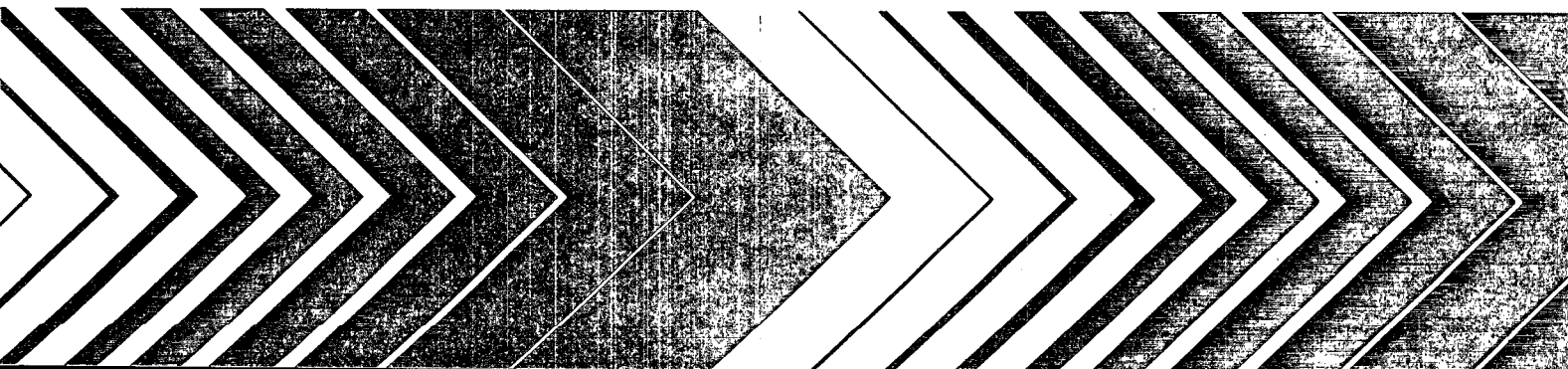
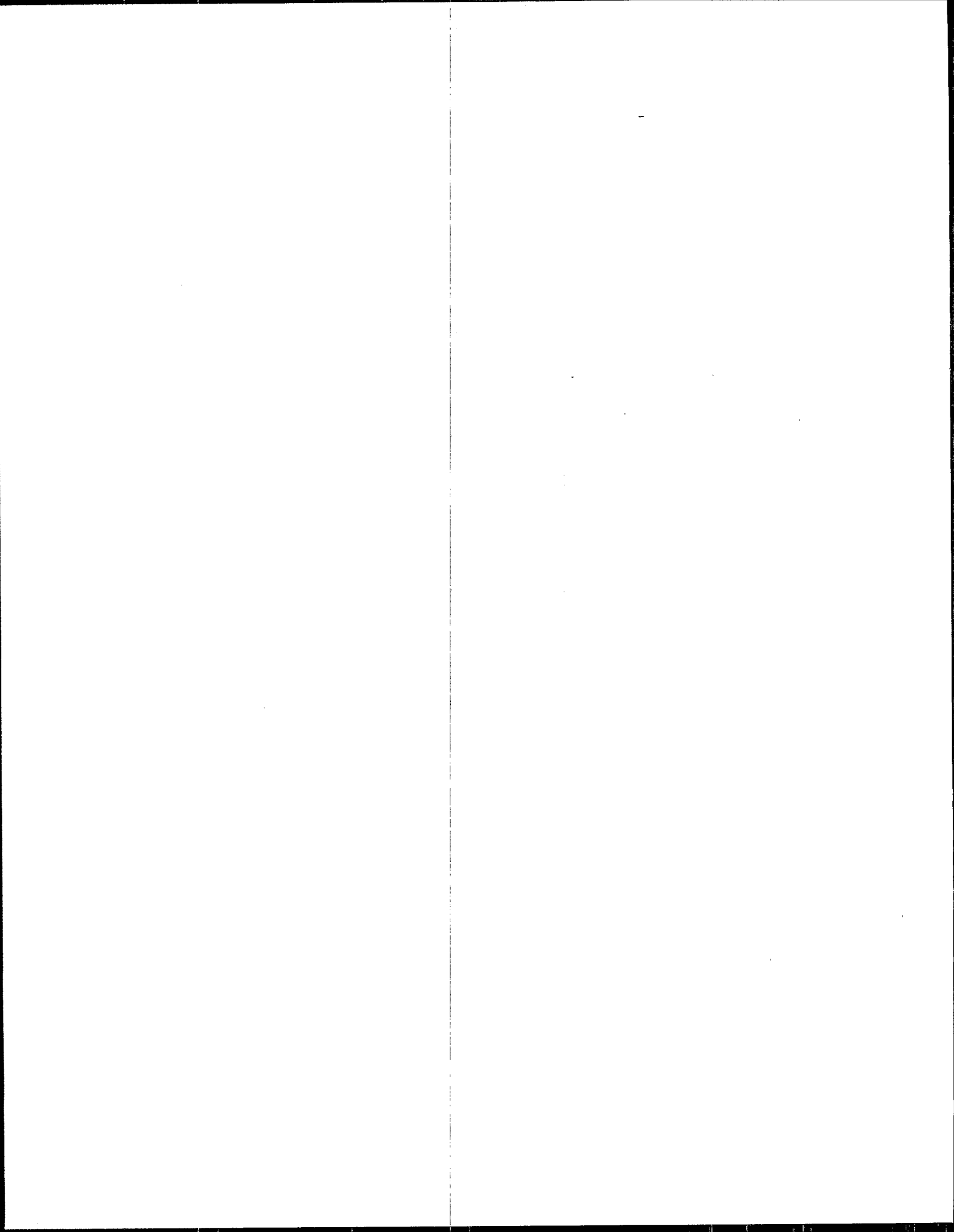




# **Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium**

## **Abstract Proceedings**





EPA/600/R-92/028

April 1992

# **Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium**

## **Abstract Proceedings**

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Sponsored by the U.S. EPA, Office of Research and Development  
Risk Reduction Engineering Laboratory

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### ***Coordinated by:***

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## FOREWORD

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

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

These Abstract Proceedings from the 1992 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 Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium was held in Cincinnati, Ohio, April 14-16, 1992. 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 into two sections, Sessions A and B, which contain extended abstracts of the paper presentations. A list of poster displays is also included. 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.

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SOLIDIFICATION/STABILIZATION OF  
HIGH LEVEL INORGANIC AND ORGANIC  
SOILS AT ROBINS AIR FORCE BASE

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## INTRODUCTION

Solidification/stabilization technologies have been applied widely and generally have been effective in immobilizing metal and other inorganic contaminants at hazardous waste sites. Solidification/stabilization technologies have been less effective in immobilizing organic contaminants, because solidification alone may not reduce the mobility and toxicity of hydrophobic constituents. In addition, treatment of wastes containing volatile organic compounds (VOC) by solidification/stabilization generally has consisted of partitioning VOCs to the air either through aeration (such as materials handling and mixing) or through heat of reaction with treatment reagents.

To constitute treatment under Superfund, a solidification/stabilization technology must demonstrate a significant reduction (90 to 99 percent) in the concentration of chemical constituents of concern. During the last 10 years, various innovative solidification/stabilization technologies have emerged that are capable of treating wastes containing organic as well as inorganic contaminants. These innovative solidification/stabilization technologies have involved the use of surfactants and other reagents that chemically stabilize contaminants in conjunction with solidification.

One innovative solidification/stabilization technology, developed by Wastech, Inc., is currently being tested in the U.S. EPA Superfund Innovative Technology Evaluation (SITE) program at Robins Air Force Base (Robins AFB) in Warner Robins, Georgia. An on-base landfill cell of approximately 1.5 acres was used for the disposal of industrial wastewater treatment sludge, as well as solvents, cleaners, paint removers, hydraulic fluids, and oils. Those wastes were deposited in the cell over a period of approximately 16 years ending in 1978. Soils at the site are contaminated with a variety of VOCs, such as 1,2-, 1,3-, and 1,4-dichlorobenzene, trichloroethylene, benzene, toluene, ethylbenzene, and xylenes, and with chromium, nickel, and lead.

The Wastech solidification/stabilization technology is being evaluated to determine the effectiveness of the technology in treating organic and inorganic contaminants. The evaluation of the Wastech technology will include determining the structural properties of the treated waste and assessing the loss of VOCs during the treatment process and during post-treatment curing.

## METHODOLOGY

The first phase of the Wastech treatment technology involves adding proprietary liquid chemicals and catalysts to the waste, which will result in the formation of micelles. According to Wastech, after exposure to the liquid reagents, the contaminants are chemically stabilized and volatilization stops. The second phase of the treatment involves physical solidification and stabilization in a mixture of pozzolanic binders and portland cement. The resulting grout-like mixture is deposited into containers or in engineered excavations for curing and disposal.

The evaluation of the Wastech technology will consist of a pilot-scale demonstration at Robins AFB. The evaluation will be based primarily on 1) determining if the technology can reduce the level of organic contaminant extractability as measured by total waste analysis (SW 846 Methods 8240 and 8270), and 2) determining if the Wastech technology reduces leachability and mobility of both organic and inorganic contaminants as measured by the Toxicity Characteristic Leaching Procedure (TCLP) and other leaching procedures such as TCLP-Distilled Water. The technology evaluation also will be based on the structural properties of the treated waste, the loss of VOCs during treatment and curing, the volume and mass increase of the treated waste, and treatment variability from batch to batch.

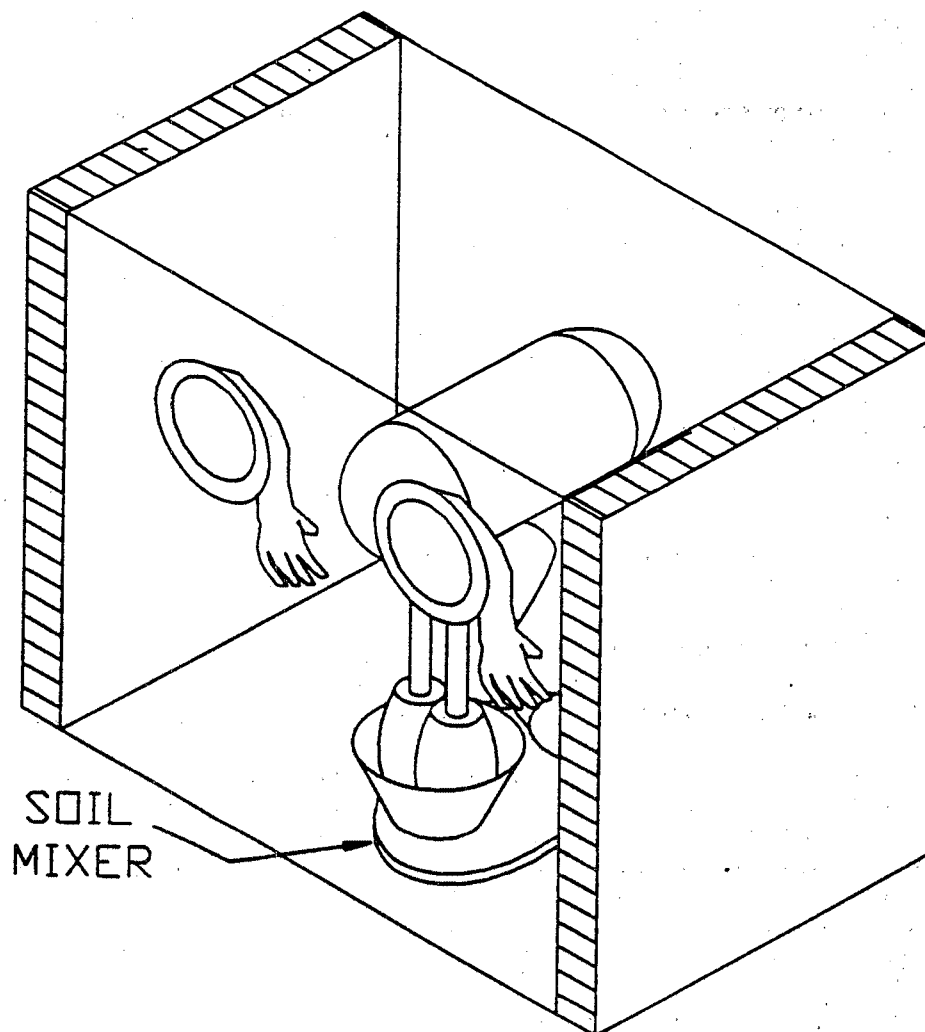
Contaminated soil from the Robins AFB site will be excavated, screened, and conveyed by a screw auger to the treatment mixer. At each excavation location, a 4-foot diameter casing, approximately 10 feet long, will be driven into the landfill, using a vibrating hammer. The casing will allow clean removal and temporary storage of overburden without adjacent overburden collapsing into the hole. After the overburden has been augered out, a modified mud bucket will collect the contaminated soil in single 1- to 2-cubic-yard lifts. The excavated waste will be transported directly to the screen and screw conveyor in the mud bucket, minimizing material handling and attendant VOC emissions. The overburden will be used to backfill the excavation following waste removal.

The mixer is trailer-mounted and contains mixing paddles and two high-speed rotary cutting blades. Calibrated load cells (scales) are located under each leg of the mixer, providing the accurate weight of all materials added. With the mixer in the trailer are storage tanks for water, liquid reagent and catalyst, pozzolanic binders, and portland cement, as well as a control booth and wet scrubber/carbon adsorption system to control air emissions. The mixer will be kept under negative pressure, with the air drawn through a tank of scrubber water and then through two canisters of granular activated carbon that are staged in series.

Raw- and treated-waste samples collected during the technology demonstration will be analyzed by a variety of chemical and physical tests (such as Methods 8240, 8270, TCLP and unconfined compressive strength). To account for any interferences introduced by the treatment reagents and process water, a reagent mix "blank" batch will be run using clean sand. The sand and water, as well as the "treated" material, will be sampled and analyzed upon discharge from the mixer.

Loss of VOCs during treatment and curing will be measured in two ways. First, for each batch of soil treated in the mixer, the scrubber water and carbon canisters will be analyzed for VOCs. Sampled clean water and carbon will be used for each treatment batch. Second, upon discharge of treated waste, a tared 5-gallon bucket will be filled with the waste, immediately covered, weighed, and placed inside a glove box with inflow and outflow ports (see figure). The glove box then will be sealed and purged with nitrogen, using a low-volume air pump. Activated carbon tubes, in series to prevent breakthrough, will be attached to the outflow port and the bucket cover removed. Carbon tubes will be changed daily for one week and analyzed for VOCs.

## REPRESENTATIVE GLOVE BOX



## RESULTS

A borehole program at the Robins AFB site to identify excavation locations for the technology demonstration was conducted in July and August 1991. Soil samples were collected from various locations at a depth of 6 to 8 feet. Representative results of the borehole sampling program are shown in Tables 1 to 3.

## CONCLUSIONS

Bench-scale testing results should be available in March or April 1992. A pilot-scale field demonstration currently is scheduled for April or May 1992.

TABLE 1. VOCs AT ROBINS AFB - METHOD 8240

Concentrations are in mg/Kg (ppm)

	Sample Location			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
1,2-Dichloroethene (total)	98	19	235	97
Trichloroethene	1,388	119	2,613	624
Tetrachloroethene	298	32	161	58
Chlorobenzene	33	17	ND	21
1,2-Dichlorobenzene	6,638	815	3,700	1,838
1,3-Dichlorobenzene	366	80	146	86
1,4-Dichlorobenzene	3,288	479	1,800	1,138
TEX*	86	145	ND	149

\* TEX = Total toluene, ethylbenzene, and total xylenes; no benzene detected.

TABLE 2. SEMIVOLATILE ORGANIC COMPOUNDS AT ROBINS AFB - METHOD 8270

Concentrations are in mg/Kg (ppm)

	Sample Location		
	<u>A</u>	<u>B</u>	<u>C</u>
1,2-Dichlorobenzene	4,867	658	5,083
1,3-Dichlorobenzene	336	72	293
1,4-Dichlorobenzene	2,560	415	2,867
1,2,4-Trichlorobenzene	127	ND	ND
Naphthalene	105	ND	ND
2-Methylnaphthalene	327	59	329

TABLE 3. METALS AT ROBINS AFB - TCLP

Concentrations are in mg/L (ppm)

	Sample Location		
	<u>A</u>	<u>B</u>	<u>C</u>
Chromium	0.371	0.358	0.370
Nickel	0.371	0.867	0.656
Lead	1.125	0.221	0.325

## REVIEW OF SOIL VAPOR EXTRACTION MICROCOMPUTER MODELS

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### INTRODUCTION

Soil Vapor Extraction (SVE) is a process in which volatilization of residual organics is enhanced and contaminated gas is removed from subsurface soils. The technology is commonly used to remediate volatile organic compounds released from underground storage tank (UST) systems. Across the nation, numerous consultants have designed and operated SVE for cleaning up gasoline and solvents contaminated soil. However, despite the wide application of SVE systems, only scanty information is available for evaluating the feasibility of SVE technology and predicting the efficiency of system performance.

The US EPA Risk Reduction Engineering Laboratory has recently prepared a document to provide guidance for designing and implementing a soil vapor extraction treatability study in support of remedy selection at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites. As stated in the guidelines, screening and evaluation of the SVE technology applicability necessitates understanding SVE processes through modeling techniques at an early stage of the technology implementation.

A model is a physical or mathematical construct that simulates or approximates the behavior of an actual physical process. Models are used to understand processes or portions of processes that have a high degree of complexity or cannot be readily understood by direct observation. In leaking underground storage tanks site or hazardous waste site evaluations, models are particularly valuable since modeling the behavior of a soil-vapor-groundwater system prior to the construction of a remediation system can reduce the cost associated with trial and error system design and operation.

If SVE processes can be adequately modeled, then the remedial design consultant will be better able to examine the process feasibility, to predict potential performance, and to develop system engineering design criteria prior to SVE implementation. This paper presents a brief overview of the identified micro-computer models that simulate soil vapor transport due to the influences of a SVE system and evaluate the feasibility of using SVE system for site remediation.

### SOIL VAPOR EXTRACTION MODELS

To effectively design a SVE system, an understanding of the mechanisms controlling the fate and transport processes and the site characteristics which affect them is required. The major processes that affect SVE are advection, diffusion, dispersion, partitioning, and abiotic and biological transformations.

Mathematical models have been developed to describe results of laboratory SVE column experiments, as well as results from field scale implementation of SVE. In order to identify models which are applicable for use in evaluating SVE systems, a larger group of models, subsurface vapor transport models, was examined. The models within this group consist of seven model types:

- Models developed to simulate laboratory column studies.
- Models developed to simulate laboratory pilot (sandbox) studies.
- SVE screening models.
- Models developed to simulate the effect of SVE at the field scale.
- 3-D vapor flow models for field scale applications.
- 3-D multi-phase fate and transport models having a vapor flow component for field scale applications.
- Groundwater flow models used to approximate vapor flow.
- Radon gas fate and transport models.

While each of these types of models is important in describing some portion of subsurface vapor transport, this presentation addresses only those models which can simulate SVE systems on a personal computer. Table 1 summarizes four general types of models which are discussed in the following sections.

1. Column Models -- Column models are developed to simulate laboratory column studies that gauge the relative importance of various fate and transport processes under simplified and controlled column conditions. SVE treatability study and research have been conducted with column studies with computer modeling.

Wilson (1991) developed a SVE column model to simulate one dimensional flow in laboratory column studies. The model considered local equilibrium between vapor phase, aqueous phase, adsorbed state, and nonaqueous liquid phase. Advection and diffusion/dispersion in the vapor and aqueous phases are taken into account, and biological degradation is also modeled as a first-order process occurring in the aqueous phase. In addition, the user can determine the sorption parameters based on the test results according to Freundlich, Langmuir, and BET adsorption isotherms characteristics.

2. Screening Models - SVE screening models are models which are primarily used in a semi-quantitative fashion to estimate whether SVE is feasible for application at a specific site. In addition, such a model may provide estimates of some design parameters for sizing a SVE system. Johnson et al. (1990, 1990a) presented a practical approach to screening the feasibility of using SVE at a particular site. The approach is based on equations which estimate VOC removal rates and pressure distributions related to various SVE design parameters. Based on this approach two models, HYPERVENTILATE and VENTING, were developed.

HYPERVENTILATE was developed as a user friendly, interactive, software guidance system that operates as a "decision tree" for investigating the potential implementation of SVE at a given site. It was designed for the Apple Macintosh Hypercard environment, and consequently requires the Hypercard program for operation. The model will not completely design a vapor extraction system, predict exactly how many days it should be operated, or

predict the overall effectiveness of a SVE system. It was designed to be used as a guide to a structured thought process to: (a) identify and characterize required site data, (b) decide if soil venting is appropriate at a site, (c) evaluate air permeability test results, (d) estimate the minimum number of extraction wells, and (e) estimate how results at a given site might differ from the ideal case. The organizational basis used in Hyperventilate is a system of multiple card files. The main card stack is called "Soil Venting Cards". Since individual cards within this stack may require further explanation, there are secondary card stacks that can be accessed through individual cards. These secondary stacks include the "Soil Venting Help Stack", the "Air Permeability Test" stack, the "Aquifer Characterization" stack, and the "System Design" stack. Most of the SVE system parameters are estimated under the topics that deal with SVE feasibility, system design and field testing.

VENTING -- This screening model for estimating the VOC removal rate from the vadose zone under SVE conditions assumes steady gas flow, equilibrium partitioning between the free product and vapor phases and complete mixing of free product and vapor to estimate the reduction in mass of each component of the contaminant over the time of extraction. The mass balance portion only considers partitioning from the free product phase into the vapor phase. It assumes contributions to the vapor phase by the aqueous and adsorbed phases are negligible. The key parameter which controls the results of VENTING is the volumetric gas flow rate which is in contact with the contaminated soil. The flow rate may either be input directly based on field measurements or may be estimated from the gas permeability of the soil and the vent pressure. If the gas permeability is not known, "VENTING" provides a method of estimating a value for this parameter using air permeability test data.

3. Three-Dimensional Vapor Flow Models -- This category of subsurface vapor transport models addresses the three-dimensional flow of soil vapor through a porous medium due to the pressure gradient established by an extraction well. Such models do not consider the contaminant concentrations in the soil vapor but do simulate the compressibility of the vapor. CSUGAS is one of this type models. It is a three dimensional, finite difference model which numerically simulates the flow field of a compressible gas in a porous medium due to the influences of a SVE system. The finite difference method is used to numerically approximate a solution to the system of equations. Use of this method allows for application to a heterogeneous and isotropic porous medium with gaseous flow under steady state or transient conditions. The model can be used to select design parameters, determine the feasibility of SVE at a particular site, or evaluate proposed modifications to existing SVE systems.

4. Ground Water Flow Models -- Another approach which has been used to predict the pressure distribution and flow of a SVE system for design purposes is to use ground water flow models. The equations describing vapor and ground water flow in a porous medium are similar enough to warrant the use of ground water flow models to approximate the pressure field and flow of a given system design. The advantages of using ground water models are that many of these models are readily available, well documented, validated, and may already be familiar to the user. MODFLOW is a commonly used ground water flow model. This model is a three-dimensional, finite difference ground water flow model developed by the USGS as a modular model capable of simulating many hydrologic systems (McDonald and Harbaugh 1985). It has several optional features which

are not applicable for simulating air flow. The model is divided into "packages", each of which represents a hydrologic or computational feature. Packages are further divided into "modules" which are subroutines designed for use in a particular package. For SVE applications, the two packages that are the most important are the Block Centered Flow (BCF) Package which simulates flow within a porous media and the Basic Package. The Basic Package includes definition of: the number of rows, columns and layers in the finite difference grid, timing of the analysis, the initial pressures (head for ground water), the boundary conditions, the timing and format of the output, and a volumetric balance.

## CONCLUSIONS

Recent designs of SVE systems for VOC removal have mostly been empirically based due to the simplicity of the process and to a lack of analytical tools capable of aiding in system design. While it is possible to empirically design a SVE system which will extract VOC vapors, design of an efficient system which will effectively target the entire contaminated soil volume and reduce VOC residuals to an acceptable level, requires predictive capabilities, especially at sites with very heterogeneous soils and/or widely varying topography. Predictive capabilities such as those provided by a correctly applied model are needed to estimate the change in effectiveness of a system due to varying the blower size, well configuration, screened interval, and other system parameters.

Many numerical model have been used in actual field situation to evaluate the effectiveness of SVE in removing organic vapors. Modeling yields meaningful results when the appropriate background information is used. Sensitivity analyses reveal the importance of soil moisture, temperature, heterogeneities of the soil and other factors in controlling the migration of volatile constituents through the unsaturated zone. Furthermore, the process of contaminants desorption from soil particles, which occurs through three consecutive mass transport steps, plays an important role in determining final cleanup efficiency and will generate significant differences in removal rate between the various types of soils and volatile organic components.

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# SUMMARY MATRIX OF MODELS

Model Name	Model Type	Developer	Availability	System Requirements	Applications	Input	Output
"SVE COLUMN"	Lab Column	D.J. Wilson	Beta Test Phase	IBM PC/AT Compatible 840 KB RAM MS-DOS 2.0 or higher. BASICA	Feasibility of SVE use; qualitative estimates of mass remaining	Flow rate, column dimension, porosity, temperature, time step, sorption isotherms	Mass remaining vs. time
"HYPERVENTILATE"	Screening	Shell Development Westhollow Research Center	Beta Test Phase	Apple Macintosh, >1 meg of RAM, "Hypercard" 2.0 or newer	Feasibility of SVE use; qualitative estimates of cleanup time and some design parameters	As above plus boiling point data on spill components; desired remediation time	Estimates of flow rates; removal rates; residual concentrations; # of wells required
"VENTING"	Screening	Environmental Systems and Technologies, Inc.	Available to public, \$300	IBM PC/AT compatible 512KB RAM, math coprocessor, hard disk with >1.5 meg	Feasibility of SVE use; qualitative estimate of cleanup times	Air flow or soil permeability or permeability test results; mass, area and composition of spill; porosity; properties of spill components, soil temperature	Mass removal rate curve for each spill component
"CSUGAS"	3-D Vapor Flow	Colorado State University Civil Engineering Department	Available to public, \$125	IBM PC/AT compatible, DOS 2.0 or higher, 840 KB RAM, graphics monitor, math coprocessor	Quantitative estimate of design parameters; evaluation of various system designs	Permeability; porosity; initial pressures; topography	Soil pressure distribution; total system flow
"MODFLOW"	3-D Ground Water Flow	USGS	Available to public, \$250-\$525	IBM PC/AT compatible, DOS 2.0 or higher, math coprocessor, graphics monitor	Quantitative estimate of design parameters, evaluation of various system designs	Vapor conductivity, initial pressures	Soil pressure distribution; total system flow

## REMEDIATION OF LEAD CONTAMINATED SOIL

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### INTRODUCTION

Lead contaminated soil in urban areas is of major concern because of the potential health risk to children. Many studies have established a direct correlation between lead in soil and elevated blood lead levels in children (Fairey and Gray, 1970; Neri et al., 1978; and Rabinowitz and Bellinger, 1988). In Minneapolis, Minnesota, Mielke et al. (1983) reported that 50% of the Hmong children with lead poisoning were in areas where soil lead levels were between 500 and 1000 micrograms per gram (ug/g), and 40% of the children suffering from lead poisoning lived in areas where soil lead levels exceeded 1000 ug/g.

In urban areas, lead pollution in soil has come from many different sources. The sources include lead paint, lead batteries and automobile exhaust. Olson and Skogerbee (1975) found the following lead compounds in soils where the primary source of pollution was from automobiles: lead sulfate, lead oxide, lead dioxide, lead sulfide, and metallic lead. The primary form of lead found was lead sulfate. Lead batteries contain metallic lead, lead sulfate, and lead dioxide. The primary form of lead found is lead sulfate. Lead sulfate, lead tetraoxide, white lead, and other forms of lead have been used in the manufacture of paints for houses.

At present, two remediation techniques, solidification and Bureau of Mines fluosilicic acid leaching, are available for lead-contaminated sites. The objective of the present investigation at the Risk Reduction Engineering Laboratory(RREL), Edison, was to try to solubilize the lead species by appropriate reagents and then recover the contaminants by precipitation as lead sulfate, using environmentally acceptable methods. A multistep extraction process was developed. The apparatus used for mixing was a LabMaster mixer, with variable speed and high-shear impeller.

Previous work had used nitric acid for dissolving metallic lead. Owing to the environmental concerns, it was decided to use acetic acid in the presence of oxygen. The theoretical justification for this approach is the favorable redox potential for the reaction between metallic lead, acetic acid, and gaseous oxygen.

In the first step a water slurry of lead-contaminated soil is reacted with ammonium carbonate to convert lead sulfate to lead carbonate. After filtration, the soil is reacted with gaseous oxygen in an acetic acid medium. In this second step metallic lead and lead carbonates are solubilized as lead acetate. The soil is filtered and then reacted (third step) with manganese acetate. This step converts lead dioxide to soluble lead acetate, leaving insoluble manganese compounds as a byproduct. The filtrates from the three steps are combined to precipitate insoluble lead sulfate, which is a usable product.

## METHOD

To determine what mixing speed and oxygen flow rate to use, 5.0 grams of metallic lead was mixed at different mixing speeds and at different oxygen flow rates in the presence of sand for one hour. The sand was added to keep the metallic lead dispersed throughout the solution. At the beginning and end of the runs, the pH of the lead-sand-acetic acid mixture was measured to determine if the desired reaction was occurring. The dissolved oxygen concentration was measured every 10 minutes. At the end of the run, three samples were taken for determination of lead by atomic absorption spectroscopy.

The second experiment performed was a rate of reaction study. In this study, every ten minutes a sample was taken out for lead determination to find how long it takes for maximum metallic lead solubility to occur in the presence of the oxygen. These tests were done for 70 minutes. Three different sets of conditions were studied. In the first set of conditions, 10,000 milligrams per liter (mg/L) of metallic lead was mixed in 1.0M acetic acid with an oxygen flow rate of 73.4 milliliters per minute (mL/min). In the second set of conditions, 20,000mg/L of metallic lead was mixed in 0.01Molar(M) acetic acid with an oxygen flow rate of 73.4mL/min. In the third set of conditions, 10,000 mg/L of metallic lead was mixed in 0.1 M acetic acid with an oxygen flow rate of 73.4 mL/min. Temperature pH, and oxygen solubility were also determined. The lead concentrations in the sample were determined via atomic absorption spectroscopy.

The solubilization of lead dioxide involves the use of manganese acetate to reduce and solubilize the lead dioxide. 1.15 grams of lead dioxide was added to a beaker containing 500 mL of 1.0 M acetic acid. To twelve beakers of this mixture, manganese acetate was added at the following levels: 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 grams. The contents were mixed for a period of one hour, then filtered. Three samples were taken from the filtered solution for lead determination.

In separate experiment, samples of silt loam from Bayou Bonfouca, Louisiana were spiked with 10,000, 5,000 and 1,000 milligrams per kilograms (mg/kg) of lead. Four different types of lead were added to the silt loam. Lead sulfate, white lead, lead dioxide, and metallic lead were added to the soil in the ratio 6:2:1:1. The extracting solutions in the following steps were added at a ratio of 8:1. The first step was to add ammonium carbonate solution to convert the lead sulfate to lead carbonate. The sample was mixed for 5 minutes. Three samples were taken from the filtrate for lead analysis. The second step was to add 1.0 M acetic acid to the sample in the presence of oxygen to solubilize the lead carbonate, metallic lead, and white lead. The lead in solution was determined by atomic absorption spectroscopy. After the second step, the residue was leached with deionized water. The leachate was analyzed for lead. The final step involved the use of manganese acetate in 1.0 M acetic acid as a means of removal of the lead dioxide from the soil. At the 10000 parts per million(ppm) lead level, the above procedure was done twice to see if any additional lead could be extracted.

## RESULTS

The solubilization of metallic lead in a sand medium showed the importance of choosing the proper mixing speed and oxygen flow rate. As the oxygen flow rate was increased from 24.1 ml/min to 59.5 ml/min, an increase in the solubility of metallic lead was observed. Oxygen flow above 59.5 ml/min did not result in an increase in metallic lead solubility. Increasing the mixing speed from 400 revolutions per minute (rpm) to 800 rpm caused almost a 25% increase in metallic lead solubility. Metallic lead solubility at 400 rpm averaged 63%, while at 800 rpm mixing speed, metallic lead solubility averaged 84%.

The complete results for the manganese acetate test can be found in Table 1. The use of manganese acetate showed that, when added at a level of 1.0gram/500 milliliter (g/mL), more than 55% of the lead dioxide (2000mg/L) dissolved. Additional manganese acetate appeared to result in a slight decrease in lead dioxide solubility.

TABLE 1. LEAD DIOXIDE SOLUBILITY AS AFFECTED BY THE LEVEL OF MANGANESE ACETATE ADDED.

Manganese Acetate Used (g/500mL)	Lead Added (ppm)	Lead in Solution (ppm)	(%)
0.5	2000	654	33
1.0	2000	1185	59
1.5	2000	1038	52
2.0	2000	997	50
2.5	2000	945	47
3.0	2000	979	49

In the rate of reaction studies, the solubilization of lead varied depending upon the ratio of metallic lead to acetic acid. When metallic lead was added at 10000 mg/L rate to a 1 M solution of acetic acid representing approximately 10 to 1 reagent to lead ratio, 72% of the added lead was in solution in 10 minutes. After 20 minutes, 89% of the added metallic lead was found to have dissolved. The increase in metallic lead solubility was then much slower and levels off at 60 minutes with 95.5% of the lead going into solution. When the ratio of reagent to metallic lead was 1.3 to 1, 73.3% of the metallic lead went into solution within 10 minutes. After seventy minutes, the metallic lead solubility had only increased to 80.2% of the added lead. When lead was added at 20,000 mg/L to a 0.01 M acetic acid solution, lead solubility leveled off at 10 minutes of 4.8% of the added lead going into solution. After the first ten minutes, lead solubility decreased and pH rose above 9.6.

The results of experiments with lead-contaminated soils are summarized in Table 2. Using soil spiked with lead at 5000 mg/kg of soil, approximately 82% of the lead went into solution from the above procedure. In the first step where carbonation was done, only 0.7% of the lead went into solution. In the oxidation step, 63.8% of the applied lead went into solution. Leaching the residue with water resulted in an additional 3.5% of the lead being removed from the soil. The final step where manganese acetate was added resulted in an additional 14.2% of the added lead going into solution.

Using soil spiked with lead at 1000 mg/kg of soil, approximately 80% of the lead went into solution. The carbonation step resulted in 1.9% of the lead going into solution. The oxidation step resulted in 57.6% of the lead going into solution. Leaching the residue with deionized water resulted in the removal of additional 4.4% lead from the soil. The addition of manganese acetate resulted in 15.9% of the added lead going into solution.

The 10000 mg Pb/kg of soil sample was run through the three-step process twice. After the first run through the three-step extraction procedure, 82.9% of the lead added was in solution. The second run through the three-step procedure resulted in an additional 6.4% of the added lead being solubilized. A total of 89.3% of the added lead was solubilized by duplicating the three step process. The oxidation step in the first set of extractions resulted in 65.1% of the lead going into solution. The manganese acetate extraction step resulted in 13.8% of the added lead being solubilized. The second set of extractions resulted in an additional 4.6% of the lead being removed in the oxidation step with the remaining lead removal being divided between the deionized water and manganese acetate leaching steps.

After the above treatment, the soil was subjected to the Toxicity Characteristic Leaching Procedure (TCLP) test. The soil passed the test with a value of 3 parts per million (ppm) in the leachate.

TABLE 2. LEAD REMOVAL EFFICIENCY IN THE THREE-STEP PROCESS IN A SILT LOAM WITH DIFFERENT LEVELS OF INITIAL LEAD

Step	Reagent used	Lead input (ppm)	Lead in solution (ppm)	Removal efficiency (%)
1	Ammonium Carbonate	1000	2.6	1.9
2	Oxygen and Acetic Acid	1000	75.3	57.6
	Deionized Water	1000	24.1	4.4
3	Manganese Acetate	1000	21.3	15.9
Total		1000	123.4	79.7
1	Ammonium Carbonate	2000	5.5	0.6
2	Oxygen and Acetic Acid	2000	428.6	63.8
	Deionized Water	2000	94.4	3.5
3	Manganese Acetate	2000	96.6	14.2
Total		2000	625.1	82.2
First Extraction				
1	Ammonium Carbonate	10000	5.0	0.4
2	Oxygen and Acetic Acid	10000	847.3	65.1
	Deionized Water	10000	207.3	3.7
3	Manganese Acetate	10000	183.2	13.8
Total		10000	1242.8	82.9
Second Extraction*				
1	Ammonium Carbonate	10000	0.7	0.1
	Oxygen and Acetic Acid	10000	62.6	4.5
2	Deionized Water	10000	32.7	0.7
3	Manganese Acetate	10000	12.2	0.9
	Deionized Water	10000	5.2	0.1
Total		10000	113.6	6.4

\* Here the removal efficiency was calculated on the starting concentration in the first step.

## CONCLUSIONS

The results in the silt soil show that a three step process involving manganese acetate, ammonium carbonate, acetic acid and oxygen has the potential for effectively removing lead sulfate, lead dioxide, metallic lead, and white lead from a soil. The three step extraction process resulted in 80% or greater solubilization of the lead that was added to a silt loam.

At present, research is continuing on the study of this process for removing the lead compounds of concern in urban environments and more data will be available when the conference is held.

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## DESTRUCTION OF ORGANIC WASTES USING CONCENTRATED SOLAR RADIATION

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### INTRODUCTION

We have recently demonstrated that the rate of many gas-phase photochemical reactions can be increased by initiating these reactions at elevated temperatures (e.g.,  $> 400^{\circ}\text{C}$ ) (1,2). The development of very high-temperature photochemistry has raised exciting possibilities for applications such as the destruction of toxic organic wastes (1-3). Since concentrated sunlight contains a considerable quantity of near-UV photons ( $\lambda > 300$  nm) that can be used to initiate photochemical reactions, as well as infra-red (IR) photons that can serve as a source of considerable thermal energy, the solar induced thermal/photolytic destruction of hazardous organic wastes appears to be technically feasible.

Our initial laboratory studies using simulated, broad-band, solar radiation (filtered xenon arc emission) in conjunction with a thermoelectrically heated flow reactor have clearly shown that the destruction rates of target compounds can be significantly increased and the production of stable reaction intermediates reduced as compared to identical thermal exposures (1,2). We have developed relatively simple global kinetic and photochemical models that empirically describe the experimental results. However, the details of the photochemistry and spectroscopy are poorly understood and the need for further investigation is clear. In this paper, we present the results of a detailed study of the high-temperature photolysis of chlorobenzene in a gas-phase, oxidative environment using a new flow reactor system utilizing a pulsed, tunable laser system as the near-UV photon source.

### METHODOLOGY

The experimental portion of this research program was conducted on two dedicated instrumentation systems. Absorption spectra were obtained on a system referred to as the High Temperature Absorption Spectrophotometer (HTAS), while the reaction data was taken with a system called the Advanced Thermal/Photolytic Reactor System (ATPRS).

The HTAS consists of a specially designed high-temperature absorption cell illuminated by a deuterium lamp, with the absorbed radiation dispersed by a 0.25 M monochromator and detected with a 512 channel optical multichannel analyzer. Temperature dependent absorption spectra were obtained up to  $750^{\circ}\text{C}$ .

The ATPRS is a modular instrument comprised of a tunable pulsed laser illumination system, high temperature reactor, and dedicated analytical systems. The tunable pulsed laser system consists of a Nd:YAG laser (Continuum, Model 682-20) coupled to a dye laser (Continuum, Model TDL-51). The reactor is a slender cylinder measuring 4 mm by 250 mm. Downstream of the reactor is a cryogenic trap that is cooled to  $-160^{\circ}\text{C}$ .



using chilled nitrogen. For analysis, the exhaust gases are purged to an in-line programmed temperature GC (Hewlett-Packard, Model 5890) fitted with a hydrogen flame ionization detector and a mass selective detector (Hewlett Packard, Model 5970) which was operated in a scanning mode. During normal operation the GC is fitted with dual columns for simultaneous mass spectrometric (GC/MS) and hydrogen flame ionization (GC/FID) detection of the effluent from the cryogenic trap. Alternatively, for analysis of light species (e.g., carbon monoxide, methane, etc.), the GC was operated as a conventional system using gas samples collected in Tedlar bags attached to the cryogenic trap's exhaust port.

## RESULTS

Figure 1 presents data on the thermal and thermal/photolytic destruction of chlorobenzene. As can readily be seen by comparison of these Figures, the rate of destruction of chlorobenzene is accelerated with the addition of ultra-violet radiation. Furthermore, fewer (and different) products are formed following thermal/photolytic treatment that are decomposed at lower temperatures than the products formed under purely thermal degradation conditions.

The photochemical quantum yield for chlorobenzene destruction was calculated to achieve a maximum of 0.536 at 700°C and the destruction of chlorobenzene was also enhanced by a factor of 4300 at this temperature.

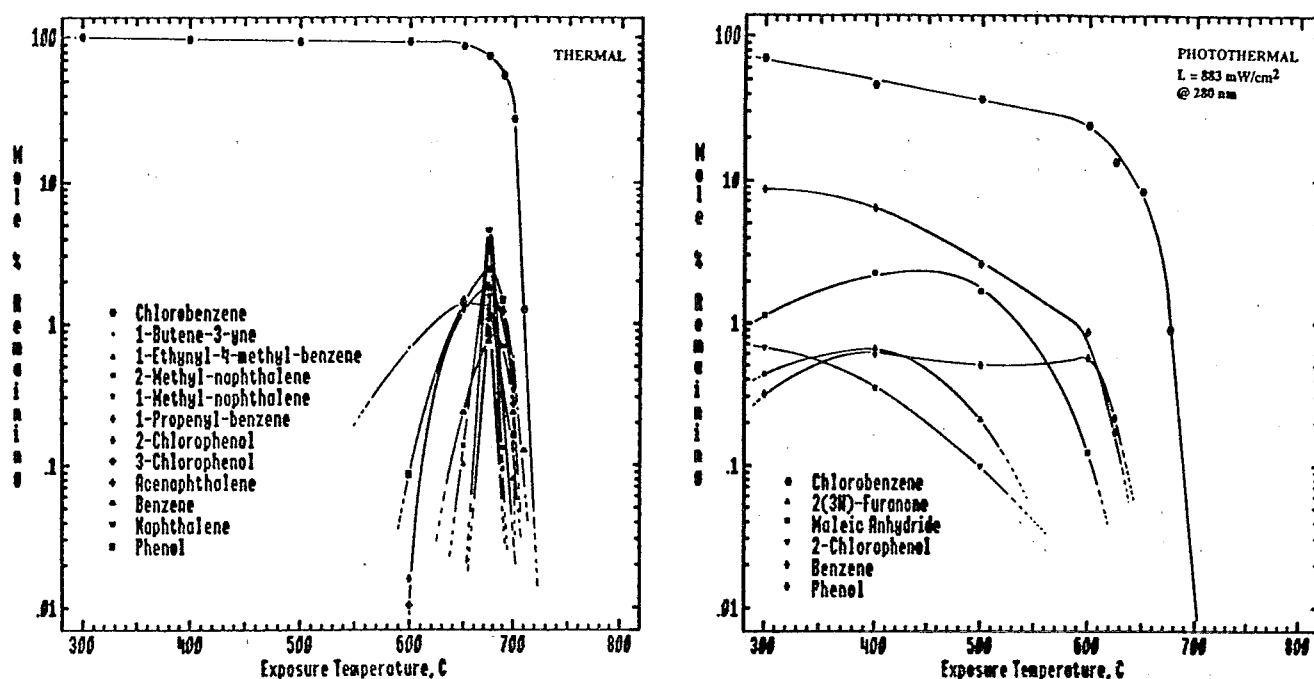


Figure 1. Comparison of product yields from the thermal and thermal/photolytic oxidation of monochlorobenzene at  $I_0 = 883 \text{ mW/cm}^2$  @ 280 nm.  $[\text{ClBz}]_0 = 2.95 \times 10^{-5} \text{ mol/L}$ . R.T. = 10.0 s. Of particular note is the reduction in quantity, yield, and stability of the thermal/photolytic by-products. Significantly, this is an apparent change in oxidation mechanism resulting in different products.

## CONCLUSIONS

Data on this and other compounds demonstrate the potential viability of destruction of toxic wastes using concentrated solar radiation.

There appears to be several advantages of solar destruction over thermal destruction which include:

1. Increased destruction efficiency of the parent and by-products;
2. Control of vaporization of toxic metals through lower operating temperatures;
3. Control of  $\text{NO}_x$  formation through lower operation temperatures;
4. Recovery of excess thermal energy that can be used for thermal desorption of solids and sludges;
5. Control of  $\text{CO}$ ,  $\text{CO}_2$ , and toxic organic emissions through substitution of solar energy for conventional fuels;
6. Cost savings due to lower fuel costs, increased materials lifetime, and reduced size and complexity of air pollution control devices;
7. Increased public acceptance through use of a renewable, non-polluting energy source for a non-incineration waste disposal technology.

Apparent major disadvantages include:

1. The unreliable availability of solar radiation;
2. Cost of collection and concentration of solar radiation;
3. Lack of an off-the-shelf technology to construct a working pilot- or full-scale system.

Our task is to develop an approach that utilizes the advantages and to minimize the disadvantages.

One approach that has been previously proposed is to develop a hybrid two-stage system targeted for detoxification of contaminated soils and other solids [3]. With this concept, a hybrid primary unit (possibly an indirectly-fired rotary drum design) may be used to thermally desorb organics from solids, while a secondary solar reactor would be used to thermal/photolytically destroy the desorbed organics. An auxiliary heat source is necessary to operate the process continuously during intermittent cloud cover and maintain night-time operation. The desorbed organic matter during dark operation may be stored by cryogenic trapping or sorption on carbon for destruction during light periods. Since the total volume of material desorbed is small, the photolytic reactor should readily handle the stored off-gases during light operation. This approach maintains the previously listed advantages for solar based waste destruction while minimizing two of the three disadvantages. The hybrid primary unit allows continuous operation, thus eliminating the concern over the unreliability of sunlight.

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ASSESSMENT OF RELATIVE POHC DESTRUCTION  
AT EPA'S INCINERATION RESEARCH FACILITY

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## INTRODUCTION

As part of their permitting process, hazardous waste incinerators must undergo demonstration tests, or "trial burns", during which their ability to meet EPA performance standards is evaluated. Among the performance standards is a minimum destruction and removal efficiency (DRE) for principal organic hazardous constituents (POHCs) in the incinerator waste feed.

In accordance with the regulations promulgated under the Resource Conservation and Recovery Act (RCRA), selection of POHCs for incinerator trial burns is to be based on "the degree of difficulty of incineration of the organic constituents in the waste and on their concentration or mass in the waste feed." (1) In order to predict the relative difficulty of incinerating specific compounds, several "incinerability" ranking approaches have been proposed, including a system based on POHC heats of combustion and a system based on thermal stability under pyrolytic conditions. (2)

The latter ranking system was developed by the University of Dayton Research Institute (UDRI) under contract to the U.S. EPA Risk Reduction Engineering Laboratory (RREL). The system is supported largely by non-flame, laboratory-scale data and is based on kinetic calculations indicating that post-flame pyrolysis of poorly-mixed waste/air pockets is the primary contributor to emissions of undestroyed organic compounds. (2-4) The subject tests were conducted to develop data on POHC behavior in a larger-scale, conventional incineration environment.

## METHODOLOGY

Testing took place in the rotary kiln incineration system (RKS) at the U.S. EPA Incineration Research Facility (IRF) in Jefferson, Arkansas. The RKS consists of a primary combustion chamber and a secondary (afterburner) chamber. Flue gas exiting the afterburner flows through a quench section, which is followed by a venturi scrubber and a packed-column scrubber. Downstream of the packed column is a secondary air pollution control system (APCS) consisting of a demister, activated-carbon adsorber, and a high-efficiency particulate filter.

Mixtures of 12 POHCs, consisting of compounds from each of 7 proposed incinerability classes, were formulated for the tests. Table 1 lists the test compounds in decreasing order of predicted thermal stability.

Feed batches, consisting of 3 lb of POHC mixture added to 5 lb of a clay adsorbent material, were fed to the kiln in 1.5 gal fiberpack containers. Compound concentrations in Mixture #1 (Tests 1, 2, and 3) ranged from 8 to 10% by weight, with the exception that n-nitroso-di-n-butylamine was present at only 2% for safety reasons. POHC concentrations in Mixture #2 (Tests 4 and 5) were tailored to achieve the desired hydrogen/chlorine ratio.

Five kiln operating modes were investigated: a baseline condition; 3 failure modes (thermal, mixing, and matrix); and a worst-case combination of the 3 failure modes. Target conditions for key test parameters are indicated in Table 2.

Permit restrictions and health and safety concerns precluded operating the entire system (kiln, afterburner, APCS) under failure mode. Therefore, failure mode operation was attempted in the kiln only and it was the kiln exit (as opposed to the stack) at which flue gas POHC concentrations were measured in order to determine relative DREs. (5)

## RESULTS

No semivolatile POHCs were detected in the kiln exit gas during Test 1 (baseline), Test 3 (mixing failure), and Test 4 (matrix failure). Only low levels of volatile POHCs were observed in these 3 tests. In contrast, Test 2 (thermal failure) and Test 5 (worst-case) yielded detectable levels of 3 of the 7 semivolatile POHCs and significant levels of all 5 volatile POHCs.

Table 3 presents kiln-exit POHC DREs for each test. A "greater than" DRE in the table indicates that the POHC was not detected in the kiln-exit flue gas for that test. The lower DRE limit in such cases is calculated using the practical quantitation limit (PQL) for the POHC in the exit gas. Since the exact POHC concentration may be anywhere between zero and its PQL, the exact POHC DRE may be anywhere between this lower bound and 100%.

In the following discussions, "incineration failure" refers to poor destruction of POHCs in the kiln, resulting in low (less than 99.99%) kiln-exit DREs. As expected, incineration failure does not appear to have taken place during the baseline operating conditions. Likewise, the attempts to achieve incineration failure in Test 3 (mixing failure) and Test 4 (matrix failure) appear to have fallen short. DREs during each of those three tests were uniformly above 99.99%. The close distribution of DREs among the POHCs makes identification of a correlation between predicted and observed POHC ranking extremely difficult. Interpretation of the data is further complicated by the fact that kiln-exit concentrations of 7 of the POHCs were below their PQL. While it may be said that DREs for those POHCs are "greater than 'X%'", their exact values are not known.

TABLE 1. POHC MIXTURE COMPOSITIONS

<u>Component</u>	<u>T<sub>99</sub>(°C)<sup>a</sup></u>	<u>Concentration (wt %)</u>	
		<u>Mixture 1</u>	<u>Mixture 2</u>
Benzene	1150	8	4
Chlorobenzene	990	8	4
Tetrachloroethene	890	8	33
1,2,2-Trichloro-1,1,2 trifluoroethane (Freon 113)	780	8	4
Nitrobenzene	655	8	4
Hexachlorocyclo- hexane (Lindane)	640	10	5
Hexachloroethane	590	10	25
1,1,1-Trichloroethane	545	10	5
Diphenyl disulfide	500	8	4
p-Dimethylaminoazo benzene (Methyl yellow)	405	10	5
Nicotine	300	10	5
N-nitroso-di-n-butyl amine	130	2	2

<sup>a</sup> Temperature required to achieve 99% destruction in 2 sec under pyrolytic conditions; based on experimental, laboratory studies of mixtures (4)

TABLE 2. TARGET TEST CONDITIONS

<u>Test</u>	<u>Failure mode</u>	<u>Kiln-exit temperature [°C (°F)]</u>	<u>Feed (Kiln) H/Cl [molar]</u>	<u>Charge weight [kg (lb)]</u>	<u>Charges/hr</u>
1	Baseline	871 (1600)	3.6 (22.8)	3.6 (8)	12
2	Thermal	649 (1200)	3.6 (22.8)	4.5 (10) <sup>a</sup>	12
3	Mixing	871 (1600)	3.6 (22.8)	7.2 (16)	6
4	Matrix	871 (1600)	1.2 (15.7)	3.6 (8)	12
5	Worst-case	649 (1200)	1.2 (10.3)	7.2 (16)	6

<sup>a</sup> Includes 0.9 kg (2 lb) water added.

TABLE 3. KILN-EXIT POHC DREs<sup>a</sup> (%)

POHC	Test 1 (baseline)	Test 2 (thermal)	Test 3 (mixing)	Test 4 (matrix)	Test 5 (worst-case)
Benzene	99.9943	99.989	99.9987	99.99916	99.954
Chlorobenzene	99.9988	99.88	99.99962	99.99937	99.9948
Tetrachloroethene	99.998	99.4	99.99947	99.99929	99.9925
Freon 113	99.9966	98.7	99.99935	99.99946	99.77
Nitrobenzene	>99.99961 <sup>b</sup>	99.84	>99.99957	>99.99909	99.958
Lindane	>99.99969	99.9927	>99.99966	>99.99928	99.9989
Hexachloroethane	>99.99969	99.966	>99.99966	>99.99986	99.9925
1,1,1-Trichloroethane	99.9971	99.993	99.99928	99.99982	99.84
Diphenyl disulfide	>99.99922	>99.99901	>99.99914	>99.9982	>99.9984
Methyl yellow	>99.99969	>99.99961	>99.99966	>99.99928	>99.9994
Nicotine	>99.99969	>99.99961	>99.99966	>99.99928	>99.9994
N-nitroso-di-n-butyl amine	>99.9983	>99.9979	>99.9979	>99.9977	>99.998

<sup>a</sup> Based on feed formulation data.

<sup>b</sup> ">" indicates POHC not detected in kiln exit gas; lower-bound DRE computed using PQL.

Tests 1, 3, and 4 did yield measurable emissions of the 4 POHCs which were predicted to be most difficult to destroy. As would be expected, this resulted in lower DREs for those POHCs than for the majority of the other POHCs. Among the more significant anomalies was 1,1,1-trichloroethane, which sometimes had measured DREs substantially lower than similarly-ranked POHCs. This may be due to the fact that 1,1,1-trichloroethane is a common product of incomplete combustion (PIC), and can be reformed during the incineration process.

Incineration failure does appear to have taken place during the thermal failure and worst-case modes (Tests 2 and 5). Low to moderate DREs were quantifiable for 8 of the 12 POHCs in those two tests, and the 4 POHCs not detected are those predicted to be the easiest to destroy. In contrast to the 1,1,1-trichloroethane discussion above, the unexpectedly-low DRE for Freon 113 in Tests 2 and 5 cannot be explained by PIC formation. Nonetheless, despite the fact that the four predicted most-difficult-to-destroy compounds did not

follow the expected rank order in Tests 2 and 5, a strong correlation with the ranking system predictions exists for the two tests. (5)

## CONCLUSIONS

As discussed above, each of the tests yielded emissions of some POHCs at concentrations below their PQLs. This presents a challenge in that the exact DREs for such compounds are essentially unknown; they are greater than the DREs computed using the PQLs. As a result of the unknowns, exact ordering of observed POHC ranking is not possible. This was the case with diphenyl disulfide, methyl yellow, nicotine and n-nitroso-di-n-butylamine during each of the five tests, and with nitrobenzene, lindane and hexachloroethane during Tests 1, 3 and 4.

In order to evaluate how well the observed POHC incinerability ranking order correlated with that predicted by the UDRI ranking system, a statistical test was applied to the data. The Spearman rank-order coefficient provides a measure of the confidence with which it can be stated that a statistically-significant correlation exists.

Because the exact DREs for several POHCs are unknown, discrete rank-order coefficients could not be determined. Rather, ranges of coefficients based on assumed DREs were computed. Best-case assumptions suggest that a statistically-significant correlation at the 99% confidence level between the predicted and observed ranking orders may exist for each of the five tests. If one were to adopt the worst-case assumptions, the correlation between predicted and observed orders would be below the 90% confidence level for Tests 1, 3, and 4. However, it can be concluded with certainty that statistically-significant correlations exist for Test 2 and Test 5 at the 99% and 95% confidence levels, respectively, even under the worst-case scenario.

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# **PACS VS CO AS SURROGATES FOR TRACE COMBUSTIBLES.**

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## **INTRODUCTION**

In the continuous monitoring of trace combustibles we are presented with two fundamental problems: there are too many trace combustibles regulated to be able to practically monitor all those compounds individually in real time, and the control of the combustion and incineration devices according to hundreds of parameters would be impractical. Therefore, surrogates, that can be easily monitored, are necessary to represent the concentrations of large groups of those trace combustibles. Traditionally, carbon monoxide has been used for this purpose because of its role in the final oxidation step of all hydrocarbons. However, it has been found frequently, that CO concentrations measured correlate poorly with concentrations of air-toxics obtained from stack sampling. This is plausible if one realizes that the critical role of CO presumes that the trace combustibles should remain reactive to the point of sampling. However, when trace combustibles escape to low temperature regions of the combustion system (eg. because of poor mixing), oxidation rates might become so low that the trace combustibles become largely unreactive, not forming any CO in the process. Thus the trace combustibles might go undetected by the surrogate monitoring system.

It was thus proposed that surrogates are measured which are more chemically similar to the trace combustibles and which are equally, or preferentially more, refractory than the trace combustibles. PACs were found to be very refractory to oxidative destruction and they can be measured in low concentrations in real time (1). In experiments being carried out the use of PACs as surrogates for trace combustibles emissions is compared to the use of CO for that purpose. In the experiments the formation and destruction of PACs, as well as of CO, is studied in detail in a turbulent natural gas diffusion flame which is doped with an aromatic compound (toluene). CO measurements are made using a conventional CEM apparatus, and PACs are monitored by means of the MIT laser induced fluorescence (now LIF) system which has been developed under a separate project(2), and characterized in detail by a physical sampling method described elsewhere.

## **METHODOLOGY**

All combustion experiments are carried out in the M.I.T. Combustion Research Facility (CRF), a tunnel furnace with a maximum thermal input of 3.0 MW. The CRF consists of a number of separate, water cooled, sections, a variable number of which may be refractory lined on the inside. It is equipped with a Variable Swirl Burner (VSB) which allows the flow and mixing pattern in the near burner region to be controlled.

Secondary ("overfire") air can be introduced through a, separate, secondary air injection section and dopants may be injected through probes. The CRF allows both physical and optical access to the horizontal plane of symmetry through ports in all sections. For the experiments described in this paper the CRF was configured as shown in Fig. 1. A detailed description of the MIT CRF is given in Beér *et al*<sup>2</sup>.

All fluorescence experiments are done using the LIF/LLS system depicted in Fig. 2. The excitation source is a 5 W (multi line) argon ion laser, operated at its 488 nm line. The laser beam, modulated (at 1000 Hz) by a light chopper, is directed to the sampling volume by two beam steerers. A sampling volume, of 2 mm diameter and 60 mm length, is observed by the detection system which consists of a single lens, colored (OG 515) filters, a Jarrell Ash 25 cm focal length monochromator (with a stepper motor wavelength selector) and an EMI 9558 QB photomultiplier tube, thermoelectrically cooled to 263 K. The PMT output is collected by an EG&G 5105 lock-in amplifier, tuned to the chopper reference frequency. An IBM PC/AT serves for data acquisition and process control. The attenuation of the laser beam by the flame, necessary for correction of the LIF signal, is determined by the use of a power meter in the port opposite to the LIF instrument.

In the combustion experiments, no windows are used to avoid effects of fouling, inevitably associated with windows. The furnace, under normal operation, is operated with a slight underpressure, so as to avoid possible damage to the optical equipment by combustion fluctuations. Due to the underpressure, and the favorable geometry of the power meter (narrow view angle), there is no observable effect, of the radiation from the flame upon the measured signal.

Physical samples from the CRF are drawn through a stainless steel water cooled probe into a Dichloromethane (DCM) Sampling system, consisting of two refrigerated baths of DCM in series (243 K and 203 K respectively) in which the PACs are to be dissolved. The DCM sample (with the PACs), including the amount used for rinsing the probe, is concentrated by Kuderna Danish evaporative concentration and analyses by HPLC-UV, GC-FID and GC-MS(SIM)

## RESULTS

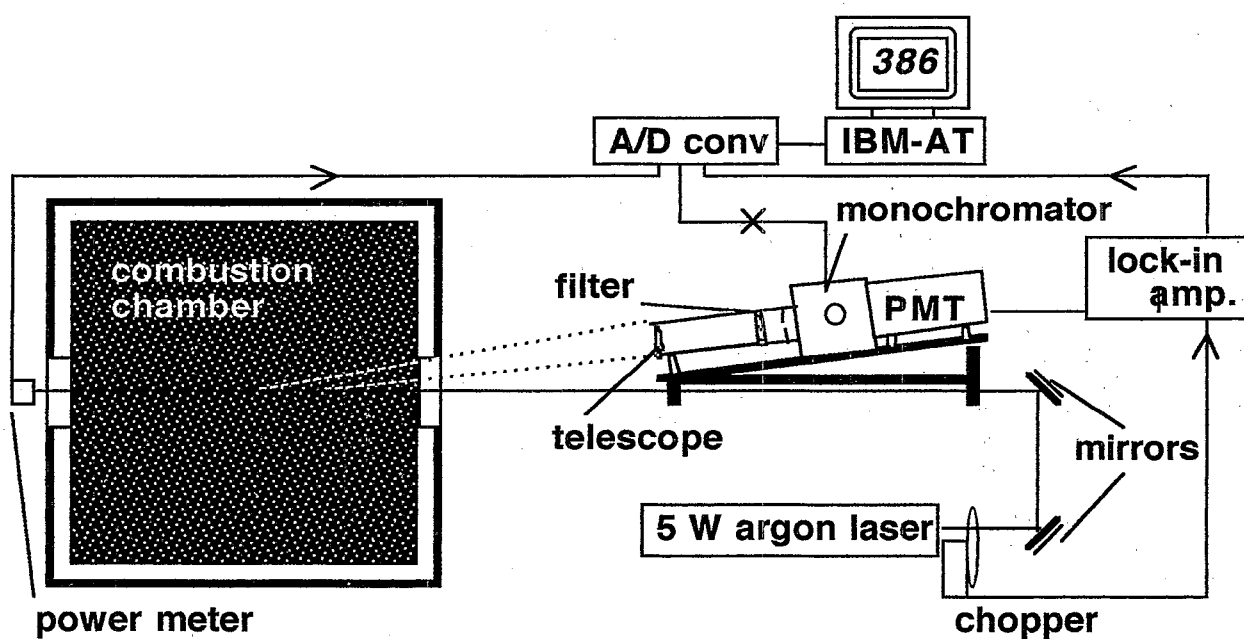
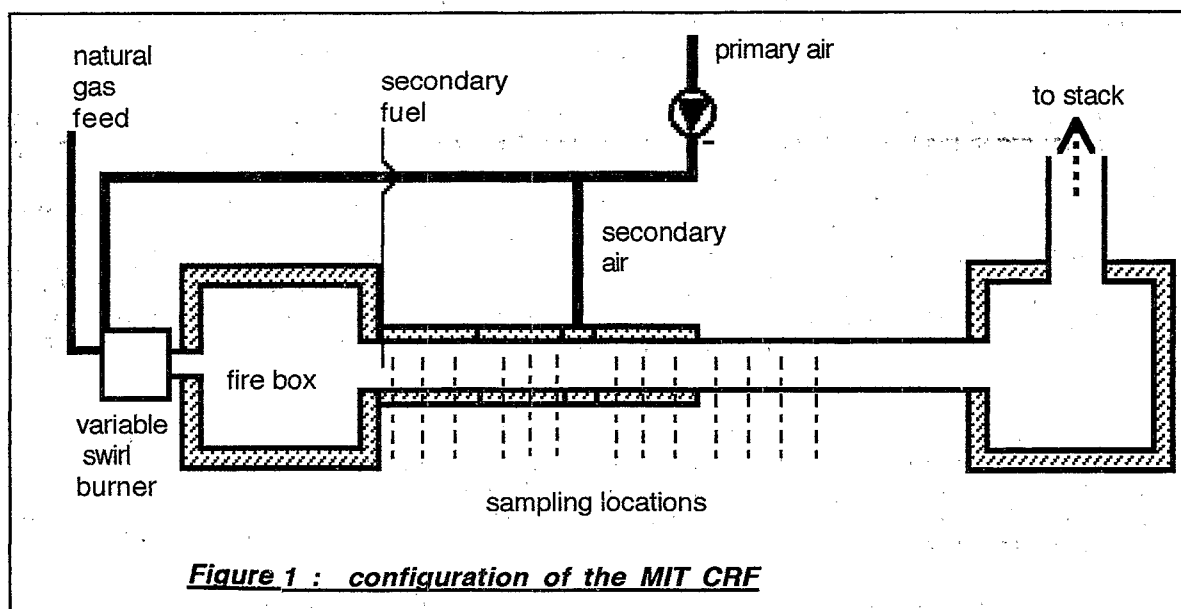
In all experiments, the fire box is run at a near stoichiometric fuel equivalence ratio. Secondary fuel, in the form of a monocyclic aromatic compound, in particular toluene, is added in the entrance of the cylindrical section. This fuel has a small concentration (order of  $10^2$  ppm), so that the fuel equivalence ratio is only marginally affected. Secondary air, to yield an oxygen mole fraction of  $\sim 0.06$ , is injected in the cylindrical section to oxidize the PACs formed.

