

# IN SITU FLUSHING & SOILS WASHING TECHNOLOGIES FOR SUPERFUND SITES

*Presented at:*

*RCRA/Superfund Engineering  
Technology Transfer Symposium*

**By:**

**Hazardous Waste Engineering Research Laboratory  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268**



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## THE DEVELOPMENT OF CHEMICAL COUNTERMEASURES FOR HAZARDOUS WASTE CONTAMINATED SOIL<sub>1</sub>

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### ABSTRACT

The U.S. Environmental Protection Agency's (EPA) Oil and Hazardous Materials Spills Research and Development Program in Edison, New Jersey, has designed a Chemical Countermeasures Program to evaluate in situ methods for mitigating or eliminating environmental damage from releases of toxic and other hazardous materials to the soils around uncontrolled hazardous waste disposal sites, and from spills of hazardous chemicals to still or relatively slow-moving surface water bodies. To date efforts have concentrated on soils-related activities to determine whether use of aqueous surfactants could significantly enhance the in situ cleanup of chemically contaminated soils with standard water washing techniques.

Laboratory studies were performed to determine the maximum cleanup efficiency under equilibrium conditions using water washes and a combination of 2 percent each Hylene PE90 (now known as NP90, Diamond Shamrock), and Adsee 799 (Witco Chemical) surfactants and to evaluate soil cleanup efficiency under gravity flow conditions. In general, overall soil cleanup approaching the 90-plus percent level was attained with intermediate molecular weight aliphatic and aromatic hydrocarbons, polychlorinated biphenyl mixtures and chlorinated phenol mixtures. Results appear to support larger scale field demonstrations, and plans are being discussed to conduct full-scale, controlled tests at appropriate hazardous waste or spill sites ("sites-of-opportunity").

### BACKGROUND

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 or Superfund recognizes the need to develop countermeasures (mechanical devices, and other physical, chemical, and biological agents) to mitigate the effects of hazardous substances that are released into the environment and to clean up inactive hazardous waste disposal sites. One key countermeasure is the use of chemicals and other additives that are intentionally introduced into the environment to control the hazardous substance. The indiscriminate use of such agents, however, poses a distinct possibility that the release situation could be made worse by the application of an additional chemical or other additive.

The U.S. Environmental Protection Agency's (EPA) Oil and Hazardous Materials Spills Branch in Edison, New Jersey, has begun a support program to define technical criteria for the use of chemicals and other additives at release situations of hazardous substances. The criteria are to ensure that the combination of the released substance plus the chemical or other additive, including any resulting reaction or change, results in the least overall harm to human health and the environment.

The Chemical Countermeasure Program (CCP) has been designed to evaluate the efficacy of in situ treatment of large volumes of subsurface soils, such as found around uncontrolled hazardous waste sites, and treatment of large, relatively quiescent waterbodies contaminated with spills of water-soluble hazardous substances. For each situation, the following activities are planned:

- a literature search to develop the existing body of theory and data
- laboratory studies on candidate chemicals to assess adherence to theory and define likely candidates for full-scale testing
- full-scale, controlled tests at a site-of-opportunity

This paper presents the results of the information search and laboratory studies for the soils-related activities of the program.

1. The work reported herein was performed by JRB Associates under U.S. Environmental Protection Agency contract No. 68-03-3113, Task 29. The content of this publication does not necessarily reflect the views or policies of the U.S. Environmental Protection Agency, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government.

## INFORMATION SEARCH

A literature search of limited scope was performed to gather information on the state-of-the-art in chemical countermeasures. The emphasis of the search was on the most recent and innovative work on the subject, and on work most likely to be fruitful for further development. The search was primarily directed toward readily available publications on subjects related to chemical countermeasures, and toward contacting key people doing research, development, and field implementation of chemical countermeasures.

The application of chemical countermeasure techniques in the field has been very limited. The main reasons are caution and scarcity of information/experience. Current technology for removal of contaminants from large volumes of soils (too large to excavate economically) having relatively low to moderate levels of contamination has been limited to withdrawal of groundwater, with or without recharge to the soil, *i.e.*, *in situ* "water washing."

Accordingly, the laboratory studies were designed to determine whether adding aqueous surfactants to recharge water used in a continuous recycle could significantly enhance the efficiency of contaminated soils cleanup by water washing. Based on the literature, it was thought that surfactant mixtures would improve the solvent properties of the recharge water, thereby enhancing the removal of chemical contaminants adsorbed onto soil particles. This approach was a direct derivative of the laboratory studies performed by the Texas Research Institute for the American Petroleum Institute on the use of surfactants for enhanced gasoline recovery from sand (Texas Research Institute, 1982).

## LABORATORY PROGRAM DESIGN

The experimental design of the laboratory program was formulated after reviewing the results of similar investigations identified during the information search. The primary purpose of the laboratory studies was to determine whether use of aqueous surfactants could significantly enhance the *in situ* cleanup of chemically contaminated soils by standard water washing techniques. A secondary objective (assuming the primary goal was successful) was to obtain information and make recommendations for designing larger scale tests under controlled conditions and field tests at sites of opportunity.

Before conducting the laboratory studies, four specific issues had to be resolved. The first issue was to identify and select a suitable soil to be used in the laboratory tests and included soil characterizations and evaluation of permeability versus compaction parameters. The second issue involved contaminant selection and determination of the concentrations required for soils studies. The third issue dealt with surfactant selection, surfactant solubility, compatibility with soil type, and efficiency of pollutant removal. The fourth issue involved the analytical methods to be used for extraction and analysis for the pollutant groups of interest in the soils and leachates.

### Selection of Test Soil

In choosing the soil to be used in the tests, native soils at each of 10 Region II Superfund sites were identi-

fied to determine the most commonly occurring soil series. Once determined, a soil type of the same taxonomic classification was located in the vicinity of the potential larger-scale test facility that could be excavated and used in the experiments. The most commonly occurring classification was Typic Hapludults (Freehold soil series), a fine-to-coarse loamy soil of humid climates, containing zones of clay accumulation. In addition to taxonomic classification, a permeability rating of  $10^{-2}$  to  $10^{-4}$  cm/s was specified as a desirable range.

Table 1 presents the grain size distribution obtained by wet sieve and pipette analyses. Approximately 95 percent of the theoretical surface area is represented by fines (15 percent silt and 8 percent clay).

To determine the mineralogical composition of the Freehold soil, x-ray diffraction studies were undertaken. The results showed quartz and feldspar to be the only measurable constituents. Quartz was the major phase, representing at least 98 percent of the total weight. No measurable amounts of clay minerals appeared.

The total organic carbon content (TOC) of the soil was determined on a sample of soil prepared by grinding and suspending in an aqueous solution of phosphoric acid and sodium phosphate, in accordance with EPA Method 415.1. The TOC value was 0.12 percent by weight. This relatively low level of organic matter in the soil implies a relatively low adsorption potential for organic contaminants.

The cation exchange capacity (CEC) of the soil also was determined by the methods of Jackson (1970), and the results were combined to yield the total CEC. The result was 8.8 milliequivalents per 100 grams, an extremely low value, confirming the absence of mineralogic clay in the soil.

### Selection of Contaminants

The compounds used for testing in the laboratory were chosen on the basis of several criteria. They should:

- occur frequently in high enough concentrations in the soil surrounding Superfund sites
- present a significant hazard to human health and the environment
- have low to moderate mobility and high persistence in soil

Table 1. Grain size distribution of Freehold soil by wet sieve and pipette analyses (Modified ASTM D-422 using U.S. Bureau of Soils sieve sizes)

Class	Size range ( $\mu$ m)	Mass (percent)	Theoretical surface area (percent)
Gravel	>1000	16	<.05
Sand	62 to 1000	61	5
Silt	8 to 62	15	34
Clay	< 8	8	61

- be treatable by an existing chemical method
- have an appropriate chemical analog, if too hazardous or expensive for experimentation

Data were gathered on the concentrations, frequency of occurrence, soil adsorption, and toxicity of waste chemicals found at Superfund sites. The incidence of the various hazardous waste and waste classes is given in Table 2. The data on soil contaminants indicate that the most widespread class of contaminant is the slightly water-soluble organics, which includes low molecular weight aromatics and halogenated hydrocarbons. The next most common contaminant classes are heavy metals and hydrophobic organics. Clearly, the occurrence of phenols also is widespread.

Based on this review and analysis, three pollutant compound mixtures were selected for use in soil testing: (1) intermediate and high molecular weight aliphatic hydrocarbons and polynuclear aromatic hydrocarbons (high boiling distillation fraction of Murban crude oil), (2) polychlorinated biphenyl mixture in chlorobenzenes (Askarel<sup>®</sup>), and (3) di-, tri-, and pentachlorophenols.

#### Selection of Surfactants

The preliminary selection of 2 percent Richonate YLA and 2 percent Hionic NP90 as the surfactant mixture was based on the results of a Texas Research Institute study (Texas Research Institute, 1979) evaluating the removal of gasoline from pure Ottawa sand. After initial studies, however, this mixture was found to be unsuitable due to its marked tendency to suspend the silt- and clay-size grains (less than 63  $\mu$ m in diameter), which resettled in small pores, thereby inhibiting column flow.

Beaker studies then were conducted to evaluate solubility properties of the surfactants and their tendency to disperse the fine clay-size particles present in the Freehold soil.

The decision was made to use a combination of 2 percent Adsee 799 and 2 percent NP90, non-ionic surfactants, based on the mixture's:

- high water solubility
- ability to disperse Murban hydrocarbons
- minimal suspension of fine soil particles
- lower content of compounds that cause analysis interferences than previously tested surfactants

Table 2. Hazardous oil contaminants at Superfund sites

Soil Contaminants	Number of sites	Examples
Heavy metal wastes	47	
Chromium	9	
Arsenic	8	
Lead	7	
Zinc	5	
Cadmium	4	
Iron	3	
Copper	2	

Table 2. Hazardous oil contaminants at Superfund sites

Soil Contaminants	Number of sites	Examples
Mercury	2	
Selenium	2	
Nickel	1	
Vanadium	1	
Fly ash	1	
Plating wastes	2	
Other inorganics	26	
Cyanides	6	
Acids	7	sulfuric acid
Alkalis	6	lime, ammonia
Radioactive wastes	3	uranium mining and purification wastes, radium, tritium
Miscellaneous	4	beryllium, boron hydride, sulfides, asbestos
Hydrophobic organics	38	
PCBs	15	
Oil, grease	11	
Volatile hydrocarbons	6	hexane, Varsol
Chlorinated hydrocarbon pesticides	5	endrin, lindane, DDT, 2,4,5-T, dieldrin
Polynuclear aromatics	1	
Slightly water soluble organics	64	
Aromatics		
Benzene	9	
Toluene	8	
Xylene	5	
Other aromatics	3	styrene, naphthalene
Halogenated hydrocarbons		
Trichloroethylene	11	
Ethylene dichloride	6	
Vinyl chloride	4	
Methylene chloride	3	
Other halogenated hydrocarbons	15	chloroform, trichloroethane, tetrachloroethylene, trichlorofluoromethane
Hydrophilic organics	20	
Alcohols	4	methyl, isopropyl, butyl
Phenols	12	picric acid, pentachlorophenol, creosote
Other hydrophilics	4	dioxane, bis (2-chloroethyl) ether, urethane, rocket fuel
Organic solvents (unspecified) and other organics	30	dioxin, dioxane, dyes, pigments, inks, paints, nitrobenzene



### Analytical Procedures

The analysis of contaminated soils and aqueous leachates involved solvent extraction, liquid chromatography (fractionation into aliphatic, aromatic, and polar fractions), and instrumental analysis by gas chromatography (GC) using flame ionization detectors (FID) and electron capture detectors (ECD), and high performance liquid chromatography (HPLC).

For leachates in which aromatic hydrocarbons or PCBs were present, EPA Method 608 was followed. The Murban hydrocarbon contaminant extracts were analyzed by FID-GC.

The extract from the PCB contaminant leachate was analyzed by ECD-GC without silica gel fractionation.

For the leachate containing chlorinated phenols, EPA Method 625 was used. The leachate was subjected to the acid/phenol extraction step only, and then analyzed by HPLC.