Test are run with equal amounts of the secondary fuel injected, as well as one blank test, in which no secondary fuel is injected at four different temperatures (in the range between 1400 and 2000 K). In each test detailed measurements are made of temperatures, velocities, and major species and trace hydrocarbon species, along all axial center line stations of the furnace in both fuel rich and fuel lean zones of the combustion system.

Those measurements illustrate the processes by which PACs, trace combustibles, and CO are being formed and destroyed and thus the propensity of both PACs and CO as surrogates for trace combustibles can be assessed from a fundamental point of view.

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# HIGH ENERGY ELECTRON BEAM IRRADIATION: AN EMERGING TECHNOLOGY FOR THE DESTRUCTION OF ORGANIC CONTAMINANTS IN WATER, WASTEWATER AND SLUDGE

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## INTRODUCTION

As a result of the widespread presence of hazardous organic contaminants in aqueous matrices, considerable research is being conducted on treatment technologies for removing these compounds from contaminated environments. Historically treatment process efficiency focused only on the removal of the solute of interest from solution, with little or no concern for the formation of potentially hazardous reaction by-products. An extension of this approach is the use of carbon adsorption and aeration stripping. In the case of carbon the solutes are concentrated and then incinerated during the carbon regeneration process. Aeration stripping for the removal of volatile chemicals at worst transfers the problem directly into the atmosphere and at best transfers it to carbon or another adsorbent.

A more realistic approach to the problem of the disposal of toxic and hazardous organic waste chemicals will be the development of 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<sub>3</sub>, most often in the presence of various catalysts for its decomposition, e.g. ultraviolet (UV) light and/or hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>. 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 in some instances worse than the starting materials.

The current innovative treatment process being evaluated is the use of high energy electrons for the ultimate disposal of hazardous organic contaminants from aqueous matrices. When high energy electrons impact an aqueous solution reactive transient species are formed. The

three transient species of most interest, in the removal of hazardous contaminants from aqueous matrices, are the aqueous electron,  $e_{aq}^-$ , the hydrogen radical,  $H\cdot$ , and the hydroxyl radical,  $OH\cdot$ .

This paper describes the use of high energy electrons for the destruction of chloroform, trichloroethylene (TCE), tetrachloroethylene (PCE), benzene, toluene, and phenol from aqueous solution. The experimental parameters examined are: absorbed dose, water quality (with and without the addition of 3% clay), and carbonate ion concentration.

## METHODOLOGY

The Electron Beam Research Facility (EBRF) is located at the Miami-Dade Central District Wastewater Treatment Plant located on Virginia Key, Miami, Florida. The facility consists of a horizontal 1.5 MeV insulated-core transformer (ICT) electron accelerator capable of delivering from 0 to 800 krad absorbed dose. 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. Total power consumption, including pumps, chillers and other auxiliary equipment is about 120 kW.

The experiments presented in this paper were conducted by preparing 3,000 gallon (11,355 L) solutions of the compounds slated for study in either a 4,600 or 6,000 gallon tanker. The tanker is then directly connected to the influent of the EBRF, where the solution is pumped and irradiated. All contaminants were studied at 0.1, 1.0, and 10 mg L<sup>-1</sup>, pH 5, pH 7 and pH 9, with and without the addition of 3% clay.

## RESULTS

Initial results using high energy electron radiation were presented at the 17th Annual RREL Research Symposium. By changing the experimental design and eliminating the use of methanol, as a carrier for the organic contaminants studied, we have begun to develop a better understanding of the removal processes and more realistic estimates of removal efficiency than previously reported.

Tables 1-3 summarizes the calculated  $d_{0.50}$ ,  $d_{0.90}$ , and  $d_{0.99}$  values for TCE with and without the addition of 3% clay at three different pH levels. That is, the absorbed irradiation dose required to remove 50%, 90%, and 99% of the initial concentration of TCE from solution. From these results, it appears that our initial removal efficiency estimates were at least 10-fold higher than when methanol is eliminated from the experimental matrix. That is, equivalent solute removal is now possible with about 10-fold less energy. In addition to increased removal efficiency we have conducted extensive studies on solutions of up to 3% clay and have shown that the presence of the suspended matter only moderately affects removal efficiency and in some instances actually increases removal efficiency.

Since carbonate ion is an excellent scavenger of  $OH\cdot$ , the *in situ* concentration of carbonate ion was controlled by pH adjustment. For trichloroethylene and tetrachloroethylene lowering of the pH (i.e., less available carbonate ion) did not seem to enhance removal efficiency. This is because these halogenated compounds are primarily removed by  $e_{aq}^-$ . Chloroform, however, did show a

decrease in removal efficiency at lower pH values. This is opposite from what was expected. At this time the reason for this phenomenon is unknown. For the aromatic compounds benzene, toluene, and phenol removal efficiency was enhanced by pH adjustment. This is attributed to the lower carbonate ion concentration available at lower pH values. That is, less  $\text{OH}^-$  scavenging by carbonate ion.

Reaction by-products identified for a majority of the compounds studied included: chloride ion, low molecular weight aldehydes and low molecular weight carboxylic acids. All organic reaction by-products were identified in sub-micromolar concentrations. From these results it follows that the remaining concentration of starting material was completely mineralized to halide acids, carbon dioxide, and water.

## CONCLUSIONS

In conclusion, the use of high energy electrons appears to be a promising treatment technology for the ultimate destruction of hazardous contaminants from aqueous matrices. This innovative treatment technique has the ability to completely mineralize a variety of hazardous compounds without the added problem of a secondary treatment technique for ultimate contaminant disposal as in carbon adsorption and/or aeration stripping. Furthermore, high energy electron radiation has demonstrated the destruction of these hazardous contaminants in a variety of water qualities ranging from treated groundwater to water containing up to 3% suspended solids.

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Table 1. Summary of the Doses Required to Remove 50%, 90%, and 99% of TCE From Aqueous Solution.

pH	Target at 0.762 $\mu\text{M}$ (100 $\mu\text{g/L}$ )							
	( $\mu\text{M}$ )	No Clay			( $\mu\text{M}$ )	3% Clay		
		$d_{0.50}$	$d_{0.90}$	$d_{0.99}$		$d_{0.50}$	$d_{0.90}$	$d_{0.99}$
5 Rep #1	0.726	9.29	30.9	61.7	0.721	6.00	19.9	39.8
Rep #2	0.970	8.74	29.0	58.1	0.753	8.97	29.8	59.6
7 Rep #1	0.660	6.18	20.5	41.0	0.822	10.8	35.9	71.7
Rep #2	0.711	9.08	30.2	60.3	0.652	9.41	31.3	62.5
9 Rep #1	0.786	8.85	29.4	58.8				
Rep #2	0.894	9.80	32.6	65.1				

Table 2. Summary of the Doses Required to Remove 50%, 90%, and 99% of TCE From Aqueous Solution.

pH	Target at 7.62 $\mu\text{M}$ (1,000 $\mu\text{g/L}$ )							
	( $\mu\text{M}$ )	No Clay			( $\mu\text{M}$ )	3% Clay		
		$d_{0.50}$	$d_{0.90}$	$d_{0.99}$		$d_{0.50}$	$d_{0.90}$	$d_{0.99}$
5 Rep #1	7.35	8.33	27.7	55.3	7.64	9.63	32.0	64.0
Rep #2	8.63	9.12	30.3	60.6	8.02	9.74	32.4	64.7
7 Rep #1	9.17	8.21	27.3	54.5	7.07	10.0	33.3	66.5
Rep #2	8.73	9.45	31.4	62.8	8.11	9.32	31.0	61.9
9 Rep #1	7.28	14.1	46.7	93.4				
Rep #2	9.38	8.67	28.8	57.6				

Table 3. Summary of the Doses Required to Remove 50%, 90%, and 99% of TCE From Aqueous Solution.

pH	Target at 76.2 $\mu\text{M}$ (10,000 $\mu\text{g/L}$ )							
	( $\mu\text{M}$ )	No Clay			( $\mu\text{M}$ )	3% Clay		
		$d_{0.50}$	$d_{0.90}$	$d_{0.99}$		$d_{0.50}$	$d_{0.90}$	$d_{0.99}$
5 Rep #1	58.7	15.2	50.4	101	55.6	15.8	52.4	105
Rep #2	47.8	15.3	50.8	102	63.8	15.9	52.9	106
7 Rep #1	65.1	14.6	48.6	97.1	70.0	17.3	57.4	115
Rep #2	51.1	15.4	51.3	103	47.7	14.7	48.9	97.8
9 Rep #1	61.4	20.8	69.1	138				
Rep #2	45.5	15.7	52.2	104				

## CARBON DIOXIDE CLEANING OF CONTAMINATED SURFACES

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### INTRODUCTION

Cleaning of contaminated surfaces presents many challenges. Surfaces can be cleaned in many ways and, depending on the cleaning method, produce many waste by-products. Many of the wastes produced will be hazardous or toxic and therefore require proper containment, capture and disposal. One cleaning or surface preparation method is blast finishing. Blasting technology is not new. Within the past two decades, modified or specialized blast media have been selected to enhance the surface cleaning and preparation process. Older methods utilize natural abrasives such as water and sand. The newer methods employ glass beads, steel shot, steel grit, aluminum oxide, silicon carbide, garnet grain, walnut or pecan shells and plastic beads to create variations in abrasive action.

A ranging study was conducted to determine the applicability of pelletized carbon dioxide as a media for removal of lead-based paint from wooden doors, and to characterize the occupational exposures to airborne lead and total particulate. Personal breathing zone and work area samples were collected to assess the airborne concentrations of lead particulate. Aerodynamic particle size distribution were determined using Marple Series 290 Cascade Impactors. Residual surface levels of lead were determined using the Housing and Urban Development (HUD) wet-wipe method and a particulate adhesive sampler (PAS).

### METHODOLOGY OF THE BLAST CLEANING PROCESS

The blast cleaning of surfaces is an art form which has been used throughout industry as a quick and highly efficient method of surface preparation for coatings or reuse. Certain applications have become more sophisticated due to environmental constraints. As a result of these considerations, containment systems and pollution recovery systems are expected. Current regulations in many states require adequate capture and disposal of blasting sand that has been used to clean chromium, lead or other coating materials.

The use of carbon dioxide as a blast media, can offer several advantages over other materials and methods. One positive feature of using CO<sub>2</sub> is the reduced volume of solid and liquid waste requiring disposal. A fifty to one ratio is not uncommon. A second favorable feature is that the surface finish of metals may not be altered; if desired, the degree of removal may be tailored so that original undercoat is left and thus remains for refinishing. One disadvantage to the use of this process is the CO<sub>2</sub> level in the work area may be high and a second drawback would be that while CO<sub>2</sub> pellets remove most rust, sand or some other abrasive media; blast may be required to meet current paint preparation specifications related to profiling and "white metal" surface.

A video dramatically presents the blasting cleaning process using pelletized CO<sub>2</sub>. This video explains applications which have a proven performance history. Carbon dioxide surface cleaning can be an effective method if it is applied properly.



Each cleaning process has five factors for evaluating the effectiveness of cleaning contaminated surfaces:

1. Surface to be cleaned,
2. Penetration of cleaning agents,
3. Type of contamination to be removed and disposed of,
4. Disposal method, and
5. Total cleaning cost.

The cleaning process can be physical/mechanical or chemical or a combination of both. Common physical/mechanical methods include polishing, sanding, grinding and blasting. The chemical methods typically are acids, alkalies, solvents, and water. Almost any combination can be used in a variety of sequences to produce the desired effect.

The most common surfaces to be cleaned are metals, concrete, plastic, fabrics, and wood. These surfaces may be contaminated with benign compounds, unknown substances, toxic substances, hazardous wastes, and radioactive substances.

The factors for evaluating the effectiveness of cleaning a surface will depend upon:

1. Thickness of contaminant,
2. Penetration of the substrate
3. Bonding characteristics,
4. Required reaction, and
5. By-products.

A good cleaning process requires surface decontamination, sub-surface removal, preparing the surface for sealant and proper collection and disposal of residues. Surface cleaning methods available should include but not necessarily be limited to, 1) mechanical wipe, 2) chemical wipe/rinse, 3) physical abrasion, 4) chemical penetration, and 5) penetration by mechanical means. The selection of abrasive cleaning agents will depend upon the surface contamination, hardness of surface, and blasting material hardness. The blasting process can be both a cleaning and a finishing method. Blasting can remove surface contamination and roughen the surface for the application of paint. Blasting is also used to remove surface irregularities and create a specific surface finish.

The CO<sub>2</sub> process utilizes pelletized carbon dioxide, which is metered into an air stream on demand. This air stream is then directed through a nozzle at high velocity and the solid CO<sub>2</sub> particles impinge on the article to be cleaned. The collision between pellets and the work piece causes the kinetic energy of the pellets to be rapidly converted to heat which causes the CO<sub>2</sub> to sublime.

The cleaning effectiveness of carbon dioxide pellets relative to the substrate being cleaned is determined by:

1. Composition of substrate
2. Mass and density of CO<sub>2</sub> pellets
3. Velocity of CO<sub>2</sub> pellets
4. Dwell time of CO<sub>2</sub> pellets
5. Angle of impact
6. Temperature of the surface
7. Distance between nozzle and surface to be cleaned.

The proven applications of carbon dioxide cleaning include material preparation, technical cleaning, paint removal, and decontamination.

## RESULTS

The ranging study conducted on lead paint removal from wood doors revealed some very important aspects of using the pelletized CO<sub>2</sub> process:

1. Personal breathing zone and work area concentrations respectively, were approximately 2 and 4 times the OSHA Permissible Exposure Limit (50  $\mu\text{g}/\text{m}^3$ ) for lead during removal of lead-based paint from wooden doors. Work area sample concentrations are higher than the personal breathing zone concentrations because they represent concentrations measured closest to the point of generation of the particulate (i.e., the samples were positioned approximately 2 feet from the workpiece).
2. Cascade Impactors were used to determine the cumulative particle size distribution of lead and total particulate aerosol. The mass median diameter (MMD) of total particulates for two personal breathing zone and two work area samples are 13.5 and 10.5 microns and 28 and 24 microns, respectively. The MMD of lead for two personal breathing zone and two work area samples are 13 and 17 microns and 38 and 41 microns, respectively. Particles larger than 10 micron equivalent diameter are essentially all removed in the nasal chamber.
3. Samples collected for assessing lead-particulate fall-out in the test room showed concentrations that ranged from 730 to 1,300  $\mu\text{g}/\text{ft}^2$ .
4. Residual surface concentrations of lead using the wet-test method ranged from 330 to 5,000  $\mu\text{g}/\text{ft}^2$  (average = 3,500  $\mu\text{g}/\text{ft}^2$ ). All but one of these samples exceeded the Department of Housing and Urban Development (HUD) interim surface guidelines of 200 to 800  $\mu\text{g}/\text{ft}^2$ . Residual surface concentrations of lead using the tape-lift method ranged from 84 to 3,800  $\mu\text{g}/\text{ft}^2$  (average = 1,320  $\mu\text{g}/\text{ft}^2$ ). Half of these samples were less than the HUD interim surface guidelines.

5. Baseline concentration of gaseous carbon dioxide in the test room was 1,000 parts per million (ppm). Measurements made at approximately 15-minute intervals during the carbon dioxide blasting ranged from 2,000 to 30,900 ppm ( $n = 11$ , arithmetic average = 10,700 ppm). By comparison, the OSHA PEL's 10,000 ppm for an 8-hour time weighted average, 30,000 ppm for a 15-minute short-term excursion limit, and 50,000 ppm for an immediately dangerous level to health.

Sampling and analytical methods used to measure surface cleanliness have been investigated recently by the Risk Reduction Engineering Laboratory. A dozen sampling methods were investigated and each technique appeared to have certain advantages. The analytical quantitative and qualitative methods will vary with the type of contamination on the surface. All of the cleaning procedures require a surface testing method to determine the appropriate cleaning agents and system to produce the desired result - a "clean" surface. The question becomes "how clean is clean?" This can only be defined using the proper sampling and analytical methods.

## CONCLUSIONS AND RECOMMENDATIONS

Major conclusions on the pelletized carbon dioxide cleaning process are:

1. Selecting proper sequence of methods for each application produces high efficiency.
2. Surface testing is a mandatory requirement for evaluation.
3. Several cleaning methods used together may enhance efficiency.

Pelletized carbon dioxide blasting appears to be a viable technology to remove lead-based paint from wooden surfaces (e.g., doors). The removal efficiency of the technology can be enhanced by final cleaning procedures. Environmental control systems can be developed to minimize fugitive particulate release and gaseous carbon dioxide. This technology can significantly reduce the quantity and nature of the waste generated during paint removal and produces no liquid waste. Hence, it offers outstanding environmental gains regarding hazardous waste minimization.

EVALUATION OF THREE OIL FILTER DESIGNS  
FOR POLLUTION PREVENTION EFFECTIVENESS

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## INTRODUCTION

Used oil and discarded oil filters are a major source of waste in the U.S. Two possible ways of minimizing these wastes are the use of reusable oil filters and the use of filters that extend oil life. Reusable filters may reduce waste since they can be cleaned and reused instead of being discarded. Filters that reduce the rate at which engine oil deteriorates in quality, allowing the oil to be used longer between oil changes without harm to engine life, generate less oil and filter wastes due to fewer oil changes.

A oil filter testing program was started in January 1991 as a part of the California/EPA Waste Reduction Innovative Technology Evaluation (WRITE) Program. The California/EPA WRITE program is now in its third year of technically and economically evaluating waste reduction technologies. The WRITE Program is a national research demonstration program designed to evaluate the use of innovative engineering and scientific technologies to reduce the amount and/or toxicity of wastes generated from the manufacture, processing, and use of hazardous materials. This work was done under a Mission of Support Policy Agreement between the U.S. EPA and the California Department of Toxic Substances Control.

In this testing program, three types of diesel engine bus oil filters (reusable wire mesh, disposable fiber, and disposable paper) underwent an engineering and economic evaluation at the Orange County Transit Association (OCTA) in Garden Grove, CA. The two major objectives of the testing were (1) to assess the performance of three different types of oil filters and (2) to determine if the oil life could be extended. Testing parameters included efficiency, ease of use, economics, and environmental impacts, such as the reduction of number of oil filters and/or the frequency of oil changes.

## METHODOLOGY

This program was designed to test alternative filters on twelve OCTA fleet buses with Detroit 6V92T diesel engines. The twelve test buses selected were identical in manufacturer and age and were dispatched from the same division. The buses were as similar as possible in mileage, type of service route, and previous routine oil analysis results. Three sets of buses were grouped at random; each set included four buses with identical primary filters and secondary centrifugal filters. Four buses

were the baseline test vehicles with regular spin-on pleated paper primary filters. The second set of four buses were equipped with a composite synthetic media primary filter. The third set of buses used a reusable screen for the primary filter.

During the 4-month test period the twelve selected buses were sampled weekly each Saturday between the dates of May 18 through September 21, 1991. On each bus a special device was installed that allowed extraction of a sample of the circulating oil. A brass fitting called a "probalyzer" was installed on the oil recirculation line downstream from the primary filter. The fitting had an internal valve that could be opened to access the flow of oil while the motor was running. The oil samples were analyzed weekly for a series of physical and chemical properties. These parameters were used as a tool to monitor and evaluate the adequacy of the motor and engine oil. In addition, biweekly particle counting tests were conducted on the samples in an attempt to gauge the particle removal efficiencies of the filters.

Data were analyzed for the following parameter groups:

1. Wear elements - Iron, Chromium, Lead, Copper, Tin, Aluminum, Nickel, Silver, Manganese, Antimony, Cadmium, Titanium
2. Contaminants - Silicon, Boron, Sodium
3. Additives - Magnesium, Calcium, Barium, Phosphorus, Zinc, Molybdenum
4. Physical and Chemical Parameters - Flash point, Fuel, Viscosity, Water content, Percent solids, Glycol, Soot, TBN
5. Particle Counts - >5, >10, >15, >25, and >50 um

Test parameters can be grouped into those that primarily reflect the quality of the oil and those that are indicative of potential engine problems. Viscosity and percent solids indicate oil quality. Metallic wear elements, water content, glycol content and contaminants are indicators of potential engine problems. These parameters were monitored based upon guidelines provided by the Detroit Engine Company.

## RESULTS

Overall, no differences could be observed among the twelve buses except for wear metals and particle counts  $\leq 25$  um. Samples from the buses with synthetic fiber filters had slightly higher metal concentrations than those with other filters due to one bus that had consistently higher concentrations throughout the test. Samples from these buses also had the lowest concentrations for particles with diameters  $\leq 25$  um. These buses were followed by the buses with reusable filters, then by buses with regular filters. In addition, all of the buses went beyond the 6,000 miles oil filter change limit currently in place by OCTA. Ten of the twelve buses operated the full 4-month period without an oil and filter change. Miles traveled ranged from 14,429 miles to 21,571 miles.

## CONCLUSIONS

Using conventional oil test methods (excluding particle count analyses) no significant differences were observed in recirculating oil quality between the reusable and non-reusable filters. With regard to particle count, the composite synthetic media filters maintained significantly lower particle counts for particles less than 25  $\mu\text{m}$  in size than the other two filters. Considering the pleated paper filter versus the reusable filter, the reusable filters showed better performance for the particles  $\leq 25 \mu\text{m}$ . The differences in performances between filters disappeared as particle sizes increased.

Oil and filter changes at OCTA are currently performed approximately every 6,000 miles. This program found that the test buses were able to travel far beyond this distance without unacceptable deterioration of oil quality. The type of filter used appeared to have no significant effect. It appears that bus engine manufacturer recommendations for oil change intervals are highly conservative and may be safely increased for fleets that conduct routine oil quality monitoring like OCTA.

Oil filter changes not including the cost of oil are estimated to cost \$30 each for the pleated paper filter and \$40 each for the composite synthetic media filter. Since the reusable filter is not replaced at each oil change, it is necessary to amortize its \$364 installed cost over an estimated 10 year life. Adding labor and expendable parts cost (e.g. gaskets) the estimated cost of cleaning the reusable filter is slightly lower at \$27.50 per cleaning, based upon 8 cleanings per year. Fewer cleanings result in a higher cost per cleaning due to constant amortization cost. Basically, there is no significant difference in the comparative cost of using the three filters tested. However, the use of the reusable reduces the disposal of 8 filters per year per bus. For a fleet of 450 buses (OCTA), this is 100 drums of oil filter waste per year.

If the interval between oil changes were increased from 6,000 to 18,000 miles, the annual cost savings would be approximately \$350 per bus per year and annual oil disposal would be 170 gal per bus per year less based on 48,000 miles driven per year. For OCTA this would be a savings of \$157,000 per year and decreased oil disposal of 1390 drums per year.

As stated previously, synthetic filters did a better job of filtering out particles  $\leq 25$  microns in the oil. The reduction of these particle counts may be helpful in extending the engine's life. However, research is needed to quantify the relationship between engine oil particle counts and engine life between overhauls. If reduced particle counts should have a significant effect in increasing engine life, the potential economic benefits are large.

## THE WASTE REDUCTION EVALUATIONS AT FEDERAL SITES PROGRAM

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### INTRODUCTION

The Waste Reduction Evaluations At Federal Sites (WREAFS) Program is a cooperative research, development and demonstration (RD&D) program between the US Environmental Protection Agency and the Federal community at large. The three primary objectives of the WREAFS Program are to : 1) conduct waste minimization assessments and case studies; 2) conduct pollution prevention research and demonstration projects jointly with other Federal activities; and 3) provide technology and information transfer of pollution prevention results. Since the initiation of the WREAFS Program in 1988 within the Risk Reduction Engineering Laboratory's Pollution Prevention Research Branch, the Federal community has initiated constructive action and demonstrated awareness of the significance of pollution prevention in the production and consumption of goods and services for the Federal government nationwide and abroad. This abstract provides a summary of the current cooperative RD&D projects within the Federal community under the aegis of the WREAFS Program.

### WASTE MINIMIZATION ASSESSMENTS

The waste minimization assessments are conducted by an assessment team that is composed of personnel from EPA, personnel from the cooperating Federal facility, and others who can provide technology and processing expertise. The assessments follow the procedures described in the EPA report, Waste Minimization Opportunity Assessment Manual, (EPA/625/7-88/003) which is available from the Center for Environmental Research Information (CERI), Publications Unit, 26 West M. L. King Dr., Cincinnati, Ohio, 45268. This Manual provides a systematic procedure for identifying ways to reduce or eliminate waste generation. The conduct of a waste minimization assessment results in the waste generating activity identifying solutions and RD&D needs. The active participation as part of the waste minimization assessment team also provides on-site training for Federal personnel, encouraging continued use of the EPA Manual at other waste generating activities within a Federal Department. This hands-on experience is one reason for targeting at least one joint waste minimization assessment between EPA and each of the fourteen Federal Departments. Results from completed waste minimization assessments are documented with a report and project summary for technology transfer to both the public and private sectors.

Completed waste minimization assessments available through CERI include:

EPA/600/S2-90/046

Waste Minimization Opportunity Assessment:  
Philadelphia Naval Shipyard

EPA/600/S2-90/031

Waste Minimization Opportunity Assessment: Fort Riley,  
Kansas

EPA/600/S2-90/062	Waste Minimization Opportunity Assessment: US Coast Guard Support Center, Governors Island, New York
EPA/600/S2-91/030	Waste Minimization Opportunity Assessment: Naval Undersea Warfare Engineering Station, Keyport, Washington
EPA/600/S2-91/024	Hospital Pollution Prevention Case Study
EPA/600/S2-91/031	Waste Minimization Opportunity Assessment: Optical Fabrication Laboratory, Fitzsimmons Army Medical Center, Denver, Colorado
EPA/600/S2-91/054	Waste Minimization Opportunity Assessment: Scott Air Force Base
EPA/910/9-91-017	Waste Minimization Opportunity Assessment: US Coast Guard Base Ketchikan, Alaska and
EPA/910/9-91-018	Waste Minimization Implementation Plan: US Coast Guard Base Ketchikan, Alaska are results of a joint project between EPA's Region 10 Federal Facilities Program and RREL.

Other planned and ongoing waste minimization assessments to be completed in FY 92 include joint assessments with the Department of Interior's Bureau of Mines, the US Army's facility in Ft. Carson, Colorado, the Department of Agriculture's Research Service in Beltsville, Maryland, the Department of Treasury's Bureau of Engraving and Printing and the US Department of Energy's Sandia National Laboratories.

The Tidewater Interagency Pollution Prevention Program (TIPPP) is a cooperative effort among EPA, DOD, and NASA to take advantage of the capabilities of well-defined communities to develop a pilot program, establishing an integrated multi-media pollution prevention plan that includes both short- and long- term projects with results that will be transferable to other Federal and public communities. Through a number of WREAFS sponsored pollution prevention assessments at selected operations at each of the host facilities, pollution prevention recommendations will be considered for implementation or further demonstration. The host facilities are located at Ft. Eustis, Langley AFB, Langley NASA, and Navy Base Norfolk. WREAFS is also developing a series of Pollution Prevention Fact Sheets on processes, products, and various activities prevalent at TIPPP installations to assist with more generic short-term issues. It is anticipated that TIPPP facility managers will utilize the P2 information to reduce the generation of wastes from selected processes and each alternative will be documented and transferred throughout the Federal community. At the end of FY 92 RREL support to TIPPP should include up to thirty waste minimization assessments and fifteen P2 Fact Sheets. Due to the importance and widespread transferability of the results from RREL support to the TIPPP, the majority of WREAFS resources have been allocated for the TIPPP projects.

#### RESEARCH, DEVELOPMENT, AND DEMONSTRATION

A number of RD&D needs have arisen from the conduct of waste minimization assessments since there are not optimum solutions available for every waste generating problem. When a solution is not technically sound or does not exist, or solutions are not economically feasible, the stage is set for



RD&D. The WREAFS Program has concentrated on waste minimization assessments during the first three years and with the successful completion of these assessments and case studies, it is felt the WREAFS Program will target RD&D within the Federal community for the next several years. The Pollution Prevention Research Branch has conducted RD&D activities within the Federal community over the past three years such as: the evaluation of emulsion cleaners at US Air Force Plant No. 6; waste reduction from chlorinated and petroleum-based degreasing operation with Auburn University for Tyndall AFB; the evaluation of a wet to dry Navy spray paint booth; reclaiming fiber from newsprint with USDA; and investigating and developing wood/plastic composites with USDA's Forests Product Laboratory.

RD&D projects planned and on-going for FY 92, in addition to what will result from the TIPPP, include support to the Air Force and Navy. The WREAFS Program is planning technical support to the Naval Civil Engineering Laboratory (NCEL) for a joint project with a FY 92 start regarding industrial wastewater treatment plants (IWTP). This in-house study calls for a feasibility analysis to determine future needs which consider pollution prevention solutions to current and future pollution generating issues as well as emerging waste management technologies. The initial meeting for this technical support project is for RREL to host a workshop on January 29, 30, and 31.

Tinker AFB and RREL are working on a joint RD&D project designed to evaluate five major chemical waste generators as the overhaul/repair processes associated with CFC's, electroplating, component cleaning, painting/de-painting, and vapor degreasing. The objective of this project is to identify and assess alternative processes that will enable the Oklahoma City - Air Logistics Center to minimize waste generation while meeting overall mission objectives. By the end of FY 92, completed activities will include baseline data gathering, alternative identification and characterization, alternative assessment, and selection of alternatives.

The objective of another Tinker AFB - RREL joint RD&D project is to minimize the amount of hazardous chemicals used in plating by implementing electrochemical metallizing (EM). Using computerized numerical control, semi-automatic, or fixed station systems for EM plating of parts which are currently bath plated, EM plating will reduce chemical usage thus reducing the amount of hazardous wastes being generated in the repair and overhaul of gas turbine engines. This project includes seeking an acceptable substitute for chrome plating, providing a demonstration line for semi-automatic EM nickel plating, performing cost comparisons between tank plating and EM, and assessing the quality of the parts being plated. The impact of EM plating could be substantial for reducing chemical requirements.

## TECHNOLOGY TRANSFER

Technology transfer continues to result from project reports and project summaries of completed WREAFS projects. As noted earlier, the waste minimization assessments provide an opportunity for training and change in culture to thinking pollution prevention rather than end-of-pipe control. It is important for the Federal community to be leaders in pollution prevention and to provide examples to others in the private and public sectors. A number of pollution prevention workshops/conferences or parts of environmental conferences which include pollution prevention have participants from the Federal community. This technology transfer allows for an integrated approach to the problems of waste generation in the United States. Stepping down from the aloofness of sovereign immunity, the Federal government and business are working together toward pollution prevention solutions. The WREAFS Program is providing the forum and technical foundation for the encouragement of pollution prevention research in the Federal community. Using lessons learned RD&D for pollution prevention answers throughout the Federal community, joining RD&D resources to find solutions to common waste generating problems, and working together to bring about the cultural change in thinking pollution prevention are the goals of the WREAFS technology transfer efforts.

Federal scientists and engineers are invited to share RREL facilities and interact with RREL scientists and engineers in promoting a research cooperative for Federal facilities. It is the vision of RREL that scientists and engineers from other Federal Agencies would be assigned to RREL for a specified period to work on a pollution prevention research project of that Agency or assist RREL with pollution prevention research projects that will be applicable to all Federal facilities. The contacts, joint RD&D, and training will benefit both EPA and the other Agencies. Participation in this "cooperative" is strictly voluntary.

#### WREAFS PROGRAM SUMMARY

The WREAFS Program takes on many facets in its endeavor to support the Federal community with pollution prevention research. There has been a number of RD&D products that have been completed and a number of on-going efforts, but perhaps the most important impact will come from any resulting cultural change brought about by conducting a waste minimization assessment or reading a RD&D report. The Federal facilities "cooperative" is one idea that should be a big benefit for the Federal community and pollution prevention once support is provided. It is necessary for all of the fourteen Departments to take an active role in pollution prevention and be an example to the rest of the world.

## MEASURING POLLUTION PREVENTION

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### INTRODUCTION

To assess progress in pollution prevention, estimates or measurements of the amounts of pollution actually prevented have to be made. Such estimates or measurements tell us how far we have come and, possibly, how much farther there is to go in utilizing pollution prevention as a tool for improving environmental quality. They can, theoretically, be used to assess progress on a scale ranging from the individual facility or even the individual process or activity generating wastes to a scale as large as a geographical area such as a county, a state or even the United States as a whole.

### INDUSTRIAL SOURCES

A major step in being able to assess pollution prevention progress by industry was the provision in the recent Pollution Prevention Act requiring the addition of a "toxic chemical source reduction and recycling report" to the annual Toxics Reduction Inventory (TRI). This report, beginning in 1992, will attempt to quantify the pollution prevention progress actually occurring with respect to certain toxic chemicals used by industry. Progress will be assessed through the tabulation of such information as the quantities of the chemicals entering wastes or otherwise released to the environment, the amounts recycled at the facility or elsewhere, etc.

Roughly a year ago, an early version of this source reduction and recycling report was evaluated "in the field" by Battelle Columbus Operations under a Pollution Prevention Research Branch support contract (1). The draft report form was distributed to nine companies which had volunteered their services to "test" it. The companies were provided with the form and its instructions and asked to complete the form and then to meet with Battelle evaluators. By interviewing the companies, the evaluators tried to ascertain 1) the clarity/understandability of the form and its instructions, 2) the ease or difficulty of responding to the questions, 3) the reliability and meaningfulness of the data reported, 4) any concerns over confidentiality of the data requested and 5) the overall "burden" of responding and to obtain suggestions for improvement.

In addition, the draft report form was sent to several industrial trade associations and public interest environmental groups for their reactions.

As might be expected, the field test participants and the trade associations had very similar comments but the environmental groups commented from a different perspective. All commenters agreed that the purpose of the forms should be to collect the data needed to describe pollution prevention progress, to encourage pollution prevention, to express progress to the public and to identify opportunities for further pollution prevention. Commenters also agreed that the definition of terms needed to be clarified, especially terms such as open-loop and closed-loop recycling.

On the other hand, industry and public interest groups differed on how closely the TRI and RCRA reporting processes should be connected. Environmental groups wanted to see a close tie between these reports while industry reviewers felt that even the qualitative connection proposed in the form would be difficult to implement. There was also considerable variance in views as to the level of detail available or appropriate for reporting. Industry commenters expressed concern that the report would not always

capture a true picture of their pollution prevention activities. They also felt that requirements to report expected progress might be converted into auditable goals. A major issue involved the "starting point" to be used as a baseline for assessing progress. It was felt that firms that had already aggressively implemented pollution prevention would suffer in comparison with firms that had done nothing to date and still had "the low-hanging fruit to pick." Another item that elicited much comment related to the so-called Production Ratio or Activity Index aimed at normalizing data from year to year based on the level of production or activity taking place at a facility. It was urged that flexibility be allowed in choosing the most appropriate Index for each chemical being reported.

With the passage of the Pollution Prevention Act, a mandated set of source reduction and recycling questions will be added to the TRI beginning in 1992. These questions and the instructions related to them have benefitted from the results of this field test and from considerable other input from a wide variety of industrial, public interest and other groups over the last year or so.

## AGRICULTURAL SOURCES

Battelle was also asked to develop a methodology for measuring pollution prevention progress in the agricultural sector (2). Focus was placed on three types of agricultural pollution: fertilizers, pesticides and concentrated animal wastes. With regard to fertilizers and pesticides, it was felt that application rates could serve as simple surrogates for "wastes generated" and that, generally speaking, reductions in amounts applied from one year to another would approximate pollution prevented. It was recognized, however, that many factors other than the introduction of pollution prevention techniques affect amounts applied. For fertilizers, amounts are impacted, for example, by type of crop, crop rotations, weather and market factors. For pesticides, one must also consider, for example, cyclical infestations and pesticide formulations available. The pesticide situation is, of course, considerably more complicated because of the many, many different types and potencies of pesticides whereas fertilizer pollution is essentially limited to the three major nutrients, potassium, phosphorus and nitrogen. Because of the normal year-to-year variations, it was felt that data on application rates would have value only to detect trends over extended periods such as 5 or 10 years.

With respect to animal wastes, the possibilities for accomplishing true "source reduction" are quite limited. The primary methodology examined from the standpoint of how to assess pollution prevention progress was the use of growth hormones to increase the amount of product (meat, milk, eggs) per unit of manure excreted.

In all cases, Battelle's proposal was to survey a representative sample of farmers to determine the rates at which various pollution prevention techniques were being applied. From this information along with data on how much pollution is prevented by each technique, an estimate of overall pollution prevented could be made.

Battelle's findings in the agricultural area, while not providing any specific methodology ready for field testing, should help in providing a basis for 1) refining and expanding the list of pollution prevention practices applicable to agricultural activities, 2) measuring reduced fertilizer or pesticide use rates under different circumstances and 3) estimating the adoption rate for various agricultural pollution prevention practices.

## PROGRESS RESULTING FROM PRODUCT DESIGN DECISIONS

A third task assigned to Battelle (3) was to develop a methodology for measuring pollution prevention progress occurring as a result of actions or decisions taken during the design stage of a product. This is important since the TRI will collect information only on pollution prevented during the manufacturing stage. Yet, through astute product design decisions, much pollution can and will be prevented during other stages of the product's life than the manufacturing stage; most importantly, perhaps, pollution prevention as a result of product design will primarily occur during product use and at the time the product's useful life ends and the product, itself, becomes a waste.

Since a designer is able to influence the raw materials used, the production process employed, the way in which the product is used, its life, its "repairability," its recyclability and even the mode of its eventual disposal, product design decisions which beneficially influence any of the above potential environmental impacts should be acknowledged. This effort is an attempt to define how this might be done.

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TWO POLLUTION PREVENTION TECHNOLOGY EVALUATIONS  
FOR THE PRINTED CIRCUIT BOARD INDUSTRY

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## INTRODUCTION

The Minnesota/EPA Waste Reduction Innovative Technology Evaluation (WRITE) Program is one of seven programs nationwide in which EPA and cooperating states or local governments evaluate and demonstrate the engineering and economic feasibility of selected waste reducing technologies in a manufacturing or fully operational setting. The program in Minnesota, which began in mid 1989, targets the metal finishing industry; specifically rinsing operations within metal finishing operations, as the focus of the evaluations. The 5 technology evaluation projects planned for the full life of the Minnesota/EPA Program and subsequent technology transfer activities are intended to speed the early introduction of cleaner, pollution preventing technologies in the metal finishing industry. This extended abstract presents final results from the first project and preliminary results from the second project conducted under the Program.

## PROJECT 1

### PROCEDURE

Micorn, Incorporated is a medium-sized job shop circuit board manufacturer employing approximately 240 people at its plant in New Brighton, Minnesota. Under a number of military and commercial contracts the company produces an average of 1000-1200 square feet of double sided multilayered panels per day. In 1989, annual revenue was \$17 million.

The evaluation took place at the sensitize line where a number of process baths including etchant ("micro-etch"), activator, accelerator, electroless copper and rinse tanks, first etch and then chemically deposit copper onto the insides of the circuit board holes. Drag out from two of the line's process baths, the micro-etch and the electroless copper baths, was a significant source of waste copper discharged in the rinse water waste stream leaving the line. This rinse water had to be treated by an on-site ion exchange unit for copper removal before it could be discharged to public sewer.

Baseline samples and measurements were taken over a two week period to determine the initial drag out rate in milliliters per square foot of board plated. Enough sample sets were taken to calculate 12 values for the drag out which were then averaged.

For the first modification, the hoist system was slowed from the baseline withdrawal rate of 100 ft/min for the micro-etch line and 94 ft/min for the electroless copper line to 11 ft/min for the micro-etch line and 12 ft/min for the electroless copper line. Samples were taken and measurements made to determine the drag out after modification 1 was put in place. Again, the number of sample sets enabled 12 drag out values to be calculated.

For the second modification, the withdrawal rate was set at an intermediate rate between baseline and modification 1, and the drain time over the bath was increased. Withdrawal rates were

40 ft/min for both micro-etch and electroless baths, and drain time was increased from a baseline of 3.4 seconds to 12.1 seconds for the micro-etch line and for the electroless line from 5.2 seconds to 11.9 seconds. Samples were taken to provide 12 calculated values for drag out.

## RESULTS

Both modifications reduced drag out significantly. Baseline drag out from the micro-etch bath, 12.1 ml/ft<sup>2</sup>, was reduced to 6.7 ml/ft<sup>2</sup> or 45% by modification 1, and the electroless copper bath drag out was reduced from 6.0 ml/ft<sup>2</sup> at baseline to 3.0 ml/ft<sup>2</sup> after modification 1, for a reduction of 50%. After modification 2, the micro-etch drag out was 7.1 ml/ft<sup>2</sup>, a reduction of 41% from baseline, and for the electroless bath, drag out was 2.9 ml/ft<sup>2</sup>, a reduction of 52%.

By reducing drag out in these amounts, 203 and 189 grams of copper per day were prevented from being discharged as waste in the rinse water waste stream, for modifications 1 and 2 respectively. Because copper concentration in rinse water was reduced, the potential for conserving rinse water flows was also shown, although this was not directly tested. Rinse water flows could be turned down proportionate to the reduction in drag out and still maintain the same rinsing efficiencies.

The economic savings due to these reductions were calculated by taking into consideration avoided cost of treatment of the rinse water and avoided charges for water and sewer service. If implemented, the first modification would save the company \$3350 - \$2640 savings in treatment costs and \$710 in avoided water and sewer costs. The same figures for implementing the second modification would be \$3120 - \$2460 in treatment costs and \$660 in avoided water and sewer charges. Since no capital costs were incurred in making the changes, payback would be immediate.

## CONCLUSION

In the first project, the waste reducing capabilities of two simple rinsing modifications were demonstrated at a Minneapolis area printed circuit board manufacturer. The no cost, low technology changes made were 1) slowing the withdrawal rate of racks containing the printed circuit boards as they were pulled from an etchant process tank and an electroless copper process tank and 2) combining an intermediate withdrawal rate with a longer drain time over the process tanks. Both modifications significantly reduced drag out of concentrated copper containing bath solutions into the rinse water systems.

## PROJECT 2

### PROCEDURE

The second project took place at a flexible circuits manufacturer which employed approximately 1800 and had annual sales of \$92 million in 1989. Two technologies were tested for their ability to reduce waste: 1) soft absorbent polyvinyl alcohol (PVA) rollers replacing hard rubber squeegees to reduce drag out in a horizontal cleaning operation and 2) adding a conductivity activated flow controller to reduce rinse water in a tin lead plating line. The company had identified the cleaning operation and the tin lead line as its largest waste generators and the areas it believed offered the largest potential for waste reduction. Waste streams from both lines were treated on site by lime precipitation, sludge pressing and drying and off site sludge disposal as hazardous waste. Treated waste water was discharged to sewer.

Initial testing was conducted in May, 1991. While testing was completed for the conductivity flow controller evaluation at that time, the company continues to monitor the cleaning line to determine sponge roller effects on cleaning bath life.

The PVA "sponge" type rollers were tested for drag out reduction at an acid cleaning tank which was part of a larger cleaning operation that removed oil, grease, and chromate conversion coating from flexible copper sheets in preparation for the application of photoresist. In testing the sponge rollers, baseline samples taken over a two hour period included enough sample sets to provide 10 drag out values. During baseline testing the line was operated using the hard rubber squeegees that come as standard equipment with the cleaning units. Next, for the evaluation phase, the squeegees were removed and replaced with PVA sponge rollers. Sampling again was performed over a two hour period to provide 10 sets of samples for drag out calculation. Samples were analyzed for copper concentration as an indicator of drag out. In both baseline and evaluation sampling, flexible circuit throughput was also tracked to enable a drag out per square foot calculation.

In the second evaluation at the flexible circuits manufacturer, a conductivity sensor and flow controller were installed at a tin lead plating line to reduce rinse water flow from the triple countercurrent rinse system. Before installation of the flow controller, baseline flow was measured using a totalizing flow meter at the influent line to the rinse system. Flows were recorded every 8 hours for a one week period; conductivity was also recorded over this period to help establish a set point for the conductivity flow controller.

After baseline sampling, a conductivity sensor was installed in the final rinse tank and connected to a controller. The controller was set to activate a valve at the rinse water influent line when the sensor reached the set point of 30 mS. When conductivity reached this level in rinse water, the valve opened and allowed rinse water to flow to the rinse tanks. The 30mS level was chosen as the approximate median level of the conductivity readings found during baseline testing. The company believed this to be a conservative estimate for the contamination that could be tolerated by the system and still maintain effective rinsing. Again during evaluation, flow was recorded every 8 hours over a one week operating period. During baseline and evaluation monitoring, throughput of flexible boards was also tracked.

## RESULTS

Testing of the sponge rollers for drag out reduction at the cleaning line showed the sponge rollers to be successful in reducing drag out. Baseline testing of the hard rubber rollers determined that drag out was originally occurring at the rate of 27.6 ml/ft<sup>2</sup>. After installation of the sponge rollers drag out was reduced to 9.8 ml/ft<sup>2</sup>, a 64% reduction from baseline. Rinse water could be proportionately reduced without compromising rinsing efficiency.

While drag out, as measured by copper concentration in the bath and rinse tank following it, was reduced, the increased rate of copper build-up in the cleaning bath tank suggested that the tank would have to be replaced more frequently since the company used bath copper concentration as a measure of bath contamination and as an indicator for bath replacement. At present, the company is conducting a longer term study to determine the impact of the rollers on bath life. This information is critical to drawing a comparison between waste generated using hard rubber versus sponge squeegees. The economic evaluation will also have to await this information before the two can be compared.



For the other evaluation conducted at the flexible circuits manufacturer, baseline testing of the rinse flows to the tin lead line showed that 1.41 gallons/ft<sup>2</sup> of rinse water were used in the triple countercurrent rinse system before installation of the flow controller. After the conductivity sensor and flow controller were installed rinse water flow was reduced to 0.64 gallons/ft<sup>2</sup>, a reduction of 55%.

The economic analysis showed that this reduction in rinse water would save \$132/yr in avoided water and sewer utility charges and \$877/yr in avoided rinse water treatment costs. The total savings per year of \$877 divided into the \$500 installed cost of the flow controller/sensor combined with its \$50/yr operating cost, results in a payback of 7.5 months.

## CONCLUSION

The evaluation of the flow controller at the flexible circuits manufacturer clearly showed that waste could be reduced and savings achieved when used on a tin lead line rinse system. The results are not yet available for the sponge rollers installed at a cleaning line; although it reduced drag out significantly, the increased build up of copper in the cleaning bath required more frequent bath replacement. The company continues to monitor the change in bath life to provide a more complete picture of waste generated and associated costs before and after the change to sponge rollers.

EVALUATION OF EMULSION CLEANERS  
AT AIR FORCE PLANT NUMBER 6

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## INTRODUCTION

The evaluation of emulsion cleaners at Air Force Plant 6 project is an offshoot of the Waste Reduction Evaluation at Federal Sites (WREAFS) Program conducted within the Pollution Prevention Research Branch. The WREAFS program consists of a series of demonstration and evaluation projects for waste reduction conducted cooperatively by the U.S. Environmental Protection Agency (EPA) and various divisions of other federal agencies. The purpose of this project is to provide assistance to Air Force Plant 6 personnel by documenting the relevant work by other aircraft fabrication facilities to support comparison of cleaner qualification performance with trichloroethylene for the vapor degreaser operations at Air Force Plant 6.

## METHODOLOGY

Air Force Plant No. 6, located in Marietta, Georgia, is operated for the Air Force by Lockheed Aeronautical Systems Company. The facility is part of the Aeronautical Systems Division (ASD), whose headquarters is located at Wright-Patterson Air Force Base near Dayton, Ohio. There are six vapor degreaser units that utilize trichloroethylene (TCE) to prepare steel and aluminum parts for a variety of subsequent manufacturing steps in the production of C-130 aircraft.

Although the usage of trichloroethylene has decreased from 1.2 million pounds in 1988 to about 650,000 pounds in 1990, the decrease has been largely due to a diminishing workload at the plant. Lockheed Environmental Department and Materials and Processes Department staffs are interested in substitution of the current solvent with appropriate cleaners due to concerns about worker safety and health in addition to the environmental impacts of the current solvent. The eventual goal of the facility is to substitute water-soluble emulsion cleaners to obviate use of 650,000 pounds of TCE.

During the initial phases of this project, it was decided to investigate research conducted by other aircraft manufacturing entities prior to conducting full scale testing of a targeted list of cleaners. As a result of canvassing various businesses within the aircraft manufacturing industry, it was determined that a substantial amount of research was currently being conducted. The facilities conducting research were cooperative in sharing information and as a result, it was decided to document research currently being conducted and submit a report to Lockheed to use as a starting point for determining where to begin their research.

The information for this report was developed by documenting research performed by Boeing Aircraft, Air Force Engineering Service Center (AFESC), General Dynamics, Lockheed Missile and Space Company (LMSC), Martin Marietta and Northrop. This research information was particularly useful since Lockheed qualification criteria are based on Air Force (military specifications), Lockheed and Boeing tests. Lockheed currently conducts significant subcontractor work for Boeing. Also, data and information for the report was accumulated from emulsion cleaner manufacturers/suppliers and an international workshop on solvent substitution.

#### Boeing Aircraft

Boeing Aircraft Corporation has been investigating the replacement of solvent and vapor degreasing processes for the past three years. Specifically, Boeing has ongoing research efforts with requirements similar to Air Force Plant 6 at three locations. Boeing is evaluating cleaners at its Wichita, Puget Sound, and Kent Space Center facilities in actual shop trials. Shop trials are pilot programs designed to evaluate the performance of a given solvent during actual production. The Puget Sound plant manufactures commercial aircraft; the other two facilities are strictly involved in military aircraft production. The Boeing site that offers data most relevant to the Plant 6 program is located at the Kent Space Center.

#### Air Force Engineering Service Center (AFESC)

AFESC has been active in solvent substitution over the past several years. One of their projects is substitution of cleaners with biodegradable solvents. This project was conducted in three phases. During Phase I, nearly 200 companies were contacted and 185 different solvents were obtained for testing. These tests looked at biodegradability, ability to dissolve soils, cleaning efficiency, and corrosiveness (if able to pass the other three). From these tests, the most promising were identified for further testing in Phase II.

During Phase II testing, solvents were subjected to extensive performance testing at the field test facility at Tinker AFB, Oklahoma. AFESC evaluated enhancement methods (ultrasonic and mixer agitation at various temperatures) on a revised list of solvents which originated in Phase I. Phase III tests evaluated solvents during implementation. The cleaners evaluated in Phase III were the same cleaners evaluated in Phase II.

The U.S. DoE is sponsoring continuation work. They are working on a related project which will study solvents and their ability to clean approximately 20 different "soils" (this term is used to refer to any processing contaminant that must be removed from a part surface). These tests will focus on performance and corrosion rather than biodegradability. Once the most promising cleaners are identified, additional tests will be performed for recyclability and VOC emissions. It is hoped that the information from the earlier report can complement this report in order to form a comprehensive database on solvents.

#### General Dynamics

Of the research efforts investigated for this study, General Dynamics is the most comprehensive program. The program is being conducted at the Fort Worth Division and is currently in shop trial. The program initially evaluated 40 cleaners and screened to five cleaners. One of the five cleaners was eliminated due to corrosion test concerns. The four remaining candidate cleaners were optimized with General Dynamics' input. One product is compatible with the solvent regeneration process in use at General Dynamics and is currently being used in the shop trial program.

### Lockheed Missile and Space Company (LMSC)

LMSC staff have been involved in evaluating non-hazardous cleaners since August 1989. Their goal has been to find suitable replacements for 1,1,1-trichloroethane (TCA) used in vapor degreasers. The LMSC program seeks to replace all TCA used in a variety of processes throughout their facility. Cleaning performance, compared with TCA, as well as the etching and corrosion effects on magnesium and aluminum surfaces were evaluated.

### Martin Marietta

Martin Marietta staff in Denver have completed an aggressive solvent substitution program that sought to replace TCA. Numerous tests were performed on cleaners to clean aluminum soiled with fish oil, mineral oil, glycerine, machining oil, layout dye, and aluminum mill stamps.

### Northrop

Northrop used a different strategy for evaluating cleaners: they simply told the manufacturers to send them their best formula with instructions for use and the product would either pass or fail. No experimentation or cleaning optimization was attempted.

## RESULTS

The final report has been compiled for this project. The report contains information on the evaluation of various substitute cleaners on the conformance of the emulsion cleaners to be implemented at Air Force Plant No. 6 with specific qualification test criteria. The document contains the specifications for qualification tests in 17 areas. The 17 test areas are:

- |  |                        |
|--|------------------------|
| • pH                                   | • Etching              |
| • Corrosiveness                        | • Sandwich corrosion   |
| • Cleaning                             | • Intergranular Attack |
| • Corrosion between<br>faying surfaces | • Corrosion Resistance |
| • Foaming                              | • Paint Adhesion       |
| • Effect on Cd plated<br>surfaces      | • Sulfur               |
| • Effect on Adhesion                   | • Phosphates           |
| • Water break-free                     | • Chromates            |
| • Visual                               |                        |

It also contains a list of ten cleaners that were targeted for evaluation. Table 1 presents a summary of the cleaners evaluated by the various organizations in the determination of a substitute for halogenated solvents. This table provides information on what cleaner(s) were tested. It also provides the reason why a cleaner was disqualified from further testing and which cleaners are currently being investigated in pilot tests. Although in most cases the companies conducting the research sought to replace TCA, the industrial processes are analogous to those conducted at Air Force Plant 6.

TABLE 1. SUMMARY OF CLEANER SUBSTITUTES EVALUATED BY VARIOUS ORGANIZATIONS

	Boeing	AFESC	General Dynamics	LMSC	Martin Marietta	Northrop
* Grace Duraclean 282	b		a	b	c	
* Turco 6778		d				
* Turco 4215 NCLT			b			a(3)
* Turco 3878					a	
* Blue Gold		d		b		
* Brulin 815 GD	b	d	b	a(1)		b
* Hurri-Klean		d				
* Quaker 624 GD			b	a	a	b
* Polychem 2000						
* Novamex						
* Rochester-Midland (Biogenic SE373)	b	d	a			
Bioact EC7					a(2)	
Simple Green					a	
Coors Bio T					a(2)	
Oakite Inproclean 2500				a(4)		
3D Supreme	d	a				
RB Degreaser	d					

\* Lockheed Air Force Plant 6 target cleaners

- a - Evaluated
- b - Selected for implementation or further evaluation
- c - Implemented
- d - To be evaluated

Eliminated due to:

- (1) Phosphates
- (2) Flammability concerns
- (3) Not easily recyclable
- (4) Unacceptable etching of magnesium substrate

The document concludes with a chart that compares the performance criteria of the various companies to the criteria required by Lockheed.

## CONCLUSIONS

EPA is continuing to work in cooperation with Lockheed Aeronautical Systems Company-Georgia and Air Force Aeronautical Systems Division to investigate the potential for implementing emulsion cleaners as a replacement for trichloroethylene (TCE). The substitution of emulsion cleaners for TCE is currently being implemented at Air Force Plant No. 6. Lockheed has selected cleaner Brulin 815 GD from this report for pilot testing. As a follow-up to successful pilot testing, further testing is planned in 800 gallon and 3400 gallon tanks respectively. Lockheed is providing funding for the pilot testing.

It is anticipated that this substitution will function as a degreasing solvent as well as an alkaline cleaner. It will reduce tankage and eliminate or reduce substantially the use of chlorinated solvents at Air Force Plant 6. EPA will be cooperating with Lockheed and Air Force personnel to document the successes, problems and costs associated with the change. The results can then be transferred to similar facilities in the Department of Defense or the Department of Energy, and can serve to expedite the use of emulsion cleaners at other facilities.

EVALUATION OF FILTRATION AND DISTILLATION  
METHODS FOR RECYCLING AUTOMOTIVE COOLANT

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## INTRODUCTION

Government regulations and high waste disposal cost of spent automotive coolant have driven the vehicle maintenance industry to explore on-site recycling. The USEPA in cooperation with the New Jersey Department of Environmental Protection (NJDEP) and the New Jersey Department of Transportation (NJDOT) evaluated two commercially available technologies that have potential for reducing the volume of spent automotive coolant. The objective of this study was to evaluate the quality of the recycled coolant, the pollution prevention potential, and the economic feasibility of the technologies.

## METHODOLOGY

Engine coolants are intended to provide protection against boiling, freezing, and corrosion. Through use, the coolants lose some measure of these functions because of accumulation of contaminants and the depletion of additives such as corrosion inhibitors and anti-foam agents. The recycling process attempts to restore the functions of the coolants to standards specified in ASTM D 3306-89 and SAE J1034 (for automotive coolants) and ASTM D 4985 and SAE J1941 (for heavy-duty coolants).

The first technology involved chemical filtration to recycle spent coolant and was manufactured by FPPF Chemical Co. This technology consisted of two separate units; a fleet size unit that operates on up to 100 gal of stored spent coolant and a smaller portable unit that operates on a per vehicle basis and does not require prior collection and storage. The process for both units is similar. The stored spent coolant is drawn into a 100 gal plastic holding tank from which it is circulated through filters, aerated to form oxides of dissolved metals, and refiltered. The coolant pH is measured after initial filtration and compared to a chart that shows how much additive is needed to raise the pH to 9.5. The high pH helps to reduce the corrosivity of the coolant. In addition to raising the pH, the hydroxide portion of the additive precipitates soluble metals which are continuously filtered out. The additive also contains a blend of inhibitors, polymers, and surfactants to improve coolant quality. Following pH adjustment, the freezing point of the coolant is checked with a hand-held refractometer. A chart tells the operator how much virgin coolant must be added to achieve a freezing point of -34 F or lower. The portable unit had an ion exchange column to further reduce metals.

Primary batches of spent coolant (as received) were run through the fleet-size unit and portable unit. The primary batches represented stored spent coolant from the automotive and heavy-duty vehicles operated by NJDOT. Three "spiked" (altered spent coolant) batches were also run. The purpose of these salts- and acid-spiked batches was to create exaggerated conditions to test the limits of the recycling process. A blank, consisting of virgin coolant and tap water, was run through the fleet-size unit. Samples of the spent, virgin, and recycled coolant were collected for analysis.

The second technology evaluated was one of distillation to recover automotive and heavy duty engine coolant. This coolant recycling unit was manufactured by Finish Thompson, Inc (FTI). The unit operates on up to 15 gallons of spent coolant per batch. Spent coolant is poured into the distillation still along with an additive to control boiling. The unit is switched on and allowed to operate until water and ethylene glycol are distilled off into two separate clean drums outside the unit. This may take about 12 to 15 hours for a full 15-gallon load of spent coolant depending upon the amount of water present. Water distills out first at atmospheric pressure into the processed water drum. As the temperature rises, the vacuum pump switches on automatically and starts drawing out the glycol. The vapors are condensed by using tap water as the heat exchanger fluid or by using an optional chiller. The condensate enters the primer tank, where it mixes with the primer (ethylene glycol) and overflows into the processed glycol drum. The processed glycol and processed water can then be mixed in equal proportions. Three gallons of distillation residue collects at the bottom of the still and is emptied out, typically after five batches. Primary and spiked batches of spent coolant, similar to those run on the filtration units, were also tested on this distillation unit.

## RESULTS

In this study, results of the analyses were compared against ASTM and/or SAE standards. After recycling with the filtration unit, the boiling and freezing points of the coolant were brought as close to standard as possible through use of the hand-held refractometer and alteration of the glycol-to-water ratio. None of the recycled samples from the primary batches met the corrosion standards as measured by the ASTM D 1384 and D 4340 tests. The spiked recycled samples, however, met the corrosion standards for the ASTM D 1384 test. This variation may be because the amount of corrosion inhibitor added is based on the pH of the spent coolant. Since the acid-spiked samples had lower pHs, adding more corrosion inhibitor to the coolant resulted in better corrosion resistance.

The spent and recycled coolants from the filtration units were characterized chemically and levels of contaminants, such as metals, chlorides, oil and grease, etc., were measured to determine if these constituents affected performance. After recycling, although levels of chlorides and sulfates were not noticeably reduced in the coolant, the level of metals was considerably reduced. This retention of chlorides and sulfates in the recycled coolant may contribute to corrosion.

After recycling with the distillation unit, freezing point was measured by a hand-held refractometer and the ratio of processed water to processed glycol was adjusted to meet freezing point specifications. The freezing and boiling points were in agreement with the recommended standard. Both pH and corrosivity of the recycled coolant were also within specified limits. Corrosivity was measured in terms of the weight loss of metal test specimens exposed to the coolant for two weeks. The recycling process was able to restore the spent coolant to within specifications as compared to the ASTM D 3306 standard. The aluminum corrosion test (ASTM D 4340) was also run. This test evaluates the effectiveness of recycled coolant to inhibit corrosion of cast aluminum alloys under heat transfer conditions. This test is important because of the growing usage of aluminum instead of cast iron in automotive engines. The batches were recycled to within the acceptable standard for this test.



The spent and recycled coolants were characterized chemically and contaminant levels were also measured to determine if these constituents affected performance. The levels of calcium, magnesium, iron, and zinc were reduced considerably in the recycled coolant. Changes in levels of lead and aluminum were hard to estimate due to low analytical recoveries and low starting levels of these metals in the spent coolant.

For both filtration and distillation, the pollution prevention potential was measured in terms of the volume and hazard reduction. Volume reduction addresses gross wastestreams ( i.e. spent coolant, filters). Hazard reduction involves individual pollutants( i.e. ethylene glycol, heavy metals ) contained in the wastestreams. The estimate of the amount of coolant that NJDOT disposes of annually was based on the amount of new coolant that NJDOT uses annually decreased by 10% to account for the environmental loss of coolant through leaks in the vehicles cooling systems. Because the coolant is recycled rather than disposed of , the volume reduction was calculated to be 8,812 gals. The volume of sidestreams generated for disposal during recycling for filtration (e.g. filters) and distillation ( e.g. residue ) were approximately equal.

For filtration, the economic evaluation took into account the capital and operating costs of the recycling equipment as well as the savings provided by decreasing the amount of raw materials (virgin coolant, water) and reducing disposal costs. Because of the relatively high price of virgin coolant and the high volume of virgin coolant purchased by NJDOT, the recycling process was found to have a payback period of less than one year. This is assuming that the filtration unit is able to produce coolant that meets quality standards.

For distillation, the economic evaluation also took into account the capital and operating costs of the recycling equipment as well as the savings provided by decreasing the needed amount of raw materials ( virgin coolant and water) and by reducing disposal costs. The purchase price of the recycling unit at the time of this evaluation was \$ 5,115. Due to the relatively high price of virgin coolant and high volume of virgin coolant purchased by NJDOT, the payback period was much less than one year. The payback varies depending on the amount of spent coolant generated annually by the user. For example, if a generator purchases 100 gals of coolant annually, the recycling unit may not be economical. A slightly larger generator, with 500 gal/yr of purchased coolant, would have a payback period of approximately seven(7) years. The payback improves as the amount of coolant purchased becomes larger.

## CONCLUSION

Although recycling by filtration has great waste reduction and economic potential, the filtration unit evaluated in this study would require additional improvements to ensure an acceptable quality of the recycled product. Some possible areas of improvement are adjusting the method of determining the amount of additive used and implementing a means of anion ( chlorides and sulfates, etc. ) removal such as ion exchange.

The distillation evaluation also shows good waste reduction and economic potential. The NJDOT facility could potentially reduce waste from over 8000 gals to approximately 400 gal/yr. The recycled product in the distillation evaluation also fared very well in the selected ASTM performance tests and the chemical characterization analyses. Boiling point, freezing point, pH, and corrosion resistance function of the coolant were restored to specifications. Metals, salts, and organic contaminants were also removed.

Several automotive and heavy-duty engine manufacturers are also beginning to evaluate

recycling. Such studies involve relatively expensive testing which may be costly for small repair shops to conduct on their own. Some repair shops have already undertaken recycling based on information provided by vendors to address the increasing cost of disposal. But in general, initial reaction to recycling coolants in the automotive industry has been cautious, given the demanding nature of the application.