Soil samples were prepared for pollutant analysis using a rigorous shaker table extraction procedure that has been shown to yield results comparable to Soxhlet extraction.

### LABORATORY EXPERIMENTATION

The laboratory experimentation was conducted in two phases. The first phase involved shaker table agitation (equilibration) to determine the soil/aqueous surfactant partitioning of the pollutants. This compared the maximum cleanup efficiency under conditions of water washes and 4 percent aqueous surfactant washes with thorough agitation. The combination of 2 percent each of Hynic NP90 (Diamond Shamrock) and Adsee 799 (Witco Chemical) in water was used.

After the surfactant efficiency was determined in the shaker table tests, the soil column studies were performed to evaluate soil cleanup efficiency under gravity flow conditions. In the column studies, different concentrations of the three pollutant groups were used. The concentration of Murban hydrocarbons was 1,000 ppm in the soil; the concentration of PCBs was 100 ppm; and the concentration of chlorinated phenols was 30 ppm.

#### Shaker Table Studies

Table 3 presents the experimental design for shaker table agitation/equilibration of contaminated

Table 3. Experimental design for shaker table agitation/equilibration of contaminated soils

Experiments sample number	Initial water equilibration			Water-plus-surfactant equilibration			Final water equilibration		
	1st wash	2nd wash	3rd wash	1st wash	2nd wash	3rd wash	1st wash	2nd wash	3rd wash
1	Extract soil Examine leachate	0 <sub>1</sub>	0	0	0	0	0	0	0
2	Examine leachate	Extract soil Examine leachate	0	0	0	0	0	0	0
3	— <sup>2</sup>	Examine leachate	Extract soil Examine leachate	0	0	0	0	0	0
4	—	—	Examine leachate	Extract soil Examine leachate	0	0	0	0	0
5	—	—	—	Examine leachate	Extract soil Examine leachate	0	0	0	0
6	—	—	—	—	Examine leachate	Extract soil Examine leachate	0	0	0
7	—	—	—	—	—	Examine leachate	Extract soil Examine leachate	0	0
8	—	—	—	—	—	—	Examine leachate	Extract soil Examine leachate	0
9	—	—	—	—	—	—	—	Examine leachate	Extract soil Examine leachate

1. "0" indicates no action taken because sample was used (destroyed) during sampling  
 2. "—" indicates no analytical activity, i.e., the soil is saved for the next step

soils with aqueous surfactant. Nine contaminated soil samples plus three controls (not shown in the table) were prepared. All 12 samples (80 to 100 g each) were placed in 500 ml Teflon® screw cap jars and subjected to a water wash (200 ml), with the leachate from the first and second samples analyzed after the first water wash and the soil from the first sample sacrificed for analysis after the first water wash. The remaining 11 samples then were subjected to a second water wash (200 ml), with the soil from the second jar sacrificed for analysis, as well as the leachate from that sample and the leachate from the third jar analyzed, etc.

In this manner, as illustrated in Table 3, soil and leachate were analyzed after each of the three initial water equilibrations; after each of three water-plus-surfactant equilibrations (200 ml each); and after each of three final water-rinse equilibrations (200 ml each). Each soil/solution mixture was agitated vigorously for a half an hour and then centrifuged to separate the aqueous and soil phases.

#### Soil Column Studies

The columns used in this study were glass, 7.6 cm (3 in) inner diameter by 152 cm (5 ft). Both ends of the column were sealed with nipples glass caps. A Teflon® O-ring placed between the glass column and cap sealed the two surfaces as they were clamped together by an adjustable stainless steel jacket. Teflon® tubes connected to the caps allowed the introduction of the aqueous solution and the collection of the leachate.

The test soil was prepared by spreading a uniform layer in aluminum pans to a depth of about 1.3 cm (0.5 in) and treated with a fine aerosol spray of the contaminant mixture dissolved in methylene chloride. The methylene chloride was allowed to evaporate, after which the soil was mixed by stirring with a stainless steel spatula.

Contaminated soil was packed into the columns using the following procedure: A plug of glass wool was pushed to the bottom of the column. About 775 g (1.7 lbs) of soil then was added to the column and packed to a height of 10.2 cm (4 in) using a controlled-drop hammer compactor designed to fit inside the column. Following compaction of each lift, the soil was tested with a pocket penetrometer to determine the compaction. The soil was packed to a total height of 0.92 m (3 ft) and compacted to a density of 1.88 to 1.76 gm/cm<sup>3</sup> (105 to 110 lbs/ft<sup>3</sup>).

A falling head permeability test, using modified American Society for Testing and Materials methods because of column design, was performed on one of the control columns before starting the column tests. Head level fall from the initial starting point was measured over time while maintaining a constant head level at the outflow. Permeabilities (K) were calculated from the following standard equations

$$K = (2.3 L/t) \log_{10} (h_0/h_1)$$

Where: L = length of soil sample (cm)

t = elapsed time (s)

$h_0$  = original head level (cm)

$h_1$  = head level after elapsed time t (cm)

Permeabilities measured in this manner ranged from  $1.1 \times 10^{-3}$  to  $9.0 \times 10^{-4}$  cm/s ( $3.6 \times 10^{-5}$  to  $3.0 \times 10^{-5}$  ft/s).

Figure 1 presents an overview of the column setup during an experiment. Water or aqueous surfactant was gravity-fed under a constant 61 cm (2 ft) head pressure to the top of each column via Teflon® tubing from reservoir carboys and collected below after passing through the column. Leachate was collected and analyzed for pore volumes 1 through 3, pore volumes 4 through 7 and pore volumes 8 through 10 for each treatment.

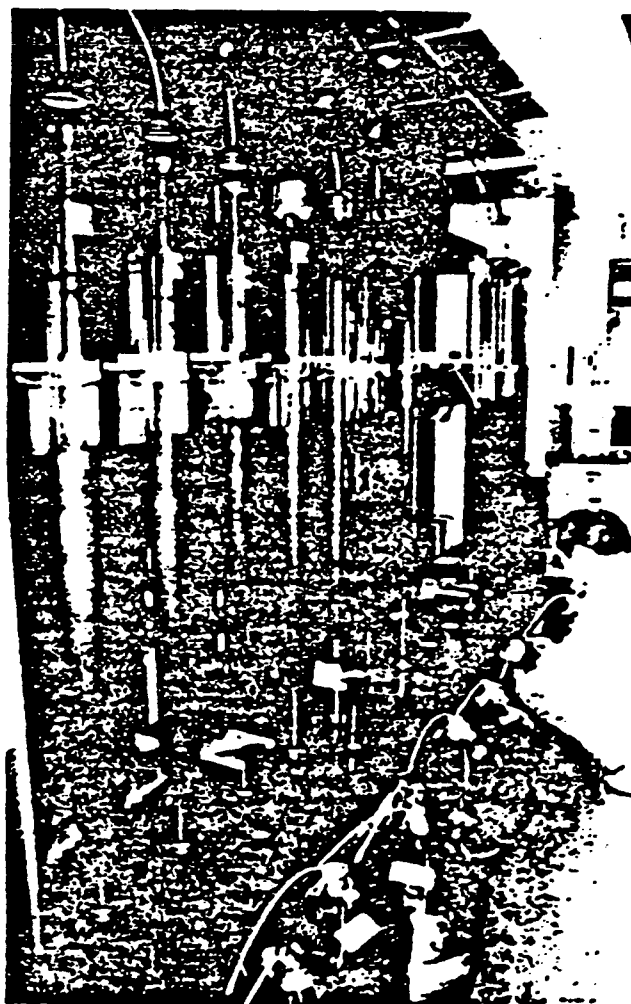


Figure 1. Overview of soil columns in a column rack designed to support water and surfactant carboys at a constant height above columns—Surfactant and water were introduced to each column through the Teflon® tubing in each 20 liter (5.3 gal) glass carboy above the rack. Leachate eluting from each contaminated soil column was collected in the glass carboys shown in the foreground.

## RESULTS

### Murban-Contaminated Soil

The quantitative data are illustrated in Figure 2 as a bar graph of total hydrocarbons present in soil and leachate after each step in the shaker table experiments. The data in the graph illustrate that very little cleanup of the soil occurred during the first three water washes, but a significant reduction (down to 41 percent of original levels) was obtained after the initial aqueous surfactant wash. Continued improvement in hydrocarbon removal was observed in the second and third equilibration with aqueous surfactant. Gradual removal of surfactant and residual hydrocarbons then was observed in the three final water washes. In general, overall mass balance approaching 95 percent was obtained in the shaker table experiment.

In the soil column studies with Murban, very limited removal of aliphatic hydrocarbons from the soil occurred even after 10 pore volumes of initial water. After three pore volumes of aqueous surfactant, however, the soil material was significantly cleaner, and after the final 10 pore volumes of water rinses, the soil was effectively decontaminated.

Significant levels of aromatic hydrocarbons were present in the soil after 10 initial water washes. After the first three aqueous surfactant washes, however, the aromatic components were completely removed, and all that remained in the soil were components from the surfactant material itself.

Soil column and leachate data are shown in Figure 3, which presents the relative contaminant concentration in the soil and leachate after each water/surfactant treatment. The distillation fraction concen-

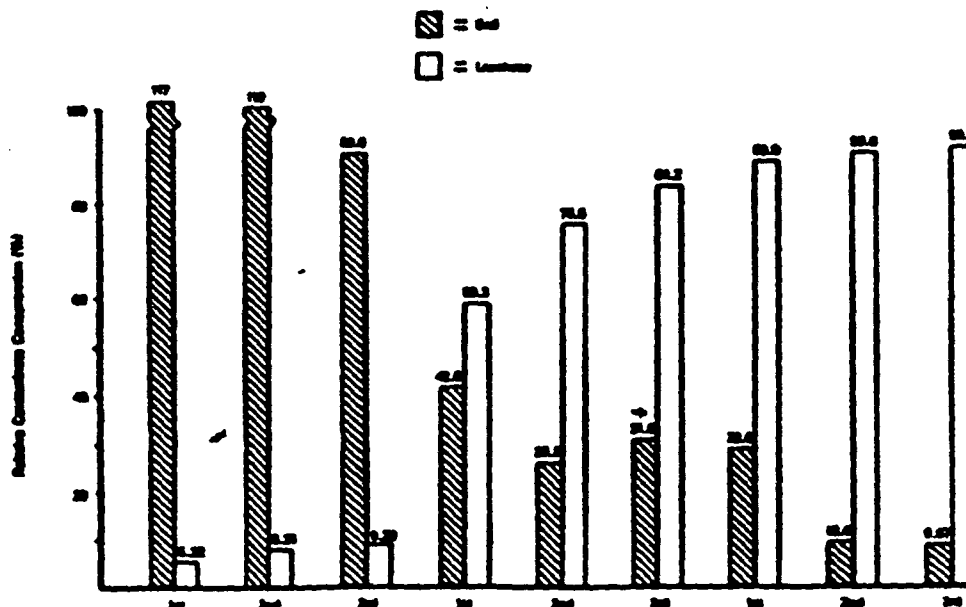
tration ranged from 80 to 100 percent during the first three water washes and then dropped to about 10 percent during the surfactant treatment, with 70 to 80 percent of the original hydrocarbons observed in the aqueous surfactant leachate. The final three water washes did not effect any additional cleanup of the soil, and the average residual soil concentration was about 7 percent of the initial spiked distillation fraction concentration.

### PCB Pollutant Mixture

The initial PCB shaker table experiments followed the same protocol as that described for the Murban hydrocarbons.

Figure 4 illustrates PCB cleanup from the shaker table experiments. After the first surfactant wash, the soil PCB concentration decreased to about 25 percent of the original level, with 45 percent of the original PCBs accounted for in the aqueous surfactant at that point. Additional surfactant rinses produced even greater cleanup of soil PCBs, with up to 82 percent of the original PCB material present in the surfactant after the third aqueous surfactant equilibration. An overall removal of about 87 percent of the original PCBs after the three final water rinses was finally obtained.