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## THE USE OF HYDRAULIC FRACTURING TO ENHANCE IN SITU BIOREMEDIATION

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### INTRODUCTION

Bioremediation was determined to be a viable method of degrading the hydrocarbon contaminants at a fuel distribution and storage facility in Dayton, Ohio. Laboratory tests done by the on-site contractor indicated that percolating water containing oxygen and nutrients through the soil would result in biodegradation of the contaminants. The site is underlain by silty clay till of relatively low hydraulic conductivity, so conventional methods of delivery were expected to result in either slow rates of percolation, and thus slow rates of remediation, or excessive drilling costs. Therefore, the site was selected as a candidate for hydraulic fracturing, a technique of creating high permeability channel ways in tight soils.

### METHODOLOGY

The site was divided into two areas: one to be treated by using hydraulic fracturing (HF) and the other to be treated using a conventional well (CW). The same injection fluid was to be introduced into each. The two areas were sampled at the beginning of the project then again during treatment.

Hydraulic fractures were created by injecting cross-linked gel at a constant rate into a lance-like device composed of a casing and an inner rod, both of which are tipped at one end with a hardened cutting surfaces that form a conical point. A drive head at one end of the lance secures both the casing and the rod. Individual segments of the rod and casing are 1.5 m long and they are threaded together as required by the borehole depth.

During the field work, the lance was driven to depths of as much as 4 meters. The rod and point were removed, leaving soil exposed at the bottom of the casing. Another device composed of steel tubing with a narrow orifice at one end, was inserted into the casing. Water pumped into the device formed a jet that cut laterally into the soil. The jetting device was rotated, producing a disc-shaped notch extending 10 to 15 cm away from the borehole. A simple measuring apparatus, built from a steel tape extending the length of the tube and making a right angle bend at the end of the tube, was inserted into the casing to verify and measure the radius of the slot.

Hydraulic fractures were created by injecting the cross-linked guar gum gel into the casing. Injection rates of 60 to 90 liters per minute were used for the tests. Lateral pressure of the soil on the outer wall of the casing effectively sealed the casing and prevented leakage of the slurry. The fractures nucleated at the notch and grew away from the borehole.

During a typical procedure to create the fractures, the onset of pumping was marked by a sharp increase in pressure of the injection fluid to between 200 and 350 kPa (30 and 50 psi). This onset of fracture propagation, however, was marked by an abrupt decrease in pressure, with pressures in the range of 70 to 170 kPa (10 to 25 psi) during propagation. After one fracture was created, the rod and point were inserted and the lance driven to a greater depth where another fracture was formed.

The conventional well was created by drilling a 10 cm borehole to a depth of 4 m. This hole was filled with sand to a depth of 1.5 meter, a half inch PVC pipe was inserted, then sealed in place by filling the rest of the borehole with bentonite.

The week after the fractures were created, continuous split spoon samples were taken to determine the location of the hydraulic fractures, to determine the soil stratigraphy and to study the chemical and microbial conditions in the soil. The borings were made at radial distances of 1.5, 3.2, and 5 meters with respect to the fractured and unfractured wells. Samples for BETX (benzene, ethyl benzene, toluene and xylene) were taken directly from the split-spoon and placed in 300 ml of methanol. The remaining sample was sealed in ziplock bags and placed in iced coolers for analysis of TPH (total petroleum hydrocarbons), moisture, and pH in the lab.

Microbial populations were determined by aseptically removing 1 gram samples, sonicating to release the organisms from the soil, then plating on R2A medium incubated at 29°C. To determine the number of gasoline degrading microorganisms in 1 gram, the samples were plated on non-nutritive salts medium and the plates incubated at room temperature in a gasoline-fume atmosphere. Microbial activity was determined by monitoring the hydrolysis of fluorescein diacetate (FDA). Fluorescein diacetate was dissolved in acetone at a concentration of 2 mg/ml. One gram of soil plus 0.5 ml of the FDA solution were added to 100 ml of 60 mM phosphate buffer (pH7.6). These were incubated on a shaker at 12°C for 24 hrs. The cultures are centrifuged, then filtered and the color development measured at 490 nm.

Water containing oxygen and nutrients is currently being injected into the wells. The flow rates and pressures are being monitored. At 8 week intervals the site is resampled for chemical, physical and microbial conditions.

## RESULTS

Four hydraulic fractures were created in the contaminated area (HF). The depth of each fracture was 2.3 m (HF2.3), 2.6 m (HF2.6), 3.2 m (HF3.2), and 4 m (HF4). We have estimated the general geometry along cross-sections through HF (Figure 1). The fractures appear to be roughly flat-lying to gently dipping toward the parent borehole. The uppermost fractures at HF appear to have the steepest dip, roughly 30°, as it climbs from the parent borehole to the ground surface north of the borehole. The other three fractures at HF dip from approximately 30° within 1.5 m of the borehole, but then flatten to dips of 10° to 15° at greater distances on the northern side of the borehole. None of the deeper fractures reached the ground surface. Two fractures were discovered 3.2 m south of HF and they were inferred to be the lowest two fractures, as shown on the cross-section. The geometry of the fractures is locally inconclusive due to lack of recovery.

Creating the fractures produced broad domes at the surface, with maximum displacements of 12 to 23 mm, over areas roughly 9 to 14 m in maximum dimension. Most of the domes are roughly equant in plan, although the point of maximum uplift is almost always at a point other than the point of injection. As a result, the fractures appear to be asymmetric with respect to the points of injection.

The results of the chemical, physical and microbiological analyses of the initial soil condition are complete. The contaminant concentrations at the site were nonuniform but the whole area was

contaminated. For example, benzene ranged from a maximum of about 14 ppm to a minimum of 1 ppm. Ethyl benzene ranged from 40 ppm to about 1 ppm. The pH of the soil was between 7.2 and 8. Starting soil moistures are in the range of 9 to 16%. The number of gasoline degrading and heterotrophic microbes ranged between  $10^4$  and  $10^5$  CFU (colony forming units)/ gram soil.

## CONCLUSIONS

Hydraulic fracturing was shown to be a feasible procedure at this contaminated site. The size and shape of the fractures were as planned. Enough information was gathered at the site in the initial assessment to evaluate the post treatment effects of the hydrofracturing as compared to a conventional injection well arrangement. The site conditions make it conducive to bioremediation (e. g. pH about neutral, significant hydrocarbon degrading microbial population). Significant progress is expected in the coming months and an update will be given at the meeting.

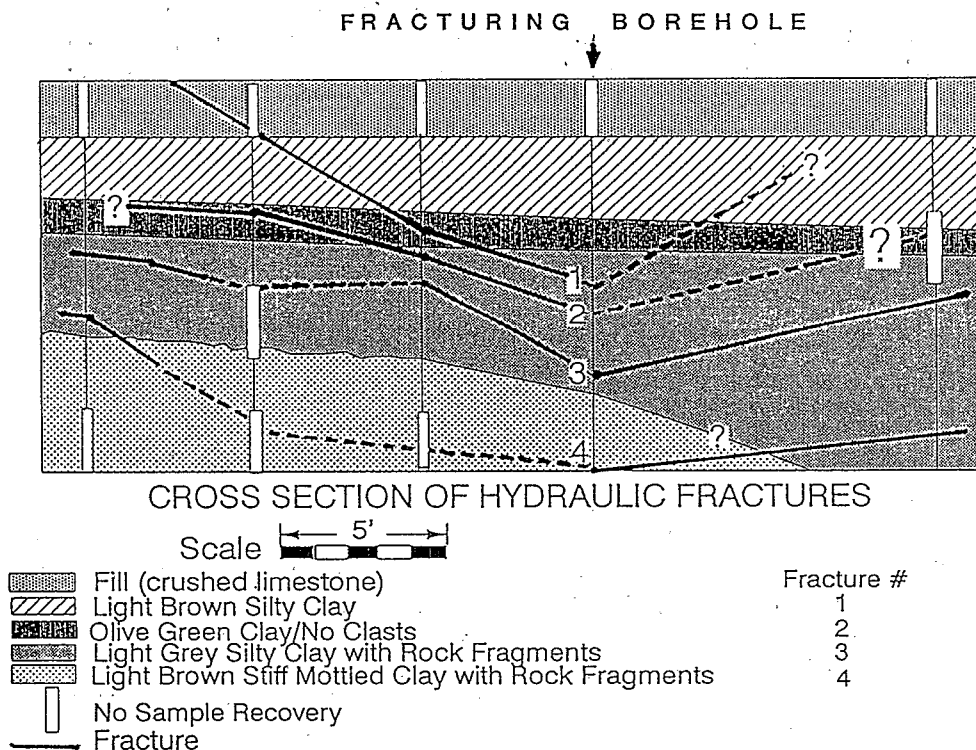


Figure 1. Cross section showing stratigraphy and hydraulic fractures in the HF treatment area.

## IN SITU TREATMENT OF SOIL CONTAMINATED WITH PAHs AND PHENOLS

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### INTRODUCTION

The wood preserving industry uses more pesticides than any other industry worldwide (1). The major chemicals used are creosote, pentachlorophenol, and CCA (copper, chrome and arsenate). It is reported that between 415 to 550 creosoting operations within the United States consume approximately 454,000 metric tons of creosote annually. When properly used and disposed off, creosote does not appear to significantly threaten human health. However, due to improper disposal and spillage at old facilities, creosote and other wood preserving chemicals have found their way into surface soils. Active wood preserving sites generate an estimated 840 to 1530 dry metric tons of hazardous contaminated sludge annually, which is classified as KO01.

Creosote, obtained from coal tar, contains a large number of chemical components. The three main families of compounds represented in creosote are: polycyclic aromatic hydrocarbons (PAH), phenolic, and heterocyclic compounds. Creosote is composed of approximately 85% PAHs, 10% phenolic compounds and 5% heterocyclic compounds. There are approximately a total of 17 PAHs present in creosote. The four most prominent compounds belonging to the PAH family are naphthalene, 2-methylnaphthalene, phenanthrene, and anthracene. These four compounds represent approximately 52% of the total PAHs present in creosote. There are approximately 12 different phenolic compounds present in creosote among which phenol is the most abundant, representing 20% of the total phenolics. In addition, the various isomers of cresol represent about 30% and pentachlorophenol (PCP) represents 10% of the total phenolics. There are approximately 13 different heterocyclic compounds present in creosote. Among these the nitrogen containing compounds are the most abundant, representing approximately 70% of the total heterocyclics. The balance is distributed between sulfur and oxygen containing heterocyclics.

All of these compounds possess toxic properties and some of them, for example, PCP, when subjected to high temperature environments are suspected precursors in the formation of dioxins.

In this paper the results of an ongoing, USEPA funded, cooperative agreement are described. The purpose of this project is to determine the treatability conditions for the removal of wood preserving contaminants present in soil by in situ thermal treatment. The goal was to find appropriate time and temperature conditions for the treatment of soils by the in situ radio frequency (RF) soil decontamination process. The in situ RF heating process utilizes electromagnetic energy in the radio frequency band to heat up the soil rapidly, uniformly, and without injection of heat transfer media or on site combustion. The in situ RF process can be used to heat the soil to a temperature range of 150°-200°C. The contaminants are vaporized and or boiled out along with water vapor formed by the boiling of native soil moisture. The gases and vapors formed upon heating the soil are recovered for on site treatment by means of a gas collection system.

The feasibility of the in situ RF soil decontamination process was first demonstrated for petroleum hydrocarbons at a site of a jet fuel spill (2). In this field experiment approximately 500 cu. ft. of sandy soil was heated to a temperature range of 150-160° C. It was demonstrated that 94 to 99 percent of the aliphatic and aromatic hydrocarbons present in the spill site were removed (2). In various other laboratory feasibility studies, the treatment conditions for the removal of the following contaminants has been established: perchloroethylene and chlorobenzene from sandy soil (3), jet fuel from clayey soil (4), PCBs from sandy/clayey soils (3), phenanthrene, pentachlorophenol and phenol from sandy/clayey soils (5). All of these studies except the one with jet fuel were done with clean soils which were spiked with the contaminants in the laboratory. In this paper we present the results of feasibility studies performed with contaminated soil obtained from a wood preservative site.

#### METHODOLOGY

Full Scale Implementation: The RF soil decontamination process is a two-step process which operate simultaneously once the average temperature of the soil exceeds 50° C. These steps are: heating of the soil, and vaporization and recovery of the contaminants.

In the first step of the process, the soil is heated to temperatures of 150° to 200° C by means of an electrode array inserted in bore holes drilled through the soil. Selected electrodes are specially designed to permit both the application of RF power while collecting vapors by application of a vacuum down hole. The vapor collection system is an integral part of the electrode array since vapor collection points are physically integrated and embedded in the array. A vapor containment barrier is used to prevent fugitive emissions, and provide thermal insulation to prevent excessive cooling of the near surface zones.

Prior laboratory and field experiments (2-5) have shown that high boiling contaminants can be boiled out of the soil at much lower temperatures than their actual boiling point. This occurs due to the presence of an autogenously established steam sweep which helps to improve the rate of vaporization of such high boiling materials. Another phenomenon which operates during in situ heating is the development of effective permeability to gas flow. The increase in permeability is confined to the heated zone, thus creating a preferred path of gas and vapor flow towards the soil surface.

The second step of the process is the collection, recovery, and on-site treatment of the vapors and gases formed by heating of the soil. The collected waste gases are transported to an on-site treatment system. The first vapor treatment step is cooling and condensation of the vapors from the gas stream. The uncondensed gases are further treated to remove contaminants. This treatment may consist of carbon adsorption, combustion in a gas-fired afterburner, and/or gas scrubbing in an alkaline scrubber. The specific gas treatment steps used depend upon the nature and amount of contaminants expected in the gas stream.

The liquid phase is separated on site into two fractions: the aqueous phase and the organic phase. The aqueous phase is treated on site through a carbon bed and a filter. The organic phase is stored, pending ultimate destruction at an approved treatment facility.

Treatability Study: The soil treatability experiments were performed by heating a 3-ft column of soil packed into a 1.5 in. diameter, 4-ft long stainless steel pipe. The pipe was connected at the top via heat traced tubing to a glass water-cooled condenser. The outlet of the condenser was connected to a vacuum flask which was pre-charged with 50 to 70 mL of methanol. The side-leg of the vacuum flask was connected to a wet-test meter. The flask was kept in an ice bath.

The bottom port of the reactor was connected to a source of heated nitrogen or superheated steam. Zero grade nitrogen was obtained from a cylinder, heated through a heat traced line and delivered at the base of the soil column. When steam was needed, a three-way valve was used to pump water into the heat traced line. The water was pumped by a positive displacement metering pump, capable of delivering 0 to 10 mL/min. The temperature of both nitrogen and steam was adjusted to approximately match the average temperature of the soil in the reactor. The soil column was heated by externally wrapped heating tapes. Both internal and external thermocouples were used to make sure that the soil was at the desired temperature.

The results of the treatability experiment were determined by analyzing and comparing the results of soil samples taken while the reactor was being packed and of treated soil removed from the reactor at the end of an experiment. The variables being studied in these experiments are the treatment temperature, time, flow rate of steam, type of flowing fluid sweep, viz., nitrogen versus steam and type of soil matrix (field soil versus Standard Analytical Reference Matrix or SARM I soil as prepared by EPA). In selected experiments mass balance will be made by analyzing the aqueous condensate phase collected in the water cooled condenser.

TABLE 1. EXPERIMENTAL CONDITIONS

	Experiment No.				
	1	2	3	4	5
Soil type	Field	Field	Field	Field	Field
Soil weight, g.	1620	1685	1772	1748	1689
Contaminants spiked	-	Aroclor 1242	Aroclor 1242	Aroclor 1242	Aroclor 1242
Treatment temp., °c	200	200	230	200	200
Treatment time at temp., hrs.	23	70	70	70	71
Sweep Gas					
Type	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>
Flow rate, L/min	0.60	0.63	0.56	0.58	0.51
Time, hrs.	22	24	12	8	8
Type	H <sub>2</sub> O(v)	H <sub>2</sub> O(v)	H <sub>2</sub> O(v)	H <sub>2</sub> O(v)	H <sub>2</sub> O(v)
Flow rate, L/min*	1.0	0.50	0.30	0.16	0.17
Time, hrs.	20	70	63	68	66

\* at treatment temperature

The experimental conditions for five experiments are summarized in Table 1 (additional experiments are underway). All experiments were performed with



soil obtained from the wood treatment site. In experiments 2 to 5, Aroclor 1242 was spiked on the soil to determine the removal efficiency of PCB by the in situ process.

## RESULTS

TABLE 2. REMOVAL DATA FOR PAH AND PHENOLIC COMPOUNDS

Analyte	Boil- ing Point °C	Melt- ing Point °C	Percentage Removal Experiment No.				
			1	2	3	4	5
Treatment Temperature, ° C			200	200	230	200	200
Treatment Time at temp., hr			23	70	70	70	71
Acenaphthalene	278	95	53	100	100	84	95
Acenaphthene	278	95	100	-	100	100	100
Fluorene	294	115	100	100	100	100	-
Pentachlorophenol	309	189	100	100	100	100	100
Phenanthrene	340	100	41	-	73	74	81
Anthracene	342	218	66	100	64	84	68
Fluoranthene	393	111	69	-	90	88	78
Pyrene	393	156	69	100	94	89	77
Benzoanthracene	439		13	17	45	60	40
Chrysene	448	254	10	25	60	46	43
Benzo(b)fluoranthene			0	6	45	12	16
Benzo(k)fluoranthene			5	10	48	21	21
Benzo(a)pyrene	495	196	15	23	43	34	31
Indenopyrene			3	8	20	34	23
Dibenzo(a,h)anthracene	524	266	8	-28	15	35	17
Benzo(g,h,i)perylene	>500	278	2	7	19	30	22

The results of experiments 1 to 5 are summarized in Table 2. In this table the percentage removal for PAHs and PCP is presented. The results show that treatment at a temperature of 200 to 230° C for a period of 70 hr. is sufficient to remove the PCP and the three ring PAHs to their analytical detection limit. Thus nearly 100 percent removal of these compounds from the soil can be achieved. High removal efficiency was also obtained for pyrene, a four-ring PAH. All of these compounds have a normal boiling point less than 400° C. For other compounds with higher boiling points and having four or more rings, the removal efficiency was lower. In experiments 2 through 5, Aroclor 1242 was spiked into the soil. The initial concentration of Aroclor was 1078, 1150, 1240, in experiments 2 to 4, respectively. The final Aroclor

concentration in the soil from these three experiments was 48, 14, and 34 ppm. Thus the average removal of the Aroclor in the three experiments was 95.6, 98.8 and 97.3 percent. Thus treatment at 230° C can reduce the PCB concentration below 25 ppm. Additional analyses of the condensate are being performed to close the mass balance for the PAHs, PCP and the Aroclor. More experiments are being done on SARM-I soil to provide comparative data for the standardized soil.

## CONCLUSION

The results of the treatability experiments performed have shown that heating of soil to a temperature range of 200° to 230° C is sufficient to remove PCP and all the four-ring PAHs with boiling point of less than 400° C. As before, it was again demonstrated that it is not necessary to heat the soil to the boiling point of the pure component in order to obtain substantial removal from soil. The results have also demonstrated the feasibility of the removal of Aroclor 1242 from soil in the temperature range of 200-230° C.

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## LONG-TERM DURABILITY OF SOLIDIFIED/STABILIZED MATERIALS

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### INTRODUCTION

One of the major concerns with the solidification/stabilization (S/S) process for final containment of hazardous wastes or other leachable materials is the uncertainty relative to long term stability of the material in the environment, where it will be exposed to many influences which may cause deterioration. The potential for and degree of weathering needs to be evaluated.

This research addresses the potential weathering of waste forms and the effects of aging and weathering on leaching from these waste forms. The overall objectives of this research are to assess the long-term durability of stabilized/solidified wastes from Superfund sites and to verify existing durability/leaching models. Specific objectives include the development of accelerated aging and weathering tests for determining long-term durability, evaluating the influence of wet/dry cycling on durability and leaching characteristics, evaluating the influence of waste form cracking on sample porosity and permeability, and use of the results obtained to validate existing durability and leaching models.

### METHODOLOGY

The stabilized/solidified waste samples were prepared from sludges containing .02 M concentrations of lead nitrate, sodium arsenite and cadmium nitrate with a water/binder ratio of 0.7. The sludge was solidified with different waste-binder ratios of portland cement, lime/flyash, and kiln dust using ASTM C-109 into 3" diam x 6" cylinders, 2" x 2" x 2" cubes, and 3" diam x 1" disks and cured for 28 days. These samples were then aged in weathering chambers, which allow specimens to be exposed to static conditions (elevated temperatures and/or pressures and/or submersions) and recirculating sprays for simulated times of 20, 50, and 100 years. The set of control samples (not aged) and the test samples (aged) were then tested for porosity, permeability, leach tested (TCLP, ANSI 16.1, and Sequential Leaching), wet/dry cycles, unconfined compressive strength, and acid weathering.

Stabilized/solidified samples were subjected to Arrhenius aging techniques to accelerate the aging process. Accelerated aging refers to accelerating the conditions a treated waste will experience during the aging process. Many environmental factors may affect a material over its lifetime, such as changes due to wet/dry, wind and rain erosion and weathering or erosion due to groundwater action. The procedure developed for artificially aging the waste forms is based on the Arrhenius model. The equivalent age function is based on the activation energy of the material.

The age function, known as the Arrhenius equation is:

$$\frac{t_s}{t_a} = \exp \left[ \left( \frac{E_a}{k} \right) \left( \frac{1}{T_s} - \frac{1}{T_a} \right) \right]$$

where:

$t_s$  = service time  
 $t_a$  = accelerated time  
 $E_a$  = activation energy  
 $k$  = Boltzman's constant  
 $T_s$  = service temperature  
 $T_a$  = accelerated temperature

This formula provides a means for determining the equivalent age (service time,  $t_s$ ) a specimen would experience at a given natural temperature (service temperature,  $T_s$ ). These times and temperatures are modelled as accelerated temperature ( $T_a$ ) for a given accelerated time ( $t_a$ ) for the material specific activation energy ( $E_a$ ).

In this research, Thermogravimetric Analysis (TGA) was used to determine the waste specific kinetic parameters for the Arrhenius aging equation. Thermogravimetry measures the weight changes in a sample as a function of temperature or time. The mode of thermogravimetry used for this study is known as dynamic thermogravimetry, in which different sample types were heated in an environment whose temperature changed in a pre-determined manner at a linear rate. The resulting mass change versus temperature curve provided information concerning the thermal stability and composition of the sample. This information was then used to determine kinetic parameters of the material, specifically the activation energy.

Cement-based immobilization systems rely heavily on pH control for stabilization of metal contaminants. Over time, acid in leachants in contact with the waste form will penetrate the specimen and gradually leach waste matrix materials and metals into the surrounding environment. An intensive study was undertaken to identify the leaching mechanisms involved by evaluating the pH profiles within leached specimens and the physical and chemical properties of the leached material. The pH profile along the acid penetration route in the cement-based waste forms was identified by splitting the samples and applying various pH color indicators. The effect of acid attack on density and porosity changes and pore size distribution was also studied.

Monolithic and crushed test specimens which have been subjected to accelerated aging procedures

based on the Arrhenius model were acid weathered using a leachant with an acidity comparable to that expected to be encountered by the waste form over the period of time simulated by the aging process. The monoliths were suspended in an extractor at a 10:1 (g leachant/sq cm monolith surface area) ratio for 48 hours. Crushed samples were extracted for 48 hours at a 20:1 (W/W) leachant: solid ratio. Aged samples were analyzed for leaching depth, leached zone porosity and wet/dry resistance, and the leachate is analyzed for contaminants. The resulting samples, which simulate aged and weathered waste forms, were then subjected to various leaching tests, including the TCLP and the ANSI 16.1 test to determine whether the aged specimens leach differently than control samples.

The possibility of leaching hazardous substances from solidified wastes in land disposal sites is increased if the solidified monolith is fractured during weathering. It is, therefore, desirable to determine if the monolith fractures during weathering and, if it is fractured, what is the extent of fracture. The method used to determine the amount of surface fracture was laser holographic interferometry. Holograms were made by recording a diffraction grating on a photographic plate. The interference of a reference beam and an object beam created by a laser beam created the fringe patterns on the photographic plate. Cracks were seen in the hologram as a discontinuity in the fringe pattern. The object(sample), optics, and plates were placed on an isolation table consisting of a 3000 pound granite table top. Epoxy dye injection was used to determine the inner fractures and cracks.

Another technique used to evaluate deterioration of solidified wastes include resonance frequency and pulse velocity. This was done in collaboration with the Department of Energy (DOE) to evaluate this technique for assessing waste form durability. The evaluation of this parameter required the determination of the natural frequency of the specimens after each aging cycle. In resonance frequency testing a sample was excited by the application of an ultrasonic wave generator. The frequency of the waves was varied until the specimen vibrated in a resonant mode. As specimens sustain damage, the resonant frequency changes and this change can be used to assess the damage.

## RESULTS

Thermogravimetric Analysis (TGA) was run on pieces from three crushed cylinders of waste forms made from a sludge containing lead nitrate, sodium arsenite and cadmium nitrate. Each sample was analyzed under different physical conditions (small solidified pieces or as powder); under different moisture conditions (saturation, air-dried, dried at 60° C and dried at 110° C); and for four different temperature ramps from 2° C/min to 16° C/min, in order to investigate the effect that the physical properties of the samples exhibited on the resulting TGA analysis.

Using the Arrhenius Equation and the kinetic parameters determined from the TGA data, an accelerated aging schedule was developed. The Arrhenius equation uses the activation energy ( $E_a$ ) found from the TGA, Boltzman's constant ( $k$ ), and a given accelerated operating temperature ( $T_a$ ) for the aging chambers. The service time ( $t_s$ ) was chosen to model two different times in the future, 50 and 100 years. The service temperature to be modelled was taken from the average temperature in the greater Cincinnati area over the last 100 years ( $T_s = 54.6^\circ \text{F}$ ).

The time of contact of a waste form with leachant could significantly alter the potential for leaching because it results in increased porosity and creation of a chemically altered surface layer. The pH in the surface altered layer was found to vary from 5.0 to 6.0, which is very close to the pH in the bulk

leachate. A reacting zone, where the pH abruptly changed from 6 to 12, sharply divided the altered surface layer from the remaining unleached waste form or "kernel". The reacting zone was white in color and was about 100 microns in width for the samples with 0.6 water-cement ratio leached in 0.4 N acetic acid solution for a total period of 29 days (Figure 1). SEM/EDX analysis indicated that in the surface layer, most of the calcium and the stabilized metals were removed by the leachants. The metal contents of the kernel, however, were very close to those of the original material. It was believed that the leaching boundary was formed by the inward diffusion and reprecipitation of calcium hydroxide crystals in front of the acid.

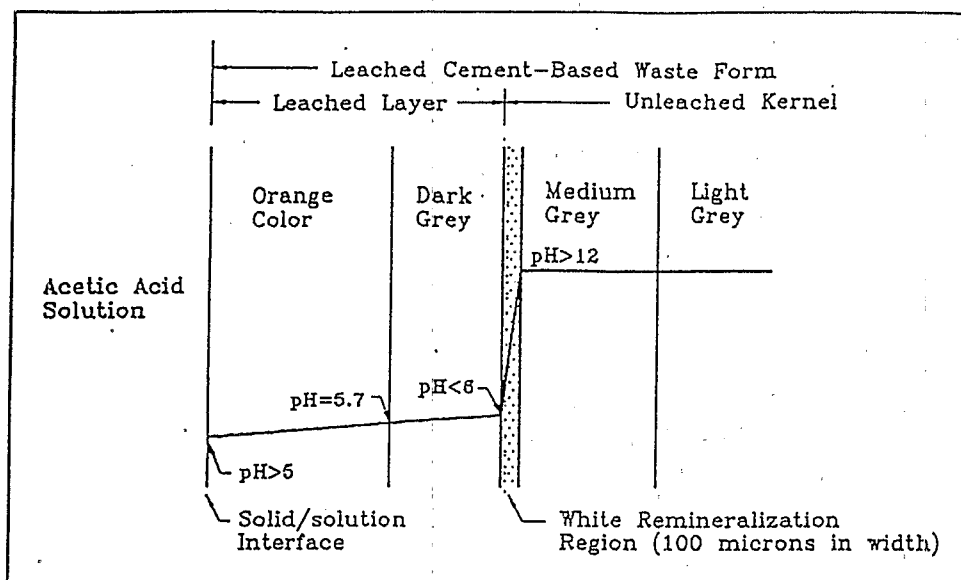


Figure 1. Schematic profile of a leached cement-based waste form.

The porosity of the kernel was essentially the same as for the unleached controls, but the porosity of the leached layer increased significantly. The pore distribution in the kernel was the same as in the unleached samples, but the leached zone was significantly different. The gel porosity of the leached layers increased greatly due to the dissolution of calcium silicate hydrate matrix.

The leaching of metals was controlled by the acidity available in the leachant. Dissolution of alkaline materials left a silica-rich layer on the surface of the cement-based waste form. This surface layer exhibited different properties than those of the unleached material. The surface layer had a higher water content, was lighter weight, and was soft and friable. Furthermore, the abundant silicate content on the solid surface detained a portion of the leached metals, while they moved through the leached layer into bulk solution. The leaching mechanisms of metals was idealized as five steps: (1) mass transfer of acids from bulk liquid to solid surface, (2) transport of acids through leached layer, (3) diffusion-controlled fast dissolution reactions at leaching boundary, (4) transport of metals through leached layer, and (5) mass transfer of metals from solid surface into bulk liquid.

## CONCLUSION

The leaching of metals is a consequence of acid penetration. The distance from the solid/solution interface to the front of the leaching boundary can be regarded as the depth of the leaching zone, where the metals dissolve and diffuse out of the waste form.

The position of the leached layer can be predicted by knowing three measurable factors- the acidity consumed in the leachant, leach time, and the buffering capacity of the waste form. By knowing the leachable fraction of metal contaminant, the total amount of metal leached can be estimated from the thickness of the leached layer.

These studies have shown that leaching is directly correlated to the amount of acid in contact with the waste form, and that the leaching front moves progressively into the sample rather than being diffused throughout the waste form depth. Further studies indicate that the amount and extent of leaching is essentially the same for samples exposed to a weak acidic leachant over a long time period as for a strongly acid leachant over a short time interval. Thus, the effect of acid leaching over a 50 or 100 year period can be simulated by using proper strength acid leachant, equivalent to that specimen would see over the exposure period.

Sample porosity and pore size distribution is very important in determining the degree of leaching that will occur in a waste, since leaching is largely controlled by the amount of available surface area. A study conducted on solidified/stabilized fly ash and flue gas desulfurization (FGD) sludge wastes showed that acetic acid leaching increases pore volumes and pore sizes. It was found that pore structures varied depending upon the wastes used and the solidification mix formulations tested. The higher the alkalinity in a sample, the greater the change of pore structure due to leaching. Changes in pore structure were primarily due to leaching of calcium hydroxide, resulting from the attack of hydrogen ions in the leachant. These findings essentially coincide with the porosity results for the metal sludge used in this project.

Future work will include the testing of radioactive/mixed waste samples obtained from DOE for utilization in the weathering chambers. Many ideas about optimum S/S techniques have originated from actual laboratory investigations and use of chemical and physical tests, but there has never been a concrete relation between field leachate quality and laboratory leachate quality. The application of leach tests in conjunction with weathering and aging techniques on field waste samples will provide valuable data on existing short-term laboratory tests. This will aid in devising better techniques for making predictions on the long-term durability of S/S waste forms.

## METALS PARTITIONING RESULTING FROM ROTARY KILN INCINERATION OF HAZARDOUS WASTE

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### INTRODUCTION

In response to the need for data on the partitioning of trace metals from hazardous waste incinerators, an extensive series of tests was conducted in the summer of 1991 at the USEPA Incineration Research Facility (IRF) in Jefferson, Arkansas. These tests were conducted in the IRF's rotary kiln incinerator system (RKS) equipped with a pilot-scale Calvert Flux-Force/Condensation scrubber as the primary air pollution control system (APCS). The purpose of this test series was to extend the data base on trace metal partitioning and to investigate the effects of variations in incinerator operation on metal partitioning. Another objective was to evaluate the effectiveness of the scrubber for collecting flue gas metals. This series is a continuation of an ongoing IRF research program investigating trace metal partitioning and APCS collection efficiencies. Two previous test series were conducted using the RKS equipped with a venturi/packed-column scrubber and a single-stage ionizing wet scrubber.

The primary objective of this test series was to determine the fate of six hazardous and four nonhazardous trace metals fed to the RKS in a synthetic, organic-contaminated solid waste matrix. The six hazardous trace metals used were arsenic, barium, cadmium, chromium, mercury, and lead. The four nonhazardous trace metals--bismuth, copper, magnesium, and strontium--were included primarily to supply data to evaluate their potential for use as surrogates. The test variables were kiln exit gas temperature, waste feed chlorine content, and scrubber pressure drop. The test program objectives were to identify

- The partitioning of metals among kiln ash, scrubber liquor, and flue gas,
- Changes in metal partitioning related to variations in kiln exit gas temperature and waste feed chlorine content,
- The efficiency of the Calvert scrubber for collecting flue gas metals, and
- The effects of scrubber pressure drop on metal collection efficiencies.

### METHODOLOGY

The IRF RKS consists of a rotary kiln primary combustion chamber, a transition section, and a fired afterburner chamber. The refractory lined kiln is 2.5 m long with an internal diameter of 1.0 m. The afterburner chamber is also lined with refractory and measures 3.0 m long by 0.9 m in diameter. For these tests, both the kiln and afterburner were fired on natural gas. Total heat input to the kiln varied with test conditions, ranging from 200 to 580 kW (0.7 to 2.0 MMBtu/hr). Calculated gas-phase residence time through the kiln and afterburner sections averaged 2.3 seconds.

The main components of the Calvert scrubber APCS used during these tests were the condenser/absorber, Calvert Collision Scrubber,<sup>™</sup> entrainment separator, wet electrostatic precipitator,



caustic tank and injection pump, and variable-speed induced draft fan. A schematic of the scrubber system is shown in Figure 1. In its normal configuration the Calvert scrubber pilot plant also includes a quencher/saturator and a cooling tower. However, these components were not used for this test program because their functions were equivalently met by the existing RKS spray quench and closed-loop heat exchanger.

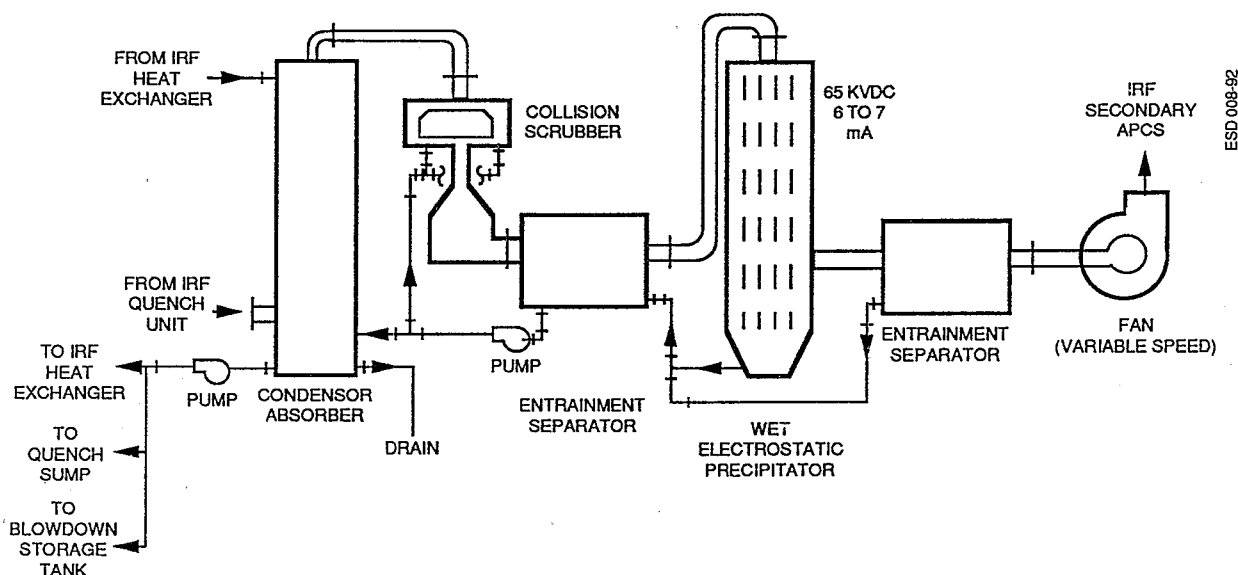


Figure 1. Schematic of the Calvert scrubber system.

The combustion gas exiting the afterburner was saturated and cooled by the IRF spray quench to approximately 82°C (180°F), then directed to the Calvert scrubber system. The first component of the Calvert scrubber is the condenser/absorber, which is designed to sub-cool the flue gas to about 50°C (122°F) and to scrub acid gases. The condenser/absorber is followed by the Collision Scrubber™. The Collision Scrubber™ splits the flue gas into two streams then uses a head-on collision to create fine droplets and a large surface area to enhance the removal of particulate and remaining acid gases as the flue gas passes through the venturi. The pressure drop through the scrubber is controlled through the use of a variable speed induced draft fan, which provides an operating range of 7.4 to 17.4 kPa (30 to 70 in WC). A three-stage entrainment separator follows the Collision Scrubber™. For this test series, Calvert Environmental installed a down-flow, tube type wet electrostatic precipitator with an entrainment separator between the first entrainment separator and the induced draft fan. Scrubber liquor collected in the sump of the condenser/absorber was pumped to either the IRF heat exchanger or quench system recirculation tank.

The synthetic waste fired throughout the test program consisted of a mixture of organic liquids added to a clay absorbent material. The base solid material was a calcined clay sold commercially as a granular absorbent for spill cleanup. The main components of the clay are hydrated aluminum-magnesium silicate, free silica, dolomite, and calcite. The organic liquid base for the synthetic waste consisted of toluene with varying amounts of tetrachloroethene and chlorobenzene added to provide a range of synthetic waste chlorine contents. Waste chlorine content in the combined feed was varied from zero (no chlorinated organics added) to nominally four percent. After mixing, the clay/organic mixture remained a free flowing solid, similar to the unspiked clay absorbent. The synthetic waste was continuously fed to the rotary kiln via a screw feeder at a nominal rate of 63 kg/hr (140 lb/hr) of which approximately 14 kg/hr (30 lb/hr) was the organic liquid matrix. For all tests, the kiln rotation rate was held constant to provide a solids residence time of about an hour.

All trace metals of interest, except chromium and magnesium, were fed to the kiln by metering an aqueous spike solution of the metals into the clay/organic liquid mixture at the screw feeder, just prior to feed introduction to the kiln. The test metals were added to the spiking solution as soluble nitrate salts, with the exception of arsenic which was added as  $\text{As}_2\text{O}_3$ . The spike solution was metered at a rate that produced the following nominal synthetic waste feed concentrations in mg/kg: As-35; Ba-420; Bi-400; Cd-20; Cu-425; Pb-50; Hg-5; Sr-430. Chromium and magnesium are native to the clay absorbent at concentrations of about 50 mg/kg and 2 percent, respectively, and so were not spiked.

The test variables were kiln exit gas temperature, chlorine content of the synthetic waste feed, and Calvert scrubber pressure drop. The test program consisted of 11 test points, with each parameter varied over three levels. Achieved conditions for the test variables are shown in Table 1. Target kiln exit gas temperatures were 538°, 816°, and 927°C (1000°, 1500°, and 1700°F). Target feed chlorine concentrations were 0, 1, and 4 percent. The scrubber pressure drop for Tests 1 through 9 was held nominally constant at 12.4 kPa (50 in WC). Test points 10 and 11 were at the same nominal conditions as test point 8, but with scrubber pressure drops of 8.7 and 17.4 kPa (35 and 70 in WC), respectively. All tests were performed at the same nominal afterburner exit flue gas  $\text{O}_2$  (9 percent) and afterburner exit temperature (1093°C (2000°F)). Excess air in the kiln varied with temperature, with measured  $\text{O}_2$  levels at the kiln exit ranging from 10.6 to 17.7 percent.

TABLE 1. TEST CONDITIONS

Test	Date	Average Kiln Exit		Waste Feed Chlorine Content (%)	Scrubber Pressure Drop	
		Gas Temperature (°C)	(°F)		(kPa)	(in WC)
1	6/5/91	541	1,006	0.0	12.9	52
2	6/6/91	819	1,507	0.0	12.4	50
3	6/13/91	909	1,669	0.0	12.4	50
4	6/18/91	555	1,031	0.6	12.4	50
5	6/19/91	842	1,547	0.6	12.4	50
6	6/21/91	919	1,686	0.8	12.4	50
7	6/25/91	543	1,010	3.6	12.4	50
8	6/28/91	817	1,502	3.4	12.4	50
9	7/9/91	944	1,731	3.1	12.2	49
10	7/11/91	829	1,524	2.3	8.2	33
11	7/16/91	827	1,521	3.4	16.9	68

The sampling and analysis protocols were designed to track the partitioning of the test metals among the RKS discharge streams (incinerator ash, scrubber liquor, and flue gas). For each test, composite samples of the clay/organic liquid mixture, aqueous metals spike solution, kiln ash, and scrubber liquor were collected. The feedrates and total quantity fed of the clay/organic liquid mixture and the metals spike solution were carefully noted. Kiln ash weights and scrubber liquor volumes were also determined for each test. The flue gas was sampled for metals at the quench and scrubber system exits using a Method 101A train for mercury and a Method 5 train modified for multiple metals capture for the remaining metals.

Sample preparation and analysis methods documented in EPA SW-846 were used for most samples. The digestion and analysis of samples for mercury were in accordance with the procedures of Method 7470 for liquid samples and Method 7471 for solid samples, with analysis by cold vapor atomic absorption spectroscopy. Solid samples analyzed for the remaining test metals were digested following the procedures of ASTM Method E886, Method A. The samples were fused in a flux containing a 4 to 1

ratio of lithium metaborate and lithium tetraborate, followed by a final dissolution of the melt in dilute HCl. The liquid samples were prepared for metals analysis in accordance with the procedures of Method 3010. Metals analysis was primarily by ICAP spectroscopy in accordance with the procedures of Method 6010, although graphite furnace atomic absorption spectroscopy in accordance with Methods 7060 and 7000 were used to analyze most samples for arsenic and bismuth, respectively.

## RESULTS

Note: At the time this abstract was prepared, the only laboratory data received were for samples analyzed for mercury. However, it is anticipated that data on the remaining metals will be received in time for presentation at the symposium.

Table 2 summarizes the mercury partitioning as a percent of the mercury fed. For all tests mercury concentrations in the kiln ash were below detection limits of 0.1 mg/kg. This is expected based on mercury's high vapor pressure. Table 2 shows that mercury recovery in the flue gas at the quench exit ranged from 17 to 113 percent of the mercury fed, averaging 66 percent. It is interesting to note that although the recovery of mercury in the quench flue gas was good, the downstream recovery in the scrubber liquor and scrubber exit flue gas was much lower. An explanation for this observation is provided by Figure 2, which shows the mercury partitioning to the scrubber liquor as a function of the waste feed chlorine content. For the three tests with no chlorine in the waste feed, mercury concentrations in the scrubber liquor were reported below detection limits of 0.004 mg/L. With increased feed chlorine content to about 0.6 percent, mercury partitioning to the liquor increased to about 7 percent of the mercury fed. Mercury partitioning to the liquor increased to approximately 30 percent with a further increase in waste feed chlorine content to about 3.5 percent. In the case of no chlorine in the waste feed, mercury is expected to be found in the flue gas in its elemental form or as mercuric oxide. Both are practically insoluble in water, but would still be expected to be scrubbed from the flue gas at the low temperatures reached in the Calvert scrubber. However, once collected in the

TABLE 2. MERCURY PARTITIONING AND SCRUBBER COLLECTION EFFICIENCIES

Test	Mercury Partitioning (% of mercury fed)					Mass Balance Closure (%) *		
	Waste Feed Chlorine Content (%)	Quench Exit Kiln Ash	Scrubber Exit Flue Gas	Scrubber Exit Flue Gas	Scrubber Liquor	Around Kiln Ash and Quench Exit Flue Gas	Around Kiln Ash and Scrubber Discharges	Calvert Scrubber Collection Efficiency (%)
1	0.0	< 2.9	112.7	< 1.4	< 1.8	115.6	6.1	> 99
2	0.0	< 1.2	23.0	0.6	< 1.3	24.2	3.1	97
3	0.0	< 0.9	16.8	3.9	< 1.0	17.7	5.8	77
4	0.6	NA <sup>+</sup>	93.8	5.6	5.2	93.8	10.8	94
5	0.6	< 1.0	67.8	25.6	6.8	68.8	33.4	62
6	0.8	< 1.0	86.5	10.4	9.9	87.5	21.3	88
7	3.6	< 1.0	69.2	28.7	30.2	70.2	59.9	59
8	3.4	< 0.8	NA	NA	29.3	NA	NA	NA
9	3.1	< 1.1	NA	NA	29.3	NA	NA	NA
10	2.3	< 1.2	77.0	32.5	34.9	78.2	68.6	58
11	3.4	< 1.1	75.1	15.0	15.4	76.2	31.5	80

\* Calculated as a percent of mercury fed using detection limit values for samples reported below detection limits.

+ NA - Data not available.

scrubber liquor, these insoluble forms of mercury likely settled to the bottom of the liquor storage tank and were not collected when the liquor sample was taken, even though the storage tank was mixed before the sample was collected. For the tests with chlorine in the feed, mercuric chloride may have formed in the flue gas. Mercuric chloride is soluble in water and is more likely to be collected during sampling of the scrubber liquor. The scrubber liquor partitioning data further suggests that the conversion to mercuric chloride was directly related to the amount of chlorine available.

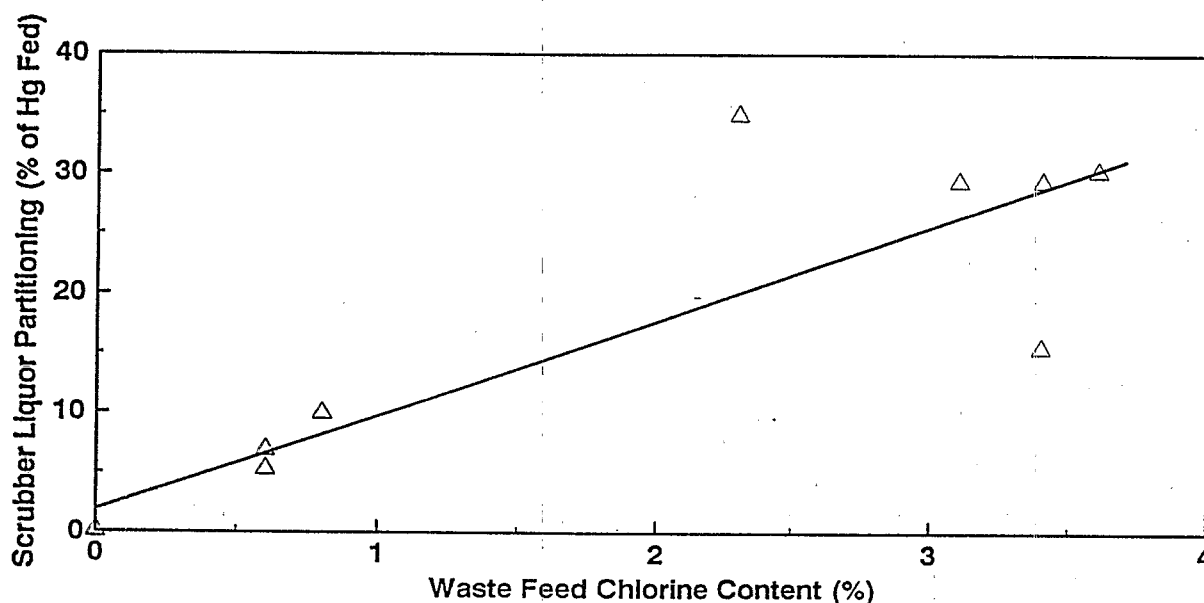


Figure 2. Mercury partitioning to the scrubber liquor versus waste feed chlorine content.

Table 2 also shows the efficiency of the Calvert scrubber for removing mercury from the flue gas. Scrubber efficiencies were determined by comparing the emission rate of mercury measured at the exit of the quench and at the exit of the Calvert scrubber system. Thus, no credit is given for removal by the quench. Collection efficiencies ranged from 58 to greater than 99 percent, averaging 79 percent. Comparing Tests 10 and 11 with the remaining tests shows no apparent relationship between scrubber pressure drop and collection efficiency over the range tested. Measured mercury flue gas concentrations ranged from 0.034 to 0.21 mg/dscm at the quench exit and from less than 0.001 to 0.028 mg/dscm at the scrubber exit.

## CONCLUSIONS

Although most of the metals data were not received from the laboratory in time for this abstract, the following conclusions can be made based on the mercury data received to date.

- As expected, mercury was volatile and was not found above detection limits in the kiln ash.
- The recovery of mercury in the scrubber liquor increased directly with increased chlorine content in the waste feed. Insoluble elemental mercury or mercuric oxide are the expected forms in the flue gas for the tests without chlorine, while the presence of soluble mercuric chloride is suspected in cases with chlorine present.
- Calvert scrubber collection efficiencies for mercury ranged from 58 to greater than 99 percent, averaging 79 percent. These efficiencies exclude any contribution by the quench for collecting mercury.

# **Engineering Analysis of Metals Emissions from Waste Incinerators Field Data**

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## **EXTENDED ABSTRACT**

Hazardous metals emitted from waste combustion devices pose a significant risk to human health. In recognition of this, EPA/RREL has initiated a study to collect and evaluate all possible metal emissions information from all combustion sources. This paper is a summary of this ongoing study.

The EPA has established risk-based limits on emissions of metals from waste combustion systems. These limits are established in the form of regulations for boilers and industrial furnaces firing hazardous waste and in the form of permitting guidelines for hazardous waste incinerators. The limits can be quite restrictive and can often be the limiting factor on the design of air pollution control devices for such facilities or on the types and quantities of wastes which can be burned. Over the past several years, a significant body of data has been accumulated on metals emissions from full scale waste combustion devices including:

- municipal solid waste incinerators,
- sewage sludge waste incinerators,
- hazardous waste incinerators,
- boilers and industrial furnaces,
- medical waste incinerators, and
- mixed waste incinerators.

In addition, a number of laboratory and pilot scale studies on metals emissions and control have been conducted. These data have been collected from tests with varying degrees of control, data quality, and completeness of reporting. Often there has been little attempt to analyze the data beyond the specific goals for which each test was conducted. Additionally, there have been few attempts to collate the data and analyze it as a single unit.

### **Scope and Advantages of this Study**

This presentation describes the analytical efforts of a project to assemble all available data on metals emissions from waste combustion devices into a single data base, and to analyze the data in an attempt to isolate and explain the fundamental parameters which control metals emissions from waste combustion devices. In particular, several concepts/questions based on fundamental mechanisms or on common observations of metals emissions from combustion systems are proposed and examined in light of the data:

- Does metals volatilization dominate partitioning ?
- Is volatilization controlled by combustion zone thermodynamic equilibrium ?
- Does the metal feed rate control metals emissions ?

- Does the air pollution control device determine emissions ?

Data and theory are analyzed and arguments are advanced to support and/or refute some of these concepts and their applications to metals behavior in waste combustion systems.

This analysis will help identify the factors which control metals emissions from waste combustion devices. Understanding of these factors and their implications will ultimately help the regulatory and permitting authorities to:

- set flexible testing procedures for facilities to show compliance with emission limits,
- determine reasonable default values for estimation of air pollution control device efficiency, and
- assess the maximum achievable control technology for metals emissions from waste combustion devices.

In addition, the analysis will help the designers and operators of waste combustion systems to minimize metals emissions.

### **Approach**

The approach is to apply the current understanding to develop hypotheses on metals behavior based on fundamental concepts and common observations. These hypotheses are then examined against data relating metals emissions to waste characteristics and design/operating parameters. The steps to this approach are:

- determine the fundamental concepts/questions of metals behavior that need to be investigated and correlated to data,
- gather data and develop a data base,
- analyze data in light of the fundamental concepts/questions proposed and link metals emissions data with theory,
- identify correlations with design and operating parameters, and
- draw conclusions from the analysis and provide recommendations for further work or testing improvements.

### **Availability and Assembly of Field Data**

A data base is being established through collection of experimental data and fundamental studies taken from various types of waste incinerators equipped with different types of air pollution control devices (APCDs) at various operating conditions. The database includes detailed information of each facility's hardware and operating parameters such as:

- size and type of incinerator,
- type of APCD,
- primary and secondary combustion zone temperatures,
- uncontrolled metals emissions,
- controlled metals emissions with detailed APCD operating parameters,
- feed rates of all wastes and metals,
- waste chlorine content, and
- other pertinent information.

The database allows the data to be easily retrieved and classified to aid comparison and analysis of the

behavior of metals and other pollutant emissions from various facilities under selected operating conditions.

## **Data Analysis**

This section presents the fundamental points of investigation in light of their relation to the engineering analysis of field test data. Discussion focuses on:

- Statement of the fundamental concept of metals behavior
- Theoretical background
- Results from the engineering analysis of field data
- Conclusions / recommendations

The key fundamental concepts will highlight what influences metals emissions in practical waste combustion systems. Therefore, to help set a base for a unified understanding of metals partitioning behavior in various types of incinerators, several concepts can be developed. Some detail of each concept follows.

### Importance of Volatilization

The influence of variation in volatilization temperature on the removal of metals from the bottom ash from field data is analyzed. Additional data are available for the impact of temperature on metals in kiln ash and fine particulates, and on the flyash enrichment of volatile metals. It is concluded that metals volatilization dominates partitioning. Notable exceptions are arsenic under certain conditions.

### Metals Emissions may be Predicted by Equilibrium Thermodynamics

If thermodynamic equilibrium is controlling, then important parameters may include:

- **Combustion zone temperature:** Temperature strongly influences the emissions of volatile metals.
- **Amount of chlorine in waste:** Chlorine in waste increases emissions of most metals.
- **Metals volatility:** Metals emissions are related to their volatility if the metals concentration in the combustion gas is the equilibrium saturated concentration. Data for the emission concentrations of some metals as a function of metals volatility ranking are available from trial burns of several hazardous waste facilities including Aptus, 3M, Bros, and DuPont.

Field data shows that trends in metals emissions are consistent with the assumption of combustion zone thermodynamic equilibrium. Effects of temperature and chlorine on metals emissions can also be thermodynamically predicted.

### Do Metals Feed Rates Control Metals Emissions ?

If a metal's concentration is undersaturated in the combustion gas, due to the vaporization of all of the metal fed to the combustor, then the metal's emission rate is dominated by the feed rate of the metal rather than its saturated concentration. Theoretical arguments and figures for the expected behavior of metals emission rates as a function of metals feed rates are discussed. A comparison plot, generated from field test data, for metals emission rates as a function of feed rates shows that metals

emissions are influenced by feed rates when all of the metal vaporizes (i.e., the metal is unsaturated in the combustion gas).

#### How Much are Metals Emissions Dictated by APCDs ?

There are several types of air pollution control devices (APCDs). Theoretical descriptions of key APCDs are discussed and field test data for control efficiencies of various types of APCDs are presented including:

- Particulate emissions from trial burns of several hazardous waste facilities with diverse APCDs including ESPs, baghouses, venturis, scrubbers, and HEPA filters.
- Metals control efficiencies from various APCDs installed at municipal waste incinerators.
- Scrubber efficiency versus volatility temperature of several metals in a rotary kiln.
- Venturi/packed bed scrubber control efficiency as a function of volatility temperature of various metals for data obtained from the Mobay/EPA trial burn test program, 1988.
- Baghouse control efficiency versus metals (ranked according to their volatility) from the Aptus/EPA trial burn test program, 1989.

In conclusion, analyses of the above mentioned data indicate that air pollution control devices dictate emissions.

#### **Recommendations for Necessary Work**

Remaining research issues include:

- Metals management requires more detailed understanding of the impact of systems design/operation and waste parameters on metals behavior.
- Important data gaps:
  1. Kinetics of metals transformation under conditions simulating waste combustion.
  2. Hexavalent chromium chemistry.
  3. Arsenic volatilization chemistry.
  4. Innovative techniques to change the size distribution of metals.
  5. Fragmentation and fly ash particle size and dependence on waste stream properties.
  6. Interactions of metals with Ca, Al, Si within burning beds of metal containing materials.
  7. Impact of physical/chemical of the waste on the behavior of metals.
  8. High temperature liquid metal viscosity.
  9. Monitoring strategies for fine particulate matter and metals emissions.
  10. Waste characterization techniques for metals behavior.

#### **Acknowledgement**

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EFFECT OF MUNICIPAL WASTE COMBUSTION ASH MONOFILL LEACHATE  
ON SELECTED CONTAINMENT BARRIER COMPONENTS

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## INTRODUCTION

This study was initiated to investigate the effects of municipal waste combustion (MWC) ash monofill leachate on lining components of an MWC monofill. This includes geosynthetic materials and natural clay (soil) liners. The ability of these materials to perform their design function for the life of the facility and post-closure period is best estimated through accelerated test methods described herein. The study consisted of two separate testing efforts, one aimed at evaluating selected natural clay linings and the other at evaluating selected geosynthetics. Both tests were performed using the same waste.

Leachate was collected from two sources, one considered modern, and the other considered older technology. Site A was a state-of-the-art MWC ash monofill leachate facility. This facility had a scrubber, and ash disposed of in the monofill contained bottom ash, fly ash, and scrubber residue. Site B was an older MWC ash monofill leachate facility. This facility did not have a scrubber. Ash disposed of in the monofill contained bottom ash and fly ash.

The following generic geomembrane types were selected at random to be tested: high-density polyethylene (HDPE), reinforced chlorosulfonated polyethylene (CSPE-R), and polyvinyl chloride (PVC). One filtration/separation geosynthetic was tested: a nonwoven polyester geotextile. Three compacted soils (Illinois, Lufkin, and Nacogdoches) were evaluated to determine their resistance to the two MWC ash leachates.

The chemical resistance of three types of geomembranes and a nonwoven polyester geotextile with samples of two MWC ash leachates was investigated in accordance with EPA Method 9090 and associated supplementary guidance by determining whether the analytical and physical properties of these materials were adversely affected by exposure to the two leachates. Analytical testing was performed to fingerprint the geomembranes and the geotextile so that the results of these compatibility studies could be used for comparison to help assess other geosynthetics that might be potential candidates for use in constructing lining systems for MWC ash monofills. In addition, a series of pouch tests was performed in which samples of the two leachates were sealed in the pouches prepared from the three respective geomembranes.

Part of the study was performed to determine any changes in the hydraulic conductivity of compacted soils exposed to MWC leachate. The purpose of this study was to determine if the selected compacted soils are chemically resistant to MWC ash leachate. Three compacted soils were evaluated to determine their resistance to two MWC ash leachates. Samples of the three soils were compacted to 90 percent of proctor compaction (ASTM D 693) in double-ring permeameters. The compacted soils were then permeated with water, followed by the MWC ash leachates, to determine the hydraulic conductivity of the soil.

The objectives of this study were: 1) to evaluate the hydraulic conductivity changes of MWC ash leachate on natural clay liners; 2) to provide study results to support requirements for lining MWC ash disposal facilities; and 3) to determine if high-salt content of MWC ash leachate will affect the permeability of natural clay liners; and 4) to determine the chemical resistance of geosynthetic products to the collected leachates.

## METHODOLOGY

A Sampling and Analysis Plan (SAP) was developed to establish procedures for obtaining samples of ash and leachate from two MWC facilities selected for this study. Leachate was collected from operating MWC facilities and their disposal monofills for use in conducting compatibility testing with geosynthetic materials, and natural clay liners.

The results of analyzing the leachate samples at the end of each exposure period show that the contents of the cells remained essentially constant throughout the exposures.

### Natural Lining Components

Permeability changes to clay soils upon exposure to the two ash leachates were assessed using SW 870's Appendix III C method, "Test Method for the Permeability of Compacted Clay Soils." Stainless steel double-ring permeameters were used to evaluate the compatibility of three compacted soils with two MWC ash leachates. Six samples of each of the soils were compacted to 90 percent of standard proctor compaction (ASTM D 693) in 15-cm permeameter molds.

The compatibility test involved determination of the hydraulic conductivity of the compacted soil to a standard leachate (0.005 N  $\text{CaSO}_4$ ) followed by one of the two MWC ash leachates. MWC ash leachates from Sites A and B were used in this study.

Compacted soil samples were prepared for hydraulic conductivity testing and their bulk density was estimated. A double-ring insert, filter, and insert guide were carefully lowered over permeameter molds until the inserts were firmly seated in the compacted soil samples. The base plate/mold assemblies were turned over and geotextile filter material was placed over each compacted soil surface. Water (0.005 N  $\text{CaSO}_4$  solution) was poured on each soil sample and a top plate was placed on each mold. Air pressure over the water was slowly increased until 3 to 5 psi was attained along with stable baseline hydraulic conductivities. The water was then removed from the surface of the soil samples and replaced with MWC ash leachate.

The pore volumes of leachate that passed through the soil samples and the time increments over which the leachate was collected were recorded for each compartment (inner and outer rings) of the double-ring permeameters. The collected data were used to calculate both the total pore volume of leachate that passed through each soil sample and the hydraulic conductivity of each sample.

Electrical conductivity (EC) was used as an index parameter to document the breakthrough of the leachate through the soil samples. Leachate that permeated the soil samples was collected and divided into two 15-mL aliquots. EC measurements were made of the saturated paste extract of each soil type, the water used in the study, and each of the MWC ash leachates.

## Geosynthetics

Tests were performed on the unexposed and exposed geomembranes. This testing protocol conformed to the testing requirements of Method 9090. U.S. EPA Method 9090, which was specifically designed to assess the chemical resistance of geomembranes and waste liquids, is divided into two parts; the first part deals with the exposure of geomembrane samples to a waste liquid, and the second part is concerned with the specific tests performed on the geomembranes before and after exposure. In this test, slab samples are immersed for up to 4 months at 23° and 50°C in a representative sample of the waste liquid or leachate that would be contained by the geomembrane. Analytical and physical tests are performed on the unexposed geomembranes for baseline data and on samples exposed to the waste liquid for 30, 60, 90, and 120 days.

Current U.S. EPA regulations require that all geosynthetics used in constructing a RCRA hazardous waste management facility must be tested for chemical resistance with the waste to be contained. Therefore, the U.S. EPA has proposed supplementary guidelines so that geosynthetics other than geomembranes can be tested in accordance with Method 9090. This guidance states that all geosynthetics are to be exposed under the conditions described in Method 9090.

The analytical properties and the extractables of the exposed samples were measured in duplicate for the unexposed geomembranes, but only single determinations were made of the volatiles contents. The volatiles and extractables were measured in accordance with Matrecon Test Methods 1 and 2. The tests indicate the type of leachate constituents that may have been absorbed by the geomembrane (i.e., volatile or nonvolatile constituents) and whether the leachate extracted components of the geomembrane compound such as plasticizers or antioxidants.

Integrity changes to geomembranes and a geosynthetic material were tested by exposing three geomembranes and one geosynthetic material to the two field-collected ash leachates. Standardized Method 9090 and current U.S. EPA guidance-specified test conditions were maintained; test criteria for assessing integrity changes specified in Method 9090 and U.S. EPA guidance were also utilized.

## RESULTS

### Natural Lining Components

The passage of more than two pore volumes of MWC ash leachate (from Sites A and B) through three compacted soil samples (Illinois, Lufkin, and Nacogdoches) showed no significant changes in hydraulic conductivity of these soils. Because the hydraulic conductivity values of the three soils to both MWC ash leachates did not significantly increase over the values to water, the soils were considered to be chemically resistant to both MWC ash leachates used in the study.

### Geosynthetics

The results of the chemical resistance test of the three geomembranes and the nonwoven polyester geotextile at both 23° and 50°C indicated that, within the 4 months of exposure to the two

MWC ash leachates, the changes in analytical and physical properties were comparatively small. The results for the HDPE geomembrane and the polyester geotextile indicate that neither of these materials were affected by the immersion and thus are considered to be chemically resistant to the two MWC ash leachates to which they were exposed. The CSPE-R geomembrane showed essentially no change in strength characteristics; however, the analytical properties which relate to the CSPE coatings showed slight increases in volatiles and weight and a decrease in extractables. The values of all three of these properties were continuing to change at the end of the 4 months of exposure. Also, there was a slight trend downward in ply adhesion. During the 4 months of exposure, the PVC geomembrane also exhibited little change in properties, indicating short-term compatibility. During the last 2 months of exposure, however, the PVC showed a trend that could indicate long-term lack of chemical resistance. To determine whether the trend is continuing, testing is underway with results expected in 1992.