As in the shaker table studies, very little cleanup of the soil column was effected with the water washes, while significant removal of PCBs was observed after pore volumes 1-3 of aqueous surfactant. The data are illustrated in Figure 5, which shows the overall concentrations of PCBs in the soil and leachate after each successive treatment. The effect of the first aqueous surfactant wash from the soil column was a 90 percent reduction in PCB concentration in the soil column.





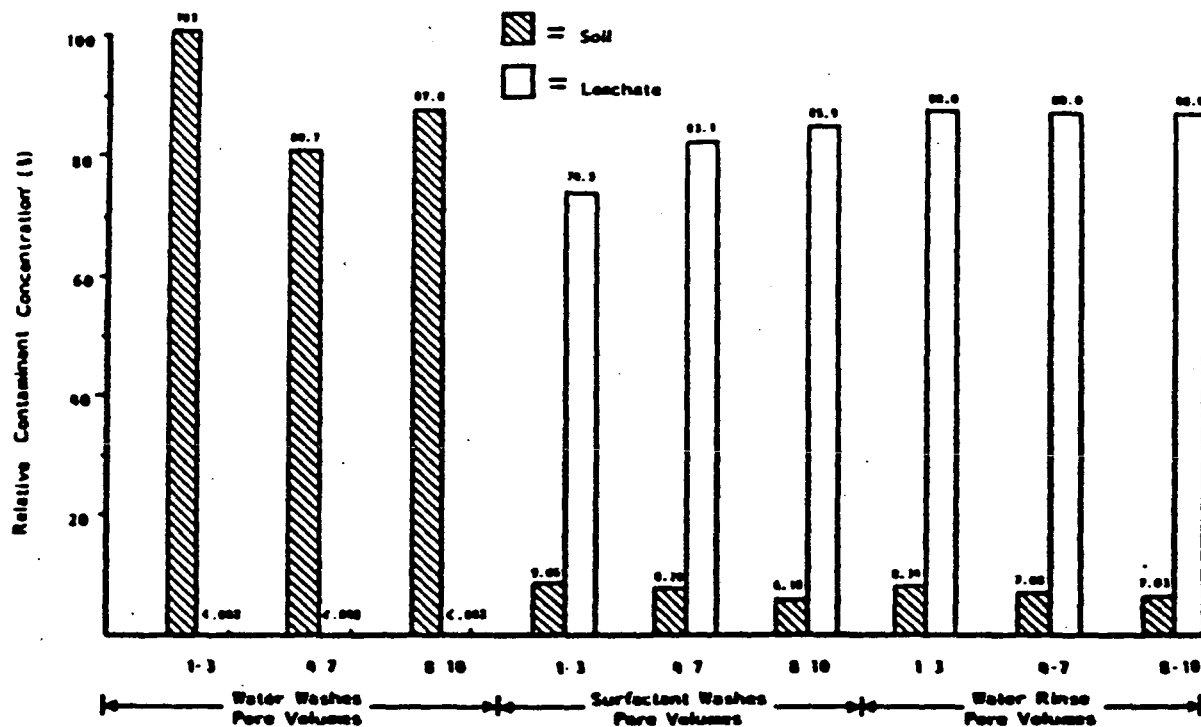
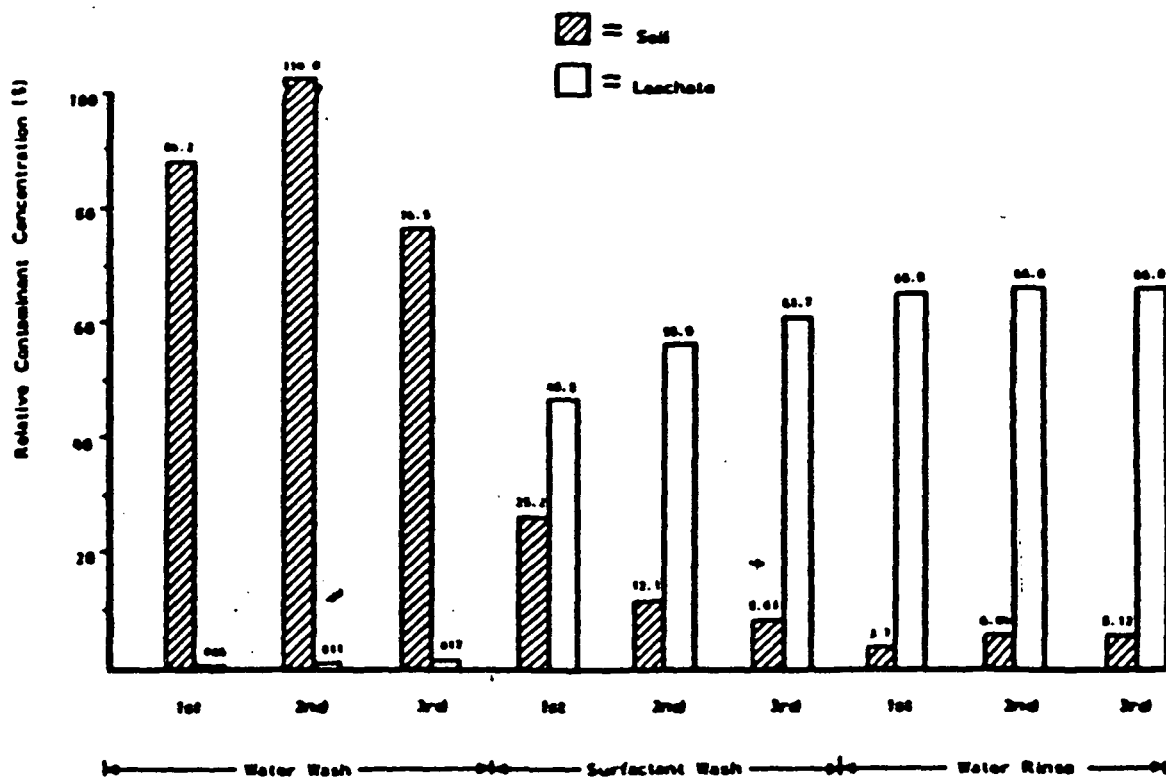


Figure 3. Results of Murban distillation fraction column experiments



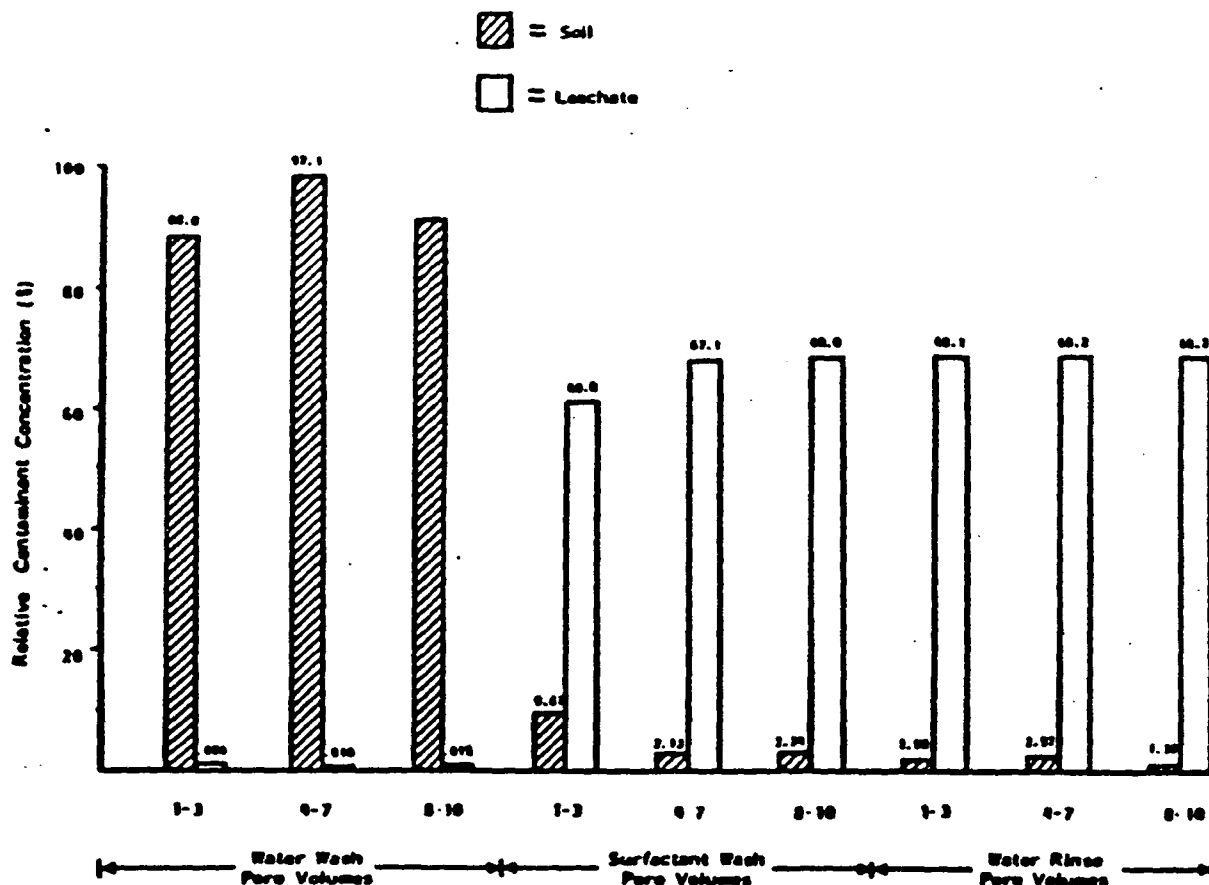


Figure 5. PCB recovery results from soil columns

During the three final water rinses, the overall PCB concentrations were reduced to less than 2 percent of the initial value. An overall mass balance of about 70 percent was obtained.

#### Chlorinated Phenols Pollutant Mixture

The overall cleanup of phenols in the soil is illustrated in Figure 6. It is clear that before initial treatment, about 93 percent of the added di-, tri-, and pentachlorophenol mixture was associated with the soil. After the three water washes, however, the residual contamination of the chlorinated phenol group in the soil had dropped to 2 percent of the amount originally present. Pore volumes 4-7 and 8-10 increased the final proportion of chlorinated phenol in the leachate to about 70 percent of the amount added to the soil originally, and the residual chlorinated phenol in the soil dropped to about 0.5 percent of the value originally introduced.

#### CONCLUSIONS/RECOMMENDATIONS

The shaker table studies and the soil column studies showed that the 4 percent aqueous solution of surfactants was extremely effective in removing hydro-

phobic and slightly hydrophilic organics from the test soil. The performance of the aqueous surfactants in removing PCBs from the soil was quite similar to their performance with the Murban distillation fraction. However, water alone was sufficient to decontaminate the chlorophenols-contaminated soil.

A small amount of aqueous surfactants solubilized substantial amounts of two lipophilic contaminant mixtures from the test soil. Although the surfactants were chosen for this function, the relative ease of removal of the contaminants from the soil is partly because of the soil's characteristics. The TOC of the Freehold soil used in the laboratory tests was 0.12 percent; this is somewhat low, and values of 0.5 to 1.0 percent might be expected for a soil mixture of A, B, and C horizons. At higher TOC values, organics would be removed from the soil less readily.

The results of the soil column tests with Murban and PCBs paralleled the shaker table test results. Because of their hydrophobic nature, little of the contaminants was removed by the initial water washes, while the aqueous surfactants removed them from the soil quite efficiently. The aqueous surfactant appeared to be somewhat more effective in the column tests than in the shaker table tests.

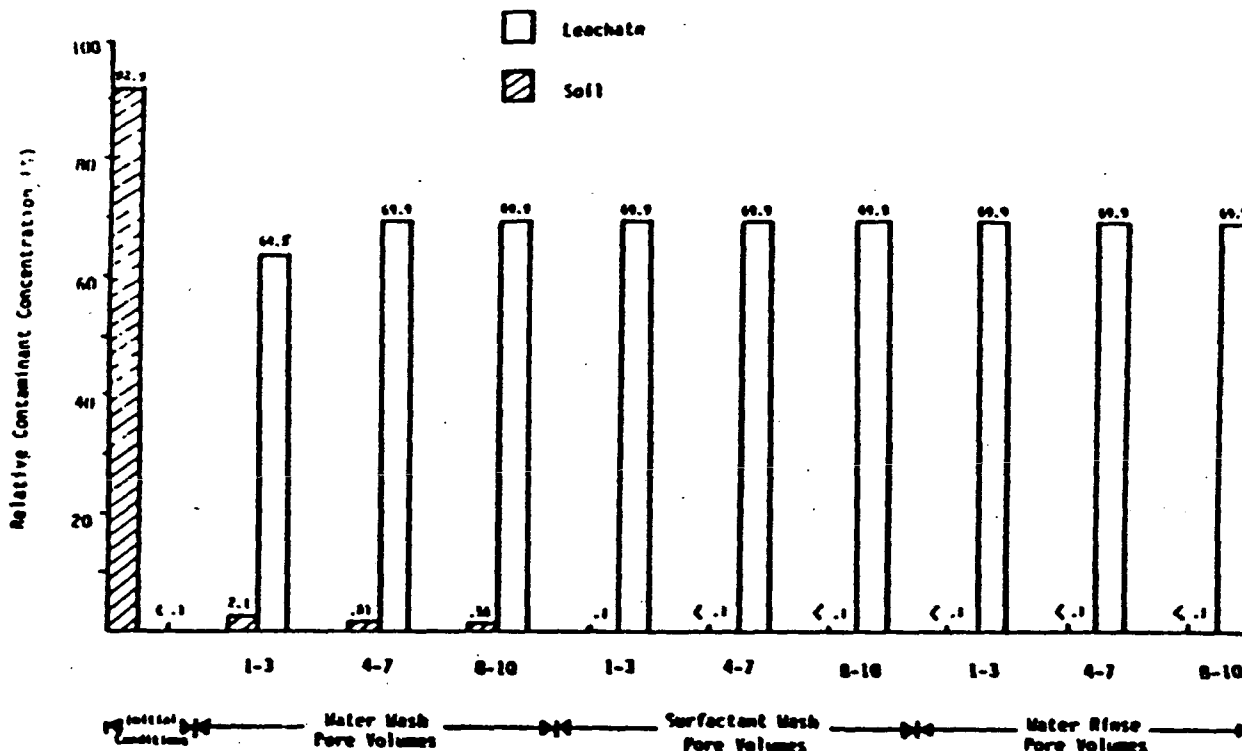


Figure 6. Results from chlorinated phenol column experiments—Concentrations summed for di-, tri-, and pentachlorophenol

For instance, in the Murban shaker table study, 50 percent of the contaminant was removed from the soil by treatment with 2 ml of aqueous surfactant per gram of soil. In the Murban soil column study, 74.5 percent of the contaminant was removed by only 0.8 ml of aqueous surfactant per gram of soil. The shaker table tests were equilibration tests and should, therefore, demonstrate optimum efficiency of the surfactant solution in removing the contaminants. The column tests were flow-through tests, but showed more efficient removal of contaminant, probably because the surfactant-solubilized contaminant micelles that formed solubilized more and more of the contaminant as they flowed in suspension down the column. The effect is similar to that observed in certain tertiary oil recovery processes (Klins, Farouqali and Stahl, 1976).

The results of the laboratory studies appear encouraging and support continuation of the Chemical Countermeasures Program into larger scale controlled field demonstrations at sites-of-opportunity.

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# 1984 HAZARDOUS MATERIAL SPILLS CONFERENCE PROCEEDINGS

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## FIELD EVALUATION OF IN SITU WASHING OF CONTAMINATED SOILS WITH WATER/SURFACTANTS<sup>1</sup>

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### ABSTRACT

Since 1981, the Releases Control Branch of the Hazardous Waste Engineering Research Laboratory has been developing techniques to wash contaminated soil in place (in situ). The project includes: design and fabrication of the hardware to carry out the washing, evaluation of surfactants to do the washing, determination of which geological characteristics to use to judge the appropriateness of in situ washing, development of a monitoring and reporting system, evaluation of two candidate sites for the field testing of the hardware, and a pilot treatment study at a contaminated site.

This paper summarizes the design and development of the In Situ Containment/Treatment Unit (ISCTU) and the evaluation of surfactants for in situ soil washing. The emphasis is on work completed at Volk Air National Guard Base, Camp Douglas, Wisconsin. The work shows that surfactants will remove otherwise obstinate contaminants from soil even without mechanical agitation of the soil. However, subsequent treatments of the surfactant laden leachate is an unresolved problem.

### INTRODUCTION

In situ soil washing is the term to describe washing of contaminated soil with-

out excavating. The washing is accomplished by applying a liquid at or near the surface

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<sup>1</sup> This report is a summary of work performed in partial fulfillment of Contract Numbers 68-03-3113 and 68-03-3203 under sponsorship of the U.S. Environmental Protection Agency. The U.S. Air Force through Interagency Agreement #RW 57931283-01-0 with the U.S. EPA has also sponsored much of the work reported here. This paper discusses

the key activities of four projects: "Treatment of Contaminated Soils With Aqueous Surfactants", "Retrofit of the In Situ Containment and Treatment Unit", "Chemical Countermeasure Application at Volk Field Site of Opportunity", and "Site Characterization and Treatment Studies of Soil and Groundwater at Volk Field."

The first washing tests were run on a shaker table and the next test series in columns. Contaminated soil was compacted in 3 in. increments into 3 in. diameter, 5 ft high glass tubes. The tubes were fitted with nipped glass caps at the bottom and top. A pressure head of 30 cm of surfactant solution was applied to the surface of the contaminated soil. The soil pores were, therefore, experiencing saturated flow of the surfactant solution.<sup>2</sup>

The soil used for the laboratory work was a Freehold series typic hapludult from Clarksburg, New Jersey. It was selected because of its grain size distribution and similarity to soil at CERCLA candidate sites in EPA's Region II. Ten percent was silt or clay, eight percent gravel and 80% coarse-to-fine sand. Its permeability of  $10^{-4}$  cm/sec is at the low end for in situ washing. Nine to eleven percent of the soil was HCl soluble. Of the crystalline structure, 98% was quartz and 2% was feldspar. Only 0.12% was organic carbon which is a low value and accounts, in part, for a low cation exchange capacity.

A topped Murban crude oil in methylene chloride was applied to the soil. This contaminant was selected because it contained many organic types including aromatics, polynuclear aromatics, aliphatics, polar and non polar compounds. The methylene chloride was allowed to evaporate and the soil was aged prior to being loaded into the test columns. Other contaminants, in separate tests, were chlorophenols and a polychlorinated biphenyl.

Gas chromatographic analysis showed that ten pore volumes of surfactant solutions passed through the columns removed 88% of the topped Murban crude oil and 90% of the PCB's. Using high performance liquid chromatography (HPLC), it was shown that chlorophenols were removed with the water alone. Surprisingly, removal in the column studies, where there is a low level of mechanical washing, was better than removal in the shaker table studies. Starting at 1000 ppm contamination in the columns, removal efficiencies as high as 98% were reported.

### Control of In Situ Washing Fluids

Accelerating the natural tendency of a contaminant to migrate through the vadose zone into the groundwater is the basic purpose of in situ soil washing. In order to do this so there is no adverse impact on an aquifer, rigid controls must be maintained to assure the contaminant is captured. The EPA's In Situ Containment and Treatment Unit (ISCTU) was designed for this purpose. The drawing in Figure 2 represents the parameters (of an hydraulic budget) that were considered for the (ISCTU).<sup>3</sup> They are: recharge  $G_a$ , discharge  $D_a$ , treatment system flow  $R$ , evapotranspiration  $E$ , precipitation  $P$ , natural groundwater flow  $U_1$ , and induced groundwater flow  $U_2$ . Variation in these qualities will change those items in lower case letters; vadose zone thickness  $w$ , mounding  $m$ , drawdown  $(h_e - h_w)$ , and radius of influence  $r_e$  (not to be confused with the radius of capture).

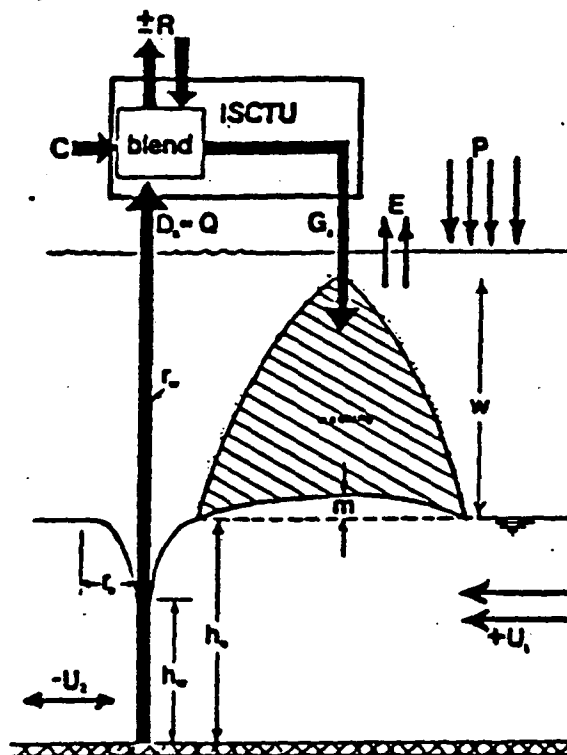


Figure 2. In situ parameters



Figure 3 is a simplified drawing of the ISCTU, which is equipped with recovery and delivery pumps, batch mixing and proportional-additive metering pumps, flow rate controls, pressure and flow meters, and a volatile organic stripping tower. Any treatment of groundwater requiring more

than air stripping must be done "off-board." A microcomputer/data logger is used to monitor environmental conditions and the effect of pumping and recharge on the aquifer. To do this, depth gauges, flow meters, moisture meters, and a weather station are connected to the data logger.

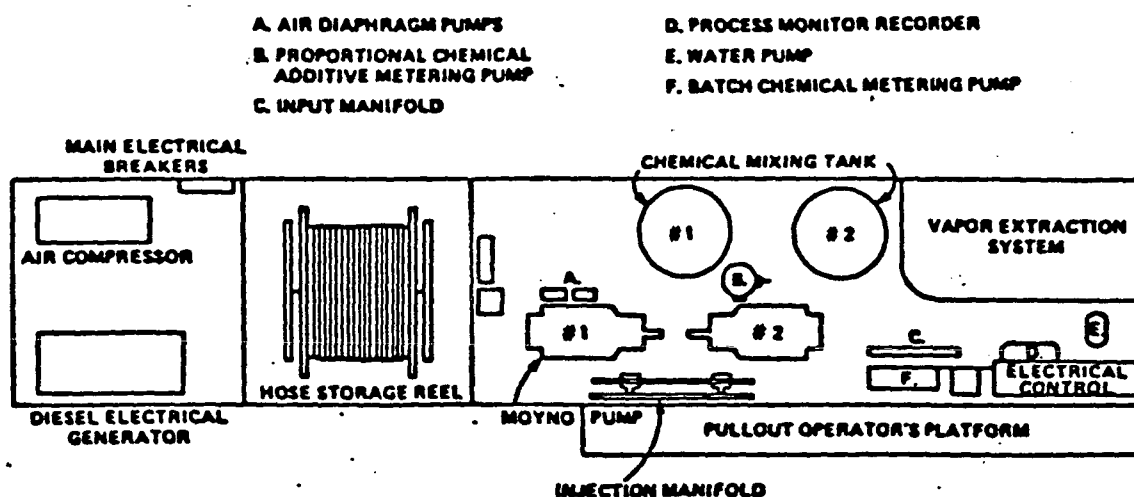


Figure 3. In Situ Containment and Treatment Unit

### Site Selection for the Field Evaluation

In September 1984 the U.S. Air Force and the U.S. EPA started in a joint effort to evaluate in situ washing technology. The primary objective of the project was to demonstrate full-scale feasibility. A secondary objective was to develop a more comprehensive strategy for the decontamination of fire-training areas of all Air Force and Department of Defense (DoD) installations. The following criteria were used in selecting a site suitable for full-scale soils washing research. A site of less than one acre was desired to reduce soil variability and reduce sampling costs. Because soil washing is best suited for permeable soils, a sandy site was sought. Contaminants at the site were to be common organic chemicals found at many other Air Force sites, i.e., trichloroethane, benzene, toluene, trichloroethylene. Officials of the selected installation and responsible environmental agencies would need to be cooperative.