The results for the CSPE-R geomembrane samples in each leachate indicate that the polyester fabric reinforcement maintained its strength during the 5 months of exposure and showed no trends toward change. The strength was judged by hydrostatic resistance, puncture resistance, and tensile properties. Thus, like the polyester geotextile, this fabric is considered to be chemically resistant to each of the MWC ash leachates. The CSPE coating showed slight effects of the immersion, however, and slight continuing trends in the analytical properties. For example, the results of testing the CSPE-R geomembrane showed that the geomembrane increased in weight (up to 7.4 percent), but that this increase resulted predominantly from water absorption. There were slight decreases in extractables, in the case of the slabs immersed at 50°C. Also, there was a slight decrease in the ply adhesion between the two layers of CSPE, which may reflect complete loss of adhesion to the fabric or some apparent loss caused by the stiffening of the CSPE-R as a result of crosslinking.

In the case of the HDPE geomembrane, there were slight increases in the values for tensile at yield, modulus of elasticity, tear strength, hydrostatic resistance, and hardness. These changes may probably be attributed to a slight increase in crystallinity and hardening of the HDPE geomembrane during the course of the exposure. There was also a trend toward a slight loss in weight during exposure, which may be a reflection of the extraction of the antioxidants from the HDPE compound.

During the 4 months of exposure to the two leachates, the PVC geomembrane samples showed an increase in volatiles contents, a decrease in weight, and signs of a slight loss of plasticizer, especially on exposure to the leachate with the higher concentration of salts. In physical properties, the tensile strength tended to decrease, and the elongation at break tended to increase. In stresses at 100 and 200 percent elongation, the trends for most of the samples were slightly downward, except during the last 2 months, when the trends were upward, as were the puncture and hydrostatic resistances. The hardness changes were small, but generally the trends were downward.

## CONCLUSIONS

Tests were conducted on selected natural and synthetic lining components involving exposure to specific collected MWC ash monofill leachate. Testing of natural lining components involved observations of hydraulic conductivity and electrical conductivity. Testing of the geosynthetics involved U. S. EPA Test Method 9090 with modifications where required. The results of the testing indicate that with proper engineering considerations, carefully selected materials can be expected to perform as designed.

These test results indicate a series of tests that are likely to be performed during the permitting and prior to construction of any waste disposal facility and are to be considered results specific to the two leachate samples and selected barrier components collected for the purposes of this study. No

inferences are to be made regarding the materials or procedures used herein regarding any other combination of lining materials or waste that is intended to be contained. Site specific testing and analyses are the only accurate way to determine lining component chemical resistance with the waste to be contained. The test methods used in this study are currently accepted methods of accelerating long-term exposure.

The intention of this study was to determine if existing lining technologies were capable of serving to contain MWC ash monofills. This study has determined that there are materials that do exist that proved their potential utility under these accelerated exposure testing scenarios, on two specific leachates. Soil, geosynthetic material and leachate quality variations preclude the authors from extrapolating any chemical resistance issues beyond the components and procedures discussed in the study and project final report.

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# SOLIDIFICATION/STABILIZATION FOR LEAD BATTERY SITE A TWO STAGE PROGRAM

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## Extended Abstract

### INTRODUCTION

Solidification/Stabilization (S/S) technology uses binders added to hazardous waste such as contaminated soil to accomplish two goals:

1. to render the toxic metal in the soil insoluble (stabilize) and
2. to develop physical strength for handling and disposal (solidify).

The binders contain a net alkalinity which resists leaching by acidic TCLP (EPA SW846, Method 3811) solutions and also react to form hydraulic binding constituents. The two goals are not necessarily synonymous however. Some solidifiers do not stabilize and some stable systems are soil like or even slurries. For disposal in land fills, both properties are desirable. The goal of this project was to collect data on these properties to support S/S as a Best Demonstrated Available Technology (BDAT) for soils contaminated by lead. This abstract is a partial summary of the on site engineering report (1).

This project consisted of two stages. Both stages are presented here chronologically since they were not planned together but do depend on each other. Both stages subjected a soil typical of lead battery sites to a spectrum of carefully designed S/S recipes. These recipes used only generic binder systems. The primary target for the project was to attain TCLP lead concentrations below 5 mg/l, and a secondary target was a minimum unconfined compressive strength (UCS) of 345 kPa (50 psi).

### Site And Soil Characteristics

The site chosen to supply the waste was a battery breaking site in Pennsylvania. This choice was made because the primary contaminant was lead, the site was accessible, and contamination from organic wastes was a minimum. Four samples were taken. Results of an on site survey with a field x-ray spectrophotometer indicated that two samples would contain over 20,000 ppm lead and the other two would contain a little less than 10,000 ppm lead. The composite was expected to fall in the range of 15,000 to 20,000 ppm lead. All soil was screened on site to pass a 3/8-inch sieve to omit battery pieces, and the appearance of the soil was a dark damp silty-clay-peat.

Analyses of the untreated soil after compositing of the four samples showed the following:

1. Metals analysis of solids
  - Iron 21000 ppm
  - Lead 21000 ppm
  - Aluminum 6700 ppm
  - All others below 1000 ppm

2. TCLP: elements failing Toxicity Characteristics level

Lead: 91 mg/l, limit: 5 mg/l

3. Total Organic Carbon: 170,000 ppm

4. Moisture: 27.7%

5. pH: 4.3

#### METHODOLOGY I

We have previously demonstrated a method to design S/S recipes that will pass the TCLP test (2). The objective of this method is to create conditions at the end of the TCLP test which minimize the solubility of lead. Lead exhibits minimum solubility at about pH 8 to 10. To attain this desired pH at the end of the TCLP test, the indigenous alkalinity of contaminated soils needs to be augmented by the amount that will neutralize the acid specified by the TCLP plus enough to raise the pH to 8 to 10. We have previously developed a laboratory procedure to measure the acid neutralization capacity of solids (3). This test has been used to determine the acid neutralization capacity of several binders (4). These binder values have been previously used in a procedure to select types and amounts of binders for treating a lead contaminated soil at a battery disposal site (5).

In this project three binder types were selected:

1. all portland cement- has a dependable chemistry and high alkalinity
2. 3 parts Type F fly ash to 2 parts quicklime- minimum weight of alkaline binder
3. 2 parts cement kiln dust to 1 part Type F fly ash- both waste products having low cost

The mix design plots of pH versus acid reactant added allow prediction of one mix design for minimum lead in TCLP leachate and another for minimum binder added to pass the TC list limit. These two criteria lead to the following recipes:

mix # 1. 16% portland cement- minimum cement level

2. 20% portland cement- minimum lead in leachate
3. 8.5% quicklime + 12.75% fly ash- minimum binder
4. 10.5% quicklime + 15.75% fly ash- minimum lead in leachate
5. 24% cement kiln dust + 12% fly ash- minimum kiln dust level
6. 28% cement kiln dust + 14% fly ash- minimum lead in leachate

These six mixes were prepared in a standard laboratory mixer with sufficient water to reach a common flow table consistency. They were cast in cylinders and cured in a 100% relative humidity chamber for 28 days while set was being monitored by penetrometer on small samples. Mixes one and two set hard. Mixes three and four stiffened but did not set completely. Mixes five and six did not set by 28 days. The UCS values for the six mixes were, in order, 462, 503, 241, 207, 0, 0 kPa.

## RESULTS I

The TCLP test were run on the UCS fragments. All the samples failed the TC level of 5 mg/l of lead. In addition, the pH's at the end of leaching were, in order, 5.26, 6.31, 5.3, 6.12, 5.44, 5.73 where the target pH was 8 to 9.75.

## CONCLUSIONS I

Another EPA project at Center Hill was evaluating the GANC/MANC test. The UCS fragments from the first phase of this project were tested using the GANC/MANC test (5). The acid neutralization capacity of the samples cured for the standard 28 days was less than was predicted from an algebraic combination of the 24 hour GANC test values for the mix ingredients. Measurements of the lead released during the GANC test (MANC) at various pH's showed that the lead in the leachate would have been low enough to pass the TC level if the pH had been in the target range of 8 to 10.

## METHODOLOGY II

The original mix calculations were studied in relation to the actual GANC results for the mixes. For each binder type, there seemed to be a single multiplier that would increase the GANC equivalents of acidity measured on the waste such that the prediction equation would give the GANC values actually demonstrated by the mixes. These factors were used to predict the increase in binder required to bring the pH to the desired level. The essence of this assumption is that the waste is more acid than the GANC showed it to be in 48 hours of contact. The following three mixes were designed by increasing the acidity of the soil by a constant factor and increasing the binder quantities accordingly. Note that the price of the high organic content was at least a doubling of the binder requirement.

mix # 7. 45% portland cement

8. 31% quicklime + 46.5% fly ash

9. 93% cement kiln dust + 46.5% fly ash

A major change in acid neutralization capacity during curing of the sample has not been observed in previous applications of the GANC test to mix designs. A study of the literature for factors that could change the acidity of a soil between 2 and 28 days in these conditions led to identification of possible organic reactions. Cellulose molecules can be oxidized to acid groups when they are activated by alkaline exposure. That suggests that the problem is the 17% total organic carbon tied up in the soil. To test this hypothesis, one more mix was prepared which removed most of the organic materials by ashing the soil at 300°C and then preparation of one of the failed mixes with correction for the loss in water and organics weight during ashing. The following mix was chosen to complete Phase II of this work:

mix # 10. 20% portland cement based on weight before ashing- comparable to mix 2.

The ashing process showed 17% weight loss from ignition excluding the water loss on drying. This is not a complete removal of organics but the structures are probably oxidized enough to show little further changes in acidity.

The mixes all set by 28 days. The UCS values were, in order, 2612, 197, 178, 1618 kPa. while the second and third mixes did not achieve the 345 kPa level desired, they did develop sufficient strength for many disposal situations and can be expected to develop strength over a longer time than the cement samples.



## RESULTS II

The pH at the end of the TCLP leaching tests was, in order, 11.11, 10.52, 11.65, and 8.90. All of these would be predicted to pass the TC level of 5 mg/l of leachable lead. The actual results from the TCLP were, in order, Below Detection Limit (BDL) of 0.2, 1.5, 0.51, BDL mg/l. All samples of Stage II passed the TC level for lead!

## CONCLUSIONS AND RECOMMENDATIONS

1. S/S is recommended as a BDAT for lead contaminated soil.
2. Natural peat type organic materials in the soil appear to interfere with the effectiveness of the binders. This can increase the binder requirement for effective stabilization to over twice the level required in the absence of the organics.
3. The current GANC test for raw soil is not able to detect the longer time organic reactions shown by this soil.
4. Any of several generic binder systems can be used to achieve TC levels of lead leachability.
5. Portland cement sets faster and provides the best strength at one month age when used at the level required for stabilization.
6. These mix design procedures will work reliably if all the acid/base reactions are detected.

### Recommendations

1. The GANC test should be revised to account for organic acid/base reactions.
2. Binder selection can be based on alkalinity and cost instead of previous testing only.
3. Biological reduction of total organic carbon contents should be researched for sites such as the Brown's Battery Breaking site. Composting is a much more desirable treatment than burning to prepare the soil for S/S.

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# ROTARY KILN INCINERATION OF SPENT POTLINER FROM THE MANUFACTURE OF ALUMINUM

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## INTRODUCTION

The process of developing treatability information on the RCRA listed waste, K088 (spent potliner from the primary reduction of aluminum), consisted of waste characterizations at three facilities, selection of the "worst case" with respect to cyanide and fluoride, and incineration. These data were made available to EPA's Office of Solid Wastes and the aluminum industry.

Incineration was selected as an appropriate treatment process as the spent potliner samples contained over 30 percent fixed carbon, greater than 5000 BTU/lb heat values, and cyanide is destroyed by thermal incineration.

## INDUSTRY AND WASTE CHARACTERIZATION

All primary aluminum produced in the United States is made by the Hall-Heroult Process. Aluminum is refined by dissolving alumina in a molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) bath and then introducing electric current. The reduction takes place in carbon-lined steel and refractory cells or pots. The carbon liner serves as the cathode. This lining becomes impregnated with the cryolite and metal over time and failures occur. A service life of 3 to 5 years for a potliner is common. The upper portions of the carbon lining from the bottom and side walls is "first cut" and is classified as K088. The "second cut" material is thermal insulation and is not K088. The mechanism by which cyanide is formed in the potliner is not discussed in the literature, but carbides and nitrides of aluminum are known to be present in the carbon lining. Table 1 presents a summary of the K088 waste characterizations. Facility Three was selected for the test burn program.

## INCINERATOR TEST CONDITIONS

The objectives for these tests were to establish whether the potliner could be incinerated and to characterize the residuals. The rotary kiln incineration system at the Incineration Research Facility, Jefferson, AK, was employed for the tests. Cyanide was considered as the principal organic hazardous constituent (POHC), and is the primary constituent of concern. Three tests were conducted under essentially the same operating conditions, except for exit temperatures. The planned incinerator operation conditions are summarized in Table 2. These conditions were chosen to maximize the carbon burn out. The actual kiln operating conditions achieved for each test are summarized in Table 3.

## TEST RESULTS

Three composite waste feed samples and two composite kiln ash samples were collected. One set of flue gas analyses was completed each test day. The

scrubber system was operated at total recycle for the three test days, and one composite scrubber liquor sample was collected. Table 4 summarizes the proximate and silica analysis results. Approximately half of the original carbon content was oxidized during the incineration test. About 80 percent of the ash content was discharged as kiln ash; the remainder was either volatilized or entrained as particulate in the flue gas.

Table 5 summarizes the cyanide concentrations for all samples analyzed. The first test samples contained an average of 5,200 mg/kg total cyanide. The waste fed during the second and third days contained less cyanide, or about 3,500 mg/kg. Kiln ash cyanide content varied from test to test, and from sample to sample within a test day. Measured levels were in the range of 60 to 330 mg/kg. Kiln ash leachates contained estimated cyanide levels, ranging from 0.5 to 0.6 mg/L for the Test 1 ash, and 3 to 4 mg/L for Test 2 and 3 ash. No cyanide was detected in the scrubber liquor or scrubber exit flue gas samples.

The cyanide destruction/removal efficiency (DRE) data are given in Table 6. The DREs were better than 99.9999 percent at both the scrubber exit and at the stack for Test 1, and 99.99987 for Tests 2 and 3. The fraction of cyanide remaining in the kiln ash was calculated to be 2.7 percent of the feed, so 97.3 percent was removed by the incineration process.

Kiln ash fluoride levels were comparable to the waste levels (1.3 to 6.8 percent). The leachate levels were generally less than 100 mg/L (one sample result was 668 mg/L fluoride). The kiln ash contained about 64 percent of the waste feed fluoride.

## CONCLUSIONS

The kiln ash contained measurable cyanide and carbon burn out was not complete. The K088 material formed slag at temperatures above 1800 degrees F. This was in contrast to the results of the preliminary ash fusion tests which indicated a 2700 degree F fusion temperature. About 20 percent of the kiln ash collected was slag removed from the kiln after completion of the tests. About a 30 percent reduction in waste weight occurred with this incineration test. Tests will be conducted to determine whether the fluoride in the kiln ash requires further treatment to restrict its leachability.

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TABLE 1. K088 CHARACTERIZATION DATA SUMMARY

Constituent	Facility 1 (mg/kg)	Facility 2 (mg/kg)	Facility 3 (mg/kg)
Fluoride	17,700	18,000	20,000
Cyanide	810	1,010	9,190
Arsenic	<2.2	<25.7	<1.1
Barium	145	153	149
Cadmium	<0.42	<0.28	0.69
Chromium	35.9	18.4	41.1
Lead	8.7	11.7	16.7
Mercury	<0.085	<0.097	<0.093
Selenium	<3.4	<2.2	10.8
Silver	<0.025	<0.37	<0.39
Nickel	13.7	6.0	52.3
Percent Moisture	0.02	0.78	0.37
Percent Ash	47.79	53.04	59.21
Percent Volatile	0.05	3.32	4.18
Percent Fixed Carbon	52.14	42.86	36.24
Btu/lb	7338	6074	5394
Ash Fusion Temp (°F)	2220	2275	2700*

TABLE 2. TARGET TEST CONDITIONS

Total waste feedrate	68 kg/hr (150 lb/hr)
Kiln temperature	980 °C (1,800°F)
Kiln exit flue gas O <sub>2</sub>	10 percent
Afterburner temperature	1,090°C (2,000°F)
Afterburner exit flue gas O <sub>2</sub>	7 percent
Scrubber blowdown flowrate	0 L/min (total recycle)
Scrubber liquor flowrate	230 L/min (60 gpm)
Scrubber pressure drop	1.5 kPa (6 in WC)
Scrubber liquor pH	7.5 to 8.0

TABLE 3. KILN OPERATING CONDITIONS

Parameter	Test 1 (1/15/91)	Test 2 (1/16/91)	Test 3 (1/17/91)
Average natural gas feedrate			
scm/hr	49	46	43
(scfh)	(1,720)	(1,609)	(1,526)
kW	504	471	447
(kBtu/hr)	(1,720)	(1,609)	(1,526)

TABLE 3. KILN OPERATING CONDITIONS (continued)

Parameter	Test 1 (1/15/91)	Test 2 (1/16/91)	Test 3 (1/17/91)
Average combustion air flowrate scm/hr (scfh)	408 (14,400)	410 (14,470)	395 (13,950)
Average total air flowrate scm/hr (scfh)	1,297 (45,790)	1,320 (46,610)	1,249 (44,090)
Average kiln draft Pa (in WC)	12 (0.05)	15 (0.06)	15 (0.06)
Exit temperature Range, °C Range, (F) Average, °C Average, (°F)	962-1,062 (1,764-1,944) 999 (1,830)	954-1016 (1,7649-1,861) 984 (1,803)	922-1012 (1,692-1,853) 972 (1,781)
Exit O <sub>2</sub> Range, % Average, %	9.6-12.3 11.0	9.9-12.8 11.6	9.7-11.4 11.4
Average waste feedrate kg/hr (lb/hr)	66.4 (146)	62.2 (137)	66.8 (147)

TABLE 4. PROXIMATE AND SILICA ANALYSIS RESULTS

Sample	Concentration, wt %					
	Fixed carbon	Volatile matter	Total Fixed plus volatile	Moisture	Ash	Silica
Test 1 (1/15/91):						
Waste 1a	33.0	2.4	35.4	0.1	64.6	3.4
Kiln ash 1a	21.5	2.1	23.6	0.1	76.3	7.3
Waste 1b	34.7	2.5	37.2	0.02	62.7	3.3
Kiln ash 1b	25.4	1.3	26.7	0.1	73.2	4.0
Waste 1c	31.3	3.1	34.4	0.2	65.4	3.7
Test 2 (1/16/91):						
Waste 2a	34.2	3.5	37.7	0.2	62.1	5.6
Kiln ash 2a	27.7	4.0	31.7	0.1	68.2	5.5
Waste 2b	34.8	4.8	39.6	0.2	60.2	5.3
Kiln ash 2b	26.1	3.7	29.8	0.1	70.1	5.4
Waste 2c	33.8	3.6	37.4	0.2	62.4	5.7
Test 3 (1/17/91):						
Waste 3a	37.4	5.4	42.8	0.1	57.1	5.9
Kiln ash 3a	28.9	2.3	31.2	0.1	68.7	5.6
Waste 3b	36.4	5.4	41.8	0.2	58.0	5.5
Kiln ash 3b	20.3	3.6	23.9	0.1	76.0	5.7
Waste 3c	38.8	4.0	42.8	0.2	57.6	6.3

TABLE 5. CYANIDE ANALYSIS RESULTS

Sample	Total CN	Amenable CN	Fraction amenable, %
Test 1 (1/15/91):			
Waste 1a, mg/kg	5,290	5,120	96.8
Kiln ash 1a, mg/kg	60	36	60.0
Kiln ash 1a TCLP leachate, mg/L	0.51	0.21	41.2
Scrubber liquor filtrate 1a, mg/L	<0.005	NA <sup>a</sup>	
Scrubber liquor solids 1a, mg/kg	<5	NA	
Waste 1b, mg/kg	4,550	4,430	97.4
Kiln ash 1b, mg/kg	130	40	30.8
Kiln ash TCLP leachate, mg/L	0.58	1.17	
Scrubber liquor filtrate 1b, mg/L	<0.0005	NA	
Scrubber liquor solids 1b, mg/kg	<5	NA	
Waste 1c, mg/kg	5,880	5,780	98.3
Scrubber exit flue gas, $\mu\text{g}/\text{dscm}$	<0.16	NA	
Stack gas, $\mu\text{g}/\text{dscm}$	<0.14	NA	
Test 2 (1/16/91):			
Waste 2a, mg/kg	3,200	2,700	84.4
Kiln ash 2a, mg/kg	90	20	22.2
Kiln ash 2a, TCLP leachate, mg/L	3.1	<0.005	<0.2
Scrubber liquor filtrate 2a, mg/L	<0.005	NA	
Scrubber liquor solids 2a, mg/kg	<5	NA	
Waste 2b, mg/kg	3,500	2,970	84.9
Kiln ash 2b, mg/kg	330	170	51.5
Kiln ash 2b TCLP leachate, mg/L	3.2	<0.005	<0.2
Scrubber liquor filtrate 2b, mg/L	<0.005	NA	
Scrubber liquor solids 2b, mg/dscm	<5	NA	
Waste 2c, mg/kg	3,500	3,000	85.7
Scrubber exit flue gas, $\mu\text{g}/\text{dscm}$	<0.15	NA	
Stack gas $\mu\text{g}/\text{kg}$	<0.14	NA	
Test 3 (1/17/91):			
Waste 3a, mg/kg	3,390	2,930	86.4
Kiln ash 3a, mg/kg	260	190	73.1
Kiln ash 3a TCLP leachate, mg/L	4.0	1.6	40.0
Scrubber liquor filtrate 3a, mg/L	<0.005	NA	
Scrubber liquor solids 3a, mg/kg	<5	NA	
Waste 3b, mg/kg	3,500	2,900	82.9
Kiln ash 3b, mg/kg	130	90	56.3
Kiln ash 3b TCLP leachate, mg/L	3.3	<0.005	<0.2
Scrubber liquor filtrate, mg/L	<0.500	NA	
Scrubber liquor solids 3b, mg/kg	<5	NA	
Waste 3c, mg/kg	3,800	3,100	81.6
Scrubber exit flue gas, $\mu\text{g}/\text{dscm}$	<0.16	NA	
Stack gas, $\mu\text{g}/\text{dscm}$	<0.15	NA	

<sup>a</sup>NA = Not analyzed. If total CN not detected, amenable CN analysis not performed.

TABLE 6 CYANIDE DREs

Parameter	Test 1 (1/15/91)	Test 2 (1/16/91)	Test 3 (1/17/91)
<b>Waste Feed:</b>			
Waste feedrate, kg/hr	72	68	72
Average CN concentration, mg/kg	5,240	3,400	3,560
CN feedrate, g/hr	377	231	256
<b>Scrubber exit flue gas:</b>			
CN concentration, $\mu\text{g/dscm}$	<0.16	<0.15	<0.16
Flue gas flowrate, dscm/min	29.5	34.6	35.2
Flue gas CN emission rate, $\mu\text{g/hr}$	<280	<310	<340
CN DRE, %	>99.99993	>99.99987	>99.99987
<b>Stack gas:</b>			
CN concentration, $\mu\text{g/dscm}$	<0.14	<0.14	<0.15
Flue gas flowrate, dscm/min	33.0	35.5	36.6
Flue gas CN emission rate, $\mu\text{g/hr}$	<280	<300	<330
CN DRE, %	>99.99993	>99.99987	>99.99987

## SELECTIVE RECOVERY OF NICKEL AND COBALT FROM ELECTROMACHINING PROCESS SOLUTIONS

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### INTRODUCTION

#### Background

An extremely large data base has been generated at Montana Tech for the treatment of a wide variety of sludge materials. Emphasis has been given to the treatment of electroplating and electromachining sludge materials. These investigations have shown that a series of hydrometallurgical unit operations can be performed to selectively recover all metal values from the hydroxide waste materials. Four publications (1-4) and ten master of science theses (5-14) have been completed that are directly related to this project, e.g., the theses include the following: Laney has investigated the effectiveness of leaching electroplating and electromachining sludge materials in sulfuric acid and the use of solvent extraction reagents to recover copper and zinc from the produced multicomponent sludge leach solutions (5); Dahnke has summarized research on zinc and iron solvent extraction, and his work produced the initial data upon which the phosphate process is based (6); Arthur investigated the application of the phosphate process to chloride-bearing sludge leach solutions (7); Konda investigated iron-zinc separations from high zinc solution in a sulfate solvent matrix (8); McGrath studied the speciation of chromium in phosphate-bearing solutions and the kinetics of chromium phosphate precipitation (9); Rapkovich studied the phosphate precipitation of trivalent cations from the ammonia/ammonium sulfate system (10); Nordwick conducted studies on the rate of conversion of ferric phosphate to ferric hydroxide (11); Quinn investigated the conversion of chromium phosphate to other more marketable products by soda ash fusion (12); Flynn investigated the use of cyanide complexation for separation of nickel from cobalt (13); and Shuey (14) is presently investigating refinements on the cyanide process for selectively separating nickel from cobalt and subsequently recovering the cobalt in a high purity form.

Because of the problem of summarizing and representing such a large amount of data in the brief space available, the approach used in this presentation is to summarize the results and conclusions without including a great deal of detail concerning the separation process. The authors are, therefore, relying on the reader to solicit copies of individual theses and publications of interest. The emphasis in this presentation will be placed on the treatment of electrochemical machining sludges; especially on the selective separation of nickel from cobalt. Also, research that is presently in progress will be reported and discussed in the oral presentation, i.e., methods studied to recover high purity cobalt from nickel depleted cyanide solutions.

#### ECM Sludges

Electrochemical machining (ECM) sludge materials are produced as a result of electrolyte solution treatment. During the ECM process, the work piece is dissolved into the electrolyte by an electrochemical deplating reaction. Because the efficiency and control of the ECM process is partly dependent on the chemistry of the electrolyte solution, simple water treatment technologies are used to control the concentration of dissolved metals in the electrolyte. A highly oxidized heavy metal hydroxide sludge results from the electrolyte treatment operations. After filtration, the sludge materials are generally supplied as a feed material to a pyrometallurgical operation or are disposed of in hazardous waste sites. The waste material contains appreciable metal values.

### METHODOLOGY

Phosphate precipitation has been investigated and demonstrated to be successful for selectively separating trivalent cations from divalent cations in complex mixed metal leach solutions produced from electroplating sludge materials by Twidwell, Dahnke, and others (1-4). These investigators have also shown that trivalent chromium can be effectively separated from trivalent iron in the presence of divalent nickel and cobalt (4). The flowsheet for the phosphate process is presented in Figure 1.



The application of phosphate precipitation technology also has been shown to be appropriate for treating ECM sludge leach solutions for the removal of iron and the recovery of chromium (2). However, the separation of divalent cations such as nickel and cobalt one from the other requires an approach other than phosphate precipitation. Figure 2 shows the unit operation sequence for the treatment of ECM hydroxide sludge materials using cyanide complexation, nickelic hydroxide precipitation, and cobalt recovery by acid baking, redissolution and electrowinning.

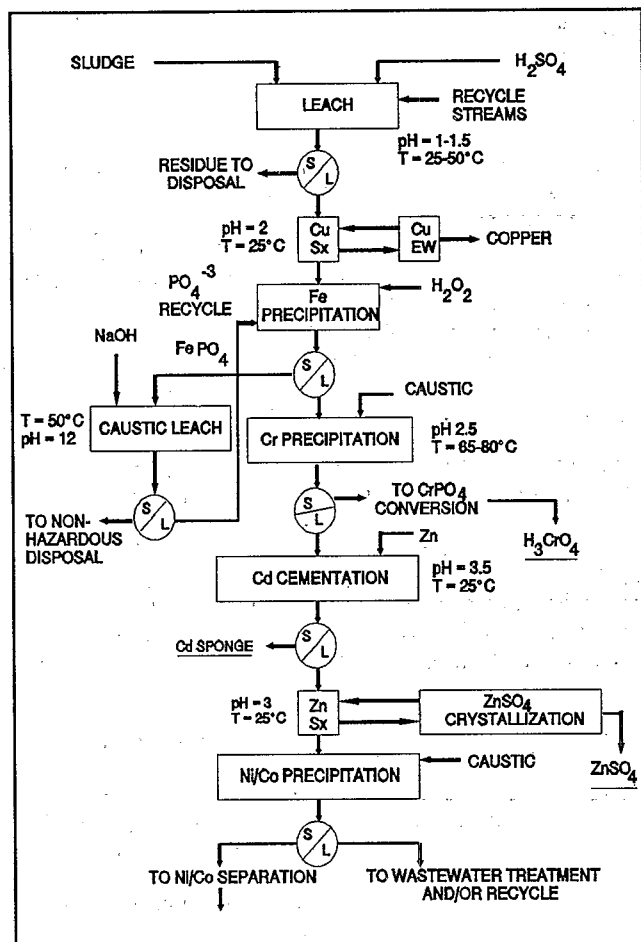


Figure 1. Metal value recovery from electroplating and electromachining sludges.

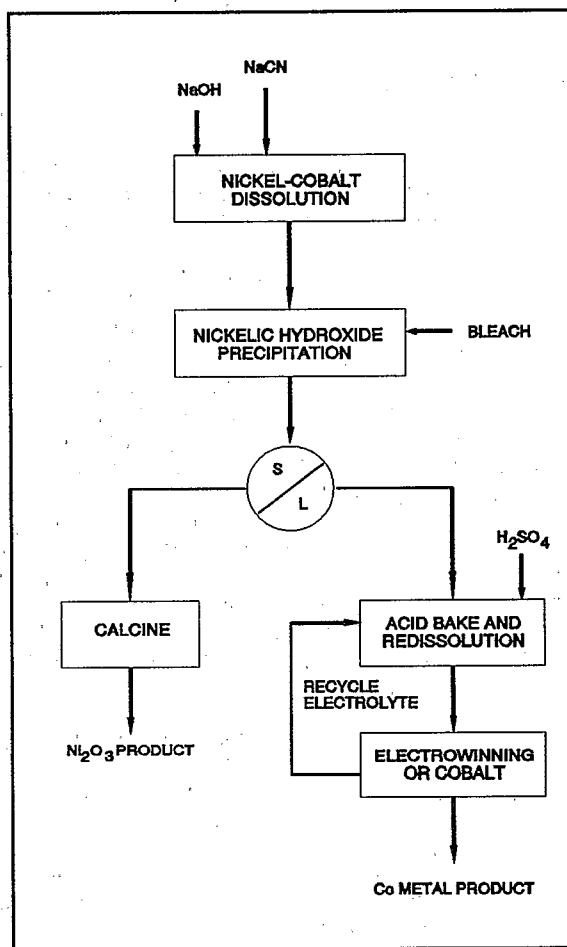


Figure 2. Selective separation of nickel and cobalt by cyanide complexation.

The nickel-cobalt starting materials were prepared by treating ECM sludge by the flowsheet (2) presented in Figure 1, e.g., the sludge was leached in sulfuric acid, filtered, iron was precipitated and filtered as ferric phosphate, chromium was precipitated and filtered as chromium phosphate, and nickel/cobalt was precipitated and filtered as hydroxides. The starting ECM sludge material was supplied by Lehr Corporation and its composition is presented in Table 1. The resulting nickel/cobalt hydroxide material composition is presented in Table 2.

The nickel/cobalt material was treated as depicted in the flowsheet presented in Figure 2. Bench scale tests were conducted in one-liter reaction vessels and large scale tests were conducted in twenty liter batches. Solution pH, Eh, and temperature were monitored throughout each test. Solutions and solids were sampled periodically during each test to establish the influence of time on the test results. Solids were examined by both x-ray diffraction and scanning electron microscopy/energy dispersive (SEM/EDX) analysis. Solid compositions were determined by digestion and induction coupled plasma (ICP) analysis. Solutions were analyzed by ICP procedures.

TABLE 1. AS-RECEIVED ELECTROCHEMICAL MACHINING SLUDGE

Source	Solids Composition, %									
	Fe	Cr	Ni	Co	Nb	Ti	Mo	Al	Ca	Na
Lehr Corp.	11.34	4.88	14.88	3.97	0.78	0.28	1.5	0.03	0.68	11.20

Starting Material Solid Content: 35.27%

TABLE 2. NICKEL/COBALT HYDROXIDE STARTING MATERIAL COMPOSITION

Batch	Solids Composition, %						
		Ni	Co	Fe	Cr	P	
Lehr #1, Dry	mean	15.97	3.97	0.05	0.23	6.63	
Lehr #2, Wet	mean	3.98	1.04	0.01	0.03	1.18	(19.88% Solids)
Lehr #3, Wet	mean	4.19	1.13	0.01	<D.L.	1.14	(18.85% Solids)
Lehr #4, Wet	mean	6.63	1.75	0.01	0.04	2.22	(18.61% Solids)

## RESULTS

A summary of experimental results are presented in this paper. Detailed experimental results and further discussion are presented by Dahnke and Twidwell (2) and Flynn elsewhere (13).

### Nickel/Cobalt Separation

Flynn (13) and Shuey (14) have investigated the influence of the variables: solution pH, residence time, amount of added cyanide and added oxidant on the product purity. The results are presented below:

- The influence of solution pH on the purity of the nickelic hydroxide precipitate and cobalt bearing leach solution was evaluated over a pH range of 12.6 to 14.0 by varying the solution pH while holding the quantity of oxidant addition constant. The initial solution concentration was five grams per liter (gpl) nickel, 1.25 gpl cobalt. The pH levels investigated were 12.6, 13.25, 13.5, 14.0. The pH of the solution was adjusted by the addition of solid sodium hydroxide pellets. Sodium hypochlorite solution (75 ml of 5.25% NaOCl) was added to the solution at a rate of 10 ml/minute following pH adjustment. A solid/liquid separation was made after a residence time of one hour and the solution and solid products were analyzed.

The appropriate solution pH for effective high purity nickel removal from solution was 14. The nickel/cobalt weight ratio present in the nickelic hydroxide product was 701/1. The cobalt/nickel ratio present in the solution phase was 98/1.

- The influence of residence time (after addition of hypochlorite at 10 ml/minute for a leach solution containing five gpl nickel, 1.25 gpl cobalt) was investigated. Four residence times were investigated at pH 14, 75 ml of hypochlorite, i.e., 15, 30, 45, 60 minutes. Following the appropriate time interval the solution was vacuum filtered and the solids and solution analyzed.

The influence of residence time on nickelic hydroxide purity was unimportant but the nickel content remaining in the solution phase was a strong function of residence time. One hour of residence was an appropriate time. The nickel/cobalt ratio present (after one hour) in the nickelic hydroxide was 690/1. The cobalt/nickel ratio in the solution phase was 93.2/1. In a follow-up large scale test study the oxidant was added all at once rather than slowly, which resulted in a nickelic hydroxide

precipitate containing a nickel/cobalt ratio of 692/1 and a cobalt solution free (within detection limits) of nickel within ten minutes.

- The influence of the amount of added cyanide on the purity of the nickelic hydroxide precipitate and cobalt bearing leach solution was evaluated for the following conditions: five gpl nickel, 1.25 gpl cobalt, pH 14, one hour residence time, and amount/rate of hypochlorite as above. The stoichiometric requirement for cyanide (for complete complexation) is eight moles of cyanide per mole of nickel plus cobalt. Any cyanide above this amount would have to be oxidized prior to the oxidation of the nickelo-tetracyano complexes thus requiring the expense of additional oxidant. Therefore, the smallest addition of cyanide that produces acceptable products should be used. The following stoichiometric amounts were experimentally investigated: 0.5, 0.75, 1.0, 1.5.

The influence of the stoichiometric amount of cyanide is not important with respect to effective removal of nickel from the solution phase but is very important with respect to the purity of the nickelic hydroxide solid. A deficiency of cyanide in solution significantly increases the level of cobalt contamination in the nickelic hydroxide precipitate. Therefore, an excess above the stoichiometric amount is required to maintain a high purity solid product. The nickel/cobalt and cobalt/nickel ratios in the solid phase and in the solution phase were (at 1.5 times the stoichiometric requirement) 690/1 and 186/1, respectively.

- The influence of the amount of added oxidant on the purity of the nickelic hydroxide precipitate and cobalt bearing leach solution was evaluated for the following conditions: five gpl nickel, 1.25 gpl cobalt, pH 14, one hour residence time, and 1.5 times the stoichiometric requirement of cyanide. The following hypochlorite (5.25%) amounts were investigated: addition (at a rate of 10 ml/minute) of 25 ml (13.125 gpl), 50 ml (26.250 gpl), 75 ml (39.375 gpl), and 100 ml (52.500 gpl) per 100 ml of starting solution.

The influence of the amount of oxidant is not important with respect to the purity of the precipitated nickelic hydroxide but is important with respect to the effective removal of nickel from the solution phase. Greater than 75 ml of oxidant were required for effective nickel removal from solution. The nickel/cobalt ratio in the solid phase for this condition was 591/1 and the solution nickel content was below the ICP detection limit (therefore, the cobalt/nickel ratio in the solution was greater than 228/1).

#### Cobalt Recovery by Acid Baking

A survey of techniques to recover cobalt from the cobalt hexa-cyano complex was conducted by Flynn (13). The techniques experimentally investigated included: direct electrowinning cobalt from solution, acid baking/electrowinning of cobalt metal, and high temperature fusion. The only treatment technique shown to be feasible was acid baking/electrowinning.

Preliminary test work was conducted to establish reagent requirements. Evaporation of one liter of cobalt solution resulted in the formation of 194 grams of solid product. The off-gases were collected, scrubbed and analyzed for cyanide during the bake operation. No cyanide was detected. This is in agreement with literature statements that no undecomposed cyanide is produced during the decomposition process. X-ray diffraction analysis of the acid bake product confirmed that the product was cobalt sulfate and other sodium, chlorine, and sulfate compounds. The cobalt concentration in the product was approximately three percent.

Sufficient quantity of this residue was produced to investigate electrowinning. The solid was dissolved in sufficient water to produce a solution containing 20 gpl cobalt (pH 5.9). This solution was placed in a small electrowinning cell using titanium anodes and lead cathodes with surface areas of 0.25 dm<sup>2</sup>. At a current density of 1.5 amperes and 6.5 volts, a deposit of 99% cobalt metal was produced in five hours.

Other test work presently underway includes: destruction of the nickel cyanide complex by hydrogen peroxide with subsequent recovery of the cobalt by electrowinning; and recovery of the cobalt by precipitation as a cobalt naphthate solid (a marketable product).

## CONCLUSIONS

Experimental test work has shown that nickel and cobalt can be effectively separated and recovered in the form of marketable products from mixed metal hydroxide electrochemical machining sludge materials by first producing a mixed nickel/cobalt hydroxide material. The nickel/cobalt hydroxide materials can be redissolved in a caustic cyanide solution. Nickel hydroxide can be selectively and effectively precipitated from the solution by a dilute hypochlorite solution. The resulting cobalt bearing solution can be reacted by acid baking/electrowinning to recover metallic cobalt.

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**U.S. EPA Symposium Presentation**

**Treatment of Dilute Hazardous Waste Streams by Sorption/Anaerobic Stabilization**

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**ABSTRACT**

Many wastewater streams contain dilute concentrations of organic pollutants that are not treated effectively by conventional activated sludge processes. These pollutants, however, can often be treated effectively anaerobically. If the pollutants were treated anaerobically, pass-through of the pollutants to the receiving stream and stripping of volatile compounds during aeration could be minimized. To treat the entire wastewater stream in an anaerobic digester would not be economical. However, if the bulk liquid stream could first be passed through a sorbent bed such as granular activated carbon (GAC) prior to aeration, only the sorbent material, a much smaller volume, would require anaerobic stabilization at elevated temperatures.

\* Presenter

Feasibility studies have been completed for a system employing GAC coated with anaerobic biomass as the sorbent material. Two 87 L/day bench-scale systems were operated for 331 days, one treating unspiked primary effluent and one treating primary effluent spiked with 5% landfill leachate and fourteen hazardous organic compounds (Table 1). Each system had two stages (Figures 1 and 2). The first stage was operated as a sorption unit, and the second stage was operated as a stabilization unit. The sorption stage was operated at a two-day carbon retention time (CRT) and an empty bed contact time of 30 minutes. The target CRT in the stabilization stage was 15 days; the hydraulic retention time in this stage approached infinity because the supernatant associated with the GAC exchanges was separated from the GAC and returned to the reactor.

In order to establish system capacity for removal of the spiked organic compounds, grab samples of the sorption stage influent and effluent were collected for GC/MS analysis of volatiles (EPA Method 1624B) and semivolatiles (EPA Method 1625B) two times every three weeks. Grab samples of the off-gases were tested for spiked volatile compounds several times during the course of the study using gas chromatography with a PID/Hall detector. Sorption stage influent and effluent samples for monitoring total and soluble chemical oxygen demand removals initially were collected as daily grab samples and later as two-day composites. Samples for monitoring sulfate reduction and for assessing the impact of the sorption stage on other wastewater characteristics important to the downstream aerobic process, e.g., total suspended solids, nitrogen forms and total phosphorus were collected and analyzed

according to EPA methods. In addition, pH, bicarbonate alkalinity, volatile acids, gas production and composition, temperature, GAC bed volume, and influent, spike and recirculation flowrates were routinely monitored throughout operation of the experimental systems.

Background concentrations of the selected organics in the primary effluent and landfill leachate used as feed stock for the study varied substantially with time; the chemical oxygen demand (COD) also varied substantially. The variability is related to the diverse industrial contributions and combined sewer stormwater flows received by the Mill Creek Plant, the source of primary effluent in the study. The variability of the concentrations of the organics and COD entering the sorption stage of the process provided a real world test of the process on low strength but complex wastewater.

The spiked organic compound removal data for the year-long study are summarized in Table 1. Average removals were the highest for the aromatic compounds. Five of the six aromatics added were removed at over 95% and the sixth, phenol, had an 85% removal. Removals of chlorinated aliphatic compound ranged from 50% for methylene chloride to 95% for trichloroethylene. Removals of phthalate compounds were approximately 60%. Removals of ketones ranged from 24% for acetone to 93% for methyl isobutyl ketone. Analytical interferences due to the ubiquitous presence of methylene chloride in the analytical laboratory may have contributed to the low removals of methylene chloride. The spiked organics that substantially passed through the process (acetone and the phthalates) are readily removed by subsequent efficient aerobic treatment.

The data for the wastewater characteristics of the sorption stage influent and effluent samples are summarized in Table 2 for both the unspiked and spiked systems. Average COD removals in both the unspiked and spiked systems consistently remained at 40-50% throughout the year-long study. The resulting reduced COD loading to the aeration process would substantially reduce air requirements and waste aerobic biomass (such as waste activated sludge) in subsequent aerobic treatment. Sulfate reduction in the range of 15% was observed in the two systems. Total and volatile suspended solids (TSS and VSS) removals in the range of 20-25% and 4-7% were observed in the unspiked and spiked systems, respectively. The difference in removal efficiency may be related to the presence of methanogenic activity in the sorption stage of the spiked system. Even at the short hydraulic retention time used in the sorption stage, methanogenic activity was noted in the spiked system; it was not observed in the unspiked system. Methanogenic activity in the spiked system was stimulated by the readily-degradable substrate, methanol, which was used as a carrier for the spike. The other parameters, i.e., nitrogen species and total phosphorus, were not significantly affected by the presence of the sorption stage.

This feasibility study, performed at bench-scale with complex real-world wastes, demonstrated that the experimental system was capable of consistently removing 40-50% of the influent COD for a year-long period. No GAC replacement was necessary during this time. The reduction of COD discharged to the aeration basin would reduce aeration requirements as well as aerobic sludge production in actual application. In addition, the stabilization process produces methane from the removed



COD which potentially would be recoverable as fuel for heating the reactor. When hazardous compounds are present in the influent waste, the sorption stage is capable of trapping significant amounts, preventing their pass-through to the aeration basin and subsequent volatilization of the strippable chemicals. The sorption stage also attenuates the effects of shock loads of compounds which may be toxic to the aerobic portion of the plant. In addition, the combined sorption/anaerobic stabilization stage retention time for GAC, and, therefore, biomass and sorbed organics, is extremely high, maximizing the potential for degradation of compounds which are normally recalcitrant at conventional treatment plant retention times.

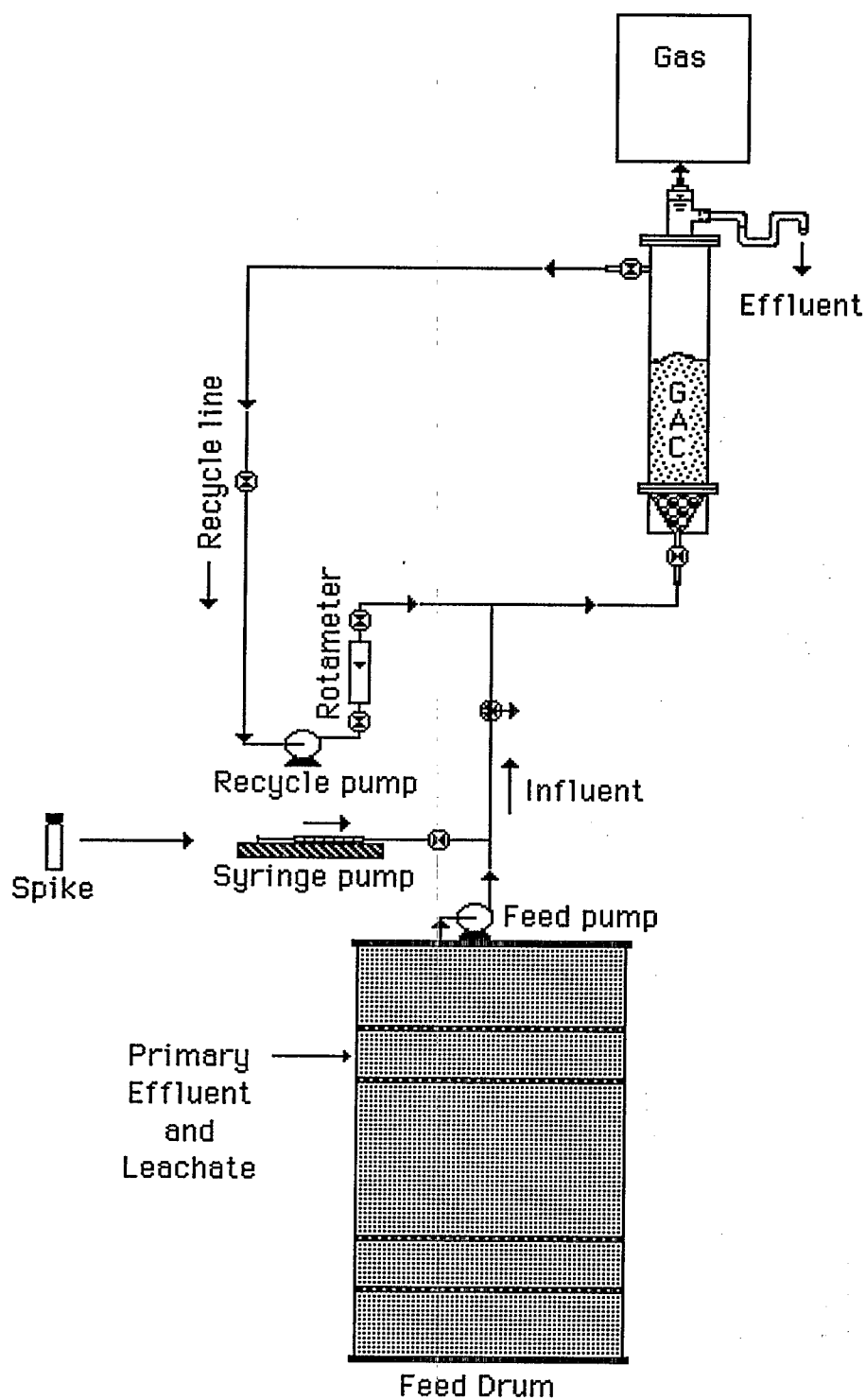


Figure 1. Sorption Stage of the Experimental Bench-Scale System

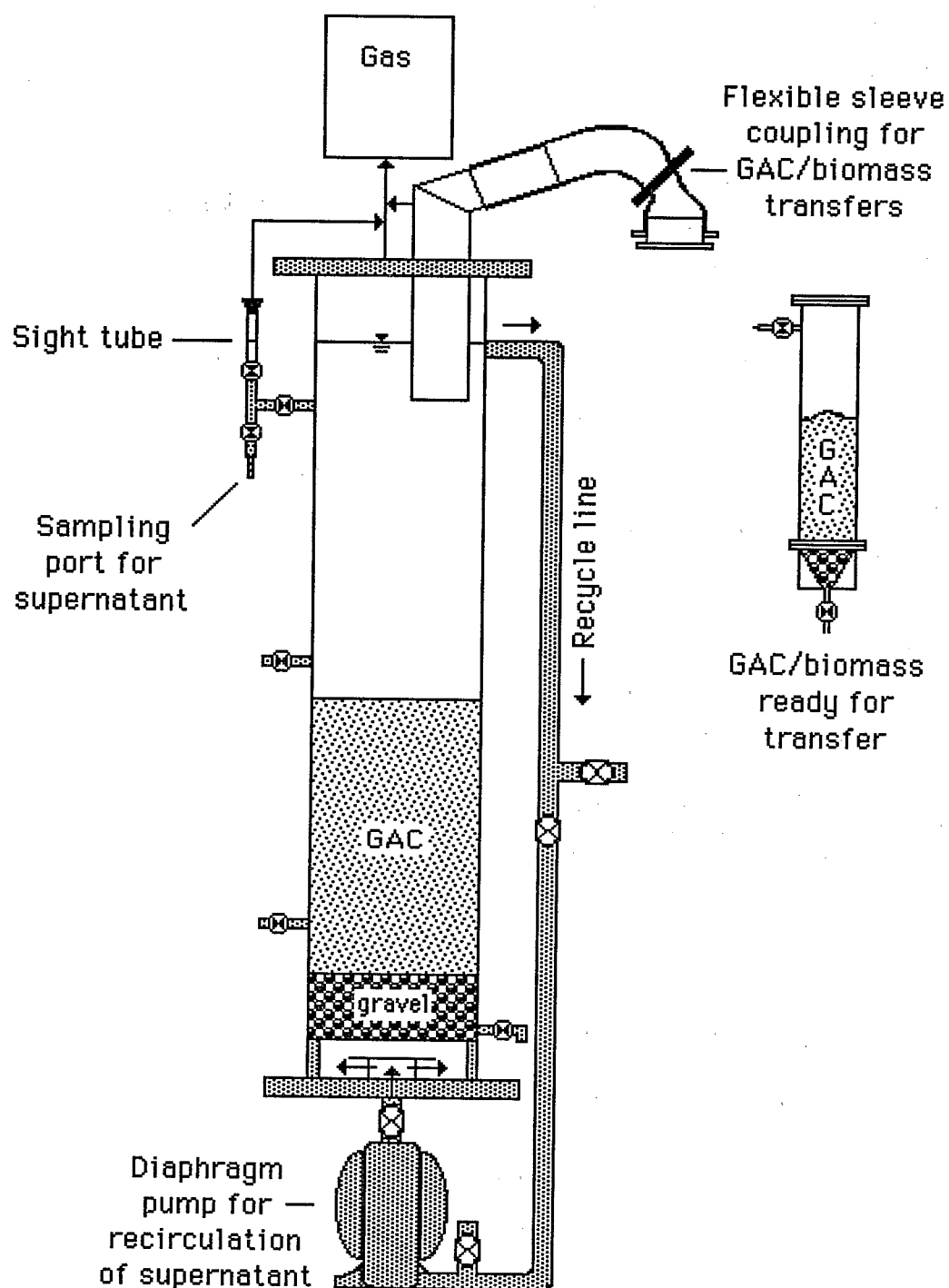


Figure 2. Stabilization Stage of the Experimental Bench-Scale System

TABLE 1. Spiked Compound Removals in the Sorption Stage of the Spiked System

	Influent (ug/L)		Effluent (ug/L)		Percent Removal
	<u>Mean</u>	<u>SD*</u>	<u>Mean</u>	<u>SD</u>	
<u>VOLATILES</u>					
Acetone <sup>1</sup>	2340	1440	1770	1170	24
Methyl Ethyl Ketone <sup>1</sup>	599	410	144	80	76
Methyl Isobutyl Ketone <sup>1</sup>	640	495	45	40	93
Toluene <sup>2</sup>	483	291	18	14	96
Ethylbenzene <sup>2</sup>	72	61	2.3	3.5	97
Chlorobenzene <sup>2</sup>	83	49	3	3	96
Methylene Chloride <sup>3</sup>	44	28	21	29	50
1,1-Dichloroethane <sup>3</sup>	65	55	14	10	78
Trichloroethylene <sup>3</sup>	57	36	2.6	2.4	95
<u>SEMIVOLATILES</u>					
Dibutyl phthalate <sup>4</sup>	47	50	16	33	66
Bis(2-Ethylhexyl)phthalate <sup>4</sup>	129	267	56	82	57
Nitrobenzene <sup>2</sup>	129	108	4	10	97
Trichlorobenzene <sup>2</sup>	55	44	3	6	95
Phenol <sup>2</sup>	132	97	20	19	85

\*SD=Standard Deviation

<sup>1</sup> Ketone   <sup>2</sup> Aromatic   <sup>3</sup> Chlorinated aliphatic   <sup>4</sup> Phthalate

TABLE 2. Wastewater Characteristics Data Summary for Sorption Stage

PARAMETER	UNSPIKED SYSTEM					SPIKED SYSTEM				
	Influent mg/L		Effluent mg/L		Percent Removal	Influent mg/L		Effluent mg/L		Percent Removal
	Mean	SD*	Mean	SD		Mean	SD	Mean	SD	
Total COD**	241	96	145	59	40	352	100	200	58	43
Soluble COD**	149	59	80	37	46	252	92	111	44	56
Sulfate #	238	56	239	70	0	228	59	231	64	-1
##	165	37	137	27	17	176	45	151	41	14
TSS #	68	53	50	44	25	91	51	87	73	4
##	62	20	49	25	21	73	26	68	24	7
VSS #	54	42	42	37	22	68	41	64	43	6
##	40	15	32	16	20	47	16	45	15	4
TKN-N #	31	10	29	9	6	42	8	40	7	5
NH <sub>3</sub> -N #	24	8	24	8	0	35	7	35	7	0
NO <sub>3</sub> -N #	0.22	0.16	0.22	0.18	0	0.27	0.18	0.26	0.18	4
NO <sub>2</sub> -N #	< 0.1		< 0.1		-	< 0.1		< 0.1		-
Total P #	3.51	1.11	3.54	1.40	-1	3.56	1.01	3.51	1.41	1

\*SD=Standard Deviation

\*\* 4/23/90 - 3/20/91

# 4/23/90 - 9/29/90

## 10/23/90 - 3/20/91

## DEVELOPMENT OF A NOVEL BIOFILTER FOR AEROBIC BIODEGRADATION OF VOLATILE ORGANIC COMPOUNDS (VOCs)

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### INTRODUCTION

In recent years, the emission into the atmosphere of volatile organic compounds (VOCs) has undergone increased regulation by EPA, OSHA and other government agencies due to potential human health hazards. The sources of these VOCs include releases during industrial production and use, from contaminated wastewaters in collection systems and treatment plants, and from hazardous wastes in landfills and contaminated ground water.

Conventional methods for treating VOC emissions include adsorption on solids, absorption in solvents, incineration and catalytic oxidation. One alternative to these conventional treatment methods is the biological destruction of the VOCs in gas phase biofilters. This method has the advantage of pollution destruction (as compared to transfer to another medium) at lower operation and maintenance costs. The biofilter method also can be combined with various stripping or vapor extraction separation processes which effectively transfer VOCs from liquid or solid matrices into the gas phase entering biofilters.

Many immobilized-cell reactors contain films of biomass growing on some type of adsorbent particle. They include trickling filters used for wastewater treatment, packed beds proposed for ethanol production, and several fluidized bed designs for anaerobic fermentations and aerobic and anaerobic wastewater treatment. Fluidized beds of floc particles, such as tower fermenters and sludge-blanket reactors can also be considered immobilized cell reactors because they represent the limiting case as the size of the support particle goes to zero.

Immobilized cell reactors provide several advantages, the principal differences being superior mass transfer at higher cell densities, no washout problems, and capability to operate in a continuous fashion.

However immobilized cell reactors share the common problem of mass transfer resistance associated with the biomass film, i.e., the substrate must diffuse in and product must diffuse out. This creates a region of low substrate and high product concentration on the inside surface of the biofilm, thereby severely inhibiting metabolic activity. This requires that biofilm thickness should be minimized to prevent diffusional limitations from occurring in the process.

Furthermore, for packed bed designs, growth of biomass causes plugging of the bed, causing high pressure drop problems in the operation. The growth of biomass is especially rapid in aerobic systems. Hence, control of biofilm thickness is an important part of immobilized-cell reactor design.

Traditionally, the term "biofilter" has been used to define processes that use compost, peat, bark, soil, or mixtures of these substances as the filter medium. These media serve as a support system for a microbial population. Filter media is underlain

with a gas distribution system, commonly perforated pipe. Gases flow through the bed where the pollutants are adsorbed to the filter media. After contact with the microorganisms the pollutants are broken down thus regenerating the adsorption capacity of the bed. Water is sprayed over the bed's surface or by humidifying the influent gases. The terms "soil filters", "soil biofilters", or "soil beds" delineate processes where the filter media is soil. Soil biofilters are generally less permeable to gas flow than biofilters that use compost, peat, or bark media thus a larger soil biofilter area is required for the same back pressure.

Biofilters and soil filters have been applied to control odors from wastewater treatment plants and industrial processes since 1953 (1). Recently, these processes have been used for volatile organic compound emissions removal from chemical and process industries (2,3,4). Other processes mentioned in the literature that employ biological treatment of waste gases include bioscrubbers and tricking filters (4,5).

Recently, experimental data has been obtained on a packed bed biofilter for the biodegradation of methylene chloride, trichloroethylene, and toluene (6,7). Complete removal of these compounds from air was demonstrated using the packed bed biofilter system.

## METHODOLOGY

This paper reports on the experimental study of the biodegradation of volatile organic compounds present in the landfill leachates in a novel aerobic biofilter. The most abundant compounds in leachate streams were targeted for study. A stripping study was carried out on the selected compounds to confirm Henry's law constant values.

The predominant VOCs from a landfill leachate stream were treated in a bench scale biofilter. The following five chemicals (substrates) were targeted for this study at the following feed concentrations: Toluene: 450 ppm; Methylene Chloride: 150 ppm; Trichloroethylene: 25 ppm, Chlorobenzene: 40 ppm, and Ethyl benzene: 20 ppm. The compounds were fed in vapor form to the biofilter in air. The required composition of the compounds in the gas phase was achieved by making the synthetic gas mixtures in a cylinder and blending with air. This was done to ensure a uniform feed concentration to the biofilter. Nutrient solution was circulated countercurrent to the gas through the bed. The inlet and outlet gas streams were analyzed for the above five chemicals using a gas chromatograph (EPA standard method 602).

The biomass acclimated to the above compounds 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 five compounds. Nutrients necessary for biomass growth were added periodically. 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 support media in the biofilter.

The novel biofilter, developed through our research, consists of a square cross-section (100 mm x 100 mm) extruded ceramic monolith structure (celite, Manville Corporation, CA), with 99 square straight passages (6 mm x 6 mm). The biomass

exists as a uniform film immobilized on the inner surface of each straight passage. The biofilm is attached to the support material and enables simultaneous diffusion and degradation of the organics.

The major differences between the novel biofilter and the other immobilized cell bioreactors are as follows:

1. The immobilized cell biofilter contains straight passages for the flow of gas/liquid phase, thereby providing liquid phase shear to maintain a thin biofilm on the support structure. This is distinctly different from a packed bed containing support particles, wherein the excessive biomass that shears off the particles becomes lodged in the interstitial spaces between the packed particles, and cannot leave the bed easily. In the biofilter, the straight passages enable the excessive biomass growth to leave the biofilter due to the shear forces exerted by the flow of liquid through the straight passages.
2. The straight passages for gas flow also minimizes the pressure drop in the biofilter. In the case of expanded packed beds, or fluidized beds, for typical adsorbents, such as activated carbon, there is significant liquid pressure needed to expand the packed bed of particles or fluidize them. Minimizing the pressure drop also minimizes the pumping cost for the gas phase, which constitutes the major operating cost for the biofilter process.
3. Stratification of the microorganisms in the biofilter occurs for a gas stream containing mixed substrates. In mixed substrate systems, the biomass culture immobilized in the biofilter at different heights gets naturally adapted to different organics, depending on their biodegradation kinetics. This stratification of the culture, not present in well-mixed systems, is a distinctive feature of plug-flow type bioreactors.

## RESULTS

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 the difference in the inlet and outlet concentrations of the compound in the gas phase to the concentration of the compound at the inlet. 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. This meant that the compound removed in the biofilter by the trickling nutrient flow was negligible as compared to the feed rate of the compound.

Figure 1 shows the percent removal efficiency for the five influent compounds as a function of time. Note that the percent removal efficiency for TCE is increasing as the microorganisms are getting acclimated to the chemical. Measurements of the cumulative net increase in carbon dioxide concentration, between the inlet and outlet gas streams, have been made to confirm the overall carbon balance. Measurements of the increase in concentration of the chloride ion in the liquid nutrient flow have been made to confirm the degradation of the chlorinated compounds. No degradation products were found to exist, as determined by GC and GC/MS analysis, in the outlet gas stream. Careful measurement of the total gas phase pressure drop allows an indirect measurement of the average biofilm thickness. This parameter has been used



to confirm the validity of a lumped parameter dimensionless mathematical model, which can be used to scale-up the biofilter.

## CONCLUSIONS

It has been shown that a biofilter is a viable technology for treating gas phase organic contaminants. Complete aerobic degradation of trichloroethylene, although at less than 100% removal efficiency, has been demonstrated in the novel biofilter. Furthermore, it has been demonstrated that the straight passages biofilter does not plug-up due to biomass growth, as in the case of packed beds, and has an overall lower gas phase pressure drop.

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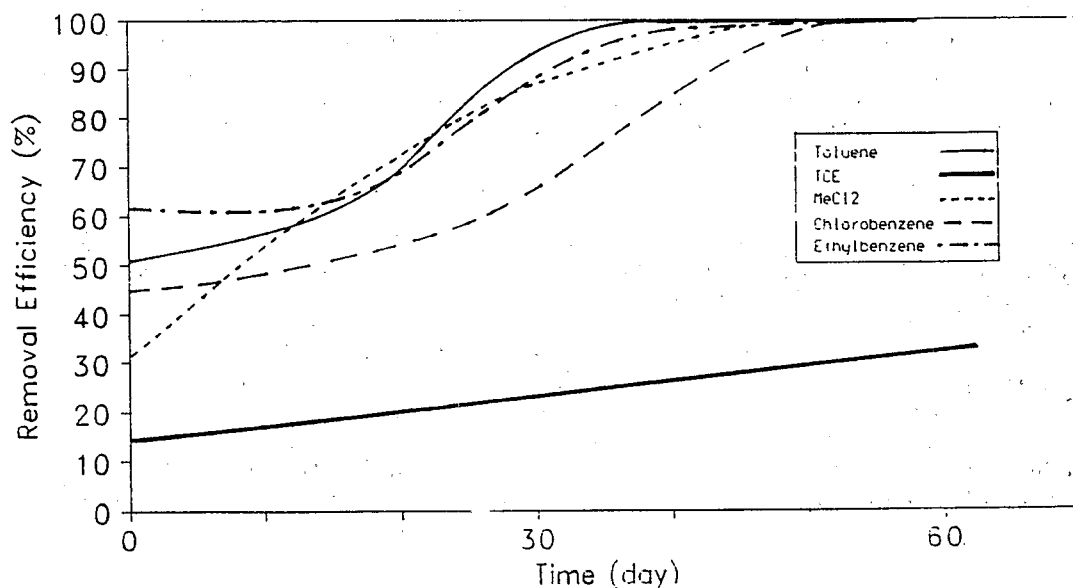


Figure 1: Removal Efficiency for the straight passages biofilter

ONSITE BIOLOGICAL PRETREATMENT FOLLOWED BY  
POTW TREATMENT OF CERCLA LEACHATES

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## INTRODUCTION

A study was conducted at the U.S. EPA's Test & Evaluation (T&E) Facility in Cincinnati, Ohio, to investigate the effectiveness of two types of anaerobic fixed-film biological reactors in pretreating hazardous landfill leachates containing synthetic organic chemicals (SOCs) prior to discharge to publicly owned treatment works (POTWs). Various anaerobic treatment processes have been used successfully in the past to treat municipal leachates, with emphasis placed on chemical oxygen demand (COD) removal. This study evaluated the processes of anaerobic biodegradation using upflow, packed-bed, anaerobic filters (bench-scale and pilot-scale) and an upflow, granular activated carbon (GAC), expanded-bed, anaerobic reactor (bench-scale). These units are highly suited for treating high strength, inhibitory wastes similar in characteristics to the leachate used in this study.