Preliminary screening of candidate sites was accomplished through a review of Air Force Installation Restoration Program (IRP) reports. Over sixty reports and nearly 800 sites were screened. During the review, it was apparent that most sites with organic chemical contamination fell into two common categories: sites of fuel spills and fire training areas.

Fire training areas were especially suited to this research because of their limited size and range of contaminants, which included chlorinated solvents, fuel components and lubricating oil. Fire training areas are found at almost all Air Force installations and, because of the long-term fuel and solvent dumping at these sites, they have significant off-site pollution potential.

Following this careful review, a fire training area at Volk Field, Air National Guard Base, Wisconsin, was selected as a research site. Historical records indicate that the Volk fire training area may

have been established as early as World War II and has routinely received waste solvents, lubricating oil, and JP-4 jet fuel. Although it is impossible to determine the quantity of chemicals that soaked into the ground versus the amount volatilized and burned in fire training exercises, one estimate is 52,000 gallons. Measurement of volatile organics from groundwater samples taken in 1980 directly below the fire pit showed chloroform, trichlorethane, trichlorethylene, benzene, toluene, and ethyl benzene totaling above 50 mg/liter.<sup>4</sup>

### Site Studies

Two site studies were made at the fire pit area during 1985. These studies were conducted to thoroughly understand the hydrology and chemistry associated with the contamination have produced as a by-product a great deal of data and insight into a chronic oil spill. Initially, the character of the contamination was misunderstood. The original concept of a floating layer of oil that could be handled easily gave way to the realization that the contamination had not remained as a water insoluble oil but had been transformed to soluble organics by biological/chemical activity. Biological activity had been nourished by the firefighting foams used in the training exercises. These fire-fighting foams may have also contributed directly to solubilizing the oils. The groundwater, 25 ft below the surface (and only 60 ft from the pit), had up to 50 mg/liter total organic carbon (TOC). Infrared spectrophotometric (IR) scans indicated this contamination was in part esters or organic acids. Upon emerging from the centrifugal pump (used for a pumping test), the groundwater frothed.<sup>5</sup> Directly below the pit the water table was at 12 ft. The hydraulic conductivity was  $5 \times 10^{-2}$  cm/sec.

### Treatment Studies of the Soil

The overall soil contamination had the physical consistency of a medium weight lube oil. At a one-foot depth average oil and grease (determined by carbon tetrachloride [ $\text{CCl}_4$ ] extraction) was 13,500 mg/kg. Deeper into the soil,

oil and grease (O&G) values decreased. At 5 ft, and continuing to the capillary zone at 10 ft, O&G values were 400-800 mg/kg. Soil samples from the aquifer taken at 15 ft produced 5000 mg/kg O&G. The chemical composition of the  $\text{CCl}_4$  extract also varied with depth. IR scans of extracts of soil from 1 ft depth match scans of paraffinic oil. Esters or acids of oil become more evident when approaching the water table. Below the water table, the oxidized oils although present, are less prominent. This profile is apparently a symptom of weathering. The more soluble oxide forms have been carried to the groundwater by percolating rain water.

The volatile contaminants also show evidence of weathering. In contrast to O&G, the weathered volatiles are found closer to the surface than to the water table and are an order of magnitude less abundant than O&G extracts. A relatively high abundance of isoprenoid compounds (includes many naturally occurring materials such as terpenes) in relation to normal alkanes also indicates long term microbial degradation.<sup>6</sup> A terpene-like odor was noticed while taking soil samples to determine the lateral extent of contamination near the surface. Within 6 in. of approaching the clean soil and at depths of 6 to 12 in. a "minty-turpentine" smell was reported by the field technician.

A part of the fire training area was prepared so that ten mini soil washings could be conducted simultaneously. The first foot of soil was not to be included. Therefore, ten 1 ft deep holes were dug and the bottom of each hole was called the "surface" of the test chamber. Each "chamber" was a 14-in. depth of soil from the bottom of the hole down. Surfactants tested were: an anionic sulfonated alkyl ester (Pit #7), a polyethylene glycol dioleate (Pit #10), ethoxylated alkyl phenol/ethoxylated fatty acid blend (Pit #8), and the contaminated groundwater (Pits #2,3,4,5,9). The dioleate caused soil plugging immediately. Compared to water, penetration rates were reduced when any surfactant solutions were used. The groundwater,

which has a low concentration of biologically produced surfactant, had the least effect on the penetration rate.

The dominant contamination in the soil was oil and grease, up to 16,000 mg/kg, where volatiles were less than 100 mg/kg.<sup>6</sup> O&G measurements were therefore used to determine the effectiveness of the soil washing. To avoid channeling during the pilot treatment, prewash O&G measurements were made on samples taken adjacent to the chambers. Statistically, the O&G measurements had a coefficient of variation (CV) throughout the test area of 35% making it difficult to draw conclusions of soil washing effectiveness. Figure 4 shows the O&G measurements after the surfactant wash process and the blank value. Pit #8 was washed with the lab-developed 50/50 surfactant blend. It is interesting to note that the O&G at 12-14 in. has increased 24% above the blank and the surface top layer O&G has decreased 50%, implying a transport of contaminant downward during the seven days of washing with 14 pore volumes. Keep in mind a CV of 35% precludes any definitive conclusion. The expected reduction of contamination at the 12 in. depth to 50% of the original level was not realized.

#### Treatment Studies of the Groundwater

Bench scale and then pilot treatment studies of the already contaminated groundwater were undertaken in anticipation of full-scale soil washing. Bench-scale studies evaluated addition of: lime, hydrogen peroxide, alum, ferric chloride, and various water treating polymers. The pilot treatment was run using the EPA's Mobile Independent Chemical/Physical Treatment Unit, a holding lagoon, and an air stripper made by the Air Force. Figure 5 is a process flow diagram that also indicates sampling points. The three treatments consistently used during the operation were lime addition, settling, and

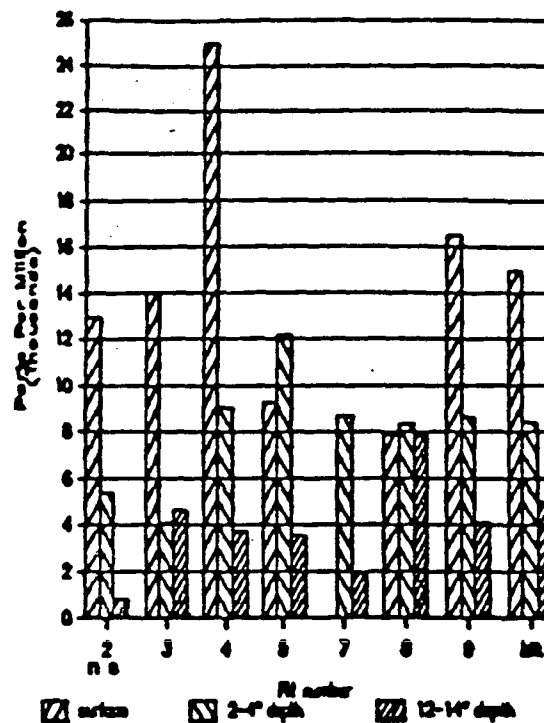


Figure 4. Soil washing data

volatilization. Total organic carbon (TOC), volatile organic analysis (VOA), and suspended solids (SS) tests were used to monitor the effect of these treatments.

Addition of lime brought about significant reductions in TOC. Organics were removed with an iron hydroxide to form a floc. (Interestingly, the contaminated groundwater had up to 56 mg/liter iron compared to background levels of 0.2 mg/liter.) Volatiles were 95 to 98% removed in the lagoon and air stripper. Figure 6 is a bar chart depicting the measured level of TOC at four points in the process. Figure 7 is a bar chart showing the measured levels of four volatiles at three locations in the process.

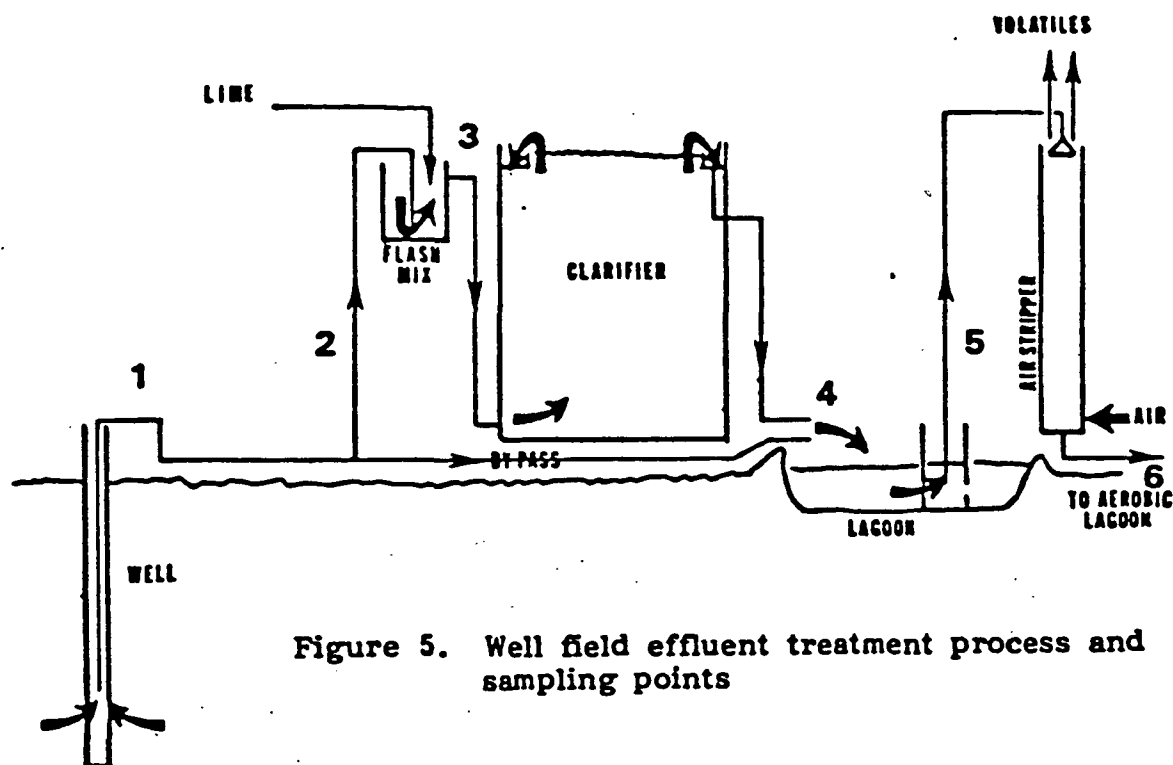


Figure 5. Well field effluent treatment process and sampling points

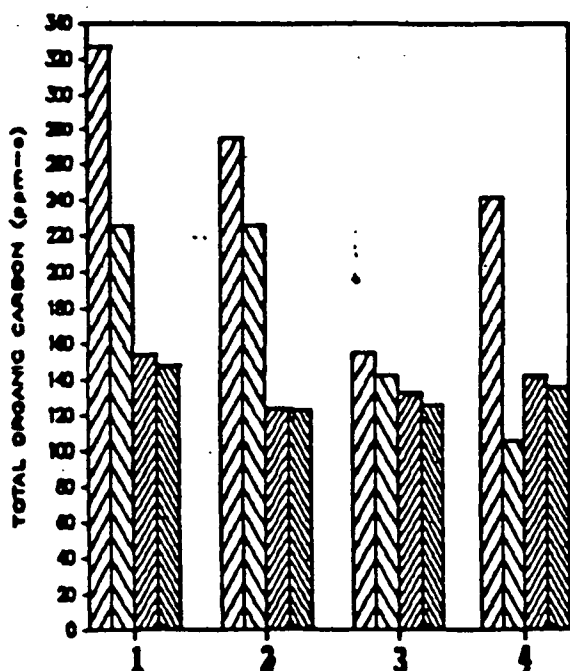


Figure 6. Four data sets showing Level of TOC at the well field, clarifier effluent, stripper feed, and stripper effluent.