Conventional wastewater treatment plants are often incapable of satisfactory removal of hazardous substances from polluted water. The current method for treating hazardous landfill leachates usually involves aerobic treatment, which may be inadequate under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) because of the following reasons:

- a) Air stripping of volatile organic compounds,
- b) Incomplete treatment of semivolatile organic compounds, and
- c) Difficulty in degrading chlorinated compounds.

Anaerobic biological pretreatment is expected to reduce such problems because of the substantially smaller volume of exhaust gas produced and the reductive dehalogenation capabilities of anaerobic microorganisms. The leachate for the study was obtained from a large commercial municipal landfill (Rumpke) in Georgetown, Ohio. The leachate was rendered hazardous by supplementing it with a mixture of ten volatile and four semivolatile organic compounds. A list of these 14 toxic organic compounds, with their corresponding target concentrations, is provided in Table 1.

The goals of this study were to: 1) establish the effectiveness of anaerobic pretreatment using GAC, expanded-bed, anaerobic reactors and upflow, packed-bed, anaerobic filters in removing organic compounds, including chloroform; 2) compare the performance of the bench-scale, upflow, packed-bed, anaerobic filter (B1) versus the GAC, expanded-bed, anaerobic reactor (B2); 3) compare the performance of the bench-scale, upflow, packed-bed, anaerobic filter (B1) versus a similarly-operated pilot-scale, packed-bed, anaerobic filter (P1); 4) evaluate the toxicity of chloroform in removal of toxic

organics in the leachate in each of the three bioreactors; 5) observe potential problems such as bed plugging and calcium carbonate deposition on the GAC medium; and 6) determine the actual retention time of the contaminants in the bench- and pilot-scale, packed-bed, anaerobic filters using lithium chloride as a tracer material. This paper reports on the performance of these systems over a period of 2 years during which effective process control was maintained. The experimental treatment systems were operated at the U.S. EPA T&E Facility in Cincinnati, Ohio.

TABLE 1. COMPOSITION OF SOC SUPPLEMENT TO THE LEACHATE

Compounds	Concentration ( $\mu\text{g/L}$ )
<b>VOLATILE ORGANIC COMPOUNDS</b>	
Acetone	10,000
Methyl Ethyl Ketone	5,000
Methyl Isobutyl Ketone	1,000
Trichloroethylene	400
1,1-Dichloroethane	100
Methylene Chloride	1,200
Chloroform	0 to 2,000
Chlorobenzene	1,100
Ethylbenzene	600
Toluene	8,000
<b>SEMIVOLATILE ORGANIC COMPOUNDS</b>	
Phenol	2,600
Nitrobenzene	500
1,2,4-Trichlorobenzene	200
Dibutyl Phthalate	200

## METHODOLOGY

The bench-scale anaerobic pretreatment units consisted of an upflow, packed-bed, anaerobic filter (B1) and a GAC, expanded-bed, anaerobic reactor (B2). These units were fabricated using plexiglass and installed to treat municipal leachates rendered hazardous by the addition of 14 SOCs. The growth support medium in the B1 column (15.2 cm diameter x 122 cm high) was 2.54-cm diameter polypropylene pall rings. The growth support medium in the B2 column (10.2 cm diameter x 106 cm high) was 1.0 kg of 16 x 20 U.S. Mesh Granular Activated Carbon (GAC). Each of these bioreactors was coupled with a second-stage, bench-scale, aerobic treatment system (simulating a POTW) consisting of a primary clarifier, aeration basin, and secondary clarifier. Raw municipal leachate was fed to each bench-scale anaerobic reactor from a sealed, chilled, mixed, oxygen-free, stainless steel reservoir through stainless steel lines. A stock solution of the SOCs was fed into the suction side of each recycle loop along with the leachate. The pilot-scale pretreatment system (P1) consisted of a 129-cm diameter by 229-cm high upflow anaerobic filter, packed with polypropylene rings, coupled with a second-stage, pilot-scale, primary clarification/activated sludge aerobic system. All three anaerobic pretreatment units were operated at 35°C and a pH range of 7-7.5.

All the bioreactors were fed with the Rumpke leachate, which was characterized by COD levels ranging between 400 and 2,500 mg/L. Due to its relatively low biodegradable content during the first 6 months of the project, the leachate was supplemented with a mixture of equal portions of organic acids (acetic, propionic, and butyric) to maintain the bioreactor influent COD at 1,600 mg/L. This practice was discontinued during the course of the study in order to evaluate biodegradation under the natural varying COD concentrations of the leachate. Leachate sulfate concentrations ranged from 3 - 300 mg/L.

The flow rate to the B1 and B2 columns was nominally set at 10 L/day. The leachate flow rate into P1 was initially regulated at 0.57 L/minute. Off gases from each of the bioreactors were measured using wet-tip gas meters, connected at the top of each of the units. Daily measurements of total gas production, feed flow rates, spike flow rates, reactor temperatures, and reactor pH values were recorded. Samples were analyzed throughout the test period for SOC<sub>s</sub>, total and soluble COD, sulfate, and off-gas composition. Metals, SOC composition in the off gas, total and volatile suspended solids, and ammonia nitrogen were measured weekly on selected sampling periods.

The experimental period can be divided into five distinct phases for the B1, B2, and P1 bioreactors. During Phase 1, each of the systems was acclimated for approximately two months to the Rumpke leachate. In this phase, the leachate flow rates in the bioreactors were gradually increased and adjusted at design specifications. The leachate flow rate was adjusted to 10 L/day in each of the bench-scale bioreactors. This resulted in an empty-bed contact time (EBCT) of 2 days in bioreactor B1, and an unexpanded EBCT of 8 hours in bioreactor B2. During this phase, the P1 bioreactor was adjusted to an EBCT of 4 days corresponding to a leachate flow rate of 0.57 L/minute (820 L/day). Bioreactors B1, B2, and P1 were inoculated with 100% concentrations (Table 1) of 13 of the 14 synthetic organic compounds (SOC<sub>s</sub>) within one month at incremental rates of 33% and 66% of the target level; chloroform was not introduced until the later stages of the study because of its potential toxicity. Phase 2 experienced the design flow rates and 100% SOC concentrations (without chloroform) for five months. During Phase 3, the leachate flow rate was doubled for pilot-scale bioreactor P1, thus establishing an EBCT of 2 days similar to that in bioreactor B1. Recirculation rate ratios were also made comparable for bioreactors B1 and P1 during this phase. During Phase 4, chloroform was included in the SOC mixture (at a concentration of 2 mg/L) for all three bioreactors. Phase 5 can be divided into several distinct stages for the three anaerobic pretreatment units. First, leachate flow rates were doubled (20 L/d) for bioreactors B1 and B2, thereby halving the EBCT in B1 and B2 to 1 day and 4 hours, respectively. Second, carbon washing was initiated on bioreactor B2 to evaluate the effects of carbon washing on the GAC system. Third, chloroform was removed from bioreactor P1's SOC spike because of possible toxic effects, and the system was monitored to determine if performance could be recovered to pre-chloroform addition levels.

## RESULTS AND CONCLUSIONS

Both B1 and B2 bioreactors were capable of removing through biodegradation most of the CERCLA compounds at efficiencies of 90% or higher, with the exception of 1,1-dichloroethane and dibutyl phthalate (which were removed at 80% efficiency). The packed-bed bioreactors removed ketones more efficiently than the expanded-bed bioreactor. Over 90% removal was observed for the following compounds in B1, B2 and P1 systems: acetone, methyl ethyl ketone, methyl isobutyl ketone, trichloroethylene, methylene chloride, nitrobenzene, and phenol. All the semivolatile compounds, with the exception of dibutyl phthalate, were removed at 95% efficiency in the B1 and B2 systems. In the P1 bioreactor, over 75% removal was observed for toluene, over 60% removal for ethylbenzene and chlorobenzene, and over 80% for 1,2,4-trichlorobenzene and dibutyl phthalate. All of the volatile aromatics showed higher removal efficiencies in the expanded-bed bioreactor compared to the packed-bed bioreactors.

The COD removal efficiency in the B1 and B2 systems averaged 42% and 48%, respectively. During the period of the volatile acids addition, the primary COD removal mechanism was methanogenic. After the volatile acids addition was stopped and the feed COD decreased, the COD removal mechanism was due to a combination of methanogenesis and sulfate reduction. The average sulfate reductions in the GAC expanded-bed bioreactor and the anaerobic filters were 71% and 65% respectively, corresponding to an influent sulfate concentration of 116 mg/L.

The performance of the B1, B2 and P1 systems was similar prior to the introduction of chloroform in the spike solution. Within 3 weeks after the addition of chloroform into the three units, however, the P1 bioreactor showed a decline in the removal of some of the SOC's (including chloroform). SOC removals continued to decline over a period of 4 months, at which time chloroform addition to the spike mixture was discontinued for the P1 bioreactor. The B1 and B2 systems continued to receive chloroform at a concentration of 2 mg/L until the termination of the study because the removal efficiency in both bioreactors averaged 95%.

During the initial period of the study (about 350 days of bioreactor operation), the less biodegradable but more adsorbable aromatic compounds were removed more efficiently in the GAC, expanded-bed anaerobic reactor than in the upflow, packed-bed, anaerobic filter. However, after about 400 days of operation, problems such as bed plugging and calcium carbonate deposition on the GAC medium disrupted the methanogenic activity in the B2 column. This problem was circumvented by periodically washing 5% of the total carbon contained in the expanded-bed system using 0.1N HCl. Therefore, in the long run, the anaerobic upflow packed-bed filter systems were less susceptible to operational problems and more conducive to the growth of methanogens compared to the expanded-bed anaerobic unit. It should be noted, however, that the bench-scale, GAC, expanded-bed bioreactor operated at one-sixth the empty-bed contact time of the bench-scale anaerobic filter and, for part of the study, at one-twelfth the empty-bed contact time of the pilot-scale anaerobic filter.

In order to verify the actual retention time of leachate in the B1 and P1 packed-bed systems, lithium chloride tracer studies were conducted. The tests were conducted first, after the fourth phase of the study (without cleaning the bioreactor media), and then after completion of the study (following cleaning and repacking of the media). Results of the first tracer study indicate some plugging in the P1 bioreactor. Results of the second tracer study are expected shortly. The observed media plugging and probable channeling in the P1 unit may explain, at least in part, the poorer performance of the pilot-scale anaerobic filter compared to the bench-scale anaerobic filter.

## TWO U.S. EPA BIOREMEDIATION FIELD INITIATIVE STUDIES: EVALUATION OF *IN-SITU* BIOVENTING

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### INTRODUCTION

Bioventing is the process of supplying oxygen *in-situ* to oxygen-deprived soil microbes by forcing air through contaminated soil at low air flow rates. Unlike soil venting or soil vacuum extraction technologies, bioventing attempts to stimulate biodegradative activity while minimizing stripping of volatile organics. The process destroys the toxic compounds in the ground. Bioventing technology is especially valuable for treating contaminated soils in areas where structures and utilities cannot be disturbed because the equipment needed (air injection/withdrawal wells, air blower, and soil gas monitoring wells) is relatively non-invasive.

The U.S. EPA Risk Reduction Engineering Laboratory, with resources from the U.S. EPA Bioremediation Field Initiative, began two parallel 2-year field studies of *in-situ* bioventing in the summer of 1991 in collaboration with the U.S. Air Force. The field sites are located at Eielson Air Force Base (AFB) near Fairbanks, Alaska, and Hill AFB near Salt Lake City, Utah. Each site has jet fuel JP-4 contaminated unsaturated soil where a spill has occurred in association with a fuel distribution network. With the pilot-scale experience gained in these studies and others, bioventing should be available in the very near future as an inexpensive, unobtrusive means of treating large quantities of organically contaminated soils.

### METHODOLOGY

#### *Eielson AFB*

At Eielson AFB, we are studying bioventing in shallow soils in a cold climate in conjunction with soil warming methods to enhance the average biodegradation rate during the year. Roughly 1 acre of soil is contaminated with JP-4 from a depth of roughly 2 ft to the water table at 6-7 ft. Initial (pre-bioventing) soil gas measurements taken in July 1991 ranged from 600-40,000 ppm total hydrocarbons, 0-13% O<sub>2</sub>, and 10-18% CO<sub>2</sub>, indicating oxygen-limited biological activity and a high degree of contamination. Thus, addition of oxygen as air to the site would be expected to increase the rate of biodegradation. In comparison, atmospheric air composition includes 21% O<sub>2</sub> and 0.03% CO<sub>2</sub>.

The test area was established by laying down a relatively uniform distribution of 24 air injection/withdrawal wells and constructing test plots within this test area (see Figure 1). Air is injected from 2-6 ft deep at an overall rate of 60 cfm to the test area or 2.5 cfm to each active well. Thus, the test plots should receive relatively uniform aeration. Three 50-ft square test plots were established. One plot is being used as a control, i.e., bioventing only, no heating. The remaining two plots are being used to evaluate separately the following two strategies of combining bioventing with warming of the soil above ambient temperature to increase the rate of biodegradation year-round: (1) passive solar warming using plastic covering, and (2) active warming by applying warm water from soaker hoses just below the surface. Water is applied at roughly 35°C and an overall rate of roughly 1 GPM to the actively-warmed plot.

In addition to the network of air injection/withdrawal wells, three-level soil gas monitoring wells and three-level temperature probes were installed throughout the site between 2 and 6 ft deep. In addition, one air injection/withdrawal well and one soil gas monitoring well was installed in a nearby uncontaminated area for

background measurements. The venting of air and the trickling of unheated water to the actively-warmed plot began in September 1991. Warming of the water began in October, 1991. A plan view of the installation is presented in Figure 1.

Periodically, *in-situ* respirometry tests are conducted to measure the *in-situ* microbial oxygen uptake rates. Such measurements indicate the relative rate of biodegradation of the contaminants. These tests involve temporarily (4 to 8 days) shutting the air off and monitoring the soil gas oxygen concentration with time. The decrease in oxygen concentration with time indicates a relative biodegradation rate at that time during the study. Oxygen uptake due to oxygen demands other than biological activity is calculated by conducting a parallel shut-down test in the (uncontaminated) control area. These tests allow estimation of the biodegradation rate as a function of ambient temperature and soil warming technique. Quarterly *in-situ* respiration tests will be conducted.

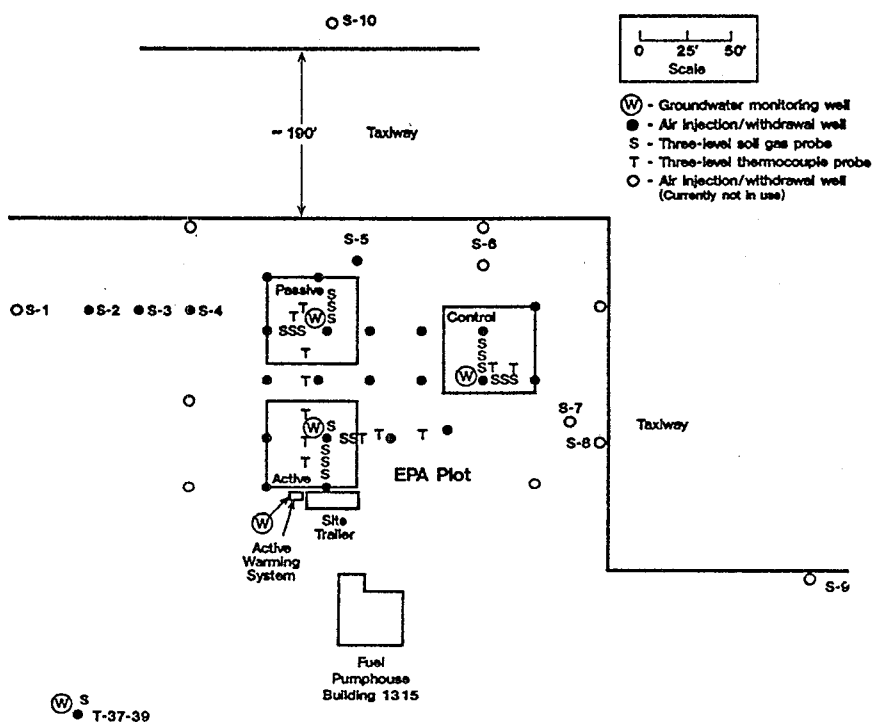


Figure 1. Plan view of the joint U.S. EPA and U.S. Air Force bioventing activities at Eielson AFB.

#### Hill AFB

At Hill AFB in Utah, we are evaluating bioventing at greater depths. A 1-acre site is contaminated with JP-4 from depths of approximately 35 ft to perched water at roughly 95 ft. Here, bioventing, if successful, will stimulate biodegradation of the fuel plume under roads, underground utilities, and buildings without disturbing these structures. A plan view of the installation is shown in Figure 2. The air injection well is indicated. "CW" wells are soil gas "cluster wells" where independent soil gas samples can be taken at 10-ft intervals from 10-90 ft deep, and "WW" wells are groundwater monitoring wells. A cross-sectional view along the path AA' in Figure 2 is shown in Figure 3. Air is currently being injected from one well into the plume at a rate of 40 cfm at depths from 30-95 ft.

An inert gas tracer study, regular soil gas measurements at several locations and depths, and semi-annual *in-situ* respiration tests are planned to demonstrate the effectiveness of delivering oxygen and stimulating

biodegradation in a large volume of soil of substantial depth. The inert gas tracer study involves temporarily replacing the injection of air with the injection of argon or helium and observing the transport of gas in the soils by monitoring for the inert gas at the various soil gas wells. The air injection rate will be increased semi-annually to evaluate the trade-off between the gain in area of influence of the injected air for bioremediation and the additional loss of air and volatilized organics to the atmosphere at the soil surface.

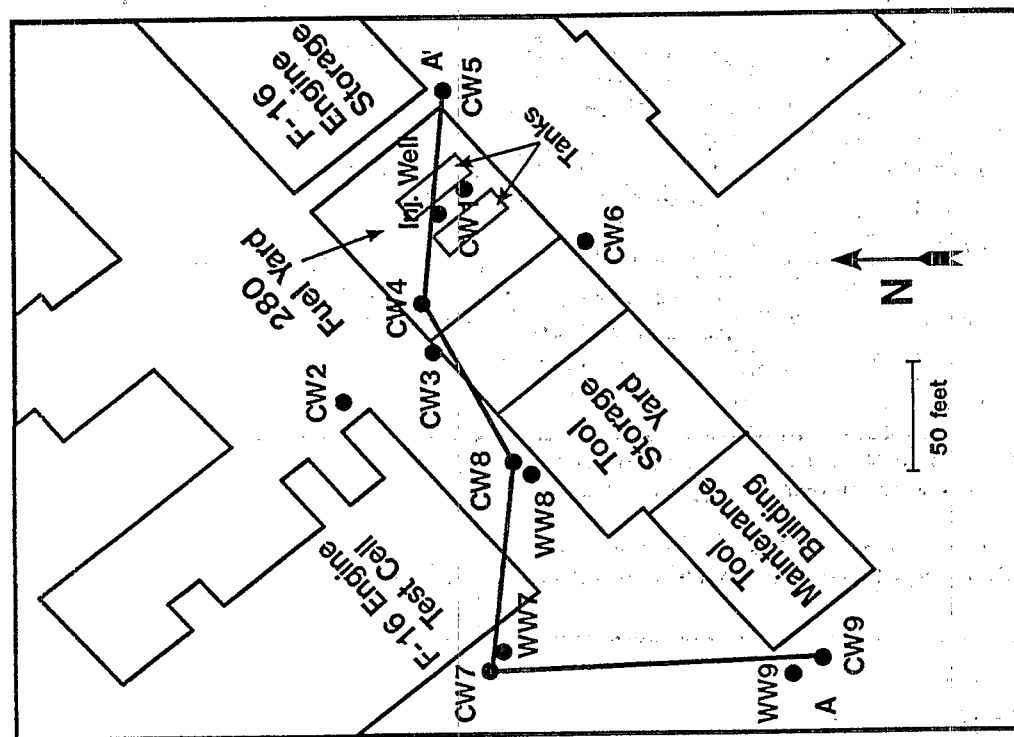


Figure 2. Plan view of the joint U.S. EPA and U.S. Air Force bioventing activities at Hill AFB. CW are cluster soil gas monitoring wells, WW are groundwater monitoring wells, and the air injection well is indicated. Path AA' indicates the location of the cross-sectional view shown in Figure 3.

## RESULTS

### Eielson AFB

Progress to date includes installation of the pilot-scale equipment and initial soil sampling for total hydrocarbons during July and August 1991, continuous soil temperature monitoring since August 25, and an initial pre-heating *in-situ* respiration test conducted in early October (data not available at this time). Figure 4 shows soil temperatures at one location at three different depths for the actively-warmed and (uncontaminated) background area as a function of time through November 15, 1991 (data for the other plots was not available at this time). Clearly, the active-warming strategy is functioning well: as ambient temperatures fell during the fall, the actively-warmed plot remained above 10°C (except for a short period when soil temperature decreased to between 8 and 9°C), while the temperature at the background location dropped steadily toward 0°C. The background area should drop well below 0°C during the winter since the annual average soil temperature at this location in Alaska is only about -2°C. Note that the active warming is maintaining the temperature in the actively-warmed plot near the average summer temperature of about 11°C.

Several problems caused inefficient performance of the actively-warmed plot in its early operation. The first problem encountered was reduced water flow rate from the buried soaker hoses due to the accumulation of silt around the hoses. The low water flow rate resulted in the steady decline of the temperature



between Day 30 and Day 56 (Figure 4). Our goal was to maintain the soil in the actively-warmed plot between 10 and 20°C. To remedy this situation, weekly high-pressure pulses are employed to clear the hoses. The pulsing began on Day 56 and quickly resulted in increased soil temperatures (Figure 4).

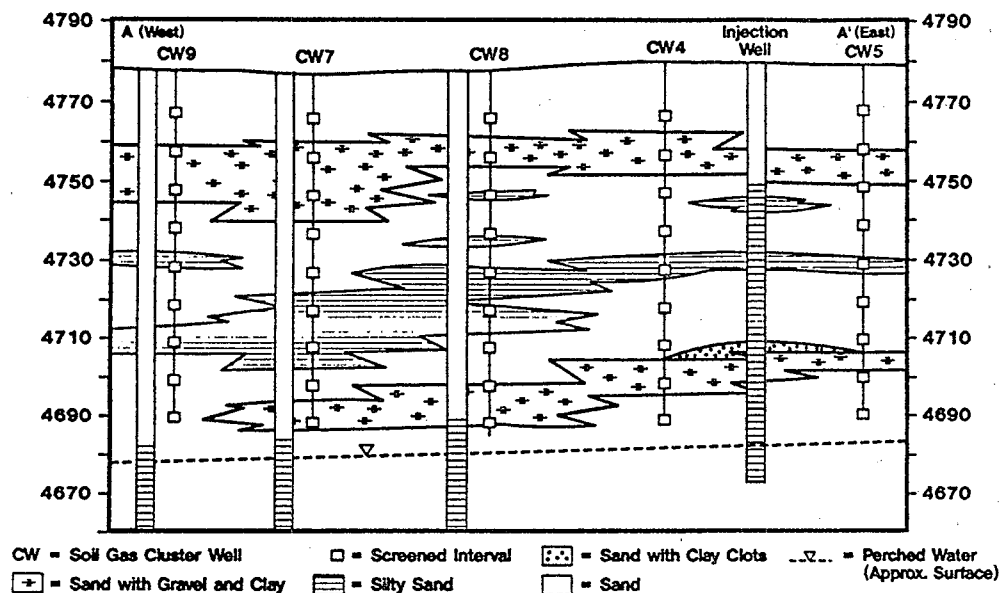


Figure 3. Cross-sectional view at Hill AFB along path AA' (Figure 2) showing the relative locations of the air-injection well, soil gas cluster and groundwater monitoring wells, and some geological features of the site.

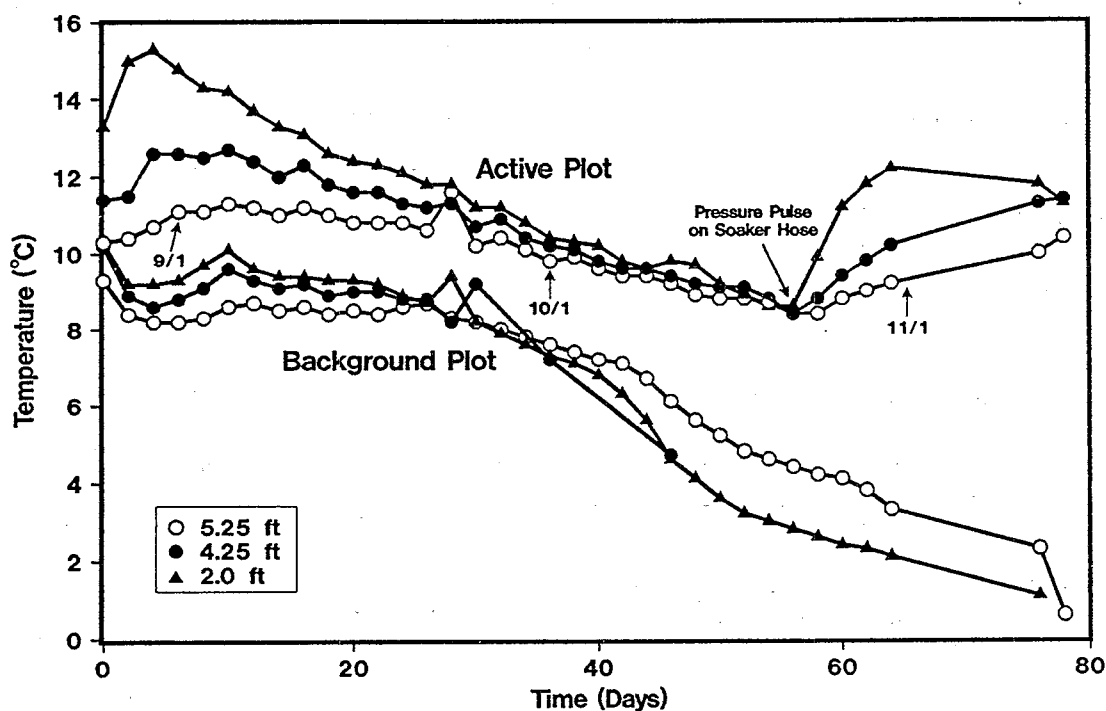


Figure 4. Temperature as a function of time at one location and three depths within the background and actively-warmed plots at Eielson AFB.

Second, the soils were not being adequately aerated, probably because a large fraction of soil pore volume flooded due to the continuous trickling of water onto the plot. Table 1 shows the range in soil oxygen concentration measured in the three plots immediately before the initial respiration test. Ideally, the forced aeration should result in a soil oxygen composition of at least 5-10% to avoid oxygen-limited microbial activity. The low oxygen concentration observed in some portions of the actively-warmed plot indicated rapid microbial activity, but also demonstrated that air was not being delivered efficiently to those areas. In December, semi-weekly cycling of the water flow rate from high to very low was initiated to decrease the average amount of water held in the soil in an attempt to increase the water-free pore volume.

TABLE 1. RANGE OF SOIL OXYGEN LEVEL DURING BIOVENTING PRIOR TO WATER FLOW RATE CYCLING. DATA ARE FROM TWO WELLS IN EACH PLOT, THREE DEPTHS EACH

Plot	Oxygen Conc. Range, %
Active	1 - 15
Passive	20 - 21
Control	7 - 20
Background	21

#### Hill AFB

Progress to date at Hill AFB includes completion of the installation of the wells shown in Figures 2 and 3 and initial soil sampling for total hydrocarbon levels as a function of depth. An example of one total hydrocarbon distribution is shown in Figure 5 for soil taken during installation of well CW6. This initial characterization will be compared to final soil sampling planned for Summer 1993 to calculate net loss of hydrocarbons due to bioventing. The inert gas tracer study is planned for Spring 1992.

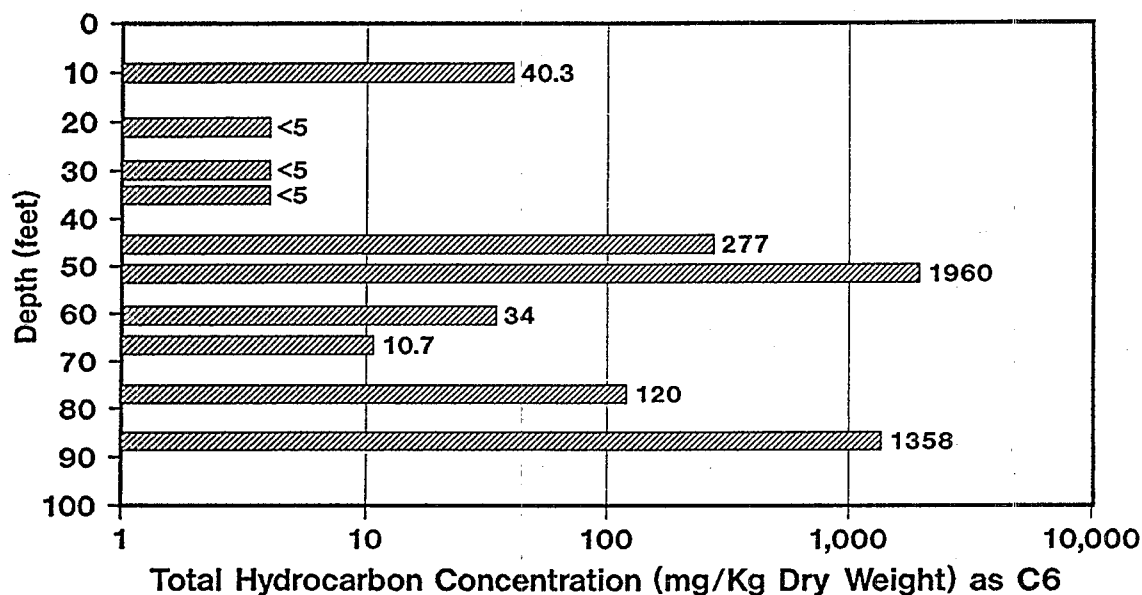


Figure 5. Initial total hydrocarbon distribution at Hill AFB well CW6. Total hydrocarbons are measured relative to a hexane standard.

## CONCLUSIONS

This paper summarizes the first 6 months of a 2-year joint U.S. EPA/U.S. Air Force study of *in-situ* bioventing. Already, the work at Eielson AFB has shown that active soil warming techniques are successful in maintaining soil at warm temperatures during cold ambient temperatures. The most efficient means of delivering warm water to avoid blockage of the buried hoses, and the optimal water and air flow rates that provide adequate warming and aeration, continue to be investigated.

The bioventing studies at Hill and Eielson AFBs are generating valuable pilot-scale performance data and field operational experience for a technology that in the near future could provide an cost-effective means of *in-situ* cleanup of organically contaminated unsaturated soils. In addition, the soil warming techniques investigated here will be applicable to enhancing biological treatment rates of unsaturated soils for any bioremediation technology at any location where a significant portion of the year is too cold to allow satisfactory biological activity.

## MEASUREMENT OF THE EFFECT OF TEMPERATURE ON OXYGEN UPTAKE

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### INTRODUCTION

The effectiveness of bioremediation products intended for use on spilled petroleum or refined petroleum products must be evaluated prior to a spill occurrence. The need for development of a test protocol for product evaluation has led to initiation of work at RREL in Cincinnati. Biological degradation of petroleum hydrocarbons requires molecular oxygen as a terminal electron acceptor. The current method for testing efficacy of bioremediation products involves monitoring disappearance of oil constituents over time by gas chromatography (GC) and gas chromatography/mass spectrometry (GC-MS), both of which are tedious and expensive. Our laboratory is developing methods by which O<sub>2</sub> consumption and CO<sub>2</sub> production can be correlated with disappearance of oil compounds. This correlation, once established, will permit examination of bioremediation products based on O<sub>2</sub> consumption/CO<sub>2</sub> production with minimal chemical analysis. The goal of this work is to establish reliable methods for assaying potential effectiveness of bioremediation products under various conditions.

Protocol development will encompass seawater, freshwater, sediments, beach material, and soils. Various types of crude oil or refined products will be examined as well as the effects of temperature and salinity on the efficacy of bioremediation products. Oxygen consumption, bacterial numbers, and changes in oil chemistry will be measured over time. When data collection is completed, the various parameters will be correlated with oil disappearance as measured by gas chromatography, and simpler, less expensive methods will be proposed as a measure of bioremediation product effectiveness.

This paper reports on the effect of temperature on microbial degradation of crude oil in closed systems. Degradation was tracked by measuring oxygen uptake in respirometers, decreases in aliphatic constituents of the oil, and changes in oil degrader populations over time. Results will have an impact on how bioremediation protocols will be conducted for determining product efficacy.

changes in oil degrader populations over time. Results will have an impact on how bioremediation protocols will be conducted for determining product efficacy.

## METHODOLOGY

Inoculum cultures were maintained by periodic (three week) transfers into Bushnell-Haas salts medium supplemented with 1.0% w/v Alaska North Slope (ANS) crude oil. Inocula were prepared by centrifuging 300 mL of culture and resuspending the pellet in a final volume of 60 mL of culture supernatant. Each respirometer flask was inoculated with 1 mL of the concentrated culture, except those flasks serving as uninoculated controls. The inoculum yielded about  $2.5 \times 10^4$  cells/mL final concentration. Flasks containing oil received 5000 mg/L of the ANS oil.

Oxygen consumption was measured using N-CON respirometers (Larchmont, NY). The N-CON system uses sensitive pressure switches to measure pressure drops in sealed flasks caused by oxygen consumption. The system then activates microsolenoid valves to feed  $O_2$  from a cylinder to balance the pressure in the flasks with reference pressure cells. The computer then calculates oxygen consumption based on the solenoid valve volume and number of pulses required to balance the system. The flask caps also include a reservoir for KOH solution for absorbing  $CO_2$  produced by oil degrading microorganisms. The KOH traps can be renewed by means of a syringe valve and cannula penetrating the flask cap.

Populations of microorganisms in the flasks were measured each time a sample series was collected for chemical analysis. Small samples (10-15 mL) of the flasks' contents were placed in a sterile reservoir on a Beckman Biomek 1000 laboratory robot. The Biomek fills a 96 well tissue culture plate with sterile medium, transfers and performs serial 10 fold dilutions of the sample, and layers oil (2  $\mu$ L No. 2 fuel oil) on the surface of each well automatically. The plates thus prepared are then covered and insulated in the dark at room temperature (22°C) for 14 days. After incubation, a multichannel pipettor is used to deliver 50  $\mu$ L of a 0.1% w/v solution of p-iodonitrotetrazolium violet to each well of each plate. After 30 minutes, positive wells were scored by counting the pink wells in each row of dilutions. The data produced were for an eight tube Most Probable Number (MPN) procedure and the MPN of oil degraders per mL was computed using a PC based Fortran program.

The remaining contents of each respirometer flask were treated by adding 50 mL of  $CH_2Cl_2$  to initiate extraction. The samples were extracted with  $CH_2Cl_2$  and had the  $CH_2Cl_2$  exchanged with hexane prior to silica gel chromatography. The crude hexane extract was applied to a 60-200 mesh silica gel column for fraction separation. The alkane fraction was eluted by washing the column with hexane and the aromatic fraction was eluted by washing the column with benzene: hexane (1:1) after the hexane washing.

The respective fractions were then concentrated to a standard volume and analyzed by GC and GC-MS. The analytical conditions were: injector

temperature, 250°C; oven temperature programmed from 5 min initial hold at 50°C to 300°C at 7°C/min; with a hold at 300°C for 35 min; FID detector, 350°C. In the case of the GC-MS the ionization voltage was 70 ev. The carrier gas was He at 5 mL/min and the column was a 0.75mm X 30mm DB-5 from Supelco, Supelco Park, PA. The GC was a Hewlett Packard 5880A and the GC-MS was a Hewlett Packard 5970A with a 0.25mm X 30mm DB-5 column. The other parameters were the same as for the GC except the program rate was 8°C/min. Oil residue weight was measured by drying a portion of the CH<sub>2</sub>Cl<sub>2</sub> extract and weighing the dried residue.

## RESULTS

The oxygen uptake curves at 15° and 25°C produced by microorganisms incubated with ANS crude were quite different. At 15°C, the onset of oxygen uptake occurred at 3 days and slowed in rate at 6 days. At 25°C oxygen uptake was rapid after 2 days and slowed after 5 days. Uptake was more rapid at 25° than at 15°. At 15°C, oxygen uptake was about 2500 mg/L, which is about 23% of theoretical. At 25°C, oxygen uptake was about 4500 mg/L, which is about 42% of theoretical. Potential oxygen uptake was calculated based on complete conversion of oil carbon to CO<sub>2</sub>. Total conversion would have consumed about 10,600 mg/L O<sub>2</sub>. The carbon content of the ANS crude was 82% based on elemental analysis of duplicate samples by an independent laboratory.

Over the period of this experiment, numbers of oil degraders followed a typical growth and decline pattern (Fig.1). At day zero the population in each flask was about  $2.5 \times 10^4$  cells per mL. By day 9 the population had increased by over five orders of magnitude, thereafter the population declining slowly to about  $10^7$  cells per mL.

Analysis of the oil content of flasks over the period of the experiment yielded interesting results. During incubation at 15°C, 95% of the resolvable alkanes were consumed by day 5 of the experiment. No aromatic hydrocarbon data were available at this writing. Degradation of labile alkanes was essentially complete by day 5. Oxygen uptake was still active after day 5, indicating that microorganisms were consuming less readily resolved hydrocarbons. Analysis of the data showed very little preference for degradation of normal alkanes over branched alkanes such as pristane. Pristane decreased in concentration almost as rapidly as heptadecane. This indicates some organisms can adapt to utilize branched chains as well as straight chains quite readily. Oil residue weight had declined from about 3500 mg/L to 3200 mg/L at the end of the experiment. Figure 2 shows the results of oil analyses from this experiment.

Even though easily analyzed hydrocarbons were consumed, significant quantities of oil persisted in the flasks. The easily resolved hydrocarbons measured by GC represent a small fraction of the total oil mass. Our laboratory estimates the n-alkane fraction to be about 1% of the oil.

The difference between oxygen uptake and oil residue weights may be due to the fact that oil residue methods only provide a general mass estimate. The extraction procedure will extract any compound that preferentially partitions

into  $\text{CH}_2\text{Cl}_2$  over water. Some of these compounds will include partially metabolized oil compounds and cellular lipids.

A subsequent experiment was conducted to evaluate the response of microorganisms to six different kinds of oil or refined products. Crude oils, light Arabian (LA), South Louisiana (SL), Prudhoe Bay (PB), and Weathered PB (WP) and Number 2 (F2), and Number 6 (F6) fuels were incubated at 15 and 25°C as previously described. Trials were conducted with nutrients or without added nutrients at both temperatures. In general, oxygen uptake at 15°C was lower than at 25°C. At 15°C, oxygen consumption was about 3700 mg/L for LA, 3200 mg/L for F2, 2700 mg/L for SL, 1600 mg/L for PB and WP, and 1000 mg/L for F6 with nutrients. Without nutrients  $\text{O}_2$  consumption was lower. The onset and early rate of oxygen uptake was the same for LA and PB crudes beginning at three days. Degradation of LA continued rapidly until 12 days and slowed. Degradation of PB slowed after six days. Degradation of SL began at four days and slowed at seven days. WP oxygen uptake began at five days and slowed at seven days. Oxygen uptake with F2 began at five days and remained mostly constant until 18 days. F6 oxygen uptake started at five days and remained slow for the entire experiment.

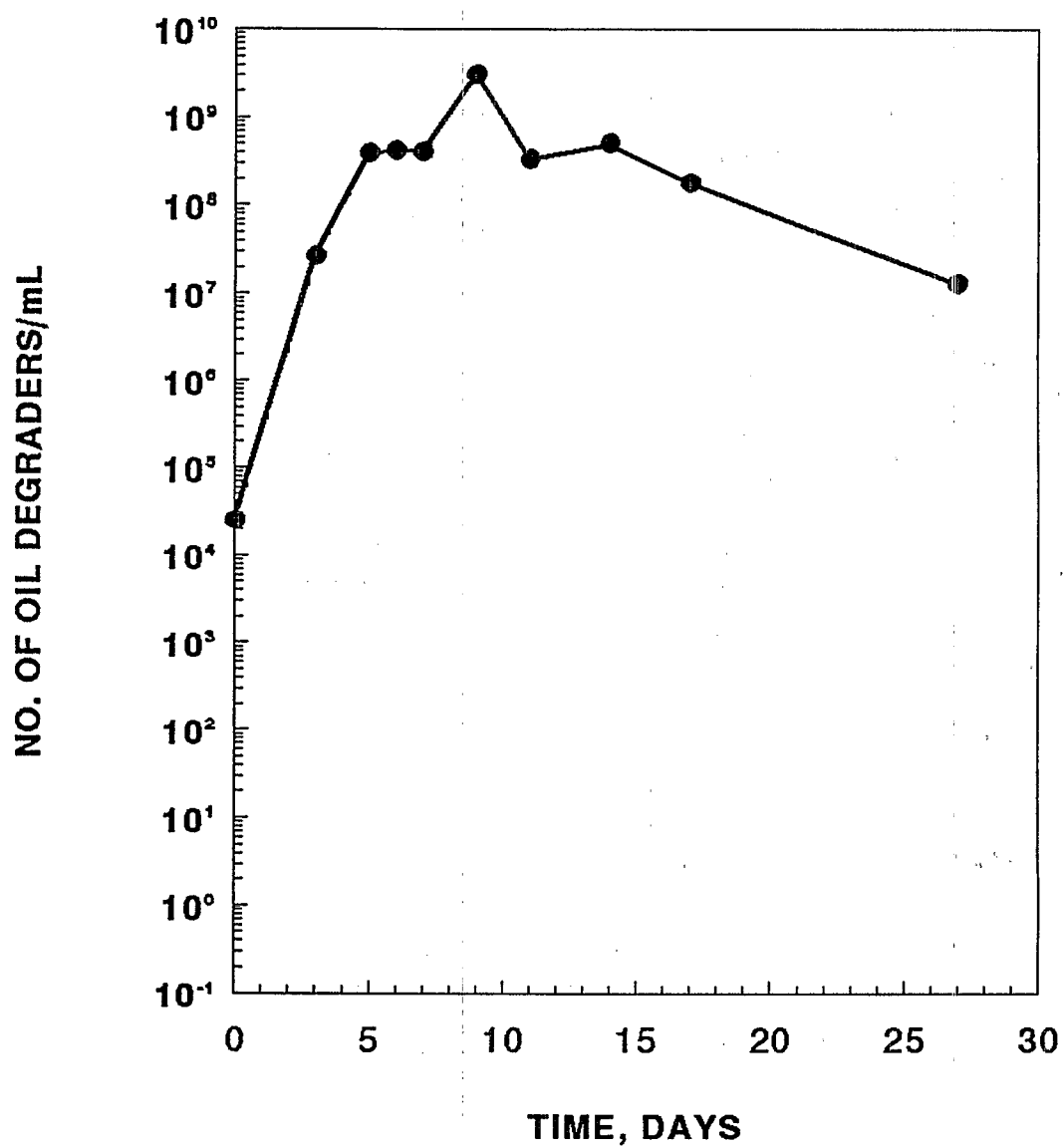
## CONCLUSIONS

The results of work to date show that the performance of microorganisms degrading oil varies significantly with temperature and nutrients as expected.

Our results indicate that the major portion of oxygen consumption is complete by less than 14 days of incubation at either 15 or 25°C. The readily degraded compounds are largely consumed in this period and therefore experiments evaluating bioremediation products may be completed in less than 30 days. Oil residue weight may not be a good indicator of degradation. Long period studies can concentrate on metabolism of resistant structures left in crude oils after preliminary weathering. The variation in  $\text{O}_2$  consumption resulting from different kinds of oils shows that bioremediation products may need to be tailored for the specific type of oil involved in a spill. The data obtained with multiple oils also will aid in planning future experiments with regard to sample collection and analysis. The lighter fuels and crude oils yielded the highest  $\text{O}_2$  consumption. The lowest  $\text{O}_2$  uptake was associated with the heavy No.6 fuel and weathered PB oils.

Testing of bioremediation products will require careful attention to the parameters of microbial growth in the testing sequence. The type of product, the oil product the remedial product is intended for, the environmental parameters affecting the remedial product, and the time scale that remedial products are intended to act in, will require that testing protocols be flexible in methodology and interpretation.

Future work will expand upon the preliminary results obtained to date in this work.



**Figure 1. Most Probable Number of Oil Degraders over Time.**



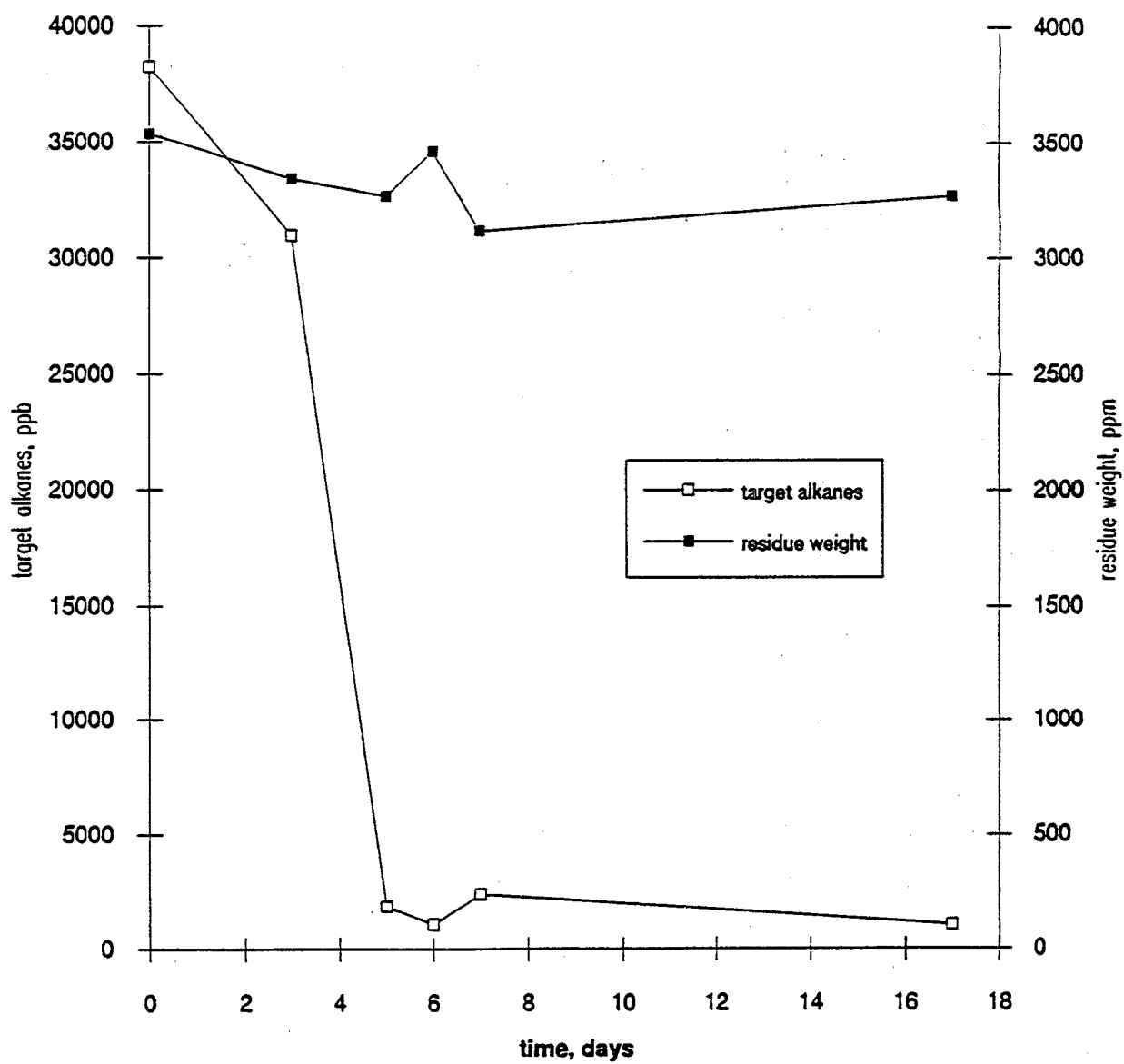


Figure 2. Decline in Target Alkanes and Residue Weight as a Function of Time at 15°C.

# A FUNDAMENTAL KINETIC STUDY OF THE ANAEROBIC BIODEGRADATION OF CHLOROFORM AND ITS PRODUCTS WITH VARIOUS CO-SUBSTRATES IN MIXED CULTURE CHEMOSTATS

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## INTRODUCTION

The highly chlorinated methanes biologically degrade only extremely slowly under aerobic conditions. For example, in conventional wastewater treatment facilities, these toxic compounds would likely be untreated and either pass through the aerobic bioreactor and appear in the plant effluent or be stripped to the atmosphere by the aeration. Cost-effective technologies to destroy these priority pollutants are required due to their prevalence at Superfund sites, in landfill leachates and in industrial effluents. For example, the 1986 National Priorities List (NPL) database indicates that chloroform and carbon tetrachloride appear at 24% and 7% of all NPL sites, respectively.

It is well known that anaerobic biological treatment can degrade the highly chlorinated methanes efficiently while metabolizing more easily degradable primary substrates. However, recently completed research by the U.S. EPA Risk Reduction Engineering Laboratory revealed that chloroform can severely limit the ability of methanogenic anaerobic treatment systems to process readily biodegradable and more refractory constituents of a multicomponent hazardous waste stream.

The type of anaerobic environment utilized appears to influence the impact that these compounds have on an anaerobic process. Recent data collected from a leachate-treatability study conducted at the U.S. EPA Test and Evaluation Facility using parallel anaerobic reactors operating under methanogenic and sulfate-reducing conditions, respectively, revealed that sulfate-reduction promoted efficient chloroform degradation while, once again, methanogenic activity was adversely affected by increased levels of chloroform in the feed.

Thus, the objective of this study is to rigorously investigate the anaerobic biodegradability of chlorinated methanes with primary emphasis on chloroform. The fundamental kinetics of transformation of carbon tetrachloride, chloroform, dichloromethane and chloromethane are studied under methanogenic and sulfate-reducing environments. These kinetics are evaluated in the presence of the co-substrates methanol, formate and acetate.

## METHODOLOGY

Six 10-liter stainless-steel chemostats were assembled. Each chemostat is equipped with two constant speed masterflex pumps to feed the nutrients and

the buffer. The nutrients contain the necessary inorganic salts and vitamins, while the buffers maintain a constant pH. The masterflex pumps are channelled through timers to enable variable flows. The organic substrates are injected with a 10-ml syringe pump. The contents of the chemostats are kept completely mixed with the aid of a variable speed mixer. The primary substrate in the feed to each chemostat and the corresponding anaerobic environment are listed in Table 1. The chloromethane will be an additional organic feed component.

TABLE 1. KEY CONSTITUENTS OF THE CHEMOSTAT FEED

Chemostat	Environment	Co-Substrate
I	Methanogenic	Methanol
II	Methanogenic	Acetate
III	Methanogenic	Formate
IV	Sulfate-reduction/methanogenic	Methanol
V	Sulfate-reduction/Methanogenic	Acetate
VI	Sulfate-reduction/Methanogenic	Formate

The chemostats are operated at a 3 g/day COD loading. Daily and weekly analyses are performed to monitor the performance of the chemostats. The daily analyses include recording the feed rates of the buffer, nutrient, and syringe pump (COD feed) solutions, and measuring the pH, total gas production, and temperature. Appropriate adjustments in the buffer solutions are made to keep the pH constant at 7.2. Weekly analyses include measuring the COD and sulfate concentration, volatile suspended solids (VSS), and volatile fatty acids (VFA) in the effluent. The percent composition of the effluent gas is also determined. These measurements allow calculation of the fraction of the COD removal attributable to methanogenesis (methane formation), to sulfate-reduction (oxidation of the organic feed components by the reduction of sulfate), and to biomass production. An example of the weekly COD balance is presented in Figure 1. Steady state is confirmed and characterized by constant levels of all parameters including measurement of the oxidation-reduction potential (ORP).

In the methanogenic/sulfate-reducing systems, an abundance of iron is required as a microbial nutrient and to precipitate the inhibitory sulfide that is produced. Iron is introduced in the chemostats with the nutrient solution. Organic chelating agents have been used in the past to solubilize iron in nutrient solutions, but these agents are not desirable as they serve as another source of COD. A detailed investigation of the chemistry of the anaerobic environment resulted in an alternative procedure that does away with these chelating agents.

## RESULTS

As of December 1991, the first phase of the project was complete. The goal of the first phase was to obtain an initial steady-state operation for all the chemostats without the presence of chloromethanes. Over four months

of stable operating data, and weekly COD balance on all the chemostats indicate that the initial steady-state was achieved (an example of the weekly COD balance for Chemostat I is presented in Figure 1). To confirm steady-state, *in-situ* ORP measurements were performed repeatedly. The steady-state values for selected parameters are shown in Table 2. Note that the sum of the percent of COD removal by methanogenesis and by sulfate-reduction does not equal 100 because a fraction of the inlet COD is used to produce biomass.

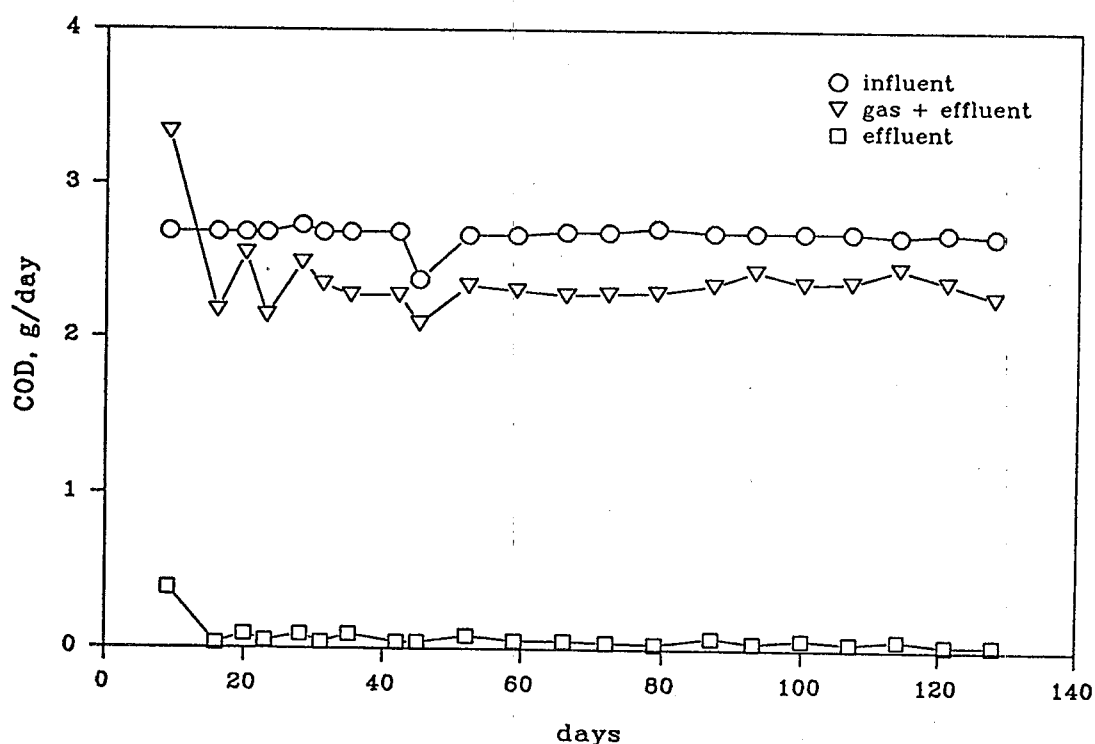


Figure 1. Weekly COD balance for chemostat I through December 4, 1991.

A computer model was developed to study the interactions of the various ions present in the systems. The main motivation for this task was to study the effect of these interactions on the availability of the nutrients, especially in the case of the sulfate-reducing systems where large amounts of sulfide are produced that can cause precipitation of the important nutrient metals. A non-steady CSTR model was prepared to simulate equilibrium interactions. Refinement of this model is continuing. The results from the

model will be compared with experimental data. These results will also be presented at the symposium.

TABLE 2. STEADY STATE RESULTS FROM CHEMOSTAT I

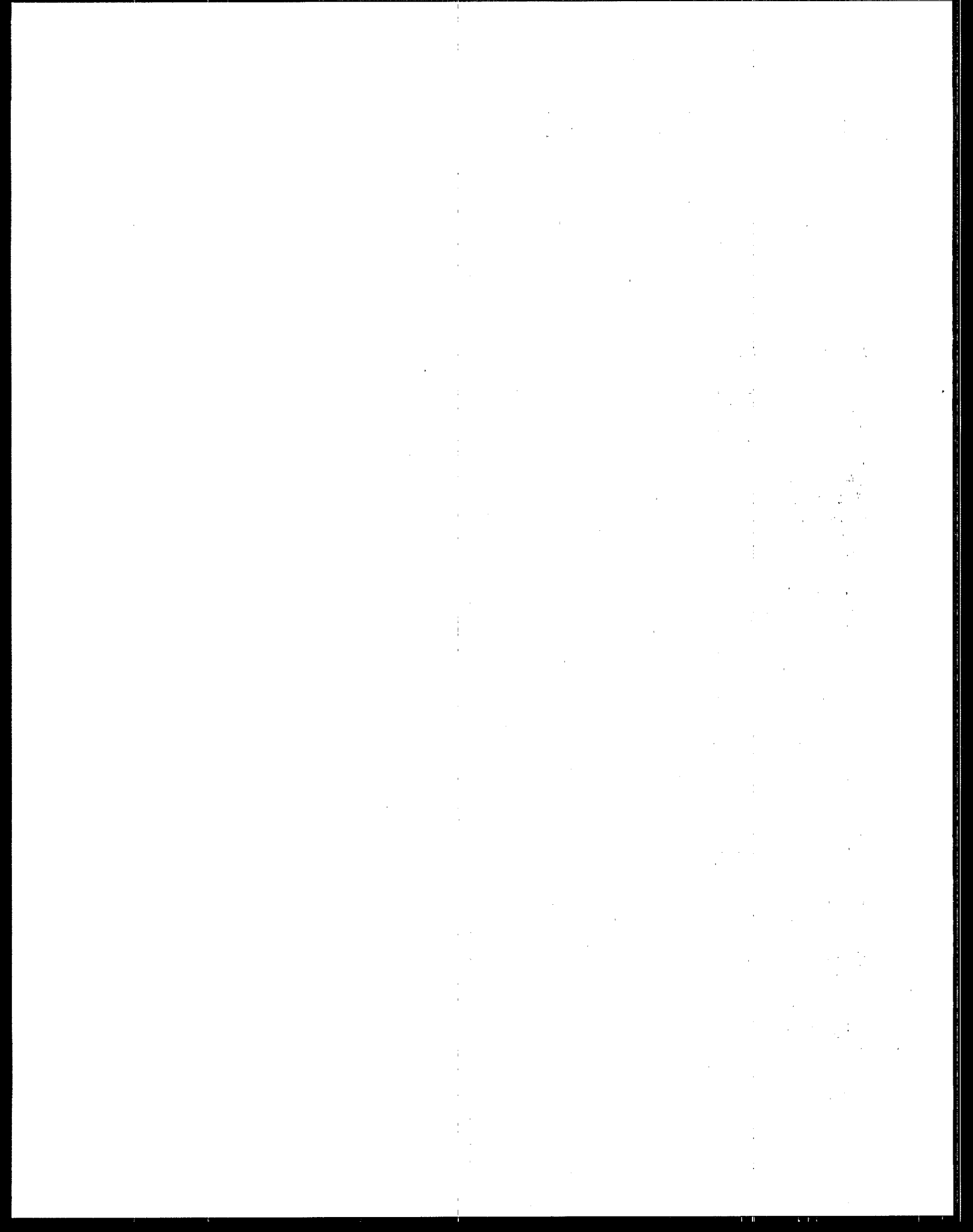
Chemostat	Removal of Inlet COD %	Fraction of COD Removal by	
		Methanogenesis %	Sulfate-reduction %
I	98	85	0
II	96	83	0
III	97	81	0
IV	96	0	66
V	94	84	0
VI	95	40	27

## CONCLUSIONS

As expected, the methanogenic systems consumed the primary substrates very efficiently with all chemostats exhibiting above 95% COD removal (Table 2). However, the sulfate-reducing systems exhibited some more interesting behavior:

- i. Acetate was readily consumed by the sulfate reducers (chemostat IV).
- ii. Although there was an abundance of sulfate in this chemostat feed (4500 mg/l), methanol was not consumed by the sulfate reducers in chemostat V and no COD was utilized via sulfate-reduction. While both the chemostats with methanol feed (chemostats II and V) exhibited methanogenesis exclusively, differences were observed in their operation. The most important was the difference in the ORPs, where the absolute value of the ORP of the chemostat with sulfate was more than twice that of the chemostats with no sulfate. Consequently, very different behaviors between the two reactors are expected once the chloroform feed starts.
- iii. A competition was observed between sulfate reducers and methanogens for formate utilization (chemostat VI). Batch tests will be performed on the chemostat contents to evaluate the kinetic parameters in order to explain this behavior.

The second phase of the project is due to start shortly. During this phase of the study, chloroform feed to the chemostats will begin. The results of part of the second phase will also be presented at the symposium.



EMISSIONS OF ORGANICS FROM BIOSLURRY REACTORS TREATING  
SOIL CONTAMINATED WITH WOOD PRESERVING WASTE

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## INTRODUCTION

This paper is a part of the work conducted for a joint Superfund Innovative Technology Evaluation (SITE) project and a study for the EPA's Office of Solid Waste and Emergency Response (OSWER) that is developing information for Best Demonstrated Available Technology (BDAT). The project was conducted at the U.S. EPA Test and Evaluation Center located at the Gest Street Waste Water Treatment Plant in Cincinnati, Ohio. The contaminated soil chosen for the test of the effectiveness of bioslurry reactors for the degradation of wood preserving wastes was a soil from the Burlington Northern NPL site in Brainerd, Minnesota. The overall results of the soil treatment are presented in a paper titled "Slurry Reactor Bioremediation of Soil-Bound Polycyclic Aromatic Hydrocarbons" by Alan Jones, Madonna Brinkmann, and William Mahaffey of Ecova Corporation.

Air sampling was conducted to characterize the off-gases emitted from the bioreactors during the operations and to determine organic constituent loss through volatilization.

## METHODOLOGY

All five reactors were vented through stainless steel piping into a manifold system before carbon filtration and eventual exhausting to the outside air. The air monitoring was conducted at a point prior to the collective manifold to obtain emissions from two individual reactors.

Two sampling trains were constructed to collect samples for volatile and semivolatile organics. Volatile organics were collected in a SUMMA passivated canister, and semivolatiles were collected in XAD-2 resin tubes. The canisters and XAD-2 resin tubes were installed in the venting systems for the tested reactors.

Four consecutive sets of samples were collected from each of the two tested reactors during the first week of operation. Two sets of samples were collected during weeks 2 through 5, and one

set of samples was collected during weeks 6, 7, and 9.

The air sampling program measured semivolatile, volatile, and total hydrocarbons during the first nine weeks of treatment. Total Hydrocarbons (THC) as methane was determined according to procedures in U.S. EPA Method 25A. This sampling was conducted continuously at the main exhaust line for the first five days of operation. Sampling for volatiles (by modified Method T014) and semivolatiles (by modified Method T013) was conducted periodically during the first nine weeks of operation.

## RESULTS

The background ambient air showed THC concentrations averaging 3ppm on a dry basis. During the charging of the reactors THC emissions gradually increased with peak concentrations averaging 390 ppm or 0.014 lb/hr from 17:51 to 18:00 on May 8, 1991. A table will be presented showing the concentrations, emission rates, and flow rates used to calculate emissions. All data are reported as methane because it was used as the calibration gas during the sampling.