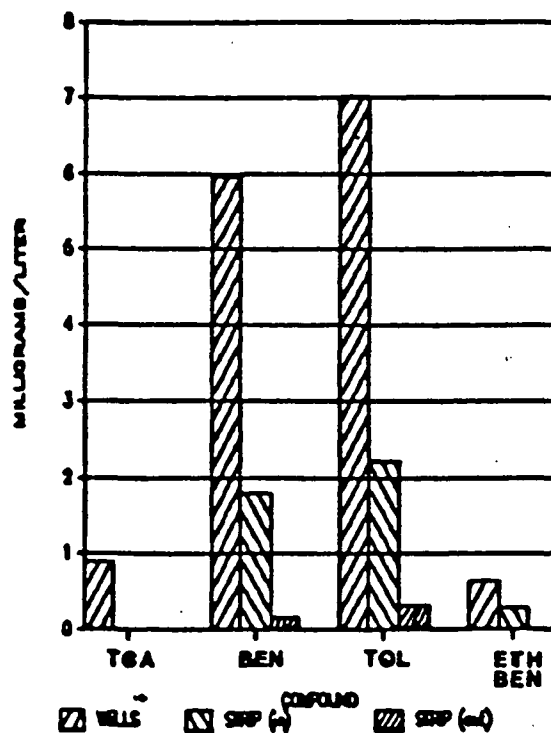


Figure 7. Volatiles at the well field, stripper feed, and stripper effluent.

In anticipation of conducting a in situ soil washing of the entire pit, tests were run to determine control of the natural groundwater flow beneath the pit. This was accomplished by a six-member well field. In total there have been 13 wells installed in the study, 7 monitoring wells and 6 withdrawal wells. Boring logs were kept during the drilling operations. Split spoon samples of the sand and weathered sandstone were used for chemical analysis and particle size analysis. The fines content of the directly

below the pit is significantly lower than in the adjacent uncontaminated soils - 2 to 5% versus 10 to 15%. Fines content of soil 8 ft below the water table, slightly down gradient, and in the plume is unusually high: 28% versus 10-15%. The production wells placed in the highest contamination zones have the poorest fluid yield. Paradoxically, according to equipotential lines constructed from water table depths, there is a convergence of flow passing beneath the pit (see Figure 8).

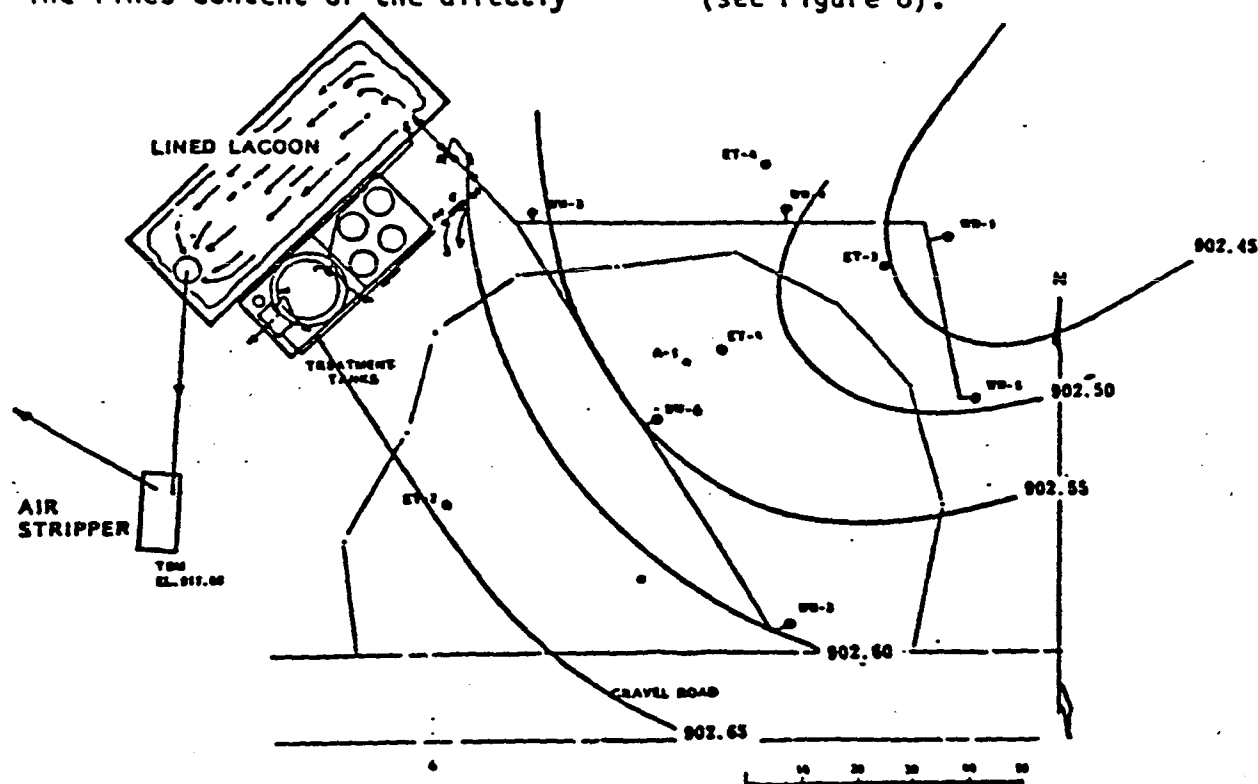


Figure 8. Treatment site showing water table equipotential lines

This is directly in line with a production well producing water containing 700 mg/ liter TOC at less than 2 gallons per minute. The average for the rest of the wells is 260 mg/liter at 6 gallons per minute. The design pumping rate for each well was 12 gpm. In spite of well yield problems the natural gradient of 0.001 (ft/ft) was easily reversed to create a radius of influence of greater than 100 ft and a radius of capture greater than the 40 ft training pit radius.

#### A Follow-up Electromagnetic Survey

An electromagnetic survey was conducted over the ground surface surrounding the training area to determine the measurable extent of the plume. The decision to do this was based on the low conductivity of the soil, high conductivity of the plume (600 micromohs), and the low conductivity of the background water (20 micromohs). A study conducted by the New Jersey Geological Survey<sup>7</sup> had been

able to map an organic plume from a fire training area in a sandy aquifer. In the report of that work, the fire fighting foam AFFF was felt to be the conductive organic that made the survey possible. In this work the high iron content of the plume is considered the reason for the success of the survey. The reason for the high iron content is the reducing conditions that exist(ed) during biological activity at the site. Figure 9 is a map of the plume based on conductivity.

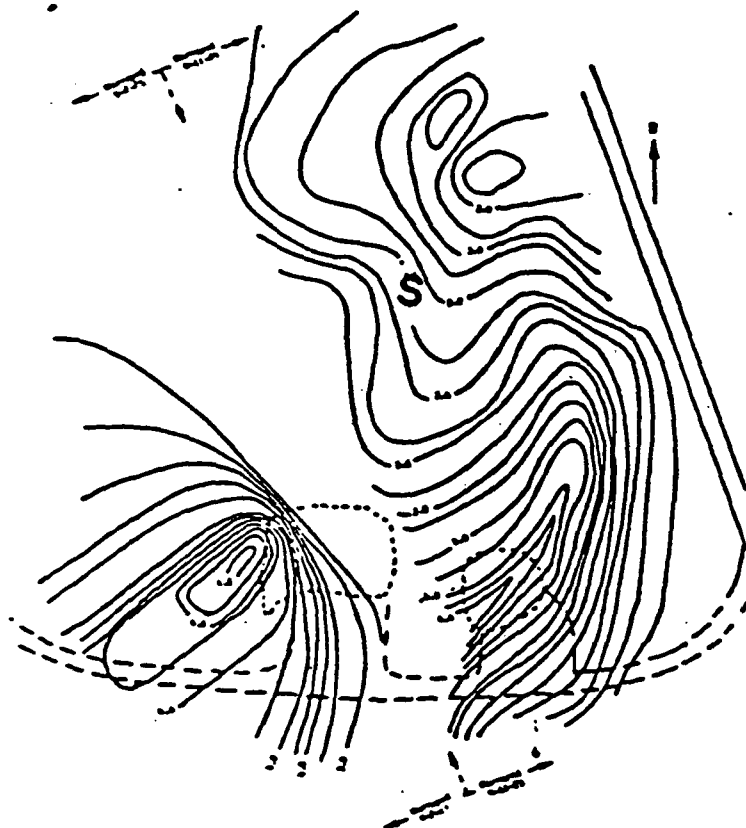


Figure 9. Electromagnetic Survey

The  $\text{CCL}_4$  extract of a soil sample taken at 12 ft at the point marked "S" in the figure was identified as an oxidized oil.

The authors wish to express their appreciation for the cooperation, encouragement and help given by a number of people from the Wisconsin Air National Guard and Department of Natural Resources. But especially we wish to acknowledge Doug Downey of the U.S. Air Force for his gentle persistence in directing the work done at Volk Field.

#### CONCLUSION

The mechanical aspects of applying a surfactant to soil and controlling an underlying unconfined aquifer to capture the wash solution have been demonstrated at a site of opportunity. Issues that remain to be addressed are treatment, if necessary, of the used surfactant solutions, isolation of the containment from the surfactant and developing a method to recycle the surfactant.



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# In Place Detoxification of Hazardous Materials Spills in Soil

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## INTRODUCTION

Spill incidents can occur in almost any known geographic area, contaminating air, water and/or soil. Containment and treatment technology for water spills has received the most attention and is the furthest advanced. However, in many instances, both water and soil are contaminated when land spill threatens a nearby water body or the groundwater table. The state-of-the-art of land spill cleanup has consisted mainly of excavation and hauling to an approved landfill site or possibly flushing of the affected area with water. These methods are appropriate in certain circumstances. However, when the groundwater is threatened, when a large soil mass is contaminated or when no suitable disposal site is available, other approaches may be needed.

It is the purpose of this effort, funded by the U.S. Environmental Protection Agency under contract number 68-03-2508, to develop a mobile treatment system which allows in place (*in-situ*) detoxification of hazardous materials spilled on soil. Detoxification in this context refers to amelioration of a spill's effect by chemical reaction. The project goals were to design and demonstrate a mobile vehicle capable of encapsulating a 10,000 gallon land spill in grout and treating the spilled chemicals in place by either oxidation/reduction, neutralization, precipitation or polymerization. The approach to achieving the design goals was to use direct injection of grouting material into the soil around the contaminated area to envelop the spill and isolate it from the groundwater, followed by detoxification by injection of treatment agents. This paper documents the results of the laboratory and pilot tests and the resulting preliminary system design. The vehicle which will be fabricated and demonstrated during 1978 should be a part of the EPA spill response arsenal by 1979.

## Project Approach

The work was divided into five phases: 1) Laboratory Study, 2) Pilot Testing and Design, 3) Fabrication, 4) Testing and Demonstration and 5) Reports. The information obtained during the laboratory and pilot tests was used to develop the final system design and, as anticipated, the end-product design was modified from that originally envisioned.

## Laboratory Testing

The laboratory tests had two main objectives:

1. To determine if *in-situ* treatment techniques could effectively detoxify chemicals present in various soil systems and,
2. To evaluate, choose and test various grout types for their potential use in spill containment.

## Choice of Chemicals and Soils

Various reagents and soil types were chosen for testing the four types of chemical reactions: oxidation/reduction, neutralization, precipitation and polymerization. Chemical compounds studied as contaminants were chosen based on the following criteria: 1) efficiency of the chemical reaction; 2) common use of the chemical and 3) potential risk of spillage. Treatment agent choices were based on: 1) the hazardous nature of the treatment chemical, 2) its availability, 3) its handling difficulties and 4) the volume needed for detoxification of the contaminant. Contaminant concentrations were established by common shipment concentrations, and the strength of the reactant was established to keep the detoxification controllable. The chemical systems are shown in Table I.

Four soil types were also included in the laboratory study. It was determined that classification of soils by grain size would be most advantageous, since this characteristic often controls the soils permeability and therefore its amenability to injection of treatment agents. The four soil types considered were clay, silt, sand and gravel. In order to simplify data interpretation, it was decided to select soils to minimize the amount of interaction of the soils with the chemical systems. This was justified because the objective of the laboratory study was to evaluate the effects of a soil's physical properties on *in-situ* detoxification and it was thought that the potential interferences from soil chemical properties could be to mask important physical effects which needed to be defined. Therefore, the following relatively inert soil types were chosen: clay—Georgia Kaolin; silt—No. 290 Silica Flour; sand—blended Ottawa Silica Sand (Flint shot and No. 1 Federal Fine); gravel—trap rock. The soil gradations were selected to be representative of the specific soil type to be tested. For example, the amount of clay or silt in the sand sample was minimal.

Table I: Chemical Reaction Systems Investigated

Reaction Type	Contaminant		Reactant	
	Compound	Concentration	Compound	Concentration
Oxidation/ Reduction	Sodium Hypo- chlorite	12-15% Cl	Sodium Bisulfite	7.5%
Neutralization	Sulfuric Acid	36N	Sodium Hydroxide	1-5N
Precipitation	Copper Sulfate	75 g/l	Sodium Sulfide/ Sodium Hydroxide	1.0 0.1
Polymerization	Styrene	100%	Persulfate	-

#### Laboratory Reaction Feasibility Testing

The laboratory testing was subdivided into three parts: design and fabrication of the testing apparatus and development of the procedures; the actual performance of the tests and evaluation of the results. Two types of testing were performed: flow through tests in which drainage of the system was allowed during the reaction and sealed tests which involved direct addition of reactant to the soil with no drainage of the soil allowed.

In order to evaluate as many of the critical variables as possible, an experimental design was established. This approach varied soil conditions (bulk density and water content), contaminant loadings (as percent of the soil void space available) and detention time (pressure). The soil and chemical systems were to be evaluated separately. After initial attempts and problems involved with developing a safe, uniform and generally applicable approach to polymerization in the soil, this reaction was not further evaluated. Therefore testing was limited to three reactions and four soil types.

The laboratory testing apparatus consisted of a 3.5 in. diameter clear column supported by machined aluminum bottom and top fittings (See Figure 1). The column was fitted with an underdrain support system for the flow-through tests and a porous plate/screen cover to distribute the chemicals placed into the column. When necessary, regulated air pressure was used to force the reactant through the contaminated soil. The sealed apparatus required elimination of the base and drainage holes. Columns of both acrylic and clear PVS plastics were used since neither material was resistant to all of the chemical species tested.

The testing procedure involved mixing specified amounts of soil and water and packing this mixture to incremental heights to achieve a specified soil bulk density. These soil columns were then contaminated with liquid to fill a certain soil void volume, the treatment agent added and samples collected at the underdrain. If sealed tests were performed on a system the contaminant/reactant/soil

mixture was allowed to stand for a given time and soil core samples were taken and analyzed.

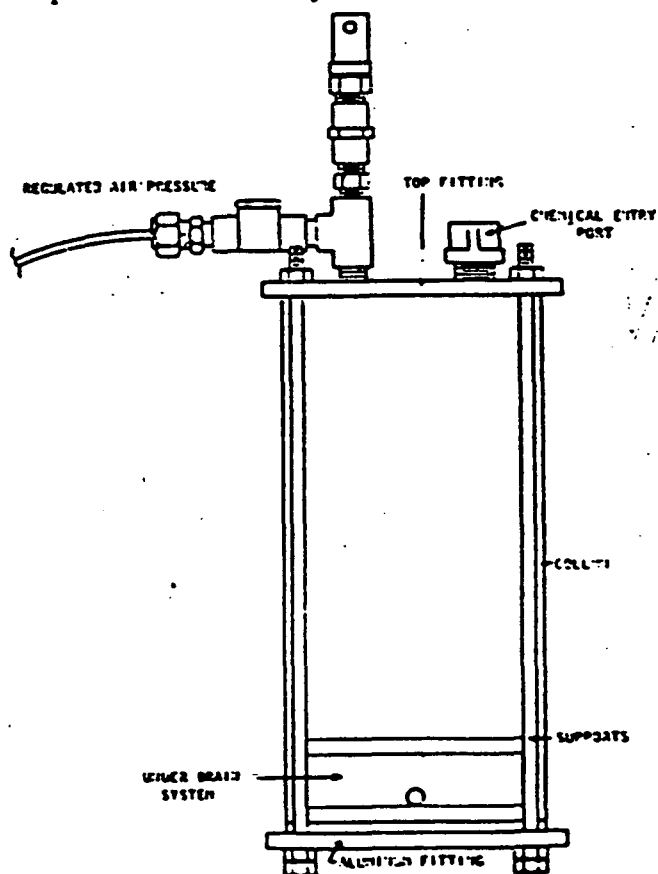


Figure 1: Laboratory Testing Apparatus

Initially, flow-through testing only was to be implemented. However, it soon became apparent that this approach was not feasible for the fine grained clays. The

high pressures required to force the reactant through the soil caused short circuiting along the column sides and no detoxification occurred. Therefore it was decided to test a surface treatment method (sealed tests) for the clay systems.

The data collected from all laboratory testing were evaluated and the percent of contaminant treated was calculated along with the residual concentration in the treated soil. Statistical analyses of these results using ANOVA design and F tests were used to identify which of the variables had significant effects on the efficiency of the reaction. The results indicate that both soil type and reaction type significantly affect the degree of detoxification, along with the three internal variables (soil conditions, detention time and loading).

The efficiency of *in-situ* treatment in gravel was much lower than with other soils (See Table II). This is a result of most of the contaminant rapidly percolating through the gravel prior to treatment. However, for the contaminants entrained on the gravel, the reaction efficiency ranged from 95-99%. The overall efficiency of the neutralization reactions was also lower since a pre-reactant water rinse was required in order to reduce the heat of reaction. Precipitation reactions were more efficient than anticipated. This may be due to the blocking affect of the precipitate which clogs some of the voids and forces the treatment agent to

flow into other contaminated areas. Redox reactions were generally quite efficient under all conditions. The detention time was critical for sand detoxification indicating that too high a pumping rate will be detrimental in final treatment.

The effectiveness of sealed detoxification (surface treatment) was not anticipated. As long as void saturation was not exceeded, the treatment agent entered the fine grained soils and mixed to a degree which detoxified most of the contaminant. This apparent mixing in the small void sizes was not expected. Reduced reaction efficiencies were apparent for precipitation because the precipitate did block the reactant's path into the soil. Overall, even this reaction was quite effective. The main problem with a sealed system is that the volumes which can be treated are limited to voids available for the reactant.

#### Grout Evaluation

The second objective of the laboratory testing was to evaluate the grout which could be used for encapsulation of a spill. The main types of grout available include particulate grouts such as cement and bentonite and chemical grouts which are mainly Acrylamide (AM-9), urea-formaldehyde resin, lignin or silicate based materials. Particulate grouts are generally used in coarse grained soils since they have a relatively high viscosity due to their suspended particles in a

Table II: Summary of Laboratory Test Results

Soil	Reaction	Test Type	Range of Effectiveness*	Average Efficiency*	Significant Variables	Number of Tests
Sand	Acid	Flow Thru	3.4-52.2	22.4	Detention Time	12
Sand	Redox	Flow Thru	18.4-66.4	37.3	Detention Time	12
Sand	PPT	Flow Thru	19.2-85.8	42.9	Detention Time	12
Sand	Avg	Flow Thru	( 3.4-85.8)	(34.2)		
Silt	Acid	Flow Thru	39.3-99.9	57.7	Soil Conditions	12
Silt	Redox	Flow Thru	12 -99.3	55.7	Loading & Soil Conditions	12
Silt	PPT	Flow Thru	42.1-98.7	74.4	Loading	8
Silt	Avg	Flow Thru	(12 -99.9)	62.6		
Gravel	Acid	Flow Thru	3.7- 5.8	4.8	None	4
Gravel	Redox	Flow Thru	12.3-26.4	20.0	Loading	4
Gravel	PPT	Flow Thru	12.6-31.3	20.1	None	4
Gravel	Avg	Flow Thru	3.7-31.3	(15)		
Clay	Acid	Sealed	74.6-78	76.3	None	4
Clay	Redox	Sealed	96.2-99.5	98	None	4
Clay	PPT	Sealed	56.5-87	74.6	None	4
Clay	Avg	Sealed	(56.5-99.5)	82.9		

\*Based on the  $\left( \frac{\text{total amount of containment-amount not reacted}}{\text{total containment}} \right) \times 100$

water base. Chemical grouts are generally in solution form and can be used to grout finer grained soils. One of the most commonly used chemical grouts is AM-9 which can

be used to grout soils of an acrylamide base which is toxic to groundwaters. Therefore it was not considered suitable for the spill containment application.

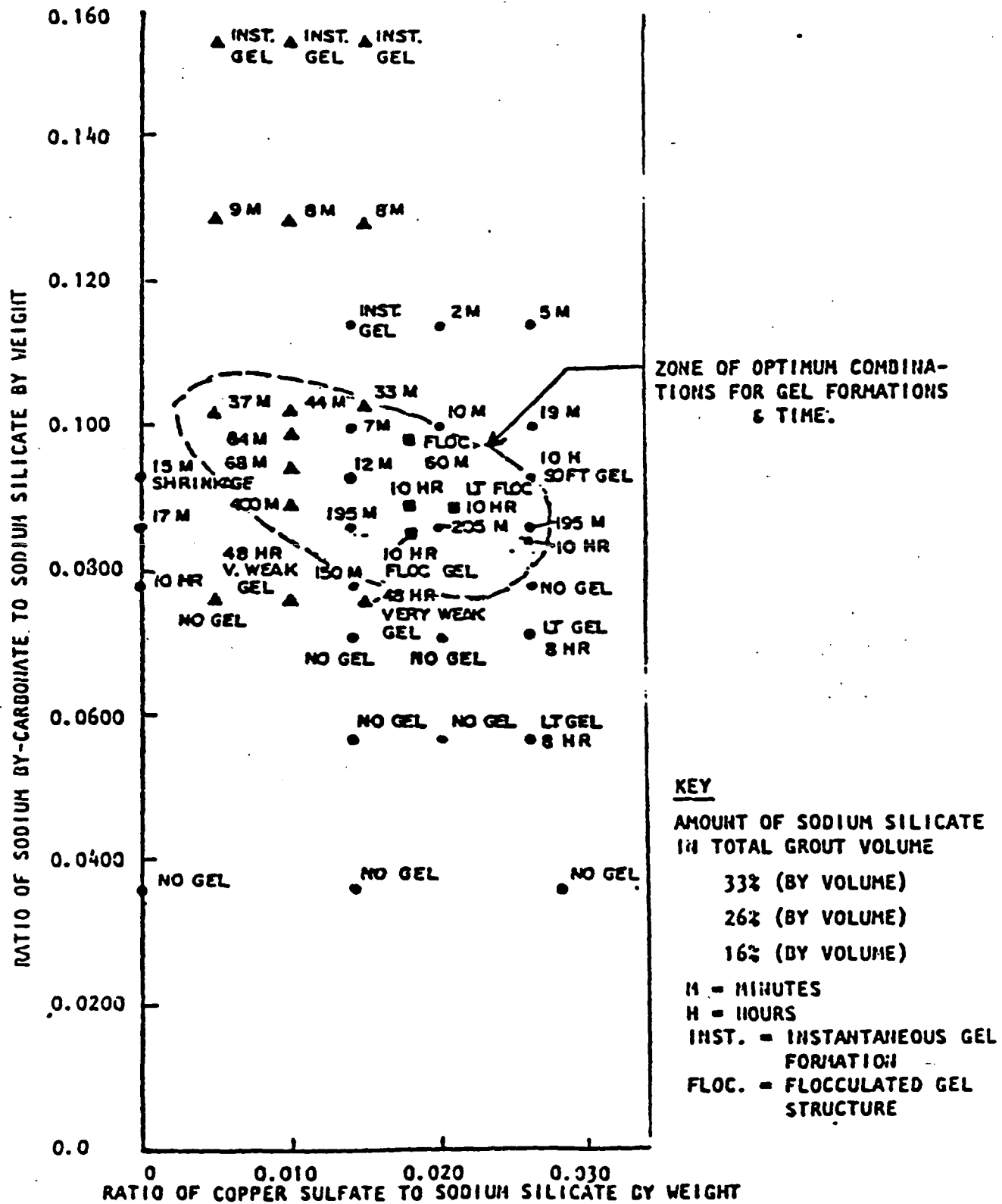


Figure 2: Affect of Various Chemical Mixtures on Gel Formation for Silicate Grout

Evaluation indicated that bentonite/cement or silicate grouts would be most feasible for spill containment. Depending on both the soil and chemical characteristics, one may be more applicable than the other. Both systems are environmentally acceptable, since the bentonite is a natural clay product and may eventually resorb into the soil and the silicate grout may break down with time; thus long term adverse effects will be minimized.