The emissions of THC dropped to 0.007 lb/hr in a little over 6 hours, and to 0.00176 lb/hr in just 24 hours. Within 48 hours the THC emissions were down to less than 0.0003 lb/hr and by 72 hours were less than 0.0002 lb/hr.

Semivolatile polynuclear aromatics were detected during the first four days of operation with naphthalene found at 8600 ug/sample, 2-methylnaphthalene at 1500ug/sample, and acenaphthene, fluorene, phenanthrene, and anthracene going in order from 703 ug/sample to 23 ug/sample. After four days all samples were below 15ug/sample. By day 3 the most volatile compounds, naphthalene and 2-methylnaphthalene had already declined to less than 20 ug/sample.

The volatile organics found in greatest abundance were: xylene, toluene, ethylbenzene, benzene, and styrene. Table 1 shows the results of the first 4 days of measurement of 12 volatile compounds. The samples again show that the majority of emissions occurred during the first few days of operation of the slurry bioreactors.

## Conclusions

It has often been stated that liquid aerated biotreatment of hazardous compounds should be avoided because of the potential for air pollution during the treatment. The testing of air emissions during this project shows that the major emissions are during the charging of the vessels and a small amount may continue for the first few days. The problem of air emissions during charging of a reactor can be similar or even greater in charging incinerators or other non-biological treatment units.



The levels of both semivolatile and volatile organics found in the air emissions of the bioreactors dropped back to near the background level within four days. Emission control systems can be devised for operation of bioslurry reactors, but the cost benefit may be low when there are no major concentrations of volatile compounds present in the waste. The microbes are quite efficient in capturing and using most of the semivolatile compounds that can be biodegraded.

TABLE 1. Volatile Organic Emissions

	DAY 1	DAY 2	DAY 3	Day 4
Concentration	ppb	ppb	ppb	ppb
Compound				
carbon disulfide	67.0	17.0	5.0	20.0
methylene chloride	-	0.8	9.2	1.1
chloroform	-	-	0.7	1.1
1,1,1-trichloroethane	-	1.6	2.8	1.6
benzene	45.0	2.3	2.4	1.2
toluene	230.0	4.6	8.0	3.2
tetrachloroethane	-	-	1.6	-
chlorobenzene	-	-	0.9	-
ethylbenzene	160.0	3.4	1.5	0.9
m- and/or p-xylene	800.0	17.0	7.3	3.0
o-xylene	320.0	14.0	3.5	1.4
styrene	44.0	3.6	0.9	0.5

## **DESIGN OF FULL SCALE DEBRIS WASHING SYSTEM**

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### **BACKGROUND**

In conjunction with promulgating Land Ban Disposal Regulations, the United States Environmental Protection Agency (EPA) published (Federal Register, May 30, 1991) an Advanced Notice of Proposed Rule Making (ANPR) in which definitions for debris and contaminated debris were suggested as quoted below:

Debris means solid material that: (1) has been originally manufactured or processed, except for solids that are listed wastes or can be identified as being residues from treatment of wastes and/or wastewaters, or air pollution control devices; or (2) is plant and animal matter; or (3) is natural geologic material exceeding a 9.5 mm sieve size including gravel, cobbles, and boulders (sizes as classified by the U.S. Soil Conservation Service), or is a mixture of such materials with soil or solid waste materials, such as liquids or sludges, and is inseparable by simple mechanical removal processes.

Contaminated Debris means debris which contains RCRA hazardous waste(s) listed in 40 CFR Part 261, Subpart D, or debris which otherwise exhibits one or more characteristics of a hazardous waste (as a result of contamination) as defined in 40 CFR Part 261, Subpart C.

The ANPR also contains suggested techniques for decontaminating debris prior to disposal. The options listed include high pressure washing based, to a large extent, on work performed by EPA/RREL. This paper gives an overview of the development and assessment of high pressure washing technology and presents an update on EPA's efforts to develop a full scale, semi-automatic, debris washing system (DWS).

### **INTRODUCTION**

Since 1987, IT Environmental Programs Inc. (ITEP, a subsidiary of International Technology Corporation) in conjunction with EPA/RREL in Cincinnati, Ohio, have been developing and conducting bench scale and pilot scale testing of a transportable debris washing system which can be used on-site for the decontamination of debris (1).

During the initial phase of the debris decontamination project, a series of bench scale tests were performed in the laboratory to assess the ability of the system to remove contaminants from debris and to facilitate selection of the most efficient surfactant solution. Five nonionic, non-toxic, low foaming, surfactant solutions (BG-5, MC-2000, LF-330, BB-100, and L-422)<sup>a</sup> were selected for an experimental evaluation to determine their capacity to solubilize and remove contaminants from the surfaces of corroded steel pieces. The pieces of corroded steel were coated with a heavy grease mixture prepared in

<sup>a</sup> Manufacturers of these surfactants are: BB-100, Bowden Industries, Huntsville, AL; BG-5, Modern Chemical, Jacksonville, AR; MC-2000, Alcolac, Baltimore, MD; LF-330, GAF Chemicals Corporation, Wayne, NJ; and L-422, DuBois Chemicals, Cincinnati, OH.

the laboratory and these pieces of "debris" were placed in a bench scale spray tank on a metal tray and subjected to a high-pressure spray for each surfactant solution for 15 minutes. At the end of the spray cycle, the tray was transferred to a second bench scale system, a high-turbulence wash tank, where the debris was washed for 30 minutes with the same surfactant solution as that used in the spray tank. After the wash cycle was completed, the tray was removed from the wash tank and the debris was allowed to air-dry. Before and after treatment, surface-wipe samples were obtained from each of the six pieces of "debris" and were analyzed for oil and grease. Based on the results, BG-5 was selected as the solution best suited for cleaning grease-laden, metallic debris.

## PILOT SCALE DEBRIS WASHING SYSTEM

Based on the results obtained from bench scale studies, a pilot scale debris washing system (DWS) was designed and constructed. The pilot scale DWS consists of a 300-gallon spray tank, a 300-gallon wash tank, a surfactant holding tank, a rinse water holding tank, an oil/water separator, and a solution-treatment system consisting of a diatomaceous earth filter, an activated carbon column, and an ion-exchange column. The pilot scale DWS was demonstrated at a PCB-contaminated site in Hopkinsville, Kentucky, and a pesticide-contaminated site in Chickamauga, Georgia.

Demonstration at the Ned Gray PCB Site, Hopkinsville, KY -- This site covers approximately 25 acres. From 1968 to 1987 a metal reclaiming facility was operated at the site, which involved open burning of electrical transformers to recover copper for resale. Approximately 70 to 80 burned-out, PCB-contaminated transformers were on site, along with large amounts of other materials, including asbestos-covered pipes, automobiles, and miscellaneous scrap metal. The entire DWS was transported to the Hopkinsville, Kentucky site on a 48-foot semitrailer and reassembled on a 24 ft x 24 ft concrete pad. A temporary enclosure, approximately 25 ft high, was also built on the concrete pad to enclose the DWS and to protect the equipment and surfactant solution from rain and cold weather. The demonstration took place during December 1989 when ambient temperatures at the site during the demonstration ranged from near 0° to 50°F.

Prior to the initiation of the cleaning process, the transformer casings, ranging from 5 gallons to 100 gallons in size, were cut into halves with a metal-cutting saw. A pretreatment sample was obtained from one half of each of the transformer casings by using a surface wipe technique (2). The transformer halves were placed into a basket and lowered into the spray tank of the DWS, which was equipped with multiple water jets that blast loosely adhered contaminants and dirt from the debris. After the spray cycle, the basket was removed and transferred to the wash tank, where the debris was immersed into a high-turbulence washing solution. Each batch of debris was cleaned for a period of 1 hour in the spray tank and 1 hour in the wash tank. During both the spray and wash cycles, a portion of the cleaning solution was cycled through a closed-loop system in which the oil/PCB-contaminated cleaning solution was passed through an oil/water separator, and the clean oil-free solution was then recycled into the DWS. After the wash cycle, the basket containing the debris was returned to the spray tank, where it was rinsed with fresh water. Upon completion of the cleaning process, posttreatment wipe samples were obtained from each of the transformer pieces to assess the residual levels of PCBs. The before-treatment concentrations ranged from 0.1 to 98  $\mu\text{g}/100\text{ cm}^2$ . The posttreatment analyses showed that all the cleaned transformers had a PCB concentration lower than the acceptable level of 10  $\mu\text{g}/100\text{ cm}^2$ .

After treatment of all transformers at the site, the spent surfactant solution and the rinse water were neutralized to a pH of approximately 8 by using concentrated sulfuric acid and were treated in the water treatment system. The before- and after-treatment water samples were collected and analyzed for PCBs and selected metals (cadmium, copper, chromium, lead, nickel, and arsenic).

The PCB concentration in the water was reduced by the treatment system to below the detection limit of 0.1  $\mu\text{g}/\text{L}$ . The concentrations of each of the selected metals (except arsenic) were reduced to the allowable discharge levels set by the city of Hopkinsville for discharge into the sanitary sewer. Upon receipt of the analytical results of the water, the treated water, which was stored in the holding tank, was pumped into a plastic-covered, 10,000-yd<sup>3</sup> pile of contaminated soil at the site. During this site cleanup, 75 transformers were cleaned in the DWS. All of these transformers were considered to be free of PCB contamination and were sold to a scrap smelter.

Demonstration at the Shaver's Farm Site, Chickamauga, GA -- The second demonstration of the DWS was conducted at a drum disposal site in August 1990. Fifty-five gallon drums containing varying amounts of a herbicide, Dicamba (2-methoxy-3,6-dichlorobenzoic acid), and benzonitrile, a precursor in the manufacture of Dicamba, were buried on this 5-acre site. An estimated 12,000 drums containing solid and liquid chemical residues from the manufacture of Dicamba were buried there during August 1973 to January 1974. EPA Region IV had excavated more than 4000 drums from one location on the site when this demonstration occurred. The pilot scale DWS and the steel-framed temporary enclosure used previously at the Hopkinsville, Kentucky Site were transported to this site in a 48-foot semitrailer and assembled on a 24 ft x 24 ft concrete pad. Ambient temperature at the site during the demonstration ranged from 75 to 105°F.

Prior to treatment in the DWS, the 55-gallon, pesticide-contaminated, empty drums were sawed into four sections. Pretreatment surface-wipe samples were obtained from each section. The drum pieces were placed in the spray tank of the DWS for 1 hour of surfactant spraying, then placed in the wash tank for an additional hour of surfactant washing, followed by 30 minutes of water rinsing in the spray tank. The drum pieces were then allowed to air-dry before posttreatment surface-wipe samples were obtained. Ten batches of one to two drums per batch were treated during this demonstration. Pretreatment concentrations of benzonitrile in surface-wipe samples ranged from 8 to 47,000  $\mu\text{g}/100\text{ cm}^2$  and averaged 4556  $\mu\text{g}/100\text{ cm}^2$ . Posttreatment levels of benzonitrile ranged from below detection limit to 117  $\mu\text{g}/100\text{ cm}^2$  and averaged 10  $\mu\text{g}/100\text{ cm}^2$ . Pretreatment Dicamba values ranged from below detection limit to 180  $\mu\text{g}/100\text{ cm}^2$  and averaged 23  $\mu\text{g}/100\text{ cm}^2$ , whereas posttreatment concentrations ranged from below detection limit to 5.2  $\mu\text{g}/100\text{ cm}^2$  and averaged 1  $\mu\text{g}/100\text{ cm}^2$ . The detection limit for wipe samples for dicamba and benzonitrile was 5  $\mu\text{g}/100\text{ cm}^2$ .

Upon completion of the treatment, the spent surfactant solution and rinse water were treated in the water treatment system. The before- and after-treatment water samples were collected and analyzed (in duplicate) for benzonitrile and Dicamba. The concentration of benzonitrile in the pretreatment water samples was 250 and 400  $\mu\text{g}/\text{L}$ , and the posttreatment concentration was below the detection limit of 5  $\mu\text{g}/\text{L}$ . The concentration of Dicamba in the pretreatment samples was 6800 and 6500  $\mu\text{g}/\text{L}$ , and the posttreatment concentration was estimated to be less than or equal to 630  $\mu\text{g}/\text{L}$  (value estimated due to matrix interferences). Since the concentration of Dicamba in the posttreated water sample was possibly as high as 630  $\mu\text{g}/\text{L}$ , the treated water stored in the polyethylene holding tank was pumped into an onsite water-treatment system for further treatment by EPA. Although the concentration of Dicamba in posttreatment water was an estimated value, it was decided to send the water to the onsite water-treatment system prior to discharge as a precautionary measure.

The test equipment was decontaminated with a high-pressure wash. The wash water generated during this decontamination was collected and pumped into the onsite water-treatment system. The system and the enclosure were disassembled and transported back to Cincinnati in a semitrailer.

#### **FULL SCALE DEBRIS WASHING SYSTEM**

The extensive experience gained under actual field conditions with the pilot scale DWS lead to the following conclusions regarding the technology: 1) the desired results were obtained using the pilot scale DWS - a marked reduction of organic contaminants on actual metallic debris from CERCLA sites was achieved; 2) the generation of large volumes of contaminated waste water was avoided by employing a process water filtration system which operates concurrently with the debris cleaning process; and 3) the pilot scale system as constructed is mechanically reliable and proved to be very rugged and amenable to being transported from site to site. Thus the field studies convincingly demonstrated that the DWS technology has definite promise for addressing the problem of decontaminating metallic debris at hazardous waste sites. In addition, important information was also gained during these field demonstrations which indicate areas where improvements in the full scale system design could be made and these are summarized in the following paragraphs.

The pilot scale system is not a high throughput device and extensive manual handling of debris is required. Due to the relatively small size of the spray and wash tanks debris larger than approximately 30" x 15" x 30" must be cut to size. Debris must be manually placed into a basket which is lifted using a fork-lift and then lowered into the spray tank. The efficiency of the spraying treatment is limited by the fact that the wire mesh on the sides of the basket interferes with the spray which emerges from nozzles on the sides of the spray tank. It was determined that during the one hour spray cycle the best results were obtained when the spray cycle was momentarily interrupted and the debris was manually repositioned to enhance contact between the debris surfaces and the spray. The spray intensity was found to be incapable of removing all of the heavy clay deposits from surfaces of drums excavated in Chickamauga. As indicated in the above discussion, it is clear that the overall pilot scale process, although generally very effective for removing hazardous contaminants, is labor intensive.

When approaching the design of the full scale system the following goals were established:

1) the manual handling of debris is to be kept to a minimum, if not eliminated; 2) the overall throughput of debris/day is to be markedly increased (on the order of ten-fold) while not diminishing the effectiveness of the process; 3) the usage of water is to be increased somewhat, however recycling of process water to minimize generation of wastewater is essential; 4) the full scale system should be mounted on one or two normal-sized semitrailers which require no special permits; 5) the system is to be rugged enough to be transported from site to site with minimal time and costs for mobilization/demobilization; 6) the system is to include appropriate features to ensure the safety of workers operating the system and to ensure containment of emissions potentially harmful to the environment. In an effort to address the goals for the full scale DWS the following features have been incorporated into the design. A schematic representation of the full scale system is shown in Figure 1.

The unit operations will entail initially loading a heavy duty basket with approximately two tons of debris (typically metallic debris) which will then be lifted by means of a crane and placed in a 3000 gallon tank. An innovative system will permit the debris to be directly impacted by high intensity detergent spray while the debris is subjected to a tumbling action. In addition to the spray/tumbling phase, the debris will be cleaned using a wash cycle in which the debris is immersed in cleaning solution and then a final spray/rinse will be utilized to remove residual contaminated liquid from the surfaces of the debris. The contaminated liquids (detergent solution, rinse solution) will be continuously treated using a transportable process water treatment system which will include various treatment modules which will be implemented to decontaminate the process water. In this fashion, the quantity of process water generated during the debris cleaning process will be significantly minimized. The full scale DWS will be mounted on two semitrailers. Site preparation will be minimal and is expected to entail leveling and placing of gravel or crushed stone on which the trailers will be parked.

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- 1) Technology Evaluation Report: Design and Development of a Pilot Scale Debris Decontamination System, U.S. Environmental Protection Agency. EPA 540/5-91-006a, August 1991.
- 2) Field Manual for Grid Sampling of PCB Spill Sites to Verify Cleanup, U. S. Environmental Protection Agency, EPA 560/5-86/017, May 1986.

## ACKNOWLEDGMENTS

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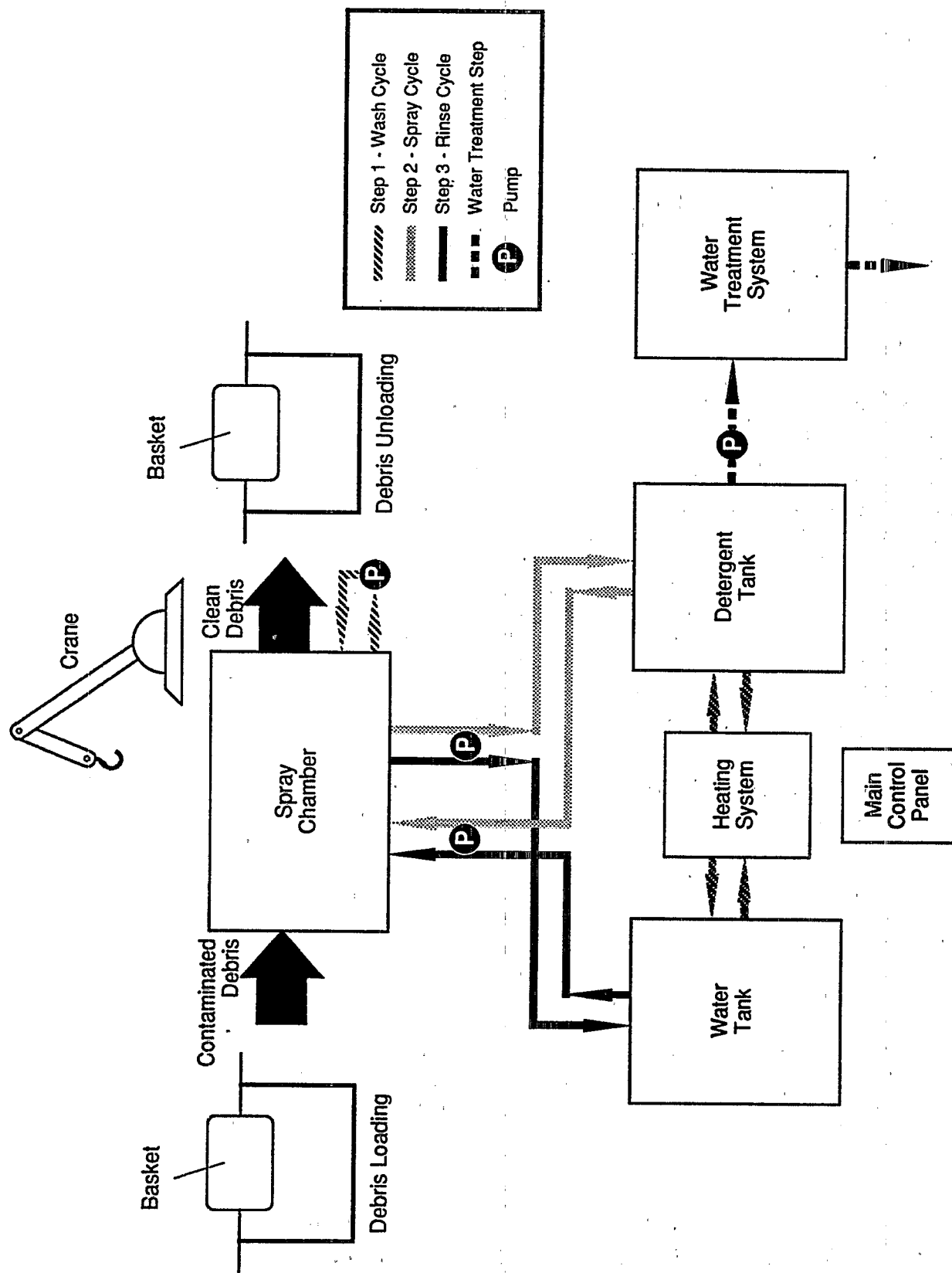


Figure 1: Schematic of Full-Scale Debris Washing System

TREATMENT OF HAZARDOUS AND TOXIC  
LIQUIDS USING ROCHEM DISC TUBE TECHNOLOGY

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## INTRODUCTION

Rochem Separation Systems, established in 1990 as a subsidiary of the international Rochem Group, has advanced the treatment of hazardous and toxic liquids with its unique, patented Disc Tube technology. Developed in 1987 at Rochem's design and production facilities in Hamburg, Germany, the Disc Tube technology is a series of membrane modules that greatly reduce the problems that hamper the effectiveness of other treatment technologies (i.e. fouling, scaling, cost, etc.). Applications of the Disc Tube technology include reverse osmosis and ultrafiltration. Rochem was recently accepted into the EPA Superfund Site program as a result of its Disc Tube technology.

## METHODOLOGY

The Rochem Disc Tube is constructed from a series of octagonal membrane cushions separated by a series of plastic spacer discs. The discs support the membrane cushions but leave an open channel flow path through the module (see Figure 1). The minimum clearance in the feed water flow path of the Disc Tube is approximately one millimeter. The flow path through the module is radial, progressing from the center of one disc to the edge of the cushion. The flow then makes a 180 degree turn and flows inward over the other side of the membrane cushion. The flow path repeats for each membrane cushion in the stack. The flow reverses direction every three inches. The turbulence created by the flow reversal eliminates the concentration polarization, minimizing scaling and fouling while maintaining high energy efficiency. Also, the Disc Tube operates effectively at increased turbidity and Silt Density Index (SDI) levels.

## RESULTS

Rochem is currently operating its Disc Tube technology in reverse osmosis (RO) systems at various hazardous landfill leachate sites throughout Europe, including one at Schwabach, Germany. The RO systems are being used at the sites to treat leachate seeping into the ground and contaminating valuable ground water. The effluent produced from the leachate treatment process meets applicable discharge standards by removing up to 99% of all dissolved solids and BOD (see Table 1).

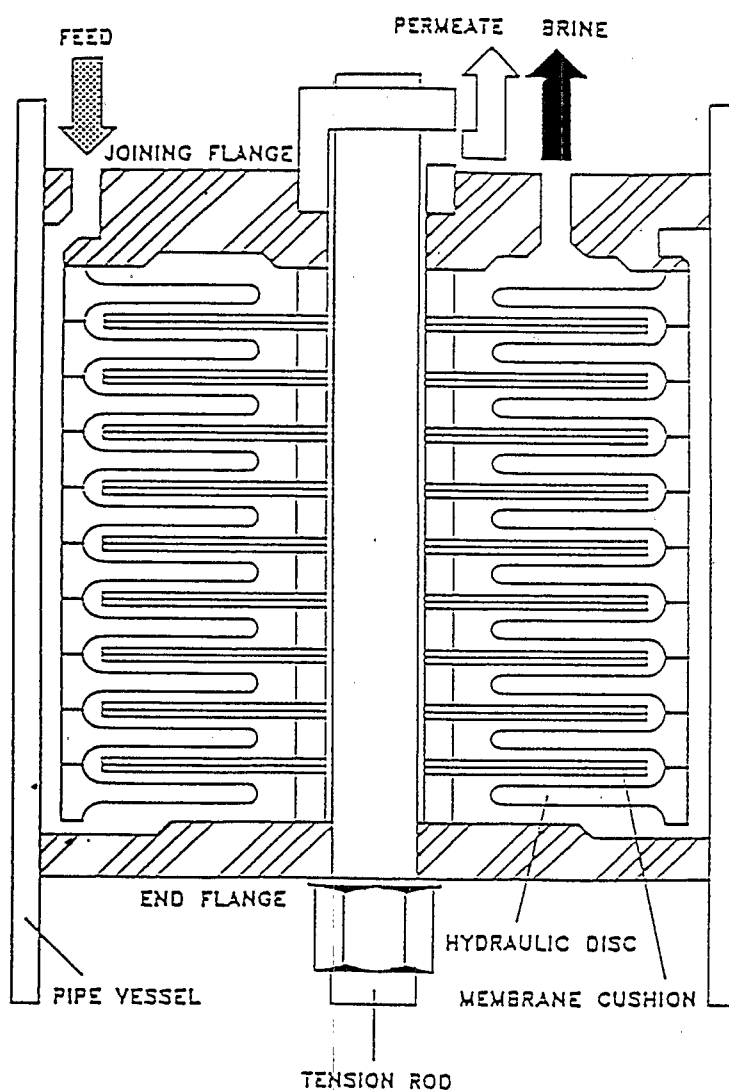
## CONCLUSIONS

The use of membranes for the reduction of difficult hazardous liquids was not economically feasible prior to the advent of Rochem's Disc Tube concept. Due to the Disc Tube's unique design, liquids that traditionally inhibit the use of membranes as a result of scale formation and biological fouling

are handled efficiently. In addition, by utilizing a combination of membrane systems to treat hazardous liquids such as multi-component waste found at hazardous landfills, cost effective and efficient treatment can be achieved. The most significant advantage this technology has over single membrane systems is that all major contaminants are reduced to within prescribed regulatory limits. Also, membrane performance is improved by selecting membranes chemically compatible with the waste to be treated.

FIGURE 1

DISC TUBE MEMBRANE MODULE  
HYDRAULIC FLOW SCHEMATIC





**TABLE 1****LANDFILL LEACHATE TREATED BY TWO-STAGE REVERSE OSMOSIS  
PLANT AT SCHWABACH LANDFILL SITE**

Parameter	Untreated Leachate	Second Stage Permeate	Rejection
El Conduct ( $\mu\text{s}/\text{cm}$ )	12.25	382	99.9%
PH Value (mg/l)	7.7	6.6	—
COD ( $\text{mgO}_2/\text{l}$ )	2,619	1.2	99.9%
BOD ( $\text{mgO}_2/\text{l}$ )	184	2.5	98.6%
TOC (mg/l)	289.0	4.0	98.6%
Hydrocarbons (mg/l)	13.40	0.3	97.8%
Sulfate (mg/l)	22093.0	4.8	99.9%
Ammonium (mg/l)	380	0.4	99.9%
Arsenic (mg/l)	0.25	ND	>99.99%
Cyanide (mg/l)	2.35	ND	>99.99%
Vanadium (mg/l)	290.0	2.2	99.2%

THE SITE DEMONSTRATION  
OF THE  
RETECH PLASMA CENTRIFUGAL FURNACE

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## INTRODUCTION

Plasma is highly ionized gas that contains equal numbers of positively and negatively charged particles. Plasmas can be created by passing gas through an electrical discharge and thereby ionizing it. The Plasma Centrifugal Furnace (PCF), developed by Retech Inc. of Ukiah, California, uses plasma generated by a transferred-arc torch to vitrify contaminated soil. In this system, soil contaminated with organic chemicals and metals is fed to the rotating PCF vessel. The plasma torch is used to heat and melt the soil at a temperature of approximately 3000°F. As the soil melts, organic contamination is driven into the gas phase which is at an average temperature of 2000°F. Organic contamination is thermally destroyed at these temperatures. Exhaust gas from the PCF is treated downstream to remove any unburned hydrocarbons, acid gas and particulate. Melted soil is intermittently discharged from the PCF and allowed to air cool into a glass-like solid mass.

## METHODOLOGY

The PCF was demonstrated as part of the EPA's Superfund Innovative Technology Evaluation (SITE) program in July 1991 at the U.S. Department of Energy's Magnetohydrodynamics Component Development and Integration Facility (CDIF) in Butte, Montana. During the demonstration, the PCF treated 1440 lb of soil contaminated with 28000 ppm zinc oxide, 1,000 ppm hexachlorobenzene and 10% by weight No. 2 diesel oil. This material was fed to the PCF at 120 lb/hr. To evaluate the performance of the system, the EPA sampled the feed and all effluent streams from the process. On cooling, the treated soil formed a glass-like matrix. During vitrification, organic contamination in the soil was volatilized and thermally destroyed.

## RESULTS

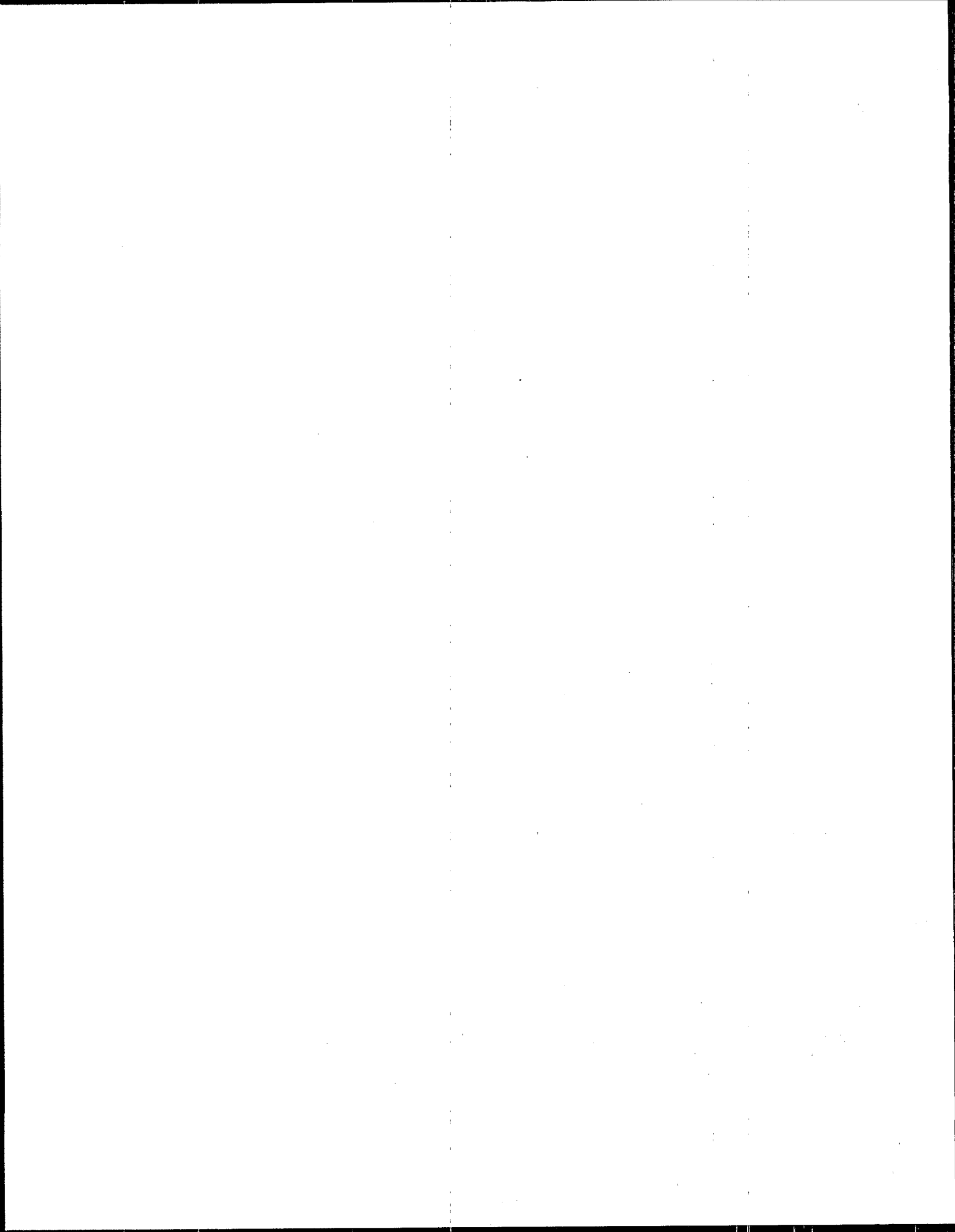
Preliminary results from the demonstration indicate that the PCF effectively immobilized the zinc contamination while thermally destroying the hexachlorobenzene. The vitrified soil produced by the PCF did not produce leachable quantities of zinc. In fact, while the feed soil produced leachate

containing 982 mg/L zinc, the vitrified soil produced leachate that contained only 0.30 - 0.45 mg/L zinc. While much of the zinc was volatilized during vitrification, acid digestion of the slag revealed that it still contained between 6000 ppm and 9000 ppm zinc. Although zinc is not regulated under the TCLP rule, these results clearly indicate that the PCF was able to immobilize the zinc that remained in the slag. The Destruction and Removal Efficiency for hexachlorobenzene was greater than 99.99%. Benzene was the only Products of Incomplete Combustion detected at significant levels.

Particulate emissions were 0.374 grains/dscf which exceeds the RCRA regulatory limit of 0.08 grains/dscf. Emissions of  $\text{NO}_x$  averaged 5000 ppm. Because the flowrate of the stack gas is very low in the PCF,  $\text{NO}_x$  emissions did not exceed regulatory limits. These emissions remain a concern, however. In full-scale PCF applications,  $\text{NO}_x$  and additional particulate control may be necessary.

## CONCLUSIONS

The results of the SITE demonstration of the Retech Plasma Centrifugal Furnace indicate that it may be a practical vitrification technology. Additional particulate and  $\text{NO}_x$  control may be necessary, but such control is readily available and should not prevent this technology from being used at sites where it is otherwise applicable.



SITE DEMONSTRATION OF THE  
SOILTECH ANAEROBIC THERMAL PROCESSOR

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## INTRODUCTION

In 1986, the U.S. Environmental Protection Agency (USEPA) established the Superfund Innovative Technology Evaluation (SITE) program to promote the development and use of innovative technologies to clean up Superfund sites. A SITE program field demonstration was performed on the SoilTech Anaerobic Thermal Processor (ATP) at the Wide Beach Development site in Brant, New York during May 1991. This technology is designed to thermally desorb organic contaminants such as polychlorinated biphenyls (PCBs) from soils and sludges. During this demonstration, the ATP was used in conjunction with dehalogenation using alkaline polyethylene glycol (APEG) reagents to chemically destroy PCB contaminants.

## PROCESS DESCRIPTION

The SoilTech ATP is an innovative, indirectly-heated rotary kiln system, using a physical separation process that thermally desorbs organics from soils and sludges. Dehalogenation is accomplished by spraying the contaminated soil with a diesel fuel and oil mixture which acts as a carrier for the APEG. The kiln provides intimate soil and reagent mixing combined with elevated temperature and residence time to accelerate the APEG dechlorination reactions.

The ATP kiln is innovative because it has four distinct zones. The first section is the preheat zone where the contaminated feed temperature is elevated to about 500°F. The next section is the retort zone where the soil is heated to 900°F, either volatilizing or coking the hydrocarbons under anaerobic conditions. The third section is the combustion zone where the kiln is heated and non-condensable hydrocarbons are destroyed. The last section is the cooling zone in which the soil is cooled by heating the preheat zone. Sand seals allow the different zones to have separate operating conditions.

The unit is designed to handle 10 to 15 tons per hour of solids containing up to 20 percent moisture and 10 percent hydrocarbon content. Wastes with greater than 20 percent moisture require dewatering to improve process economics and wastes with greater than 10 percent hydrocarbon content may require multiple passes through the unit.

During the remediation, the contaminated soils were excavated from yards and roadways, and staged in the contaminated feed storage area. Prior to entering the processor, contaminated soil passed through a grinder.

#### SITE DESCRIPTION

Between 1968 and 1978, about 40,950 gallons of waste oil, some contaminated with PCBs, was applied to area roadways for dust control. In 1980, a sanitary sewerline was installed, and PCB-contaminated soils were excavated and used as fill in several residences. As a result of these activities, approximately 42,000 tons of soil were contaminated with PCBs. Contamination levels in these soils ranged from the low tens of parts per million (ppm) to over 5,000 ppm.

#### DEMONSTRATION OBJECTIVES

The SITE technology demonstration had the following objectives:

- 1) Assess the technology's ability to remove PCBs and other organic contaminants from the soil,
- 2) Determine whether polychlorinated debenzo-p-dioxins (PCDD) or polychlorinated dibenzofurans (PCDF) are produced in the system,
- 3) Document the operating conditions of the SoilTech ATP,
- 4) Determine capital and operating costs of the ATP Technology.

## SITE DEMONSTRATION

For the SITE demonstration, three tests were conducted during full-scale remediation while the ATP was operated under typical operating conditions. Each test run consisted of 5.5 hours of solids and liquids sampling and 5 hours of concurrent stack sampling. The solid and liquid samples included contaminated feed soil, treated soil, combined flue gas cyclone fines and baghouse dust, preheat vapor cyclone fines, scrubber liquor, condensed water (before and after treatment), vapor scrubber oil, and preheat oil. In addition to stack gases, the non-condensable preheat and retort off-gases also were sampled during each run. Laboratory analyses included analyses of solid, liquid and stack gas for PCBs, dioxins/furans, volatile organic compounds (VOCs), and semivolatile organic compounds (SVOCs). Extractable organic and inorganic chlorides were also analyzed in an attempt to trace the fate of chlorine throughout the system. A variety of other general chemistry and macronutrient analyses were performed to characterize the feed and treated soils.

The unit was operated at an average 6.3 tons per hour during the three runs. Other parameters, such as kiln temperature, stack flow rates, etc., were maintained at essentially constant conditions.

## DEMONSTRATION RESULTS

Key findings from the Wide Beach SITE demonstration are:

- 1) The SoilTech ATP removed PCBs from the contaminated soil to levels below the EPA-required cleanup concentration of 2 ppm. The highest average treated soil PCB concentration was 0.073 ppm.
- 2) Dioxins and furans did not seem to be created.
- 3) No major operational problems affecting the ATP's ability to treat the contaminated soil were observed.
- 4) The average stack gas emissions were:

Particulate	0.362	gr/dscf (7% O <sub>2</sub> )
HCL	0.054	lb/hr
PCB	$3.87 \times 10^{-4}$	lb/hr
Dioxins/Furans	$1.37 \times 10^{-7}$	lb/hr
- 5) No VOC and SVOC degradation products were found in the soil.

## **EXTENDED ABSTRACT**

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### **THE SITE INVESTIGATION ROBOT**

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Non-invasive imaging of the underground is an essential component of hazardous waste site investigations, yet, despite advances in sensor technology, high quality maps of the subsurface are difficult to obtain. Subsurface mapping depends on the spatial correlation of individual sensor measurements taken at multiple locations. Current manual data collection techniques, however, are suboptimal for precisely positioning subsurface imaging sensors and are generally inefficient. In addition, considerable experience on the operator's part is required to interpret the sensor data.

In the Site Investigation Robot (SIR) project, we are applying robotics and image processing technologies to the investigatory phase of hazardous waste site cleanups. Our current focus is development of an automated subsurface mapping system to locate buried objects and geological structures so that sources and migratory pathways of contaminants can be identified and cataloged.

The subsurface maps that we produce are based on a non-invasive sensing method called ground penetrating radar (GPR). GPR operates on principles similar to conventional radar, but processing GPR data is more complicated due to the non-homogeneous nature of the subsurface medium. Though sometimes used in waste site characterization, GPR deployment, data acquisition and interpretation are human-driven processes. The potential of GPR to generate accurate three dimensional subsurface maps is thus not fully realized in current practice.

We use robots to position GPR transducers to exploit the accurate, repeatable positioning available from automated equipment. A linear scanning mechanism is used to precisely locate the transducer transverse to the path of a position cognizant, all-terrain mobile robot (Figure 1). Together, these devices acquire GPR records in a two-dimensional grid on the ground surface, with grid resolution as low as 5 cm.

The robots are commanded through a graphical interface that displays a map of the site and known obstacles. The user prescribes an area from which data are to be collected by drawing the boundaries of that region. A simple planner then determines a safe route to drive that avoids



obstacles while maximizing coverage of the surface.

At each point in sampling grid, a pulse is transmitted into the ground and the energy reflected to the receiving antenna is recorded, digitized and pre-processed to remove pulse transmission effects and noise. Three dimensional data arrays are then formed using the position information associated with the records. The waveform recorded at each grid point is actually a composite of all radar reflections within the antenna's conical beam pattern due to the poor focusing of the GPR antenna. However, since the spacing between surface grid points is accurately measured, we are able to correlate all of the measurements and synthetically focus the antenna. Vertical and horizontal sections of the resulting subsurface map are then displayed as color or gray-scale images and enhanced further with several filtering and feature detection algorithms.

SIR is an example of an emerging class of robots dedicated to the solution of hazardous waste problems. The spatially correlated information that Site Investigation Robot generates will be used to more effectively conduct the costly phase of site remediation. This, along with reduction of human exposure will ultimately lower the expense of site cleanups. This project is a preliminary step towards broader capabilities in automated waste site investigations, such as acquisition of a wider variety of data, environmental sampling, centralized site databasing, and computer-aided site modeling.

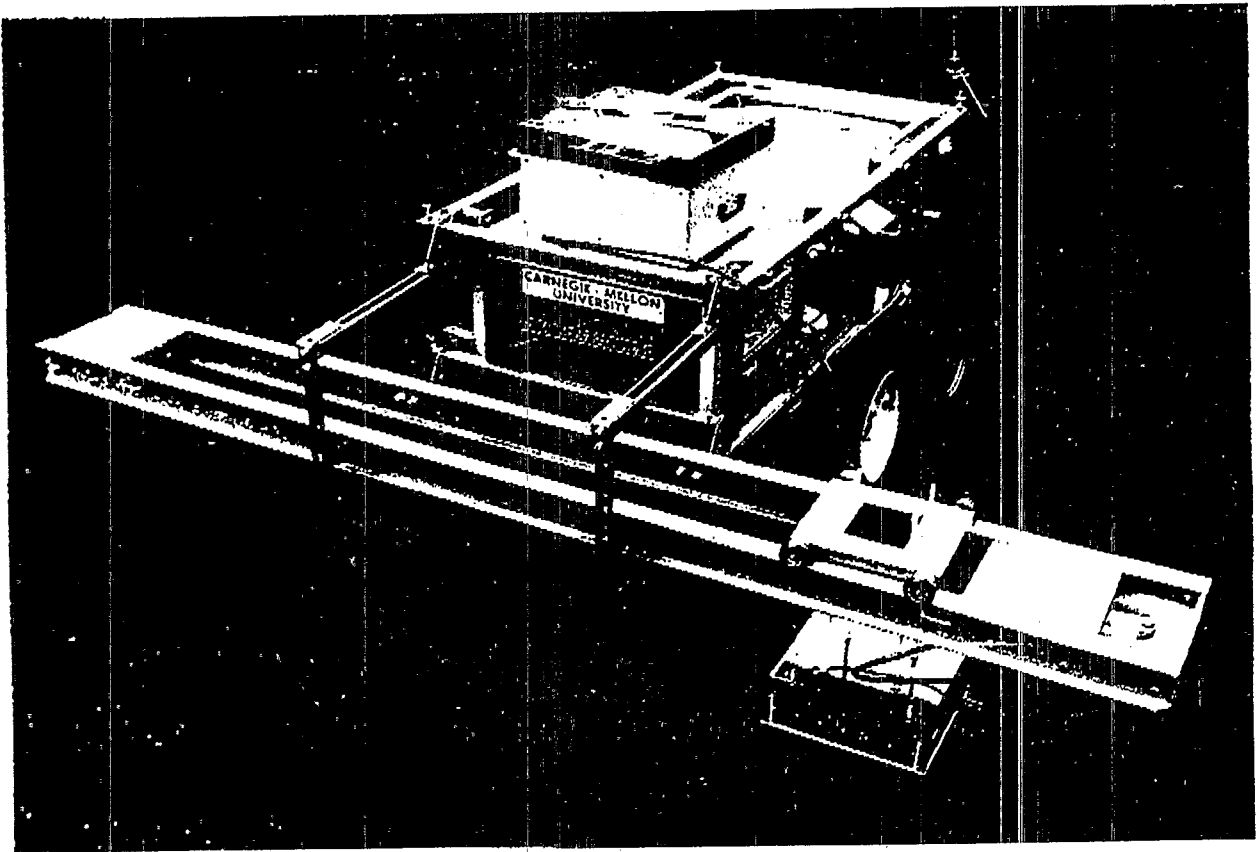


Figure 1. The Site Investigation Robot prototype

## EVALUATION OF THE AIR-SPARGED HYDROCYCLONE

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### INTRODUCTION

Throughout history, both the mining of ores and the extraction of metals from them has been guided by economic considerations. Thus, the miner took those ores that were easiest to mine and the processor extracted those values that came out readily. Processing focused on improving metal recovery to the extent that the cost of increased yields was more than compensated by the values recovered, but those minerals whose extraction cost exceeded their value were left behind. The result has been the accumulation of thousands of tons of partially depleted mineral resources, generally known as mill tailings.

Over one hundred years of extensive mining and milling operations has left the area of Butte, Montana, "The Richest Hill on Earth", with millions of tons of tailings containing varying amounts of metallic minerals. The initial mode of occurrence of these minerals was in the form of sulfides, the primary source of base metals such as copper, lead, zinc, nickel, etc. Substantial amounts of such minerals remain in the tailings impoundments. Through exposure to the atmosphere, the elements and bacterial action, the sulfides, which are relatively insoluble in water, oxidize to soluble sulfates, creating acidic drainage, laden with heavy metals and harmful to plant, animal and aquatic life. The watershed from this area, known as the Clark Fork Drainage, comprises the largest collection of Superfund Sites in the United States.

Naturally, extraction technologies have improved over the course of Butte's mining history, while ore grades have progressively diminished. Thus, the oldest tailings are those containing the highest content of sulfides. Sometimes overlain by more recently-produced and cleaner tailings, they still produce acidic effluent.

The work undertaken in this project is directed toward developing means to reprocess old tailings in order to remove a substantial percentage of the acid producers and, hopefully, to recover sufficient mineral values to offset some of the cost of removal and retreatment.

The most modern method of separating sulfide minerals is froth flotation (hereinafter referred to simply as flotation), wherein mineral surfaces are selectively rendered water repellent by subjection to a suitably controlled chemical environment within an aqueous slurry. Prior to the advent of flotation early in the 20th century, the primary method of separating sulfides from associated waste minerals was by gravity concentration, which is quite sensitive to particle size. While the lower particle size that can be separated by gravity concentration is in the range of 300 micrometers, flotation reduced the lower size limit to about 50 micrometers. This development was especially significant in the processing of Butte ores, since the values in them are concentrated in the finer size fractions.

The Butte area thus contains two general types of tailings, those from older gravity operations and more recently produced flotation tailings. As would be expected, the flotation tailings have been ground to a finer size and contain less mineral values than do the gravity tailings. Thus, the older gravity tailings are the more obvious target for remediation through removal of sulfides left behind by earlier processors, but retreatment of either type of tailing would be enhanced by the development of technology that would recover particles finer in size than those recoverable by flotation.

Tailings from the old Colorado Mill, a Superfund site containing about 250,000 cubic yards of gravity concentration tailings, was the initial target of this project. Preliminary tests indicated that this material was an ideal candidate for retreatment through the Air-Sparged-Hydrocyclone (ASH), to be described later. A proposal to evaluate the ASH with Colorado tailings was submitted to the U. S. Environmental Protection Agency (EPA), but shortly after its acceptance, the Potentially Responsible Party (PRP) for Colorado Mill tailings withdrew permission for removal of a quantity of the material for the work. Subsequently, a more recent tailing, resulting from a flotation operation, was obtained and tested.

## METHODOLOGY

Flotation is conventionally carried out in stirred tank reactors in which ground mineral particles are held in suspension in water, which disperses the necessary chemical reagents and to which air is added and fractionated into fine bubbles by a rotor/ stator arrangement. In the agitated slurry, particles and bubbles collide, with water repellent particles adhering to bubbles when collision takes place. The bubble/particle agglomerate levitates to the slurry surface and overflows to a suitable container, thus separating water repellent from water wettable particles. Poor flotation recovery of small particles is thought to result from low probability of collision due to the reduced inertia attendant with light weight.

Most of the attempts to develop more effective means of flotation have focused on flotation machine design. One such device is the Air-Sparged Hydrocyclone (ASH), which was developed by Dr. J. D. Miller of the University of Utah in the 1980's. The ASH, diagrammed in Figure 1, increases the probability of particle/bubble collision in two ways: 1) particles enter the ASH at a high tangential velocity and, 2) the porous inner wall of the ASH admits a great number of fine air bubbles in a swirling layer in line of contact with the particle stream. As in conventional hydrocyclones, lighter particles exit upwards through the vortex finder and heavier particles leave through the bottom of the device. In the ASH, the lighter particles are the particle/bubble agglomerates.

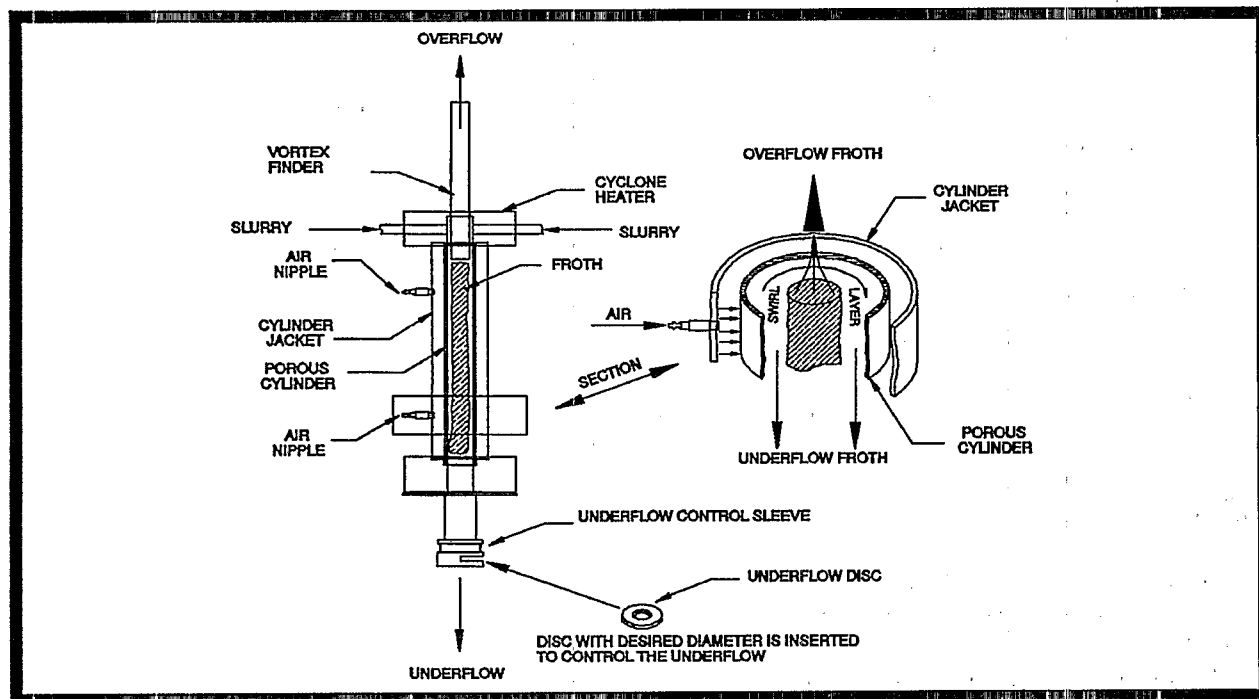


Figure 1. Air-Sparged Hydrocyclone

The ASH is licensed in Montana to Hydroprocessing and Mining of Montana (HPM), who have set up a pilot plant for its evaluation.

## RESULTS

Chemical analyses of the metal content of various size fractions of a randomly-selected sample of Colorado Mill tailings, before and after size reduction by grinding, are presented in Table 1.

TABLE 1. METAL DISTRIBUTION IN SIZE FRACTIONS OF COLORADO TAILINGS

Tyler Mesh	Weight %	Assay, %			Distribution, %		
		Pb	Zn	Cu	Pb	Zn	Cu
As Received							
+35	42.3	.04	.12	.11	24.9	13.9	29.2
-35 + 48	18.3	.04	.17	.08	10.2	8.5	9.2
-48 + 65	14.7	.04	.26	.10	8.2	10.4	9.3
-65 + 100	9.7	.05	.43	.12	6.7	11.3	7.3
-100 + 150	4.8	.06	.82	.15	4.1	10.7	4.5
-150 + 200	3.0	.07	1.30	.20	2.8	10.4	3.7
-200	7.2	.42	1.77	.80	43.1	34.7	36.7
Calculated Head Assay		.07	.37	.16			
After Grind							
+35	NIL						
-35 + 48	0.9	.04	.15	.08	0.4	0.4	0.5
-48 + 65	11.0	.04	.06	.04	4.8	2.0	2.9
-65 + 100	17.5	.04	.09	.04	7.6	4.8	4.6
-100 + 150	18.8	.05	.20	.05	10.2	11.4	6.2
-150 + 200	11.0	.05	.32	.07	6.0	10.7	5.1
-200	40.8	.16	.57	.30	71.0	70.7	80.8
Calculated Head Assay		.09	.33	.16			

Inspection of the table points out the tendency of the metal-bearing minerals to report in the finer size fractions.

Ground material was then passed through the ASH repeatedly to see if repeated treatment ("scavenging") would bring about progressive flotation of a number of potentially toxic elements. Resulting data are summarized in Table 2, in which UF signifies the underflow or rejected portion and OF the overflow or concentrate. (Underflow from the first cycle becomes feed to the second cycle and underflow from the second cycle is feed to the third cycle.) Since concentrate is removed after each test, feed to the succeeding cycle is lower in grade, which accounts for the progressive decrease in both

underflow and overflow grade. In commercial milling operations, it is normal practice to scavenge the ore stream to the extent required to give a desired recovery. The lower grade concentrates are returned to preceding process cycles in order to achieve acceptable concentrate grades.

TABLE 2. METAL CONTENT OF PRODUCTS AFTER REPEATED PASSAGE OF UNDERFLOW THROUGH THE ASH

Analysis in Milligrams per Kilogram (ppm) in Solids from:						
Element	UF #1	UF #2	UF #3	OF #1	OF #2	OF #3
Arsenic	980	820	790	10,780	8200	4650
Barium	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Cadmium	30.60	13.75	12.00	78.75	28.50	27.00
Copper	288	285	220	6,278	3,100	1,550
Chromium	7.49	1.87	1.56	29.60	23.80	13.10
Gold	1.12	0.28	0.28	56.08	13.95	5.30
Iron	4,108	3,694	2,656	35,628	30,598	20,958
Lead	5.00	3.75	30.20	8,152	5,280	866
Manganese	158	147	140	383	315	225
Mercury	0.004	< .002	< .002	0.77	0.51	0.09
Selenium	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Zinc	2,640	2,420	1,870	35,350	15,150	14,170
Silver	48.55	18.14	14.51	473.78	405.70	202.85

The above results led to submission of the proposal to EPA. Due to the refusal of the PRP to supply sufficient material for complete testing, a sample of about 28 tons of tailings from the defunct Marget Ann mill was obtained from New Butte Mining Company, who are interested in ASH technology and had earlier cooperated with HPM in testwork on dump ore from the Butte area. The Marget mill operated briefly in the 1950's and appears to have been a technical success but an economic failure.

Preliminary examination showed the material to be quite low in metal values and somewhat contaminated with organic matter. It was also found that, like most local tailings, metal content increased with decreasing particle size. This is illustrated in Table 3.

Three factorial design experiments at different levels of grind, collector and activator showed only minor concentration of lead or zinc by flotation in a conventional laboratory machine. Tests in the ASH pilot plant were carried out under various conditions, since success with this difficult material would indeed demonstrate the utility of the ASH in the flotation of fine mineral particles.

Nine campaigns were completed with results similar to those obtained from the conventional flotation machine. The low grade of the starting material made accurate analysis difficult and material accounting was poor. Work on Marget Ann tailings was terminated after analysis of data from the ninth run and remaining material and test products were returned to the tailings site.

TABLE 3. LEAD AND ZINC DISTRIBUTION IN MARGET ANN TAILS SIZE FRACTIONS

Tyler Mesh	Weight %	Assay, %		Distribution, %	
		Pb	Zn	Pb	Zn
+ 100	7.0	.042	.076	3.7	4.0
-100 + 200	12.6	.062	.138	9.8	12.9
-200 (Dry)	3.0	.077	.141	2.9	3.1
-200 (Wet)	77.4	.086	.139	83.6	80.0
Calculated Head Assay		.080	.134		

### CONCLUSIONS

It is concluded that the Air-Sparged-Hydrocyclone shows promise for recovering sulfide minerals from materials typified by Colorado Mill tailings but that each candidate for such treatment must be evaluated by testing.

Pilot plant work in the immediate future will focus on the quantity of Colorado Tailing that remained after the preliminary work that led to submission of the project proposal. If this shows promise, another tailing sample will be sought. If results are negative, the project will be terminated.

## ASSESSMENT OF BINDING ENERGIES BETWEEN ORGANIC CONTAMINANTS AND SOILS AND SEDIMENTS

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### INTRODUCTION

Accurate assessment of the extents to which various hydrophobic organic contaminants will sorb to different types of soils is critical to the development of realistic models of contaminant fate and transport, as well as to the selection of effective remedial strategies. Results of field studies show that hydrophobic organic compounds persist longer and migrate more slowly than predicted by commonly used ground water transport models, which are predicated on simple linear, reversible, equilibrium sorption phenomena. The goals of this research are to develop: 1) an improved model of complex sorption behavior in soils and, 2) a protocol which can be employed as a basis for the more realistic selection of appropriate transport models and remedial technologies for contaminated subsurface sites.

### CONCEPTUAL MODELS FOR SORPTION REACTIONS

Three general classes of binding interactions between contaminants and soils can be identified (1). Chemical sorption occurs when a bond, having all of the characteristics of a true covalent bond, is formed between a functional group on the soil surface and the sorbed chemical. A second type of interaction, which is common for polar solutes, is electrostatic or ionic bonding between the solute and charged functional groups on the soil surface; an example is the binding of calcium ions to a clay. Non-polar solutes are typically bound to soils by relatively low energy dipole interactions with functional groups on the soil surface. Adsorption of a hydrophobic compound results from the cumulative effect of these binding interactions and repulsive interactions between the solute and the solvent that serve to drive solute molecules out of solution and onto soil surfaces.

The wide range of forces contributing to sorption phenomena results in great variations in binding energies between particular solutes and soils. Most soils are intrinsically heterogeneous, generally being comprised of a conglomeration of various mineral and organic surface types. The binding strength and isotherm shape for sorption of a given contaminant on a given soil surface is determined by the distribution of the energies of individual soil fractions. Uniform distributions of binding energies usually result in linear isotherms at low surface coverages, while variations in the binding energies of the various components comprising a soil will commonly yield non-linear isotherms (2).

Sorption of hydrophobic organic contaminants on soils is frequently described by models that are predicated on the assumptions that 1) soil organic matter is the principal, if not the only, soil fraction exhibiting significant reactivity and 2) all soil organic matter has similar binding energies for non-polar organic compounds. Sorption is therefore treated in these models as a linear, reversible process dominated by weak physical binding reactions. Several investigators have generalized this concept by developing correlations that allow the prediction of partition coefficients from the knowledge of a solute's hydrophobicity and a soil's organic carbon content (3).

A number of limitations have been observed in applying these correlations to diverse soil systems. The correlations generally fail for soils of low organic carbon content, such as those typically found in subsurface environments. Non-linear isotherms have been reported for a number of low organic carbon subsurface soils (4,5). The nature of the organic carbon present in the soil has also been shown to influence the sorption of non-polar organic molecules. More reduced organic matter, reflected by higher C/O or H/O ratios, has a higher capacity to adsorb organic compounds than more oxidized organic matter (2,6,7). Furthermore, the assumption of local equilibrium between contaminants and soils in ground water systems has been shown to be invalid in a number of experiments (1,8). Explanations for non-equilibrium



include extremely slow sorption rates (1,8,9) or hysteretic effects (10). Consequently, contaminants present in a soil for an extended time period may be more difficult to desorb than freshly added material (11). The total effect of the foregoing limitations is to call into question the accuracy of the microscopic, linear, reversible, local equilibrium sorption model for describing macroscopic solute transport in many subsurface contamination situations.

#### IMPLICATIONS FOR FIELD SCALE MODELING

Selection of an inappropriate microscopic model of contaminant sorption can lead to significant macroscopic modeling errors. For example, when a literature correlation developed for high organic carbon surface soils is used to predict linear partitioning coefficients for low organic content subsurface soils, the amount of sorption may well be underestimated, and the time required to complete a pump-and-treat remedial scheme may therefore be far longer than predicted. Problems with literature correlations can be avoided by conducting laboratory studies to generate isotherms specific to the soil-contaminant system at a particular site. This method is not without pitfalls, however. When the data span too small a range of solution concentrations, isotherm non-linearities may be overlooked. Short equilibration times in the laboratory may cause hysteresis or aging effects to be missed, resulting in underestimates of true levels of contaminant binding by soils in the system. In each case the results will be overly optimistic estimates of the ease of soil remediation. Ideally, the reactivity of each type of soil fraction could be measured and a soil's binding strength for a contaminant could be calculated by using an appropriate distributed reactivity model (2). The complexity, immense diversity, and unknown structure of most soil organic matter represent great obstacles to obtaining the data needed for routine use of this approach. Alternatively, a tool might be developed to quantify binding strengths between specific contaminants to be removed and soil samples from the site in question.

#### SUPERCRITICAL FLUID EXTRACTION IN SOIL SORPTION STUDIES

Supercritical fluid extraction using non-polar gases such as carbon dioxide appears to offer a reasonable basis for development of such a tool. The chief advantage in using non-polar supercritical fluids as extraction solvents lies in their controllable solvent strength and minimal solvent-solute interactions. The solvent strength of supercritical fluids is directly related to their density, which can be varied easily by changing the pressure in the extraction vessel. Moreover, mass transfer is often orders of magnitude faster in supercritical fluids than in liquid solvents because supercritical fluids have more favorable diffusivities and viscosities. Finally, supercritical fluids offer important practical advantages because they are usually inert, non-toxic and relatively inexpensive. Efficiencies approaching or exceeding those of Soxhlet extractions have already been demonstrated for removing several organic solutes from soil and other solid matrices using supercritical carbon dioxide-cosolvent mixtures. Solute studies include polynuclear aromatic hydrocarbons (12,13), polychlorinated biphenyls and DDT (14).

In order to quantify the binding strength between a contaminant and a soil, non-quantitative extractions can be performed at different pressures. Successive increases in extraction efficiency with increasing energy input at higher pressures can then be used to calculate a distribution of binding energies for the contaminant/soil system of interest. Changes in binding strength with aging of the contaminant will be measured to develop a model of contaminant aging effects. Finally, the binding strengths measured in the supercritical fluid extraction experiments will be compared with the effectiveness of remedial schemes for soils including bioremediation, soil washing, and pump-and-treat methods. If a correlation is found, supercritical fluid extraction may be a useful screening tool for predicting remedial effectiveness.

#### CONCLUSION

Supercritical fluid extraction appears to have great potential as a new tool for examining the sorptive behavior of soils based on the results of studies that have already been conducted in this area. The need to improve our understanding of these processes is amply demonstrated by the number and severity of soil and sediment contamination incidents that have been reported and by current difficulties in modeling the removal of hydrophobic compounds from soils and sediments. It is our objective that the research being conducted under this project will improve our knowledge of the microscopic sorption

mechanisms operative in diverse types of soils and, consequently, increase the accuracy with which macroscopic transport and remediation of contaminants can be predicted.

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## BIOAVAILABILITY AND BIODEGRADATION KINETICS OF ORGANICS IN SOIL

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### INTRODUCTION

As EPA begins to remediate Superfund sites using permanent treatment technologies, such as bioremediation, a fundamental understanding of the kinetics and the factors that control the rate of bioremediation will be required (1). Biological treatment technologies hold considerable promise for safe, economical, on-site treatment of toxic wastes (2). A variety of biological treatment systems designed to degrade or detoxify environmental contaminants are currently being developed and marketed. Knowledge of the kinetics of biodegradation is essential to the evaluation of the persistence of most organic pollutants in soil (3,4). Furthermore, measurement of biodegradation kinetics can provide useful insights into the favorable range of the important environmental parameters for improvement of the microbiological activity and consequently the enhancement of contaminant biodegradation.

A major effort is currently underway to clean up aquifers and soils that are contaminated by organic chemicals, which has generated increased interest in the development of in situ bioremediation technologies. Although considerable data exists for rates of biodegradation in aquatic environments, there is little information on biodegradation kinetics in soil matrices, where irreversible binding to the soil phase may limit the chemicals bioavailability and ultimate degradation. Knowledge on biodegradation kinetics in soil environments can facilitate decisions on the efficacy of in situ bioremediation.

Recently, increased interest has been directed towards obtaining quantitative information on pollutant sorption equilibria in soils, since the physical state of the compound can influence its bioavailability. Information concerning the availability of hydrocarbons sorbed on soil can be useful in choosing the appropriate technology to treat subsurface contamination by gasoline, which is released to the environment as a result of accidental spills and leaking underground storage tanks.

The main objective of this research is to quantitate the bioavailability and biodegradation kinetics of organic chemicals in surface and subsurface soil environments, examine the effects of soil matrices and soil conditioning (drying, aging, compaction), and develop a predictive model for biodegradation kinetics applicable to soil systems.

### METHODOLOGY

Four separate soil microcosm reactors were designed, assembled and installed, to simulate contaminated sites. Each microcosm reactor consisted of a glass aquarium (12 in.x 20 in.x 12 in.) with about 6 in. depth of soil. Undisturbed, uncontaminated forest soil from Northern Kentucky was placed in each microcosm reactor. The reactor was then brought into the laboratory, and contaminated with a known class of compounds. Initially, our study was confined to phenols, PAHs,

chlorinated phenols, and aromatic hydrocarbons. Nutrients were periodically sprayed on top of the soil surface, to simulate rainfall. A known flow rate of carbon dioxide free air was introduced into the headspace of each microcosm reactor, and the carbon dioxide concentration in the exit gases was carefully monitored.

Each microcosm reactor represents a controlled contaminated site, which eventually will have acclimated microorganisms for the contaminating organics. Samples were taken from the microcosm reactors for measuring oxygen uptake respirometrically, carbon dioxide generation kinetics, and other studies.

Studies were conducted with soil slurry reactors, wherein the oxygen uptake was monitored respirometrically (5). Various concentrations of soil (2%, 5%, 10%) and compound were mixed with the nutrient medium and stirred in the reactor flask. The flask was connected to the oxygen generation flask and pressure cell of a 12 unit VOITH electrolytic respirometer.

The oxygen uptake data was then analyzed on the computer, using the Monod equation combined with a linear adsorption isotherm, to determine the soil adsorption parameter, and the Monod biodegradation parameters. The model equations for a soil slurry respirometer reactor flask have been summarized below.

$$O_2 = (S_0 - S_{aq} - S_s) - (X - X_0) - (S_p - S_{p0}) \quad (1)$$

$$\frac{dX}{dt} = \mu \frac{S_s}{K_s + S_s} X - \frac{K_s}{K_s + S_s} bX \quad (2)$$

$$\frac{dS_s}{dt} = -\frac{\mu}{Y} \frac{S_s}{K_s + S_s} X \quad (3)$$

$$\frac{dS_p}{dt} = \frac{Y_p \mu}{Y} \frac{S_s}{K_s + S_s} X \quad (4)$$

$$S_s = C_{aq} K_d S_{aq} \quad (5)$$

where

$C_{aq}$  soil concentration [ mg/L ]

$K_d$  soil adsorption coefficient [ L/mg ]

$K_s$  Michaelis constant [ mg/L ]

$O_2$  oxygen uptake [ mg/L ]

$S_{aq}$  substrate concentration in aqueous phase [ mg/L ]

$S_p$  bioproduct [ mg/L ]

$S_s$  substrate [ mg/L ]

$t$  time [ Hr ]

$Y$  yield coefficient [ mg/mg ]

$Y_p$  bioproduct yield coefficient [ mg/mg ]

$\mu$  growth coefficient [ 1/Hr ]

Carbon dioxide generation rates were measured in shaker flasks, wherein the soil sample was shaken with the nutrients and compound. A packed bed of soda lime pellets was used to absorb the generated carbon dioxide. The upper bed of soda lime pellets was used to absorb the carbon dioxide from the influent air, and the lower bed of soda lime pellets was used to absorb carbon dioxide generated in the flask, due to biodegradation.

The soda lime pellets were then removed periodically from the shaker flask, and analyzed for the amount of carbon dioxide generated.

## RESULTS

Three chemical compounds, phenol, p-cresol, and 2,4 dimethyl phenol, were selected for the soil respirometric degradation test. Three different compound concentrations: 50 mg/l, 100 mg/l, and 150 mg/l, and three different soil concentrations, 2%, 5% and 10% were selected for the initial studies.

Figure 1 shows the oxygen uptake curve for phenol at 100 mg/l concentration and various soil concentrations: 2%, 5%, and 10%.

A newly developed adaptive random search technique was used to determine these parameters from the experimental data. Table 1 presents the results of the analysis for the experimental data presented earlier in Figure 1. It can be seen that the Monod biokinetic parameters,  $\mu$  and  $Y$  do not vary with soil concentration, while other parameters change dramatically at 10% soil concentration. This is expected due to the fact that at higher soil concentrations, significant mass transfer effects occur in the bioreactor system. This finding can have a significant impact on the design and operation of soil slurry reactors. Furthermore, the physical soil adsorption parameter,  $K_d$ , decreases as the substrate concentration increases, which is expected from a nonlinear adsorption isotherm.

The experimental value for the soil adsorption parameter,  $K_{oc}$  reported in the literature (6) is 27. Since  $K_d$  is defined as  $K_{oc} \times$  (percent organic carbon in soil), the experimental value of  $K_d$  is  $27 \times 0.06 = 1.62$ . The soil adsorption parameter values obtained from respirometry are in the range of 1.02 - 3.899.

Figure 2 shows the cumulative carbon dioxide generation data for 5% soil concentration and phenol concentration varying from 0 to 150 mg/l. The total amount of carbon dioxide generated increases with the compound concentration.

The carbon dioxide generation data provides unambiguous measurement of biodegradation kinetics for complete mineralization of the compounds. Reconciliation of carbon dioxide generation data with oxygen uptake information is important in determining the biokinetics of not only biotransformation reactions, but also for complete mineralization of the compound.

## CONCLUSIONS

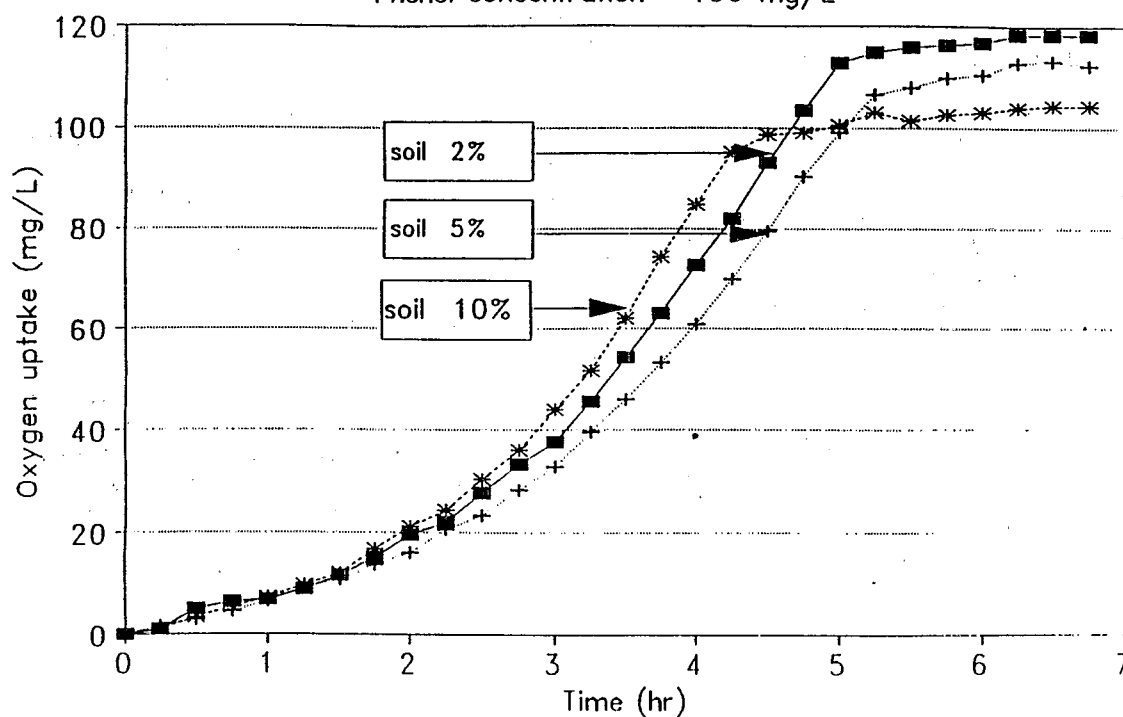
Respirometric studies with soil slurry reactors provides valuable insight into the biodegradation kinetics of compounds adsorbed in soil phase. It has been shown that a Monod kinetic equation in conjunction with a linear adsorption isotherm can provide reliable estimates of the Monod kinetic parameters. Experiments conducted in our laboratory have demonstrated that cumulative carbon dioxide measurement can be made for soil slurry systems.

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**FIGURE 1** Phenol biodegradation in soil slurry reactor

Phenol concentration = 100 mg/L



**FIGURE 2** Phenol biodegradation in soil slurry reactor

Phenol concentration = 150 mg/L

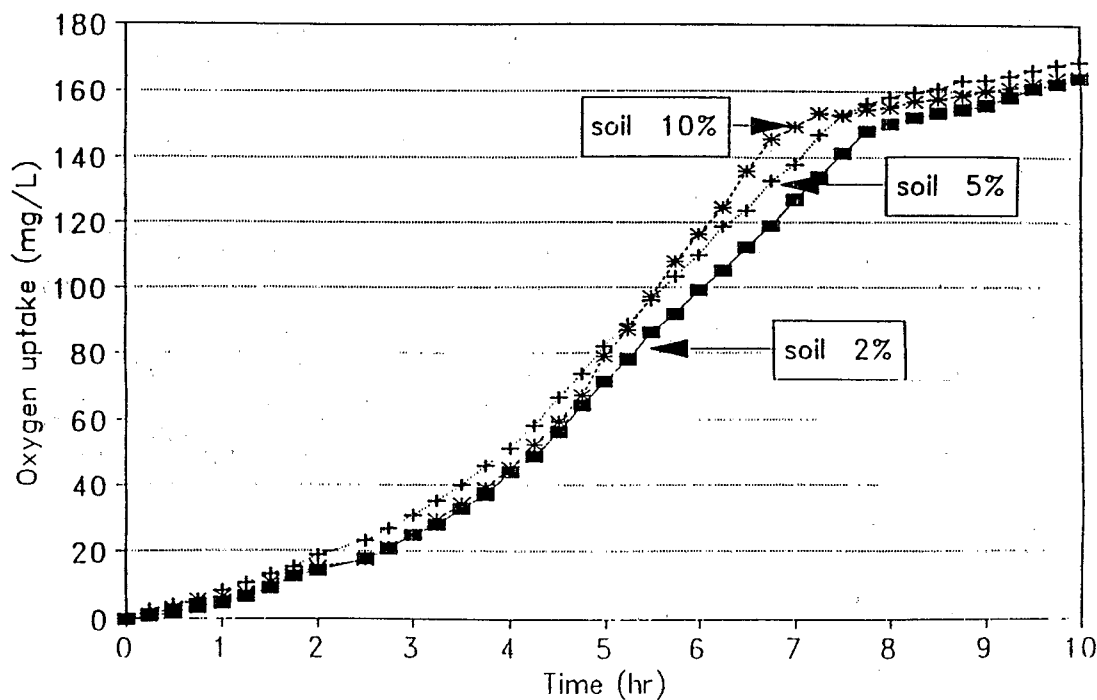


Table 1: Phenol concentration = 100 mg/l

Soil concentration :	2%	5%	10%
Monod parameters:			
$\mu$ [1/hr]	0.577	0.535	0.551
$K_s$ [mg/L]	14.6	11.4	1.12
$Y$ [mg/mg]	0.499	0.477	0.388
$Y_p$ [mg/mg]	0.0304	0.0209	0.00709
$b$ [1/hr]	0.0110	0.0295	0.00709
Adsorption parameter :			
$K_d$ [L/g]	3.899	3.84	2.54
RSSE:			
	13.3	3.84	16.5

RSSE: Residual sum of squared errors  
All mass measurements are as COD

Table 2: Phenol concentration = 150 mg/l

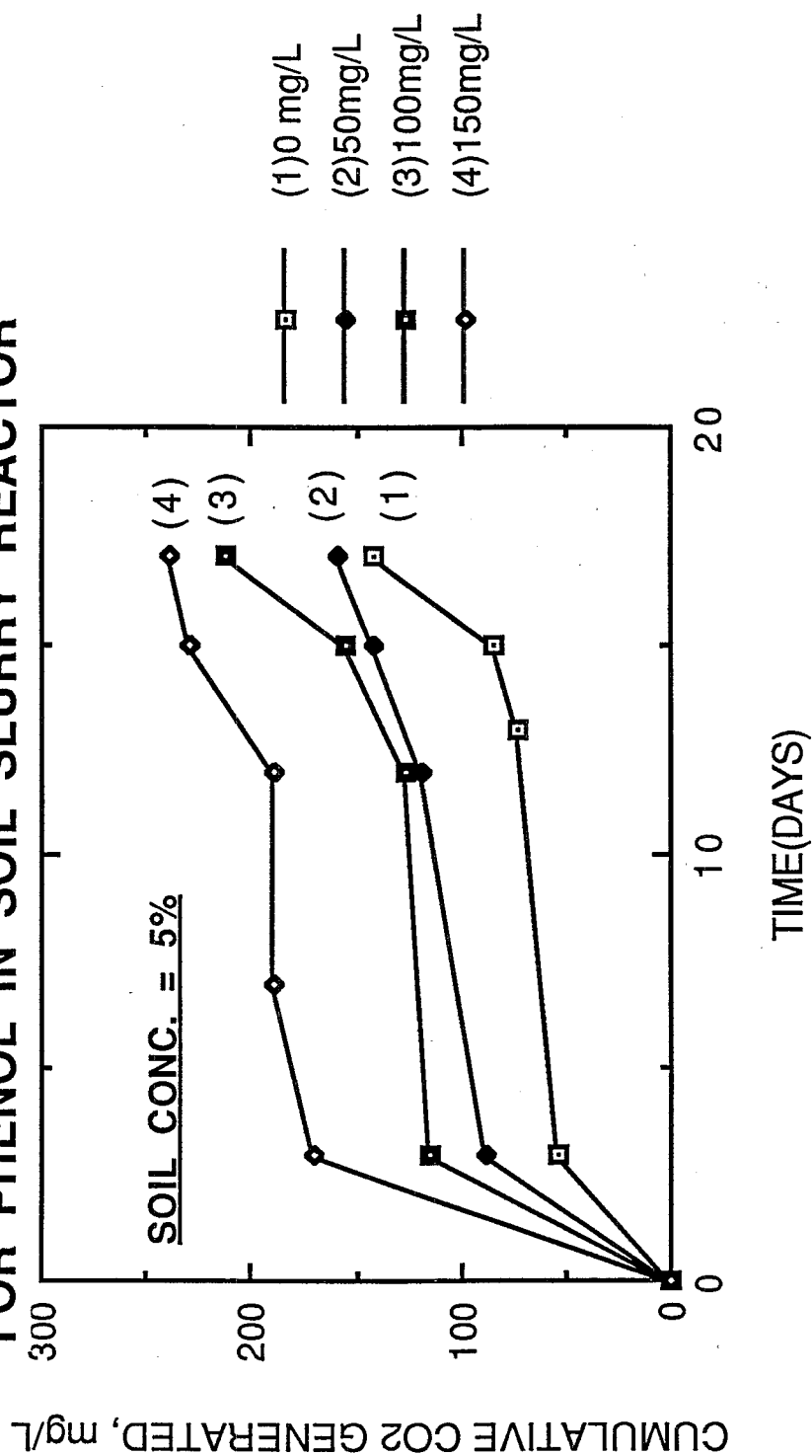
Soil concentration :	2%	5%	10%
Monod parameters:			
$\mu$ [1/hr]	0.388	0.327	0.342
$K_s$ [mg/L]	29.9	24.7	1.94
$Y$ [mg/mg]	0.406	0.272	0.369
$Y_p$ [mg/mg]	0.0360	0.0782	0.00103
$b$ [1/hr]	0.0299	0.0234	0.0162
Adsorption parameter :			
$K_d$ [L/g]	1.02	1.22	3.07
RSSE:			
	185	139	318

RSSE: Residual sum of squared errors  
All mass measurements are as COD



**FIGURE 3**

**CUMULATIVE CO<sub>2</sub> GENERATED, mg/L  
FOR PHENOL IN SOIL SLURRY REACTOR**



# REMOVAL OF CREOSOTE FROM SOIL BY THERMAL DESORPTION

by

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## INTRODUCTION

Contaminated soil and debris (CS&D) pose a special problem because of their complexity and high degree of variability. Therefore, the EPA has determined that a detailed evaluation of treatment technologies for CS&D is needed to develop separate Land Disposal Restriction (LDR) standards applicable to their disposal. These standards are being developed through the evaluation of best demonstrated available technologies (BDATs). Once these LDRs are promulgated, only CS&D wastes that meet the LDR standards will be permitted to be disposed of in land disposal units.

As part of the effort to establish the standards, a thermal desorption treatability study was performed for the U.S. EPA to supply information as part of the data base on BDATs for CS&D remediation. Thermal desorption has been successfully tested at both the bench and pilot scale on a wide range of organic contaminants. During this study, thermal desorption was investigated for removal of creosote from soil at a process temperature of 550°C.

The contaminants of concern in the soil were polycyclic aromatic hydrocarbons (PAHs), semivolatile contaminants that boil at temperatures ranging from approximately 215°C to greater than 525°C. Vapor pressures of these compounds vary depending on whether the contamination consists of one compound or a mixture of compounds. Because the boiling points of various mixes of contaminants are not known, bench-scale thermal desorption tests were performed to determine the optimum temperature and residence time required for removal of these compounds from the soil. The thermal desorption study was performed in two phases--bench-scale and pilot-scale. Based on the results of the bench test, a pilot-scale test for the thermal desorption technology was performed at an operating temperature of 550°C and a residence time of 10 minutes to reduce the PAHs present in the soil.

## METHODOLOGY

The thermal desorption pilot plant evaluated under this project consisted of a continuously rotating desorber tube partially enclosed within a gas-fired furnace shell. Small baffles were located at intervals within the tube to provide soil mixing. A stationary thermowell was extended from the discharge end into the tube with six thermocouples to monitor the soil temperature and three to monitor the gas temperature along the tube length. The furnace was a refractory-lined chamber. The 14 equally

spaced burners were controlled by a standard burner control system with appropriate safety features. Temperature measurements for furnace burner control or monitoring were taken by four thermocouples that contact at various locations on the outer metal wall of the rotating tube beneath the furnace refractor. The furnace flue gas was discharged directly to the atmosphere through a remotely positioned exhaust duct. The desorber was rated at 320,000 British thermal units (Btu) maximum heat duty. A nitrogen purge was continuously introduced to the desorber at a low rate of 2 cubic feet per minute to help flush contaminants and to maintain an atmosphere that does not support combustion (i.e., <6 percent oxygen). The residence time was measured before the study by placing colored aquarium gravel into the feed hopper and visually observing its discharge from the desorber. The average retention or residence time in the tube was calculated as the difference between the time the colored gravel was placed in the screw feeder and the time it was discharged. Solids discharged from the desorber during steady-state operation were weighed on a digital electronic scale to determine the soil feed rate.

The Superfund soil that was tested during the project was a fine, sandy soil (75 percent of the particles were between 0.1 and 0.4 mm in diameter). The soil had a relatively low moisture content of approximately 10 percent and a heating value below 500 Btu/lb.

Various temperatures and soil residence times were evaluated throughout the bench-scale testing program. The results obtained for the removal of semivolatile organics from the soil under various operating conditions are summarized as follows:

- Run No. 1 (300°C at 10 min.) removed 96.4 percent
- Run No. 2 (425°C at 10 min.) removed 99.97 percent
- Run No. 3 (550°C at 10 min.) removed 99.995 percent
- Run No. 4 (300°C at 20 min.) removed 97.4 percent
- Run No. 5 (550°C at 5 min.) removed >99.9999 percent

Based on the results obtained during the bench-scale study, temperature and residence time operating conditions of 550°C and 10 minutes were established for the pilot-scale testing program. The total residence time for the soil in the thermal desorption system was 20 minutes. This total residence time included three phases: 1) bringing the soil to 550°C, 2) treating the soil at that temperature for 10 minutes, and 3) cooling the soil before its discharge. Although the bench-scale results indicate that the run at 550°C and a 5-minute residence time provided the highest removal efficiencies for the semivolatile contaminants, larger particles were expected to be introduced into the pilot-scale unit, in which case the feed streams might not be totally uniform and could contain "hot spots." Therefore, a temperature of 550°C and a residence time of 10 minutes were chosen to obtain better treatment of the contaminated soil.

Six sets of temporally related soil samples (waste feed and treated residual) were collected during the thermal desorption pilot test to evaluate the performance of the technology for the treatment of creosote-contaminated soil. Additional samples of the off-gases were collected to characterize the emissions from the unit prior to the air pollution control equipment to determine if any degradation products were being formed.

## RESULTS

Table 1 presents the average concentrations of organic contaminants in the soil before and after treatment on a dry weight basis. On the average, total semivolatile organic contaminants were reduced from 4635 milligrams/kilogram (mg/kg) to less than the detection limit. Hence, average removal of total semivolatile organics was greater than 99.9 percent.

**TABLE 1. AVERAGE CONCENTRATION OF SEMIVOLATILE  
ORGANIC CONTAMINANTS IN TREATMENT SOIL  
(mg/kg)**

Contaminant	Pretest	Posttest	% Removal
Phenol	<2.5	<0.043	NA <sup>a</sup>
2-Methylphenol	<1.4	<0.023	NA
4-Methylphenol	<2.0	<0.033	NA
2,4-Dimethylphenol	<7.0	<0.120	NA
Naphthalene	14.3	<0.016	>99.99
2-Methylnaphthalene	180	<0.190	>99.89
Acenaphthylene	38	<0.007	>99.98
Acenaphthene	342	<0.210	>99.94
Dibenzofuran	237	<0.081	>99.97
Fluorene	388	<0.020	>99.99
Phenanthrene	1028	<0.034	100.00
Anthracene	415	<0.073	>99.98
Fluoranthene	668	<0.010	100.00
Pyrene	580	<0.052	>99.99
Benzo(a)anthracene	172	<0.023	>99.99
Chrysene	158	<0.120	>99.92
Benzo(b)fluoranthene Benzo(k)fluoranthene	158	<0.047	>99.97
Benzo(a)pyrene	77	<0.110	>99.86
Indeno(1,2,3-cd)pyrene	25	<0.035	>99.86
Dibenzo(a,h)anthracene	<1.0	<0.016	NA
Benzo(g,h,i)perylene	26	<0.320	>98.77
Total	4635	<1.35	>99.97

<sup>a</sup> NA = Not applicable.

No appreciable reduction in lead or arsenic was observed during the study because of the low operating temperature in relation to the boiling points of lead and arsenic; however, mercury, which has a boiling point of 356°C, was reduced from 19.3 mg/kg to 0.8 mg/kg.

Air sampling was performed to characterize the gases coming off the treatment system before they reached any air pollution control equipment. The results of the air analyses showed a predominance of aromatic compounds. All of the more complex aromatics detected in pretreatment soil were also detected in the off-gas. In addition, phenolic compounds as well as volatile organic compounds such as benzene, toluene, and xylene were detected in the air samples. The fact that these compounds were not detected in the soil indicates they could have been masked by the more concentrated contaminants in the soil or the possible degradation of the more complex PAHs to form lower-ring compounds.

## CONCLUSIONS

Bench tests should be performed first to determine the best operating temperature and residence time for the pilot-scale desorber with specific soils. For this study, a residence time of 10 minutes at a temperature of 550°C was selected from bench-test results for optimum operation of the pilot-scale desorber. Volatile organic contaminants were below the detection limit in both the pretreatment soil and the posttreatment soil.

On the average, the pilot-scale desorber reduced total semivolatile organic contaminants from 4635 mg/kg to less than the method detection limit, a removal rate of greater than 99.9 percent. All of the individual semivolatile organics were reduced to concentrations below the method detection limits. The highest average individual contaminant concentration in the pretreatment soil was 1028 mg/kg for phenanthrene, and this concentration was reduced to less than the method detection limit of 0.034 mg/kg in the posttreatment soil.

The off-gas from the pilot-scale desorber contained all of the semivolatile organics in approximately the same proportions that were present in the pretreatment soil. Some phenols and volatile organic compounds (e.g., benzene, toluene, and xylene) were detected in the off-gas. This indicates that some degradation of the higher-ring compounds to lower-ring compounds was taking place.

No appreciable volatilization of lead or arsenic occurred in the pilot-scale desorber. Mercury, which has a boiling point of 356°C, was 90 percent vaporized from the soil in the pilot-scale desorber. Release of the mercury to the atmosphere was prevented by the high-efficiency particulate air (HEPA) filter and carbon adsorber.

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## SLURRY REACTOR BIOREMEDIATION OF SOIL-BOUND POLYCYCLIC AROMATIC HYDROCARBONS

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### INTRODUCTION

ECOVA Corporation conducted pilot-scale process development studies in 1991 using a slurry-phase biotreatment design to evaluate bioremediation of polycyclic aromatic hydrocarbons (PAHs) in creosote-contaminated soil collected from a superfund site. Bench-scale studies were performed as an antecedent to pilot-scale evaluations in order to collect data which would be used to determine the optimal treatment protocols. This study was performed for the U.S. EPA to supply information as part of the database on Best Demonstrated Available Technology (BDAT) for soil remediation. The database will be used to develop soil standards for land disposal restrictions. This paper is a summary of the complete on-site engineering (OER) report that is available from the U.S. EPA.

The site is a former railroad tie-treating facility. Two surface impoundments were used for the disposal of wastewater generated from wood-treating processes (Resource Conservation and Recovery Act waste code K001). Although all wastewater and liquid creosote have been removed from the impoundments, there is an estimated 12,500 cubic yards of soil and sludge remaining that is contaminated with 2-, 3-, and 4+-ring PAHs. There is also some groundwater contamination restricted to a relatively small area downgradient from the site.

A landfarming operation has been conducted on contaminated soil and sludges at the site since 1986. Although this work has attained significant reductions in 2- and 3-ring PAHs, the degradation of the 4+-ring PAHs and benzene-extractable hydrocarbons has been less successful. A significant improvement in biodegradation rates of the 4-ring and larger PAHs is possible through the use of slurry-phase biological treatment vs. landfarming. In this process, the soil is suspended to obtain a pumpable slurry which is fed to a large-capacity continuously stirred tank reactor (CSTR). The reactor is then supplemented with oxygen, nutrients, and, when necessary, a specific inocula of microorganisms to enhance the biodegradation process. This method of treatment has several advantages because the engineering and biotechnology required to provide an optimal environment for biodegradation of the organic contaminants can be controlled with a high degree of confidence. Often, biological reactions can be accelerated in a slurry system because of the increased contact efficiency between contaminants and microorganisms due to the higher sustained levels of bacterial populations in the aqueous phase (e.g.,  $10^8$ - $10^9$  colony-forming units/milliliter (cfu/mL)). In a 30% slurry this translates to  $10^9$ - $10^{10}$  cfu/gram of soil which is 10- to 100-fold higher than typically attainable in solid-phase treatment processes.

### METHODOLOGY

Physical characterization of the site soils indicated that there was a substantial amount of heavy, coarse-grained particles. The percentage volume of soil fines which was less than 100 mesh was only 9%. This suggested that there would be appreciable difficulties in generating a manageable slurry with this soil. Another important observation was the presence of hardened inclusions of creosote which were pulverized when substantial shearing forces were applied. Consequently, a soil pretreatment was required prior to charging pilot-scale reactors. Normally, a soil of this nature would be subjected to soil washing to remove contaminants from oversize materials (+ 100 mesh) and yield a pregnant slurry enriched in smaller particulates (- 100 mesh). However, to meet the requirements of the EPA's program, the pretreatment step chosen was a soil milling process which crushed larger particles yielding a soil enriched in - 100 mesh particles.

Pilot-scale bioreactors (5) were EIMCO 64-liter stainless steel containers incorporating an airlift system and rotating rake attachment. The reactors were filled with a 30% slurry (w/v, soil in water) amended with nutrients and an inocula of PAH-specific degrading microorganisms. Nutrients were adjusted to provide an optimal ratio of Total Organic Carbon (TOC) : Nitrogen (N) : Phosphorous (P). A microbial evaluation of the contaminated soil was conducted to determine the size and diversity of bacterial populations and the ability of these organisms to degrade polycyclic aromatic hydrocarbons. Enrichment culture techniques and selective plating procedures were used to isolate and characterize PAH degrading organisms. Reactors were inoculated with specific PAH degrading organisms indigenous to the soil (*P. fluorescens*, *P. stutzeri*, and *Alcaligenes sp.*) at a concentration of  $9.3 \times 10^7$  per gram of soil. Rake speed, airlift volumes, temperature, pH, dissolved oxygen, and foaming were all monitored over the course of the study.

Chemical analyses were performed on composited soil samples to determine contaminant levels. Analysis for semivolatile contaminant levels was performed according to EPA Method 8270 (SW-846). In addition, soil was analyzed for polycyclic aromatic hydrocarbons by HPLC (ECOVA Site Support Chemistry [SSC-6]), total petroleum hydrocarbon (TPH) by infrared spectroscopy (IR) (EPA method 418.1), and total organic carbon (TOC) and inorganic nutrient ions ( $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$ ,  $\text{SO}_4$ ) by standard chemical methods (ECOVA SSC-17, ECOVA SSC-14, ECOVA SSC-15, and EPA 375.4, respectively). The inorganic nutrient data were used to determine whether, based upon TOC, the levels and ratio of nitrogen (N), *ortho*-phosphate phosphorous (P), and sulphur (S) were sufficient to support optimal microbial activity. In addition, a soil toxicity test was performed using Microtox procedures. The pilot-scale study was conducted for 12 weeks.

## RESULTS

This project demonstrated optimum treatment of PAHs by slurry-phase biotreatment in stirred batch reactors. Baseline analyses of PAH concentrations in the soil are illustrated in Table 1. Naphthalene, acenaphthene and fluoranthene were the constituents present at the highest levels. Total PAH levels in these soils averaged  $10,970 \pm 1,515$  gr. / kg dry soil (parts per million, ppm). The 2- & 3-ring PAHs constituted  $5,890 \pm 1,469$  ppm and the 4- to 6-ring PAHs constituted  $5,080 \pm 367$  ppm of the total.

PAH	Mean (5) (ppm)	Std. Dev. (ppm)
Naphthalene	2143.3	710
Acenaphthylene	17.4	7.6
Acenaphthene	1937.1	1016.8
Fluorene	967.8	288.4
Phenanthrene	518.9	12.1
Anthracene	307.0	34.7
Fluoranthene	2428.7	732.6
Pyrene	161.1	51.2
Benzo(a)Anthracene	957.2	284.8
Chrysene	468.1	129.6
Benzo(b)Fluoranthene	389.4	112.7
Benzo(k)Fluoranthene	279.6	83.1
Benzo(a)Pyrene	260.2	75.4
DiBenzo(a,h)Anthracene	119.9	94.1
Indeno(1,2,3-cd)Pyrene	17.2	4.8

Pilot-scale results for PAH biodegradation paralleled the bench-scale study results. Optimum reductions in total PAH of  $89.3 \pm 3.9\%$  occurred during the first two weeks of treatment (see Figure 1)

with an overall PAH reduction of  $93.4 \pm 3.2\%$  over 12 weeks. With respect to the more biodegradable and bioavailable 2- & 3-ring PAHs, a reduction of  $95.9 \pm 1.8\%$  occurred within two weeks with only a slightly increased overall reduction to  $97.14 \pm 2.2\%$  over 12 weeks (see Figure 2). Reductions in the 4- to 6-ring PAHs, which are less biodegradable and bioavailable and usually are not preferred carbon sources for bacterial growth, were  $81.58 \pm 6.7\%$  after two weeks. After 12 weeks, further significant reductions were observed in the 4- to 6-ring PAHs totalling  $89.06 \pm 4.8\%$  (see Figure 3). After nine weeks, two of the five reactors were resupplemented with inoculum and two with inoculum and surfactant (Tween 80). These amendments did not stimulate further reductions in PAHs during the time period from week 9 to week 12.

Specific PAH-degrading bacterial populations were monitored over time. Bacteria were grown on mineral salt agar and salicylate-amended mineral salt agar with phenanthrene or pyrene as carbon sources. Salicylate-amended

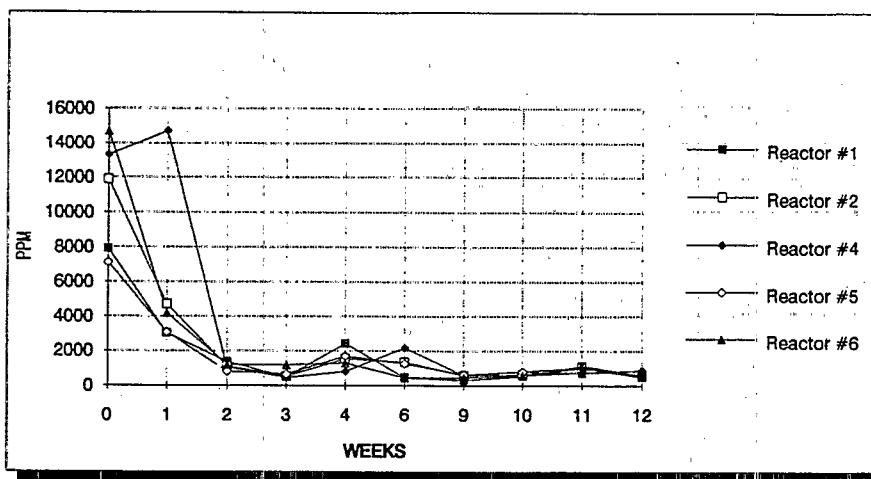


Figure 1. Total Polycyclic Aromatic Hydrocarbons

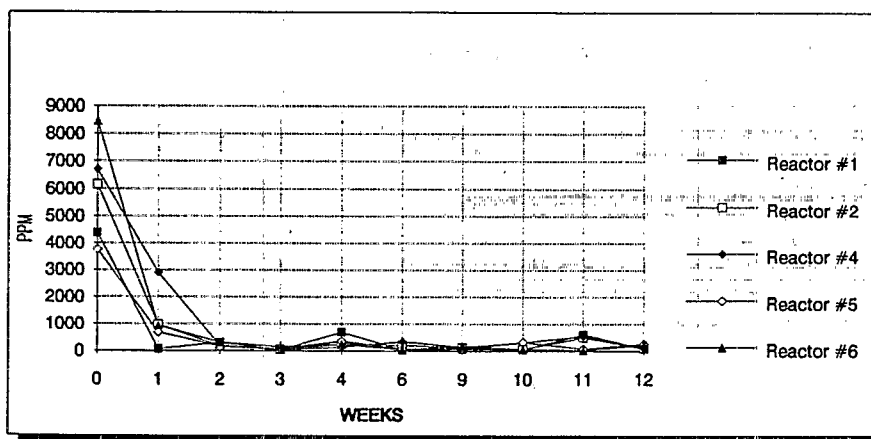


Figure 2. 2- & 3-Ring Polycyclic Aromatic Hydrocarbons

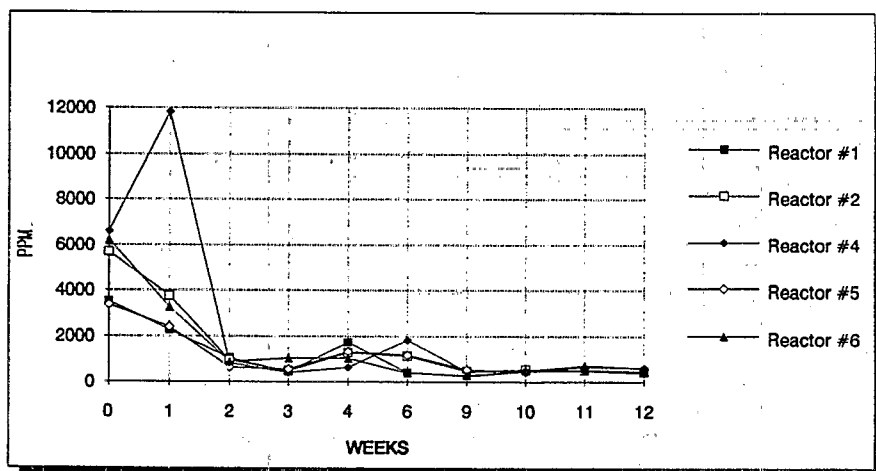


Figure 3. 4- to 6-Ring Polycyclic Aromatic Hydrocarbons



media was used to screen for strains which might be capable of cooxidizing PAH's while growing on an alternate carbon source. Specific PAH degrader population levels declined over the course of the project (see Figure 4). The PAH cooxidizing populations exhibited the most significant and rapid declines. This may reflect that bacteria that utilize salicylate are more likely to degrade naphthalene. Once naphthalene levels have been depleted, these populations may become carbon-source limited and death will occur. An interesting observation is that populations capable of utilizing pyrene and phenanthrene as sole carbon sources appear to be sustained throughout the study.

Between weeks 10 and 12, pyrene degraders exhibit the most significant population declines. Total heterotrophic bacterial counts also do not appear to decline over the 12 weeks. These data suggest subtle shifts in bacterial populations from low-molecular weight PAH degraders to higher-ring PAH degraders.

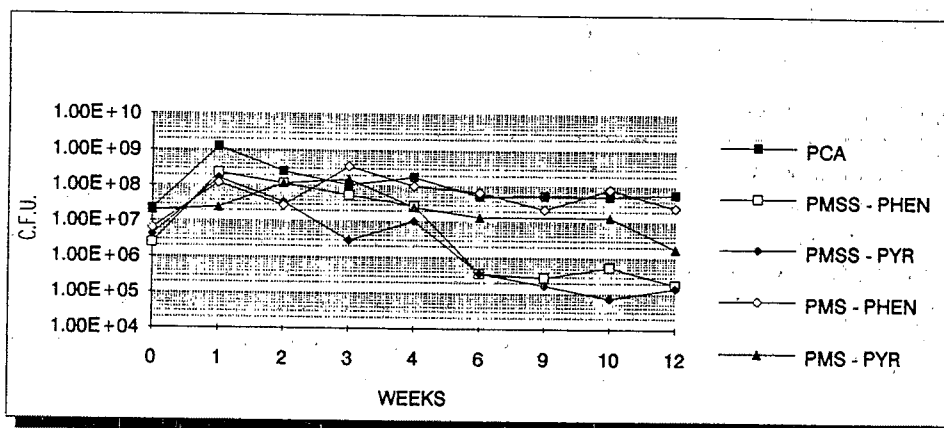


Figure 4. Mean Value of Microbial Enumerations

An important phenomenon that occurred with these soils in the continuously stirred tank reactors (CSTRs) was a further comminution of the soil despite extensive ball milling. Figure 5 shows the effect of both the milling and CSTR comminution on particle size distribution. After milling, there was an enrichment of the particle fraction smaller in size than 0.21 mm at the expense of larger size particles. This allowed development of a manageable slurry.

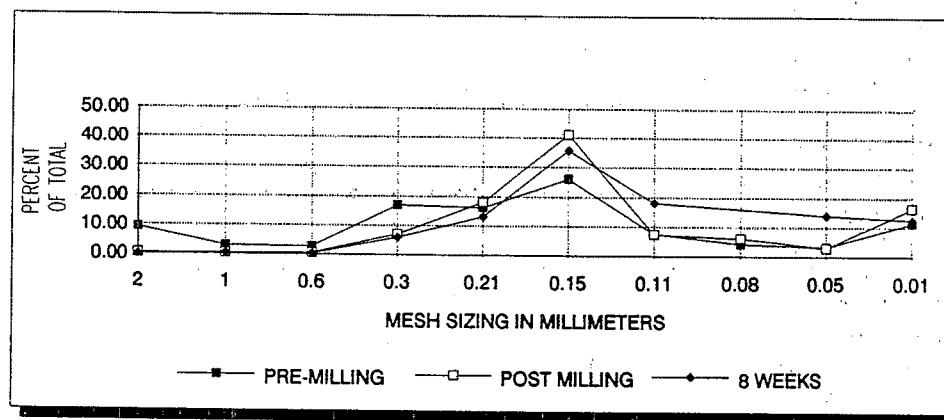


Figure 5. Particle Sizing Data

After 8 weeks of CSTR stirring there was an enrichment in the fraction with particle sizes less than 0.15 mm. This resulted in an appreciable thickening (viscosity) of the slurry itself and also an increase in the extraction efficiency of PAHs from soil particles. Between weeks 3 and 9 the levels of PAHs increased with the most significant increases observed in the 4- to 6-ring PAH fraction. These phenomenon may reflect the increased bioavailability of soil-bound PAHs due to comminution of soil particles which would also contribute to increased slurry viscosity. PAHs were reduced by 94%, of which 2- and 3-ring compounds were degraded 97% and 4- to 6-ring compounds degraded by 90%. Factors contributing to

the lack of further decline of total PAHs may be: bacterial utilization of metabolic degradative intermediates as a preferential carbon source, a reduction of the more readily biodegradable 2- and 3-ring PAHs to below levels which sustain an acclimation of biomass, the low bioavailability of the more recalcitrant 4-, 5-, and 6-ring PAHs, or the generation of inhibitory metabolic end-products which repress catabolic activity.

## CONCLUSIONS

Slurry-phase biotreatment of creosote-contaminated soils offers an efficient and rapid process for reducing the toxic PAH components of this waste class (K001). Soils from this superfund site possess a robust population of PAH degrading bacteria capable of efficient biodegradation of these compounds. Optimal biotreatment of these waste components can be stimulated by adjusting inorganic nutrient levels, providing adequate aeration with mixing, and controlling the pH. Finally, material characterization of soils is critically important in assessing the feasibility of using slurry-phase reactors to bioremediate contaminated soils.

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## ACKNOWLEDGEMENTS

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## ADSORPTIVE FILTRATION FOR TREATMENT OF METALS AT SUPERFUND SITES

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### INTRODUCTION

This project investigated the potential application of a combination adsorbent-filtration media for treatment of heavy metals from Superfund sites. The media is comprised of ordinary filter sand onto which a layer of iron oxide had been coated. The coating was applied by heating a solution of iron nitrate to dryness under controlled conditions in the presence of the sand. The final product was about 1 to 2% Fe by weight. The coating was a few micrometers thick on sand grains of diameter around 400  $\mu$ m, and it increased the surface area of the bulk solid from about 0.04 to about 7 m<sup>2</sup>/g.

Since iron oxide is known to be a good adsorbent for heavy metals, it was hoped that the modification of the surface of the sand would allow the sand grains to adsorb soluble heavy metals as they passed through a column packed with the media. At the same time, it was anticipated that the coated sand would perform comparably to plain sand as a media for collecting particulate metals. Thus, the goal of the project was to assess the ability of the coated sand media to remove soluble and particulate metals simultaneously as water containing those species passed through the column.

### METHODOLOGY

Runs were conducted using synthetic influents and a treated, metal-bearing water from a Superfund site. Preliminary runs used laboratory-prepared solutions containing 0.5 or 5.0 mg/L each of three metals (Cu, Cd, and Pb). Most of these tests were conducted at pH 9.0 using a 2-minute empty bed detention time, corresponding to a hydraulic loading rate of about 11 gal/min-ft<sup>2</sup>. Runs were also conducted to characterize the effects on metal behavior of ammonia (as a complexing agent), EDTA (as a chelating agent), or sodium dodecyl sulfonate (a surfactant) in the influent solution, and of biogrowth in the column. At the end of the project, a few tests were run with a solution collected from a Superfund site where conventional treatment is currently being applied. During all runs, influent and effluent metals concentrations were monitored, and, in most cases, soluble and particulate metals were analyzed independently.

After most runs, the media was backwashed to remove the particulates that had been collected. It was then regenerated at pH around 2.0 to remove the soluble metals that had sorbed. The backwashing step was skipped if the influent in the previous run did not contain particulate matter. Regeneration efficiency was monitored and characterized as a function of operating conditions during the regeneration step.

### RESULTS

In runs with 0.5 mg/L each of uncomplexed Cu, Cd, and Pb in the influent, the majority of the influent metal load was soluble. Between 7000 and 13000 bed volumes of influent were treated

effectively prior to substantial metal breakthrough. Before breakthrough, the metal concentrations in the effluent were quite steady, with virtually no short-term fluctuations. Typical effluent concentrations of total Cu, Cd, and Pb were substantially less than 0.1 mg/L each.

In the runs with influent nominally containing 5 mg/L of each uncomplexed metal (in reality, influent metal concentrations varied between about 3 and 7 mg/L), most of the influent metal load was particulate; soluble influent concentrations were typically around 1.5 mg Cd/L, 0.8 mg Pb/L, and 0.2 mg Cu/L. For the purposes of this discussion, a "run" is defined as the time between sequential regeneration cycles. Several batches of influent were treated during each run. During the course of these runs, the media was backwashed over 20 times and regenerated about 10 times over a period of a few months, with no apparent deterioration in performance.

A typical breakthrough curve for these tests is shown in Figure 1. The total concentrations (corrected for background) of all the metals in the effluent were well below 0.1 mg/L until about 150 to 200 bed volumes had been treated. Removal of soluble metal was always significant throughout these runs, and was very good at least until the point of particulate breakthrough. Particulate metals began breaking through the column after about 200 to 400 bed volumes had been treated over a 6- to 12-hour period. Typical removal efficiencies for soluble metals in the influent were 80% for Cu, 90% for Pb, and 98% for Cd, and typical overall removal efficiencies (comparing total effluent and total influent) were 99% or greater for all three metals (Table 1).

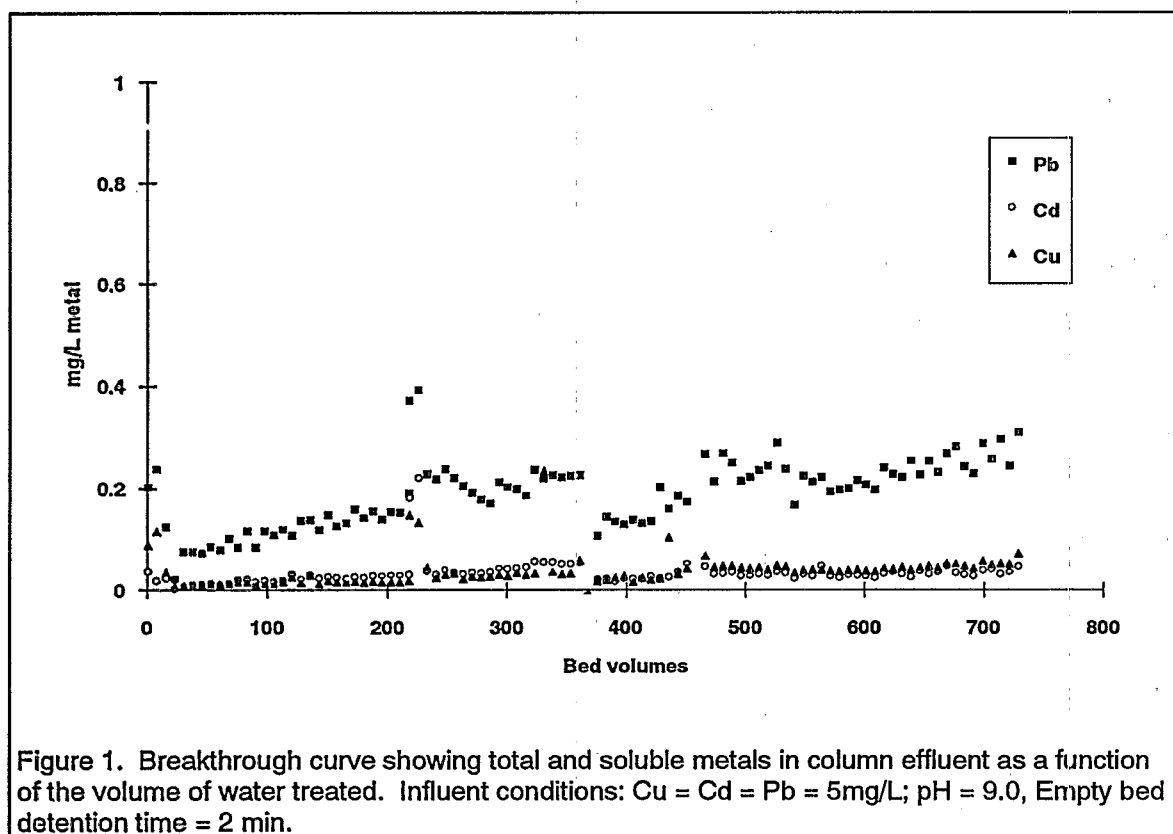


Figure 1. Breakthrough curve showing total and soluble metals in column effluent as a function of the volume of water treated. Influent conditions: Cu = Cd = Pb = 5mg/L; pH = 9.0, Empty bed detention time = 2 min.

TABLE 1. Soluble metals in column influent and effluent at various times during run 15.

Time of Sample	Soluble Influent, mg/L			Soluble Effluent, mg/L			% Removal of Soluble Metals		
	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb
Batch 1, BV 3	98	825	523	23	26	3	77	97	99
Batch 1, BV 13	105	863	548	23	17	39	78	98	93
Batch 2, BV 3	355	933	468	16	0	0	95	>99	>99
Batch 2, BV 45	127	1603	683	25	27	84	80	98	88
Batch 2, BV 63	160	1891	739	24	31	140	85	98	81
Batch 3, BV 6	77	578	392	23	12	83	70	98	79
Batch 3, BV 260	248	1710	697	63	59	109	75	97	84

Headloss usually reached 25 psi near the time when particulate breakthrough occurred. At this point, the column was backwashed with pH 9.0 water, and the next batch of influent was fed into the system. The backwash water typically contained a few hundred mg/L of each metal. After the first batch of water had been treated, particulates broke through relatively soon after each backwash step. Thus, backwashing with water adjusted to pH 9.0 did not return the column to its original filtration capacity. However, despite the fact that particulates broke through the column more rapidly in batches 2 and 3 than in batch 1, the effluent values prior to breakthrough during treatment of all three batches were comparable. When breakthrough did occur, it was due to particulate metals passing through the column; the columns did not appear to reach adsorptive saturation in any of the three batches. Thus, it appears that additional batches could have been run successfully before the column needed to be regenerated.

The regeneration protocol was to circulate either 4 or 8 bed volumes of water adjusted to pH 2.0 through the column. After two hours, an additional 4 to 8 bed volumes was passed through the column and not recirculated. The metal concentration in the recirculation fluid increased rapidly at first and then only slowly thereafter. Based on these results, it appears that a recirculating period as short as 10 minutes would release a large fraction of the available metal. Metal concentrations in the first and second regenerant solutions were as high as 3000 and 500 mg/L after the 5 mg/L runs, and about a factor of 5 lower after the 0.5 mg/L runs.

Interestingly, only about 40 to 75% of the particulate metal load that was removed by the column was recovered during the backwashing step. Most of the remainder was recovered during the acid regeneration step, suggesting that once the particles collide with the media, they form strong bonds to it. Overall recovery efficiencies (backwash plus regeneration) were almost always greater than 80% and were often 100%  $\pm$  10% (Table 2).

TABLE 2. Recovery of metals from the column after various treatments after run 15.

Metal, Batch #	Estimated Cumulative Particulate Me Removed (mg)	Metal Recovered by Backwashing (mg)	Cumulative Soluble Me Removed (mg)	Metal Recovered by Regeneration (mg)	Total Metal Recovery Efficiency (%)
Pb, 1	80.7	35.4	29		
Pb, 2	63.0	67.3	36		
Pb, 3	<u>163.9</u>	<u>150.1</u>	<u>37</u>		
	307.6	252.7	102	161.1	101
Cd, 1	119.0	29.0	47		
Cd, 2	41.4	54.3	85		
Cd, 3	<u>158.8</u>	<u>135.9</u>	<u>77</u>		
	319.2	219.2	209	234.1	86
Cu, 1	109.3	46.2	5.5		
Cu, 2	85.1	84.7	12.3		
Cu, 3	<u>201.4</u>	<u>164.0</u>	<u>11.0</u>		
	395.8	294.9	28.8	59.8	84

When sufficient ammonia was added to the solution to keep all of the influent Cu and Cd (5 mg/L) soluble, about 4000 mg each of Cu and Cd could be sorbed onto the media at pH 10. Regeneration of this column using a total of 16 bed volumes of regenerant solution at pH 2.0 recovered 93% of the sorbed Cd and 100% of the Cu. Thus, at least some complexing agents do not interfere with the performance of the media. On the other hand, when EDTA was added at a ratio of 1.25 mols EDTA/mol metal, breakthrough occurred very quickly, both at pH 10 and pH 4.5. The adsorptive filtration process appears not to be applicable for waters containing such a strong chelator. In situations where complexed metals need to be treated, tests investigating the behavior of the specific complex will be required.

Sodium lauryl sulfonate is a surfactant that might interfere with the process by interacting either with the metals or the surface of the media. Thirty mg/L of this surfactant had no noticeable effect on metal sorption.

In the one test that was run using media on which biogrowth had occurred, the biofilm apparently reduced the capacity of media for the metals by about 50%. This interference could probably be reversed by exposing the column to a high pH solution, which would solubilize a substantial amount of the biofilm.

One set of tests was conducted using a treated, metal-bearing wastewater from a Superfund site. Unfortunately, this solution could not be treated under optimal conditions for our process, since massive amounts of  $\text{CaCO}_3$  precipitated when the pH was raised to 9.0. Therefore, the water was treated at pH 8.0. The only metal present in significant quantities in this water was Zn, for which the total and soluble concentrations were in the ranges 0.6 to 4.0 and 0.3 to 0.6 mg/L, respectively. As shown in Figure 2, typical total and soluble Zn concentrations in the effluent were 0.15 and 0.05 mg/L, respectively. Thus, even though the test could not be run under optimal conditions, it did demonstrate that the adsorptive filtration process could work on such a water. Chances are that the outcome would have been more impressive if a water with lower Ca or alkalinity had been chosen for the test.

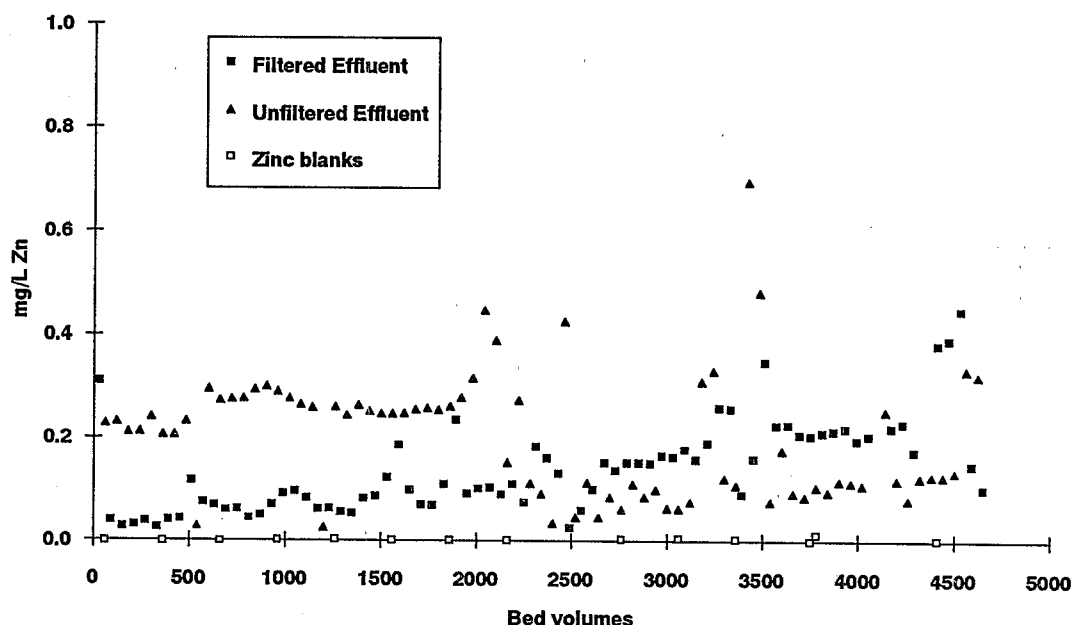


Figure 2. Breakthrough curve showing total and soluble Zn in the column effluent during treatment of water from a Superfund site (Run 3). Prior treatment involved precipitation and settling at pH = 8.0. Influent Zn concentrations quite variable with a mean value and standard deviation of  $0.73 \pm 0.28$  mg/L total and  $0.40 \pm 0.22$  mg/L soluble Zn.

## CONCLUSIONS

To summarize, simultaneous sorption and filtration of Cu, Cd, and Pb are feasible using iron oxide-coated sand under reasonable engineering conditions. Soluble effluent concentrations of a few tens of  $\mu\text{g/L}$  or less are achievable. The media can remove particulate metals simultaneously from the water, probably with an efficiency comparable to that achievable with conventional sand filtration. The media can be regenerated by exposure to an acid solution, yielding regenerant solutions containing metal concentrations a few hundred times as concentrated as the influent. In our tests, filtration limited process performance moreso than sorption, although this outcome is not generalizable; the limiting factor would certainly depend on the specific chemical composition of the influent solution.

## PHASE SEPARATION AND SOLUBLE POLLUTANT REMOVAL BY MEANS OF ALTERNATING CURRENT ELECTROCOAGULATION

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### INTRODUCTION

Electro-Pure Systems (EPS) has undertaken a two-year laboratory program to investigate the technical and economic viability of alternating current electrocoagulation technology (ACE Technology) for Superfund site remediation. The ACE Technology offers a technologically simple mechanism to achieve phase separation of liquid-solid slurries and liquid-liquid emulsions, and to remove soluble ionic pollutants (metals, alkaline metals, phosphate) from solution. Alternating current electrocoagulation 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 offers 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, gelatinous sludges which are difficult to dewater and slow to filter. As an alternative to chemical conditioning, alternating current electrocoagulation introduces into an aqueous medium highly-charged polymeric aluminum hydroxide species which will neutralize the electrostatic charges on suspended solids and oil droplets to facilitate their agglomeration (or coagulation). These species will also coprecipitate many soluble ions. ACE Technology prompts coagulation without adding any soluble species and produces a sludge with a lower contained water content and which will filter more rapidly. 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.

Presented in this paper are preliminary results from the laboratory testing program conducted by EPS under the auspices of the U. S. EPA's Superfund Innovative Technology Evaluation (SITE) program. Performance data from a field test of a pilot-scale alternating current electrocoagulation unit are summarized as well.

### METHODOLOGY

Laboratory experiments were conducted in a bench-scale electrocoagulation apparatus, referred to as an ACE Separator™, on a series of synthetic wastes. Two designs of the ACE Separator™ were used: a Parallel Electrode unit in which a series of parallel, vertically-oriented, aluminum electrodes form a series of monopolar electrolytic cells up through which the effluent passes, and a Fluidized Bed unit which consists of non-conductive cylinders equipped with rectilinearly-shaped, non-consumable metal electrodes between which is maintained a turbulent, fluidized bed of aluminum alloy pellets. Application of an alternating current field to the electrodes prompts dissolution of the aluminum and formation of highly reactive polymeric hydroxide species. The Parallel Electrode ACE Separator™ was used in the first year EPS participated in the SITE program when the basic mechanism of electrocoagulation was



believed to be electrostriction (polarization of electrical charges on colloidal particles by imposition of an alternating current electric field). Experiments conducted with this version of the ACE Separator™ primarily addressed the influence of frequency, residence time, field strength (electrode spacing), and current density of the applied AC current field. The realization that treatment efficiency was primarily dependent upon aluminum ion production instead of upon the characteristics of the applied AC current field prompted development of the Fluidized Bed ACE Separator™ which dissolves aluminum at least one order of magnitude more efficiently than the Parallel Electrode ACE Separator™. Experiments in the second year were conducted primarily with this newly-designed ACE Separator™.

Experiments were conducted on two surrogate wastes which were prepared by EPS by combining measured quantities of the EPA's Synthetic Soil Matrix (SSM), supplied to EPS by EPA's Edison, NJ laboratory, with hydrocarbon and/or metal contaminants selected by EPS. Both were prepared as stable aqueous suspensions of silt, clay and top soil containing approximately 1% suspended solids, with or without spikes of toxic metals (Cd, Cr, Cu, Pb) and diesel fuel. The clay surrogate waste contained solely the -40 mesh synthetic soil matrix fines while the second incorporated the fines fraction mixed with 1.5% No. 2 diesel fuel and 1% of a strong surfactant. Experiments on metals and phosphate reductions were conducted on aqueous end-member solutions at neutral pH at two solution conductivities (1,500 and 3,000  $\mu\text{S}/\text{cm}$ ). Metals and phosphate matrix experiments were conducted to determine the treatment conditions that would yield both acceptable metal reductions and a reasonable operating cost (electrical power, aluminum consumption). Electrocoagulation treatment efficiency was primarily determined by reductions achieved in the supernant phase of total suspended solids (TSS), turbidity, and soluble contaminant concentrations (metals, Chemical Oxygen Demand (COD) for diesel fuel-spiked surrogates). Improvements in solids settling rates and decreases in the moisture content of coagulated solids filter cakes were also measured. Based upon the encouraging results of bench-scale tests of the Fluidized Bed ACE Separator™, a portable, pilot-scale ACE Separator™ of this design with a nominal throughput capacity of 70 gpm was designed, fabricated and tested for recovery of suspended colloidal-sized pigment ( $\text{TiO}_2$ ) from an industrial waste stream. The results for treatment of the clay suspension surrogate, diesel-fuel contaminated soil slurry and metals-bearing solutions are summarized below.

## RESULTS

### • Clay-Metals Surrogate

The clay suspension surrogate was spiked with four metal salts ( $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ ) 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 approximately 50% of that required for the untreated surrogate waste (3:02 minutes versus 6:00 minutes). Comparative chemical coagulant experiments with alum ( $\text{Al}_2(\text{SO}_4)_3$ ) 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 seemed 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 supernant 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. CLAY- METALS-SPIKED SURROGATE EXPERIMENTS

ANALYTICAL PARAMETERS	UNTREATED SLURRY (mg/l)	ACE SEPARATOR TREATED		
		SUPERNANT (mg/l)	FILTRATE (mg/l)	FILTER CAKE (ug/l)
TOTAL SOLIDS	17,000	1,700	1,700	540,000
TOTAL SUSPENDED SOLIDS	22,000	25	3.0	N.D.*
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

\*N.D.: Parameter not determined.

#### • Clay-Metals-Diesel Fuel Surrogate

Electrocoagulation of the clay surrogate waste containing 1.5% diesel fuel and metals (Cu, Cd, Cr, Pb) 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). Copper is reduced by 90-94%, cadmium and chromium by 91-97% and lead by 86-89% (Table 2). No appreciable change in TOC loadings in the supernant 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 required approximately 30% longer filtration times, ACE Separator™ and polymer treatments reduce the total solids (TS) and TSS loadings to an equivalent degree (equal to four times the reduction achieved by alum treatment) 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. The mean size of the ACE Separator™-treated particulates both in the supernant 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 2. CLAY- DIESEL- METALS-SPIKED SURROGATE EXPERIMENTS

ANALYTICAL PARAMETERS	UNTREATED SLURRY (mg/l)	ACE SEPARATOR TREATED		
		SUPERNANT (mg/l)	FILTRATE (mg/l)	FILTER CAKE (ug/l)
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

\*N.D.: Parameter not determined.

#### • Metals and Phosphate Experiments

Matrix electrocoagulation experiments on the surrogate metals and phosphate-bearing solutions indicated excellent nickel, copper and phosphate concentration reductions. Electrocoagulation by means of either design of the ACE Separator™ enabled in excess of 90% (concentration basis) of the phosphate and copper to be removed from solution at low aluminum and electrical power requirements. Reductions in the nickel concentration varied between 78 and 91% (concentration basis). **Table 3** presents the analytical results for reductions for these three species from neutral solutions by means of both the Fluidized bed and Parallel Electrode ACE Separators™ for representative matrix experiments.

#### • Pilot-Scale ACE Separator™ Demonstration

A pilot-scale, portable Fluidized Bed ACE Separator™ equipped with four, 6" diameter electrocoagulation cells having a combined nominal throughput capacity of 70 gpm was designed and manufactured. This unit was field-tested at a TiO<sub>2</sub> pigment manufacturer to recover fine-grained (<30μ) product from the overflow of a clarifier which contains 500-3,000 mg/l TiO<sub>2</sub>. Electrocoagulation of the overflow at a rate of 1-2 ampere-minutes/liter, corresponding to introduction of ~15-17 mg/l aluminum, followed by 5-10 minutes of gravity settling allowed recovery of 85-95% of the pigment. Such treatment reduces the TSS of the overflow stream from 2,000 mg/l to ~50 mg/l; direct electrocoagulation of the filtrate entering the clarifier is another treatment possibility for enhancing its operation. The direct operating cost for this ACE Separator™ treatment required 5 KWH/1000 gallons of electrical power and ~0.25 lb. Al/1000 gallons for a total treatment cost of \$0.50/1000 gallons. Electrocoagulation enabled recovery of ~17 lbs. TiO<sub>2</sub>/1000 gallons that would otherwise have been lost to a settling lagoon. Assuming a pigment price of \$0.85/lb. and an electrocoagulation operating cost of \$0.50/1000 gallons ACE Separator™ treatment will enable recovery of ~\$14.00 of TiO<sub>2</sub> from every 1000 gallons of clarifier overflow.

TABLE 3. PHOSPHATE, NICKEL AND COPPER REDUCTIONS

EXPERIMENT* AND ACE SEPARATOR OPERATING CONDITIONS	INITIAL CONCENTRATION (mg/l)	FINAL CONCENTRATION (mg/l)
• PHOSPHATE		
FB 1.1 AMP, 180 SEC RT, 123 VAC	75	6.7
FB 1.5 AMP, 540 SEC RT, 74 VAC	95	1.8
PP 11.2 AMP, 240 SEC RT, 16 VAC	98	18
PP 19.6 AMP, 168 SEC RT, 27 VAC	98	6.2
• NICKEL		
FB 2.7 AMP, 150 SEC RT, 130 VAC	91	22
FB 4 AMP, 120 SEC RT, 120 VAC	87	13
PP 22.6 AMP, 144 SEC RT, 20 VAC	100	24
PP 31.9 AMP, 221 SEC RT, 13 VAC	100	8.6
• COPPER		
FB 1.1 AMP, 144 SEC RT, 97 VAC	84	1.9
FB 2.3 AMP, 14 SEC RT, 111 VAC	47	0.38
PP 23.8 AMP, 60 SEC RT, 110 VAC	75	1.4
PP 21 AMP, 225 SEC RT, 23 VAC	50	4.3

\*ABBREVIATIONS: FB: Fluidized Bed ACE Separator™, PP: Parallel Electrode ACE Separator™, RT: Retention Time

## CONCLUSIONS

ACE Separator™ treatment is effective in removing particulates from the soil suspensions, increasing the resulting mean particle size and, consequently, improving filtration properties. 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. The ACE Technology is particularly applicable to zero discharge applications in which addition of chemicals, and the inevitable build-up of residual concentrations would adversely affect the effluent quality or inhibit its reuse. Other applications of the ACE Separator™ are foreseen for the remediation of groundwater and leachates (metals, COD/BOD removal), for enhancement of clay separation from aqueous chemistries used in soil-washing operations, for the breakage of oil-in-water emulsions produced in the pumping of hydrocarbon-contaminated groundwater and for removal of suspended solids from storm water runoff. Industrial applications are envisioned for fine-grained product recovery (pigments, PVC) and for extraction of suspended solids from waste streams which contribute to high BOD and COD loadings and thus reduce POTW discharge surcharges. Overall treatment operating costs are nearly equivalent to those for traditional chemical treatment; refinement in the engineering design of the electrodes and process control mechanism are expected to further reduce these costs and thereby enhance the economic attractiveness of this innovative treatment technology.

## FLUID EXTRACTION-BIOLOGICAL DEGRADATION OF ORGANIC WASTES

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### INTRODUCTION

The Institute of Gas Technology (IGT) Fluid Extraction-Biological Degradation (FEBD) Process extracts hydrocarbon contaminants from soil and then biologically degrades the pollutants in aerobic bioreactors. The FEBD process has the potential to be an environmentally benign means of safely and economically degrading pollutants by overcoming bioavailability limitations of the pollutants in soil. The process consists of three stages; extraction, separation, and biodegradation. Contaminants are first removed from the soil by solubilization in supercritical carbon dioxide in an above-ground extraction vessel. The hydrocarbon contaminants are then collected in a separation solvent, and clean  $\text{CO}_2$  is recycled to the extraction stage. Separation solvent containing the organic wastes is sent to the biodegradation stage where the wastes are converted to  $\text{CO}_2$ , water, and biomass. All stages of the FEBD process have been successfully demonstrated.

The extraction stage of the FEBD process relies on the unique properties of supercritical fluids (SCF) to remove organic contaminants from soil. An SCF is a compound at conditions exceeding its critical temperature and pressure. Fluids in the supercritical range have viscosities and diffusivities between liquids and gases with densities close to those of liquids. Supercritical fluids have the solution characteristics of liquids with better mass transfer capabilities. Extraction and separation are easily controlled because changes in the pressure (density) of an SCF can be used to change the solvation ability of the fluid (1).

Different compounds and classes of compounds have varying degrees of solubility in individual SCFs. Hydrocarbon compound solubilities in supercritical  $\text{CO}_2$  as a general rule decrease with increasing molecular size and with increasing aromaticity (2). Alkanes are highly soluble in supercritical  $\text{CO}_2$ , and larger molecules as diverse as phenols, pesticides, PCBs, dioxins, and coal tar residues have been extracted from soils with supercritical  $\text{CO}_2$ .

The biodegradation stage of the FEBD process uses an aerobic bioreactor. In studies reported here an aerobic, PAH degrading mixed-culture derived from contaminated soil was used. The bacterial cultures used for biodegradation at a specific site will be selected based on site-specifics of the particular contaminants.

## METHODOLOGY

The soil used for testing the FEBD process was collected and provided to IGT by Biotrol, Inc. (Chesha, MN). Three soil samples were taken by Ebasco from the North Cavalcade Superfund Site in northeast Houston, Texas near the intersection of interstate 610 and U.S. highway 59. Biotrol mixed the three samples and generated a composite sample which was sent to IGT. The site was a wood preserving business, and the principal pollutants are polynuclear aromatic hydrocarbons (PAHs) present in creosote used as the wood preservative. The soil was stored frozen at IGT until needed. Analysis of the composite soil labeled FEBD-1 by EPA method SW-846, 8100 revealed a total of 1925 ppm of PAH compounds. This includes 50 ppm of 2-ring, 1132 ppm of 3-ring, 670 ppm of 4-ring, and 73 ppm of 5-6 ring PAHs.

Extraction tests were performed in a batch supercritical fluid extraction (SFE) unit purchased from LDC Analytical, Inc. and modified at IGT. Three 316 stainless steel vessels; a 55 ml. extraction cell and two 150 ml separation vessels, are connected in series and have individual pressure regulators and heaters. A metering pump with head chiller supplies CO<sub>2</sub> to the system.

Before each extraction test, 35 grams of soil is placed between inlet and exit screens in the extraction cell. Methylene chloride is placed in the separation vessels. The extraction cell is pressurized with supercritical CO<sub>2</sub>, and the separation vessel pressures are set at 500 and 200 psig, well below the critical pressure of CO<sub>2</sub>. The extraction cell temperature is then set.

Extraction of contaminants begins when supercritical CO<sub>2</sub> is passed through the extraction cell. After leaving the extraction cell, the CO<sub>2</sub> passes through an on-line UV spectrophotometer and the two separation vessels. Contaminants are collected in the separation solvent and the scrubbed, depressurized CO<sub>2</sub> is vented from the unit through an activated carbon filter. The fluid flow is continued until the desired fluid to contaminant ratio is reached. After a test is completed, both the extracted soil and the separation solvents are analyzed.

All biodegradation tests were performed in batch mode in clean 1000 ml Erlenmeyer flasks containing 250 ml of Basal Salts Medium (BSM). FEBD-1 soil extracts in ethanol (2.5 ml) were added to the flasks. A 250 ul of 0.1 OD at 550 nm bacterial suspension was added to the flasks which would give about 10<sup>5</sup> cells per ml. The flasks were incubated at 30°C on a rotary shaker operating at 150 revolutions per minute throughout the experiment. Triplicate or duplicate flasks were sacrificed at

each sampling time to monitor bacterial numbers as measured by viable cell counts, biomass as measured by protein content, and residual PAH levels. Bacterial cell counts were performed using the drop plate method (3). Biomass was measured as ug of protein per ml of culture using a protein assay kit by Pierce Chemicals.

## RESULTS

More than twenty supercritical carbon dioxide extraction tests have been conducted with sample FEBD-1 in the lab-scale SFE unit. The base test conditions were 2000 psig at 115°F using a CO<sub>2</sub> to contaminant ratio of 6800 lb/lb and no methanol additive. These four operating variables were changed in the test matrix.

When the extraction pressure was 2000 psig and the temperature was 90, 115, and 170°F, the highest extraction levels were achieved at 115°F. Extraction of 2 to 6 ring compounds increased from 90.6 percent at 90°F to 93.7 percent at 115°F and declined significantly to 79.3 percent at 170°F. The largest declines in extraction levels at high temperature were for the heavier 4 to 6 ring compounds.

The effect of the ratio of carbon dioxide to contaminants on extraction levels was studied with ratios of 2200 to 12300 lb/lb. Extraction levels of 2 to 6 ring compounds increased from 84.2 percent at 2200 lb/lb to 93.7 percent at 6800 lb/lb. No increase in extraction was obtained with higher CO<sub>2</sub>/contaminant ratios.

Pressure effects on extraction were studied between 1100 and 4000 psig, all in the supercritical range. The results of tests conducted with and without 5 weight percent methanol added as an extraction modifier are summarized in Table 1.

Table 1. THE EFFECTS OF PRESSURE AND METHANOL ADDITIVE ON EXTRACTION AT 115°F USING 6700 lb CO<sub>2</sub>/lb CONTAMINANT

Test	E-5	E-4	E-3	E-6	E-12	E-13
Pressure, psig	1100	1500	2000	2000	4000	4000
Methanol, %	0	0	0	5	0	5
PAH Removal, %						
Naphthalene	99.2	97.8	98.7	98.2	99.4	98.5
Phenanthrene	97.0	97.9	98.0	97.8	98.1	98.8
Benzo(a)pyrene	78.0	81.4	78.9	93.1	90.4	93.7
2 Ring PAH	99.2	97.8	98.7	98.2	99.4	98.5
3 Ring PAH	96.7	97.4	97.3	97.5	97.4	98.6
4 Ring PAH	90.0	91.9	90.9	97.2	96.2	97.1
5-6 Ring PAH	52.1	53.5	58.2	90.6	70.4	84.3
Total PAH	92.6	93.8	93.7	97.2	96.0	97.5

Extraction levels increase with increasing pressure between 1100 and 4000 psig. The largest extraction increases are obtained for the heavier 4 to 6 ring compounds. Adding 5 weight percent methanol to the extraction CO<sub>2</sub> significantly increases the extraction levels. The greatest increases are again for the

heavier 4 to 6 ring contaminants. A comparison of contaminant levels in the soil after extraction using CO<sub>2</sub> with and without the methanol additive is presented in Figure 1. Total contaminants in the soil are reduced from 1925 to 50 ppm using carbon dioxide with 5 percent methanol.

The biodegradation of PAHs present in supercritical extracts of FEBD-1 soil is presented in Figure 2. The cells used for biodegradation were pregrown in naphthalene and phenanthrene and were washed thoroughly in BSM before inoculation. After a lag period of 40 hours, the total PAHs concentration reached a treatment endpoint of 52 percent of the initial concentration in 30 hours. The same trends are evident with 2 through 6 ring PAH compounds.

In a second series of similar batch experiments, the lag period observed in the earlier experiments was eliminated by pregrowing the culture in an ethanol Soxhlet extract of FEBD-1 soil. Growth, as measured by protein content or bacteria numbers, indicates that there is no increase in cell numbers due to the presence of supercritical extract containing PAHs. However, there is a significant increase in the protein content due to the presence of supercritical extract.

## CONCLUSIONS

All three stages of the FEBD process; extraction, separation, and biodegradation have been studied in batch reactors on the laboratory scale. Supercritical carbon dioxide extraction at 2000 psig and 115°F successfully removed more than 93 percent of 2 to 6 ring PAHs from a contaminated soil. The addition of 5 weight percent methanol as an extraction modifier increased the extraction levels to more than 97 percent and enhanced particularly the removal of heavier 4 to 6 ring PAHs.

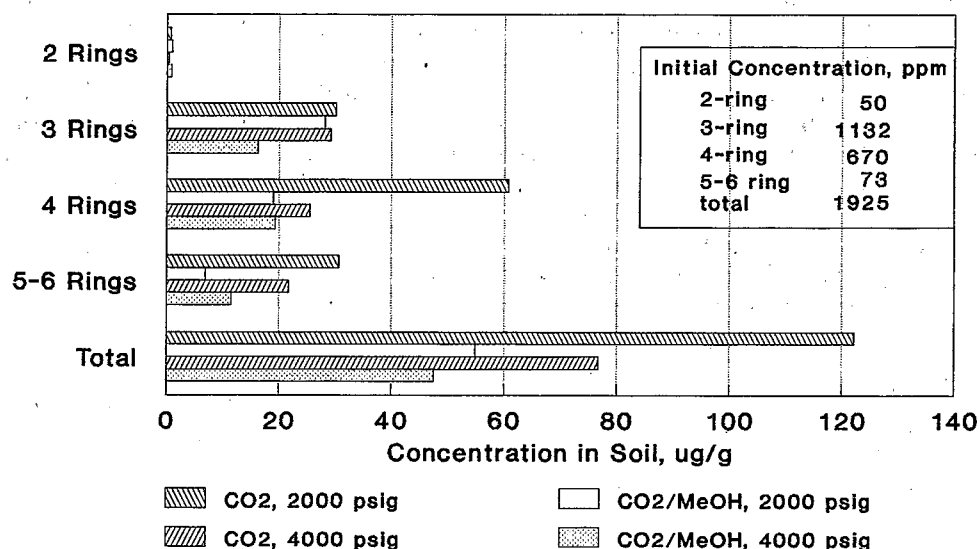
The concentration of PAH compounds extracted with supercritical CO<sub>2</sub> was decreased by 53 percent in a bioreactor after a 40 hour lag time and a 30 hour incubation time. The lag period was eliminated by pregrowing the bacterial culture in an ethanol extract of the FEBD-1 soil.

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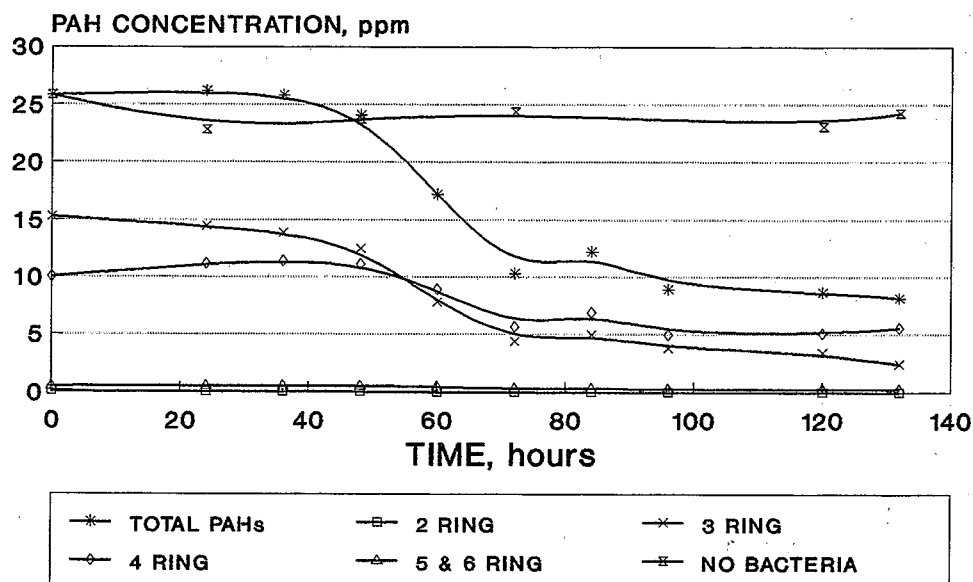


FIGURE 1: METHANOL EFFECTS ON EXTRACTION



Temperature = 115 F  
 CO<sub>2</sub>/Contaminants = 6700 lb/lb  
 CO<sub>2</sub>/MeOH = 95 % CO<sub>2</sub>, 5 % Methanol

FIGURE 2: BIODEGRADATION OF PAHs PRESENT SUPERCRITICAL EXTRACTS OF FEBD-1 SOIL



## REMEDIATION OF LEAKING USTS ON NATIVE AMERICAN LANDS

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### INTRODUCTION

Cleaning up sites contaminated by releases from leaking underground storage tanks (LUSTs) has become a priority issue for EPA as the gap between known releases and sites remediated continues to widen. Nowhere is this gap more prevalent than on the Native American reservations in this country. In most States it is common to see mounds of contaminated soil being removed from service stations; old rusty tanks being removed and new tanks being installed. These activities are promising signs that owners and operators of UST/LUST facilities are trying to comply with the Federal and State regulations. Unfortunately, such common occurrences outside the reservation are uncommon within.

This problem is primarily attributed to jurisdiction in that most of the funds that support UST/LUST activities are being channeled into State programs which employ anywhere from 10 to 50 employees. These programs are not responsible for managing or implementing UST/LUST regulations on Native American lands. Although the Indian lands represent a small percentage of the National UST population, a unique situation is created whereby only one or two Federal employees are responsible for overseeing and enforcing the Federal UST/LUST regulations from regional offices. Region 9, for example, has only one FTE (full time employee) to manage the UST/LUST activities on reservations in California, Arizona, New Mexico, Nevada, and Utah. Clearly, this is a difficult if not an impossible task.

Recently, however, a few programs are being established within some of the Tribal governments to address LUST issues and ensure compliance and enforcement. The first steps taken in tackling the LUST issue was the development of an UST/Lust tracking and prioritization system for managing sites and ensuring that those sites which pose the greatest environmental threat are addressed first. The system would be utilized by both the US EPA in Region 9 and by Tribal authorities on different reservations.

### SYSTEM DESIGN

The new system, named RUSTI (Reservation UST Information), was developed by the Risk Reduction Engineering Laboratory and the EPA Region 9 UST/LUST program. RUSTI enables users to manage all UST related activities using a PC. The system was written in Clipper V. 5.01 with several functions coded in Microsoft C. These languages offer considerable flexibility in operating system environments (eg. LAN, stand-alone PC, multi-user PC) as well as allowing for easy modification of the code.

LUST sites involve enormous amounts of file review and paperwork; RUSTI greatly simplifies and automates this "paper trail" by means of a customized electronic filing system and database. Key UST/LUST information is stored and presented in the system in an easy to use and comprehend manner. For example, if an individual needed to access information on a particular site, one could access RUSTI and pull up a comprehensive file that illustrates all previous activities (ie: tank removals, site assessments, etc.) conducted at that site. Even an individual not directly involved with the site could quickly understand the previous actions which occurred there; answer site-related questions or make an educated decision as to the next logical step of remediation.

A set protocol established by the Regional office dictates the kind of information needed to manage UST/LUST sites from new installations through tank removals and closure. The following UST/LUST activities represent the bulk of their program:

- Tracking UST/LUST Notification Forms
- Oversight of UST Removals and Site Assessments
- Enforcing Leak Detection Requirements
- Managing Financial Responsibility
- Evaluation of Corrective Actions for Site Remediation
- Technical Support to Owners and Operators
- Compliance and Enforcement of Federal Regulations

These activities are stored in three primary files, each file related in some way to each other. These files are:

TRIBE: Tribe name/code  
Associated correspondences

SITE: Site specific information  
Owner/operator information  
Tracking information  
Prioritization information  
Narrative sections

TANK: Site tank information

All of these files are accessed either directly or indirectly via the user interface of the system. RUSTI is tailored in such a way that users can make quick assessments of the above activities within any of the three primary files with just a few simple key strokes. For example: If the user were to receive a telephone call requesting information about a site on the Navajo Nation, the user would search the "Tribe" files under Navajo. Other tribes on-line would be filtered out, and the user would be presented a list of sites which reside on the NAVAJO nation.

Additional searches can be made on any field which exists in any of related databases previously mentioned. These searches can then be combined using "AND" or "OR" conjunctions and the results displayed as in any simple search. Such search mechanisms, which are currently being used in many large and small scale database systems, provide unlimited flexibility in tailoring a search to meet any users' needs.

After performing the search and selectively filtering it using "AND" or "OR" combinations, one or more records are presented which adhere to the search criteria. The user then selects the site of interest by scrolling through a list of sites. The Site Information Screen (see Figure 1) is then displayed.

## NAVAJO - SITE # 3

Name: Chevron - St. Michaels Contact: Dan J. Gallagher Add 1: AZ State Highway 264 Add 2: City/St: St. Michaels AZ Zip/Tel:		Chevron USA, Inc. Dan J. Gallagher PO Box 2833 1300 South Beach Blvd. La Habra CA 90632-2833 (213)694-7903	
Notific. Form: Removal Noti.: Removal Appr.: UST Removal: 05/01/87 Confirmed Rel: 05/01/87 LUST Resp Let: Site As. Recv: 12/13/89 RP Workpl Rec: 10/11/90 04/18/91 Remed. Init.: Remed. Compl: Site Clos App:	RP EPA A	Installation (Y/N): Operation (Y/N): Closure (Y/N): Abandonment (Y/N): Subst. Rel.: GASOLINE Qty. Rel.: UNKNOWN Violation (Y/N): N EPA Enforcement: EPA PM:	
Class: 3 No. Tank Records: 5		Groundwater Cont.: YES Soil Cont.: YES	

Enter <F>, <B>, <E>, <R>, <C>, <T>, <P>, <Q>, or <H>?

Figure 1

This screen display gives the user a comprehensive account of the Site activities, dates of correspondence, EPA approvals, release information, soil and groundwater contamination data, telephone numbers and addresses of owners/operators, classification rating and violation information. A variety of selections are available at the bottom of the Site Information Screen that pull up other files relevant to the Site selected. For example: if the user was interested in searching information on the types of tanks and contents stored at the example Navajo Site, they would select "<T>" and tank screen information would be displayed (see Figures 2 and 3).

In addition RUSTI allows users to enter and edit specific site information into narrative files using standard word processor functions. By selecting <R> on the site information screen (figure 1), the user accesses a menu for the narratives which include: (1) General information, (2) Site characterization, (3) Effects, (4) Corrective actions, (5) Operational considerations, (6) Enforcement, (7) Accounting information, and (8) Circuit Rider notes. These narrative "notepads" provide the user with a mechanism for managing and documenting all UST/LUST activities beyond the basic Regional protocol.

# NAVAJO - SITE # 3

Name: Chevron - St. Michaels Contact: Dan J. Gallagher Add 1: AZ State Highway 264 Add 2: City/St: St. Michaels AZ Zip/Tel:		Chevron USA, Inc. Dan J. Gallagher PO Box 2833 1300 South Beach Blvd. La Habra CA 90632-2833 (213)694-7903	
--	--	---	--

Select tank record to view/edit						
No.	Capacity	Contents	Const.	Mat.		Rel.
1	6000	PETROLEUM	STEEL,	SINGLE	WALL	Y
1	6000	PETROLEUM	STEEL,	SINGLE	WALL	Y
2	4000	PETROLEUM	STEEL,	SINGLE	WALL	Y
3	3000	PETROLEUM	STEEL,	SINGLE	WALL	Y
4	550	USED OIL	STEEL,	SINGLE	WALL	N

Figure 2

# NAVAJO - SITE # 3 - TANK # 1

Confirmed Release (Y/N): Y	Installation Date: 01/03/80
Tank Capacity: 6000	Removal Date: 05/01/87

Material of Construction: STEEL, SINGLE WALL  
 Tank Contents: PETROLEUM  
 Corrosion Protection: UNKNOWN  
 Piping: UNKNOWN  
 Ownership: PRIVATE/CORPORATE  
 Compliance: INVENTORY RECONCIL.  
 Overfill Protection (Y/N): Y  
 Upgrade (Y/N): Y  
 Financial Responsibility (Y/N): N

**Comments:**  
 During the transfer of hydrocarbon product from one tank to another for the installation of cathodic protection equipment, inattentive workers allowed approx. 200 gallons to spill into the subsurface.

Figure 3

## PRIORITIZATION/CLASSIFICATION

The prioritization algorithm utilized in this system provides a methodology for site ranking using a variety of site characteristics. These characteristics are determined by posing a series of questions for the site. Several answers are available for each question with each answer having a different point value. These values are summed and a classification number is determined from this total. Ten questions are provided and are as follows:

- Soil contamination (Y/N)
- Volume of soil contaminated
- TPH level in situ soil
- TPH level in stockpiled soil
- Groundwater contamination (Y/N)
- Free product on groundwater
- Contamination near domestic well
- Contamination near municipal well
- Benzene concentration
- Health / environmental risk (Y/N)

A classification scheme was developed which associates a class number to the site based upon the point summation from the above questions. The classes are summarized as follows:

- Class 1      This is the most severe classification which represents significant human health and environmental risk.
- Class 2      This is the second most severe classification which represents significant soil and groundwater contamination. TPH levels in soil exceed 2000 ppm and free product contamination is near either municipal or domestic wells.
- Class 3      This class represents significant soil contamination and low level groundwater contamination. Groundwater contamination is not in the proximity of municipal/domestic wells.
- Class 4      This class indicates soil contamination that requires remediation. No groundwater contamination is present at this site.
- Class 5      This is the least severe classification denoting minimal soil contamination and no groundwater contamination.
- Class 6      Insufficient/incomplete prioritization information.

## CONCLUSION:

A centralized computer tracking and prioritization system serves as a powerful and versatile tool for users that must deal with the remediation of a large number of UST/LUST sites. RUSTI provides considerable information at the touch of a keystroke on all UST/LUST activities on Native American Lands and classifies the sites based on potential and real environmental risk. More importantly, RUSTI provides the users with up-to-date information so that the likelihood of work duplication is minimized both in the Regional offices and in the Tribal governments.

RUSTI also provides a standard reference structure to EPA and Native American personnel not familiar with UST/LUST operating protocols. By prompting for data in a systematic format, users are made aware of what site-related questions should be asked. They are also reminded if critical site information is missing from a given site file. The system generates reports and statistical information required by the Program Office quickly, efficiently, and with a high degree of accuracy. RUSTI may not be the answer to the limited staff assignments that are responsible for the Native American lands, but it does help EPA and Tribal authorities maximize their efficiency and productivity when cleaning up UST releases.

LABORATORY STUDY OF INTERACTIONS BETWEEN  
POLYCHLORINATED BIPHENYLS AND QUICKLIME

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## INTRODUCTION

Polychlorinated biphenyl (PCB) contamination is a major concern at many sites across the country, including more than 10% of the Superfund sites for which Records of Decision are available. Under the Toxic Substances Control Act, material containing more than 50 parts per million (ppm) PCBs must be treated by incineration (or equally effective treatment) or disposed in a chemical waste landfill. Chemical destruction techniques equivalent to incineration have been the subject of numerous research projects over the past 10-20 years. High cost is the main disadvantage of conventional remediation techniques; siting of both incinerators and landfills is becoming an additional obstacle.

Liquids and sludges that contain PCBs are often solidified to improve waste handling characteristics prior to remediation. Solidification usually involves the addition of an alkaline material, such as quicklime (calcium oxide, CaO) or cement kiln dust. In the course of such bulking operations, EPA staff noted an apparent reduction in PCB levels following solidification, which might be attributable to dilution during treatment, vapor phase emissions, decomposition, or incomplete extraction of PCBs from the solidified matrix prior to analysis.

A laboratory study on this process commissioned by EPA yielded a draft final report in which the principal investigator concluded that quicklime could completely destroy PCBs. Reviewers determined that the experiments and results described in the report did not justify the conclusions. Therefore, EPA began a study to repeat and expand the initial study, as well as to confirm field observations (1).

## METHODOLOGY

The basic experimental approach was patterned after the experimental design used in the initial laboratory study conducted for EPA<sup>1</sup>. A stock solution containing 1330 milligrams per liter (mg/L) 3,5-dichlorobiphenyl (DCBP), 1050 mg/L 3,3',5,5'-tetrachlorobiphenyl (TCBP), and 1330 mg/L 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP) were prepared in methylene chloride/methanol solvent. The stock solution was used to spike a matrix comprised of equal-weight parts of diatomaceous earth, silicon dioxide and

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<sup>1</sup> Reference 1 includes experimental details and the draft final report on the initial laboratory study.



acid-washed Ottawa sand. Replicate 50-g samples of the matrix were prepared, spiked with 50 mL of the PCB stock solution, and allowed to dry at ambient temperature or at about 80 °C on a hotplate, yielding matrix contaminated at 1330 ppm DCBP, 1050 ppm TCBP, and 1330 ppm HCBP.

A series of open-vessel tests were conducted in which each of 10 PCB-spiked samples was mixed with 120 g quicklime (91.4% CaO by Ca content). At the start of the test, 50 mL reagent grade water was added to each sample with vigorous manual stirring to promote lime slaking (hydration), a strongly exothermic reaction. After cooling to <100°C, water was added to the treated mixture to produce a thick slurry; the beaker was covered with a watch glass and the slurry was heated at 80-90°C for 3 hours (h), then left at ambient temperature. Duplicate samples were acidified and prepared for analysis at nominal times of 5-72 h after lime slaking. In addition to the treated samples, 5 control samples were prepared exactly as described, with the exception that no quicklime was added.

A series of four 24-h closed-vessel tests was performed in which 50-g PCB-spiked samples were treated with 120 g alkaline material and a solvent. The alkaline materials used in three tests were quicklime, kiln dust, and an equal-mass mixture of the two, each slaked with 50 mL water. The fourth experiment used quicklime slaked with 50 mL water/methanol (9:1 volumetric). The reaction was carried out in a resin reactor, fitted to connect a mechanical mixer, a thermocouple, a slaking-solvent reservoir, and a solvent-trap system to collect volatiles and particulates emitted during the reaction. At the start of each experiment, the vessel was charged with a well-mixed sample of PCB-spiked matrix and dry alkaline material. After connecting the lid, a slight vacuum was drawn at the end of the solvent trap (cold trap and bubbler). The slaking solvent was added to the dry mixture and stirred mechanically, while vapor temperature and steam evolution were monitored. After slaking appeared complete, the treated mixture was allowed to cool, then slurried and heated as described for the open-vessel tests.

Acidification of the treated mixtures with 7.2 molar hydrochloric acid was used to terminate any reaction between hydrated lime and PCBs. Control samples received 600 mL water instead of acid. After settling, the aqueous layer was decanted. The solid residue underwent three sequential extractions, using methanol, 50% methanol/50% methylene chloride, and methylene chloride. After each solvent addition, the mixture was sonicated and then centrifuged. All solvent phases were combined with the aqueous layer in a separatory funnel, shaken and allowed to separate. The methylene chloride layer was drained through sodium sulfate and diluted quantitatively with additional solvent. Analysis was performed by gas chromatography/mass spectrometry (GC/MS). The overall method performance on PCB-spiked matrix samples carried through the extraction and analysis procedure was 87.3-93.1% recovery of the three congeners at relative standard deviations of 1.5-2.0%.

A field sample was obtained from a site where lime solidification was applied to PCB-containing sludges. The sample was homogenized, then portions were acidified and extracted as described above. Additional portions were extracted by the Soxhlet method (EPA Method 3540) using methylene chloride. The extracts from both methods were subjected to additional florisil and gel permeation chromatography to remove interfering constituents. Cleaned extracts were analyzed by gas chromatography on a fused silica capillary column followed by electron capture detection.

## RESULTS

### Open-Vessel Tests

Open-vessel tests showed large losses of PCBs following the addition of quicklime and water (Table 1). The greatest incremental decrease in concentration was observed at a nominal reaction time of 5 h, immediately following the heating induced by quicklime slaking and subsequent heating on a hotplate. As soon as water was added to the spiked matrix/quicklime mixture, the temperature rose to a

maximum of 171-189°C and a particulate-laden steam column emanated from the beaker, suggesting that vaporization or steam stripping could be occurring. A substantial fraction of the DCBP loss in treated samples can be attributed to vapor losses, since the control (no quicklime) samples also showed high losses of DCBP. The control samples showed much lower losses of TCBP and HCBP, indicating that these congeners have lower vapor pressures in the temperature range from ambient to 90°C. TCBP and HCBP losses in the treated samples could be due to vaporization and/or steam stripping at the higher temperature attained during quicklime slaking, as well as decomposition.

Table 1. Percent PCB content remaining\* at various times in open-vessel tests.

TIME h	DCBP treated	DCBP control	TCBP treated	TCBP control	HCBP treated	HCBP control
0	100	100	100	100	100	100
5	28	44	41	96	16	101
12	23	39	32	93	17	99
24	13	32	25	93	13	95
48	8.5	18	21	85	9.7	75
72	21	47	18	82	5.5	85

\* Values for treated samples are averages of two; controls were not duplicated.

Extracts of the quicklime-treated materials were analyzed for possible PCB decomposition products. Tentative identifications were based on comparison of measured mass spectra with library spectra of known compounds. Concentration estimates were based on a response factor for each product equal to that of deuterated chrysene. Products included lesser-chlorinated biphenyls (mono-penta congeners), and chlorinated biphenyls in which a methoxy or hydroxy group was substituted for one chlorine. In addition, tetrachlorodibenzofuran (TCDF) was observed in all treated samples at concentrations ranging from 1 to 14 ppm (0.07-1% of starting HCBP concentration). This is the only product where a response factor was calculated for the pure compound; a response factor of 0.359 relative to deuterated chrysene was calculated.

Total product concentrations were estimated to range from 12 to 229 ppm, with a striking dependence on how the spiking solvent was removed from the sample prior to treatment. In four samples that were evaporated solely at ambient temperature, cumulative product concentrations were 48 to 229 ppm; three of these four samples produced 205-229 ppm total products, 1-5 ppm TCDF, and peak temperatures above 180°C. The remaining six samples were heated at about 80°C prior to treatment to remove residual spiking solvent. These pre-heated samples yielded total products of 12-50 ppm, including TCDF concentrations of 4-14 ppm. It appears that the presence of residual spiking solvent favors formation of all observed products except TCDF.

Total product concentrations in the open-vessel samples after 5 to 72 h reaction times ranged from 0.3-6% of initial PCB concentration. These products in no way account for the bulk of the absent PCB mass. Losses to the vapor phase were suspected, based on DCBP loss in the control sample and apparent temperature dependence of losses of each congener. A wipe test of interior surfaces of the glove box in which these experiments were conducted showed significant contamination by all three congeners. Modelling showed that the observed time-dependent loss of PCBs was consistent with

volatilization expected for Aroclor mixtures at the experimental temperatures.

#### Closed-Vessel Tests

Closed-vessel tests were conducted to determine if PCB losses observed in the open-vessel tests were, in fact, due to vapor-phase losses of the spiked congeners, and not losses of decomposition products. The apparatus was under slight negative pressure to prevent vapor concentration buildup above the reaction mass. Four tests were carried out, each allowing 24 h reaction time after the addition of alkaline material and water. Test results are shown in Table 2. Extracts prepared from the solids in the reaction vessel and solvent in the cold trap were analyzed separately for residual PCB and decomposition products.

Table 2. Percent recovery of PCB congeners from closed-vessel tests after 24 h reaction time. PCBs from the solid matrix plus the cold traps are summed to yield total recovery.

TREATMENT	DCBP	TCBP	HCBP
Quicklime	$50 + 17 = 67$	$75 + 2.0 = 77$	$64 + 1.0 = 65$
Quicklime/Methanol*	$84 + 3.9 = 88$	$89 + 1.3 = 90$	$89 + 0.5 = 90$
Kiln dust	$102 + 3.5 = 106$	$110 + 1.0 = 111$	$122 + 1.0 = 123$
Quicklime/Kiln dust	$87 + 6.7 = 94$	$102 + 1.0 = 103$	$87 + 2.5 = 90$

\* Water added to slake the lime was spiked with 10% methanol (v:v).

This set of experiments yielded essentially full recovery of the spiked PCBs in three of the four variations. In the first experiment, using quicklime alone, some PCBs may have been lost due to vapor emission through poorly-fitted thermocouple and stirrer ports, or due to incomplete extraction of solids adhering to reaction vessel walls, lid and cold trap connections. Vapor or particulate emissions are consistent with increasing recoveries of all congeners observed as quicklime was replaced with kiln dust: the temperature should have decreased as CaO content in the alkaline material decreased, thereby decreasing the tendency of gaseous species to escape the vessel. Temperature could not be measured during the reaction, since the thermocouple interfered with the stirrer.

Although the closed vessel tests were expected to yield higher total recoveries than the open-vessel tests if vapor phase losses were dominant in the latter, we expected higher recoveries of PCBs from the cold trap in the closed vessels. At 24 h, open-vessel samples had lost 75-87% of the initial PCB spikes, with less than 6% accounted for in reaction products. Closed-vessel tests yielded only 0.5-17% of the initial spikes in the solvent traps at the same reaction time. Vapor condensation and particulate deposition on reaction vessel surfaces were visually observed during the closed-vessel tests. These factors probably account for the apparent reduction in PCB volatilization but could not be quantified separately from the bulk solid matrix. Another factor that may have contributed to reduced volatilization is reduced reaction temperature, resulting from poorer mixing (thus slower slaking) or from lower CaO concentration in kiln dust (thus less heat of hydration produced).

#### Field Sample

A sample was obtained from a site where lime was used to solidify PCB-containing waste. According to sample documents, a bucket of material had been taken after various wastes were composited and solidified, and then stored on-site.

The sample was homogenized and then sub-sampled as needed for analysis. Four replicate samples were acidified and extracted using the same procedure applied to open- and closed-vessel test samples. Two additional samples were extracted using the Soxhlet method. Gas chromatography with electron capture detection (GC-ECD) was applied to cleaned extracts. Peak profiles were compared to Aroclor standards; the best agreement was found for a mixture of Aroclors 1242 and 1254; equal mass mixtures of these Aroclors were then used for calibration to quantify the field sample extracts.

The acidification/extraction procedure yielded an average PCB concentration of 200 ppm with a relative standard deviation of 4.2% for four replicate samples. The Soxhlet procedure yielded 218 and 222 ppm PCBs on duplicate samples. Prior to treatment, samples taken at various locations across the field site were reported to contain up to 157 ppm PCBs. The field sample analyzed in this study showed that the treatment did not destroy PCBs to any measurable extent. Although both extraction procedures successfully extracted PCBs in this study, the characteristic Aroclor pattern was completely indiscernible when extracts were analyzed by GC/MS, owing to interference by numerous other compounds extracted from the sample. If an analytical laboratory attempted to analyze PCBs by GC/MS techniques, heavily contaminated samples might result in non-detection owing to masking by other contaminants. GC-ECD is less subject to these interferences.

## CONCLUSIONS

Addition of quicklime and water to PCBs on an inert matrix resulted in very little PCB decomposition. Less than 6% of the starting material was identified in reaction products. Products found routinely included partially-dechlorinated biphenyls, hydroxy-substituted PCBs, and TCDF. The variety of products was decreased and total concentration of products was less than 1.4% of starting PCB content when heat was applied to remove spiking solvent prior to treatment. These heated samples typically exhibited more TCDF than unheated samples, but lower concentrations and less variety of other compounds. Only the unheated samples yielded methoxy derivatives.

Vapor-phase losses of PCBs were significant in open-vessel tests. The effect was temperature dependent, with the dichloro congener quite susceptible to evaporation at 90°C or lower, and the other congeners more subject to evaporation or steam stripping at higher temperatures. High temperatures were achieved by slow water addition and vigorous mixing.

A stored sample from PCB-containing sludge solidified with lime was found to contain about 200 ppm PCBs as Aroclors 1242 and 1254. The PCB content was extractable by both the acidification/sonication/extraction procedure used in this study and the more conventional Soxhlet extraction. No conclusions can be drawn regarding previous reports of PCB losses since splits were not reserved of samples analyzed by other laboratories.

Treatment of PCB-contaminated materials by quicklime and water, as performed in these experiments, did not result in the degree of dechlorination required for remediation of contaminated sites.

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**RISK REDUCTION ENGINEERING LABORATORY (RREL)  
TREATABILITY DATABASE**

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Water and Hazardous Waste Treatment Research Division

**1. Purpose**

The purpose of the RREL Treatability Database is to provide a thorough review of the removal/destruction of chemicals in various types of media, including water, soil, debris, sludge and sediment. There are currently thirty-three treatment technologies, thirteen aqueous matrices and five solid matrices presented in the database. Version 4.0 was released in January 1992 and is free of charge.

**2. Target Group**

The users of the database include federal, state and local governments, universities, industry and consulting engineers. These diverse groups share a common interest in needing reliable treatability data for specific chemicals of environmental interest. Current distribution is approximately 1500.

**3. Organization**

The program contains physical/chemical properties for each compound, as well as treatability data. The treatability data summarizes the types of treatment used to treat the specific compound; the type of waste/wastewater treated; the size of the study/plant; and the treatment levels achieved. In addition, each data set is referenced with respect to source of information and each reference is quality-coded based upon analytical methods, reported quality assurance and quality control efforts and operational information on process(es) sampled.

**4. Computer Hardware and Software**

The requirements are as follows: IBM personal computer or compatible; 8 megabyte hard disk storage; 640 K RAM memory; DOS version 2.0 to 5.0, except version 4.0; and a 12 pitch printer. The program has been compiled and does not require any specialized software to operate it and it is menu driven for ease of use. The program can also be accessed through EPA's Alternative Treatment Technology Information Center (ATTIC). Please contact Joyce Perdek at 908-342-4380 for additional information.

## DEVELOPMENT OF BIODEGRADATION KINETICS FOR MIXED SUBSTRATE SYSTEMS

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### INTRODUCTION

Mixed substrate systems are often encountered in pharmaceutical, food, wastewater processes and chemical manufacturing industries. In wastewater treatment systems, a number of organic compounds are present at the same time. In these cases it is inevitable that the toxic, or inhibitory substrates will be found in mixtures with nontoxic, or conventional wastes. In the presence of alternative carbon sources, a number of possible substrate interactions can occur. Extensive studies on biodegradation of single components have been conducted (1). However, there is insufficient information on the performance of biological treatment facilities for the removal of a specific chemical from wastewater, consisting of a mixture of organic pollutants. There is a strong need for extensive studies of multisubstrate systems. A broad data base will help to understand the interaction and removal rates of organic compounds in mixtures. These studies will also help to establish control mechanisms that regulate the relative utilization rates of mixtures. In this paper, emphasis will be given on a comprehensive review of mechanisms, experimental methods, and modeling studies for biodegradation of mixed substrates.

In biological treatment plants, the substrate removal pattern in a multisubstrate system may include simultaneous, preferential, or sequential utilization. The diauxic growth observed by Monod (2) in *Escherichia coli* suggests that the very presence of a particular substrate in a wastewater stream might prevent an organism from acclimatizing to another substrate until the first one has been completely metabolized. The blockage of metabolism of one compound by another may lead to preferential or sequential substrate removal from a multisubstrate environment. Chian and Dewalle (3) have presented evidence for the sequential removal of waste components during biological treatment of a leachate from a sanitary landfill. Deshpande and Chakrabarti (4), in a batch reactor, demonstrated preferential removal of m-nitrobenzenesulfonate, sodium salt (m-NBS), from a mixture of m-NBS and resorcinol, compounds that are known to be present in m-aminophenol (m-AP) manufacturing wastewaters.

The mechanism of substrate utilization by a bacterial cell can be generally described as a sequence of three complex processes: contact of a cell with the molecule of a substrate; transport of the molecule into the cell; and formation of the substrate intermediate. On the basis of this general mechanism, it is possible to classify various types of substrates into three main groups: (a) single components substrates, which are directly transportable; (b) multicomponent substrates, which are represented by a mixture of several single substrates; (c) complex substrates, which have to be changed externally prior to transportation into the cell.

The specific research objectives of this project are as follows: (1) Evaluate the effect of co-metabolites on biodegradation kinetics; (2) Develop appropriate kinetic data for organics with a variety of functional groups; (3) Develop appropriate kinetic data of a toxic organic in presence of multiple toxics from homologous and non-homologous series, as sole carbon source or in wastewaters containing background concentrations of biogenic or toxic organics; and (4) Validate the structure-activity

relationship model for the biodegradation kinetics of the toxic compounds as single or multiple components in a variety of municipal / industrial wastewaters.

## METHODOLOGY

Experiments were conducted using a 12 unit VOITH electrolytic respirometer for the following mixed substrates: (1) Mixture of chemical and raw wastewater from the primary effluent stream of a domestic activated sludge treatment plant; four chemicals were studied at a concentration level of 100 mg/l : Aniline, Catechol, Phenol and Benzene. (2) Mixture of chemical and wastewater from the secondary basin of a domestic activated sludge treatment plant; four chemicals were studied at a concentration of 100 mg/l: Aniline, Catechol, Phenol and Benzene. (3) Raw wastewater from the primary effluent stream with no compound; and (4) Wastewater from the secondary basin with no compound.

The VOITH electrolytic respirometer 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, with 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 the oxygen generator. The carbon dioxide generated is absorbed by soda lime, placed 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, which is 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.

The nutrient solution used in our studies was an OECD synthetic medium (5) consisting of measured amounts per liter of deionized distilled water containing (1) mineral salts solution; (2) trace salts solution; and (3) a solution (150 mg/l) of yeast extract as a substitute for vitamin solution.

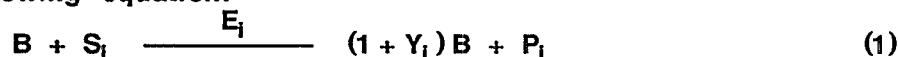
The microbial inoculum was an activated sludge from The Little Miami wastewater plant in Cincinnati, Ohio, receiving municipal wastewater. The activated sludge sample was aerated for 24 hours before use to bring it to an endogenous phase. The sludge biomass was added to the medium at a concentration of 30 mg/l total solids. Total volume of the synthetic medium was 250 ml in the 500 ml capacity reaction vessels. Reactor flasks either contained 62.5 ml of primary effluent wastewater mixed with 164 ml of deionized distilled water or 125 ml of secondary wastewater mixed with 101 ml of deionized distilled water.

In a typical experimental run, duplicate flasks were used for the test mixture, and reference compound (aniline). The reaction vessels were incubated at 25° C in the temperature controlled bath and stirred continuously throughout the run. The microbiota of the activated sludge were not preacclimated to the substrate. The incubation period of the experimental run was between 28-50 days. A comprehensive description of the procedural steps involved in the respirometric tests have been presented elsewhere (6).

Kompala et al. (7) studied the cybernetic modeling of microbial growth on multiple substrates. In this model, the internal regulatory processes, which underlie a variety of behavior in microbial growth on multiple substrates, are viewed as a manifestation of an invariant strategy to optimize some goal of the cells. The model proposed in this paper for describing the degradation of multiple substrates is based on the cybernetic model, and allows the prediction of microbial growth behavior based on growth data for single substrates. The framework of this model can be applied to batch or continuous culture growth of several bacteria on different combinations of substrates.

In the sequential growth on multiple substrates, the cells grow first on the fastest assimilated substrate in the medium. The cells may have acquired such a strong capability to optimize their growth behavior in the following manner: Assume that in a multisubstrate environment, there exist cells with different strategies of responding to the environment. The cells that arbitrarily choose to grow first on the fastest substrate available proliferate much faster than the cells that responded differently. Very quickly all the cells that remain in that environment will be those that have responded in the most optimal manner. Hence, it is reasonable to postulate that over many years of evolutionary processes, in environments with varying menus of substrates, microbes have acquired the capability to control their regulatory processes to optimize their pattern. The basic merit of the cybernetic approach is that it adopts a mathematical simple description of a complex organism but compensates for the oversimplification by assigning an optimal control motive to its response.

The microbial growth on multiple substrates can be simplistically represented by the following equation:



where:  $B^-$  is the biomass excluding the key enzyme  $E_i$ .

Instantaneous maximum biomass productivity model was proposed by Kompla (6). This model proposes that, in a multiple substrate environment, at any instant  $t$ , the organism chooses to synthesize the enzyme for the substrate which maximizes the biomass growth rate at that instant. The major limitations of the cybernetic model is that it only predicts an optimal allocation of existing resources to the enzyme synthesis alternatives.

The cybernetic model equations for biodegradation of multiple substrates are given below:

$$r_{B,i} = \frac{\mu_i^0 \mu_f e_i S_i C}{K_i^0 K_{sf} + S_i} \quad (3)$$

$$r_{E,i} = \frac{\alpha_i S_i C}{K_i^0 K_{sf} + S_i} \quad (4)$$



$$O_2 = \left( \sum S_{i0} - \sum S_i \right) - (C - C_0) - \left( \sum S_{pi} - \sum S_{pi0} \right) \quad (5)$$

$$\frac{de_i}{dt} = \frac{\alpha_i S_i}{K_i^0 K_{sf} + S_i} u_i - \frac{d}{dt} (\ln C) e_i - \beta_i e_i \quad (6)$$

$$\frac{dS_i}{dt} = -\frac{1}{Y_i} r_{B,i} v_i \quad (7)$$

$$\frac{dC}{dt} = \sum r_{B,i} v_i \quad (8)$$

$$\frac{dS_{pi}}{dt} = Y_{pi} \left( -\frac{dS_i}{dt} \right) \quad (9)$$

where:

$$v_i = \frac{r_{B,i}}{\max(r_{B,j})} \quad (10)$$

$$u_i = \frac{r_{B,i}}{\sum r_{B,i}} \quad (11)$$

where:

**B** biomass

**C** biomass concentration [ mg/l ]

**e<sub>i</sub>** specific enzyme level

**E<sub>i</sub>** ith key enzyme [ mg/l ]

**K<sub>i</sub><sup>0</sup>** Michaelis constant [ mg/l ] for pure compound i

**K<sub>sf</sub>** inhibition factor for Michaelis constant

**P<sub>i</sub>** ith bioproduct [ mg/l ]

**r<sub>B,i</sub>** rate of biomass production through consumption of S<sub>i</sub> [ mg/l/Hr ]

**r<sub>E,i</sub>** rate of E<sub>i</sub> synthesis [ mg/l/Hr ]

**S<sub>i</sub>** ith substrate [ mg/l ]

**S<sub>pi</sub>** ith bioproduct concentration [ mg/l ]

**t** time [ Hr ]

$u_i$	cybernetic model variables
$v_i$	cybernetic model variables
$Y_i$	yield coefficient [ mg/mg ]
$Y_{pi}$	ith product yield coefficient [mg/mg]
$\alpha_i$	enzyme synthesis rate constant [1/ ]
$\beta_i$	enzyme decay rate constant [ 1/ ]
$\mu_i^0$	growth coefficient [1/ ] for pure compound i
$\mu_i$	inhibition factor for growth coefficient

Note that the Monod equations in the cybernetic model was modified to include inhibition from other substrates, products or biomass as initially proposed by Levenspiel (8).

The cybernetic model equations were used to obtain the kinetic parameters from the cumulative oxygen uptake data obtained for mixed substrate systems.

## RESULTS

Figures 1 through 4 show the cumulative oxygen uptake curves for aniline, catechol, phenol and benzene in clean water, primary effluent and secondary effluent. The oxygen uptake curve obtained for the wastewater without the compound has been shown for comparison.

Similarly, oxygen uptake curves were obtained for binary mixtures of the four chemical compounds in clean water, primary effluent and secondary effluent. Figure 5 shows the oxygen uptake curve for a mixture of benzene and aniline in clean water. The cybernetic model was applied using the single compound Monod parameters, and the calculated and experimental curve for clean water are shown in the Figure. The cybernetic model parameters are summarized in Table 1.

## CONCLUSIONS

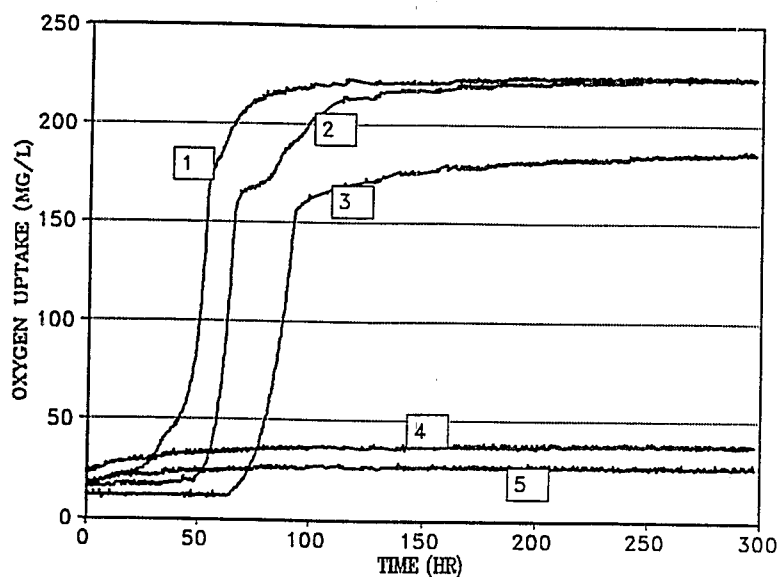
It has been shown that the Monod kinetic parameters obtained for the degradation of single compounds in wastewater are statistically the same as those obtained in clean water. This result is significant, since most of the available Monod kinetic parameters in the literature, were obtained using clean water. Furthermore, it has been demonstrated that the oxygen uptake curves for binary mixtures of compounds can be derived from single compound Monod kinetic parameters using the cybernetic model. This allows the prediction of biodegradation of compound mixtures in clean water systems from single compound studies. The extension of this result for dirty wastewater is currently being developed.

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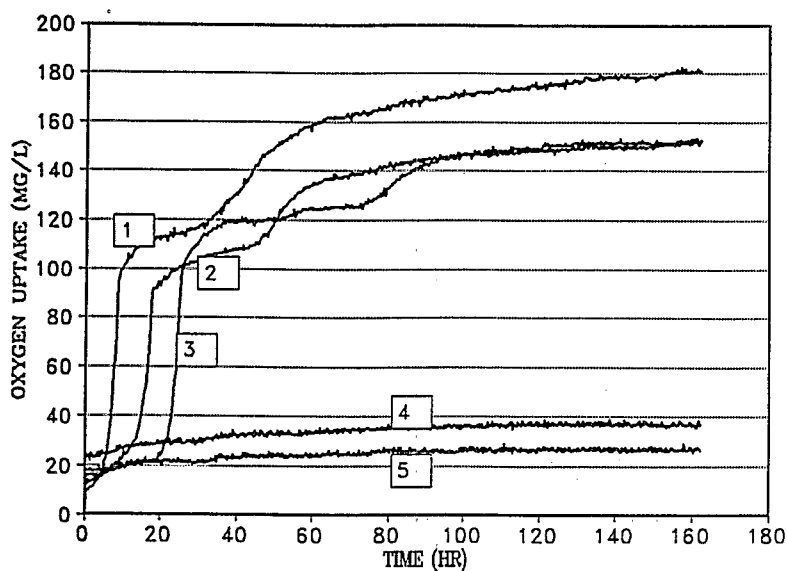
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**Table 1 Values for the cybernetic model parameters**  
(For all substrates,  $\alpha_i = 0.001$ ,  $\beta_i = 0.05$ ,  $e_{10}/e_{20} = 4.47/84.8$ )

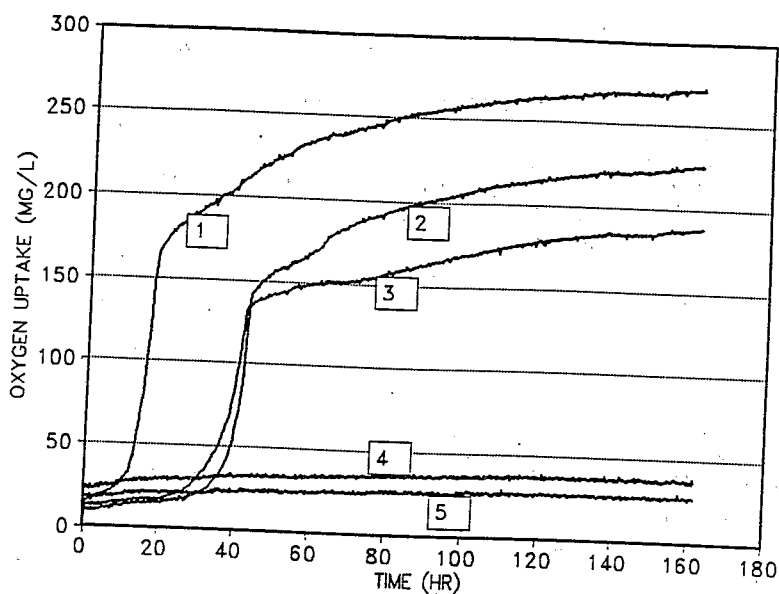
Substrate	$\mu$	$K_s$	$Y$	$Y_p$	$\mu_f$	$K_{sf}$
Aniline	0.25	28.9	0.43	0.01	1.26	5.34
Benzene	0.28	6.50	0.27	0.02	1.52	7.55



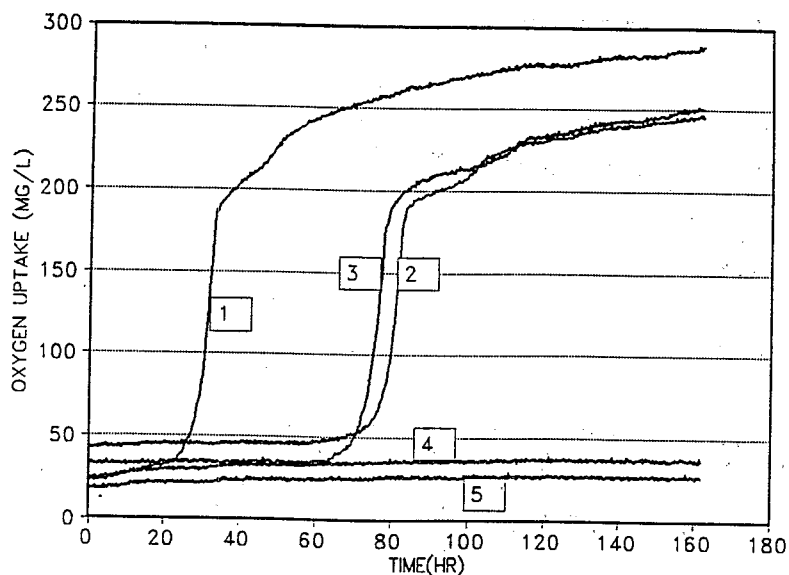
**FIGURE 1. Cumulative oxygen uptake curve for the following mixtures: [1] Primary effluent and aniline (100 mg/l); [2] Secondary effluent and aniline (100 mg/l); [3] Clean water and aniline (100 mg/l); Primary effluent; [5] Secondary effluent.**



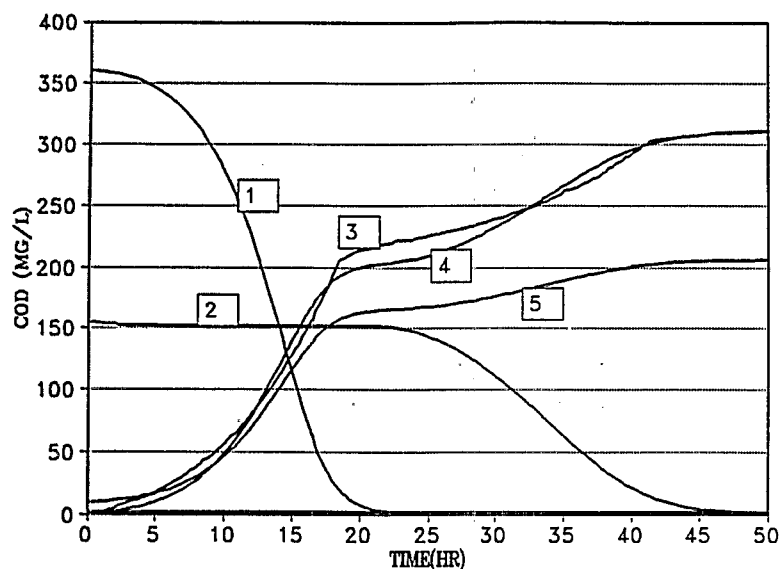
**FIGURE 2. Cumulative oxygen uptake curve for the following mixtures: [1] Primary effluent and catechol (100 mg/l); [2] Secondary effluent and catechol (100 mg/l); [3] Clean water and catechol (100 mg/l); Primary effluent; [5] Secondary effluent.**



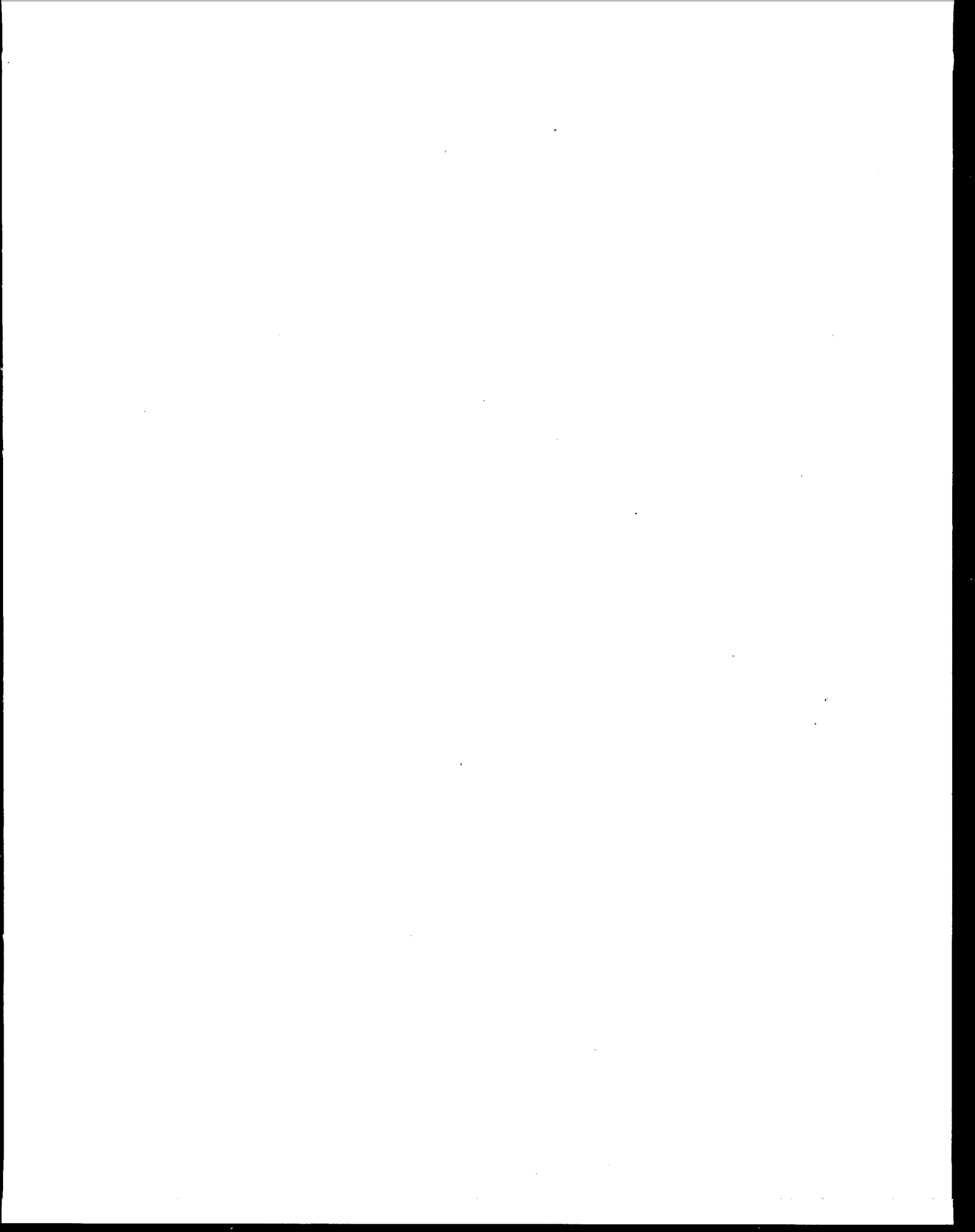
**FIGURE 3.** Cumulative oxygen uptake curve for the following mixtures: [1] Primary effluent and phenol (100 mg/l); [2] Secondary effluent and phenol (100 mg/l); [3] Clean water and phenol (100 mg/l); Primary effluent; [5] Secondary effluent.



**FIGURE 4.** Cumulative oxygen uptake curve for the following mixtures: [1] Primary effluent and benzene (100 mg/l); [2] Secondary effluent and benzene (100 mg/l); [3] Clean water and benzene (100 mg/l); Primary effluent; [5] Secondary effluent.



**FIGURE 5. [1] Concentration of aniline varying as a function of time, during the biodegradation of a mixture of benzene and aniline; [2] Concentration of benzene changing as a function of time, during the biodegradation of a mixture of benzene and aniline; [3] Experimental oxygen uptake curve for a binary mixture of aniline and benzene; [4] Calculated oxygen uptake curve using the cybernetic model; [5] Biomass concentration in COD units.**



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