There are several silicate grout formulas in general usage. The silicate grout used in this survey was formed using a mixture of sodium silicate, sodium bicarbonate and a copper sulfate catalyst. Extensive laboratory testing was performed to establish the most feasible dosages. The results are plotted in Figure 2. It is anticipated that this type of presentation will be included in the final systems operation and maintenance manual with instructions for choosing an appropriate mix. Chemical tests to determine the grout's resistance to treatment chemicals were also performed. The results indicated that the silicate grout while resistant to bisulfite, hypochlorite, sodium sulfide and copper sulfate, had very low resistance to acids and relatively low resistance to bases. This was expected because the silicate is an alkaline material and the gel is affected by pH. When a high pH occurs, a bentonite grout would be recommended.

The final output of this effort was to develop an approach for establishing a specific chemical's treatability by *in-situ* techniques. This involved determining if neutralization,

oxidation/reduction or precipitation would detoxify the hazardous material and establishing which type of grout would be most resistant to chemical penetration. These results will be presented in the final report and Operation and Maintenance Manual in tabular form for quick reference.

### Pilot Testing

Based on the results of the laboratory tests, two reaction types and two soil types were chosen for pilot scale evaluation. Precipitation and redox reactions were selected to further define effect of solids formation. Sand and clay soils were chosen so that both flow-through and sealed procedures could be tested on a larger scale. The main objectives of the pilot testing were: 1) to determine if the detoxification procedure was feasible on a larger than laboratory scale and 2) to establish critical parameters such as pumping rate, injector placement and back pressure, for consideration in the development of the final system design.

### Testing Equipment and Procedures

Special test cells were constructed for the two types of tests as illustrated in Figure 3. Both were made from coated plywood, the larger box having heavy reinforcing. Additional tanks, pumps, tubing and mixers were procured and used during the test operations, as needed. The test procedures for the surface and injection treatments were quite different. The surface testing was basically similar to the laboratory tests. The soil and water were compacted in the

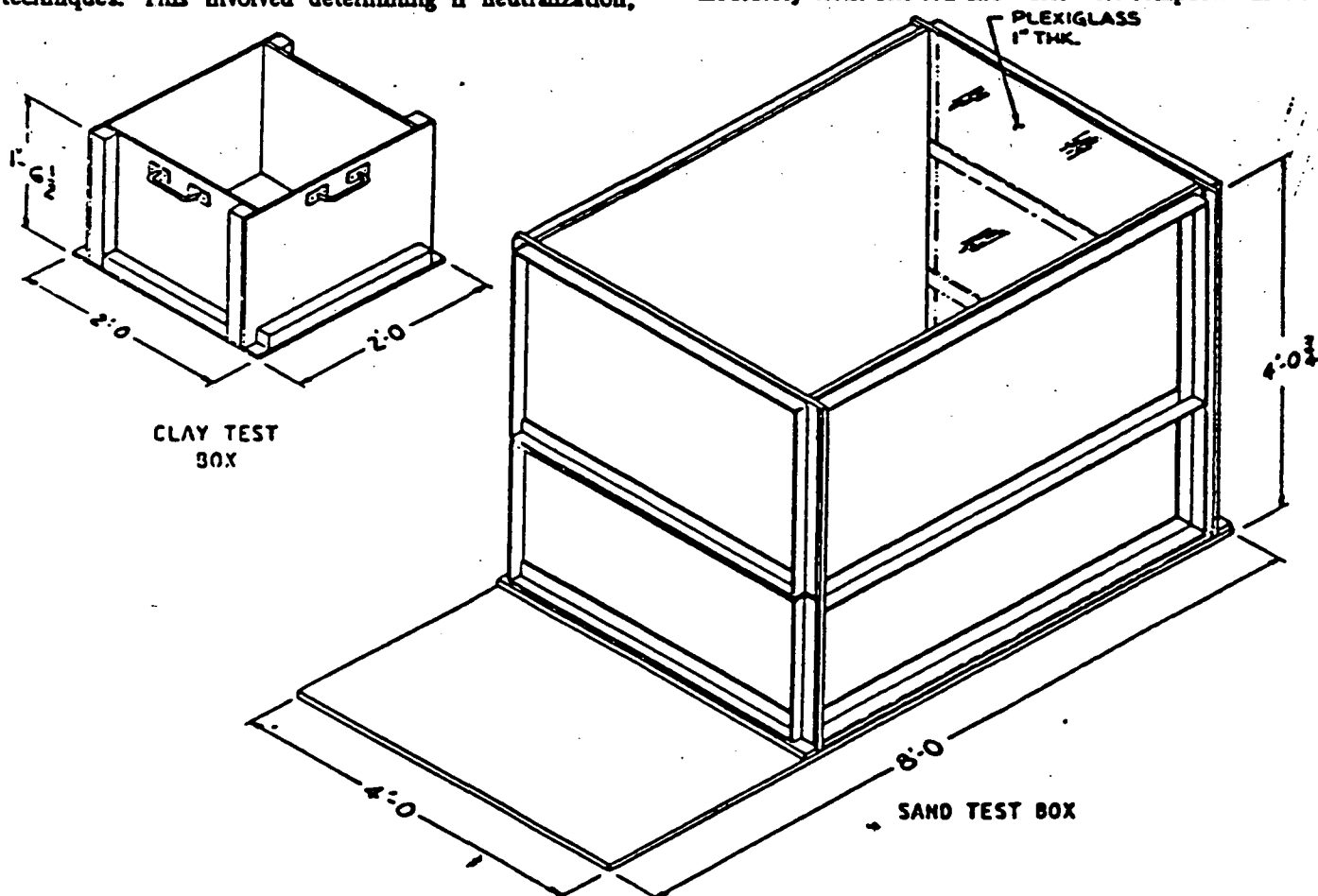


Figure 3: Pilot Test Cells



box to a given bulk density and the specified amount of contaminant was sprinkled over the surface and allowed to migrate. After 24 hours, the reactant was sprinkled on the soil surface and allowed to detoxify the soil for 48 hours. Core samples were taken at specified locations in the box and analyzed for contaminant concentration.

The flow through testing required that the box be filled with 5600-5800 lb of sand which was placed and compacted in 3.5 cm layers to achieve the desired bulk density. Water was added to yield a 5% water content. The contaminant was again placed on the surface, and the reaction was performed the same day as contamination. An injector and wet well were placed on opposite ends of the box and then the specified volume of reactant was forced through the injector into the soil. After the reactant was pumped into the system, a volume of water was injected to rinse the soil of excess reactant. Throughout the pumping period, the wet well was continuously emptied into a separate holding tank. After all liquids were pumped into the soil, core samples were collected and analyzed for moisture content and contaminant concentration.

Two pilot grouting tests were also performed to aid in choosing injector types and establishing anticipated pumping pressures and to define some of the problems associated with grouting. Various mixes of grout were pumped and the resultant grout wall observed and tested, where possible.

#### Results of the Pilot Tests

Data on the percent of contaminant removed in the pilot tests are shown in Table II. This measure of extent of reaction was based on residual concentrations found in the soil as opposed to the total amount of contaminant which had reacted as calculated for the laboratory testing. This percent reaction is generally higher than the contaminant percentages, but for a large system it is a better measure of the overall effectiveness of detoxification. However, direct comparisons to the laboratory results should not be made.

The effectiveness of detoxification for all of the pilot tests was quite high. As expected, the geometry of reactant injection and the shape of the pilot study box affected the detoxification. When evaluating the results of flow-through testing, it was apparent that the detoxification was most effective within a radius of 1.5 ft from the injector. However, detoxification effects did extend beyond this radius. The surface treatment results reflected those predicted from the laboratory testing. The redox reactions were very effective, removing most of the contaminant which was entrained in the surface layers. Precipitation reactions were less efficient than the redox reaction. This can be attributed to the blocking of voids by precipitate formation. Shrinkage cracks which formed when the surface dried allowed more effective reaction in some of the lower layers. However, as with the redox system, the majority of the contaminant entrained in the surface layer was detoxified.

Evaluation of the grout test results indicated that injection of chemical grout on an angle was possible, while grouting near the soil surface was not feasible because of short circuiting caused by grouting pressures being larger than the soil over burden weight. The particulate grout was difficult to handle in the shallow testing box and the

only injection device which proved feasible was one with a single outlet hole.

The pilot tests also indicated: 1) the importance of driving an injector directly into the soil as opposed to boring and then placing the injector, 2) the necessity of a wet well equipped with a self priming pump for liquid removal, 3) the need for pumping systems equipped for pressures up to 80 psi., 4) the requirement for volumes of rinse water was not as critical as originally anticipated, 5) the back-pressure caused by higher void volume loadings of contaminant reduced the forward flow rate significantly and 6) the neutralization chemicals could be added using a multi-holed injector (which allowed for much faster treatment). It was determined that pilot test grout gel times were shorter than in the lab and that the chemical grout injection could be controlled by the volume added while the particulate grout addition was best regulated by pressure in the injection lines.

#### Prototype Design

##### Preliminary Design

After the pilot tests were completed, the design of the prototype system was begun. Much of the information obtained throughout both the laboratory and pilot tests significantly influenced the design. A process and instrumentation diagram is shown in Figure 4 and a layout is shown in Figure 5. The system provides much flexibility for spill cleanup. The grout or chemicals are to be mixed in alternate batches in the two 1500 gal fiberglass tanks. Batching eliminates potential problems associated with exact mixing of grout constituents at the point of injection and thereby allows closer system control.

Two pump types were included. For grouting, positive displacement pumps will provide the most control and the simplest operation, however they were not sufficiently chemically resistant for chemical injection which will be accomplished by the air pumps, available in Hastelloy C. It was also determined that multiple pumps instead of extensive manifolding of injectors would allow more control of the volumes pumped into the soil. If necessary, the injectors can be manifolded in pairs to allow higher pumping rates, however this approach may not always be feasible when difficult soil conditions are encountered. The volume of liquid added is to be metered and totalized, since in most instances the chemical solutions will be added until a calculated amount is pumped into a specified area. The injector will then be withdrawn a certain distance and the pumping process repeated.

The vehicle will be equipped with a diesel-electric generator and an air compressor. An "air-hammer" type device will be used to drive the injectors (1½ in. OD, 1 in. ID) into the ground. Separate multiholed injectors will be used for chemical addition. Since the cost of chemical resistant injectors would be excessive, standard steel pipe injectors will be replaced when they corrode to the point where they are no longer usable. All components would be accessible either on the vehicle or from the side. The controls will be centralized on a panel permanently mounted on the truck. Accessory equipment will include standard test apparatus

to measure soil conditions and chemical concentrations, well points for use as wet wells, some small air pumps to empty wet wells, and a surface holding tank.

Costs are presently being developed and this design may be modified depending upon the complete economic considerations.

Table III: Summary of Pilot Testing Results

Test No.	Media	Test Conditions		Location	Results		
		Containment	% Loading		Avg Cont Conc	Avg Percent Removal (Tot)	Avg Percent Removal (Inj)
1	sand	NaOCl	25	top	411	Cl 85	SO <sub>2</sub> 99.78
				mid	2066	95.2	99.79
				bot	3374	97.6	99.76
4	sand	NaOCl	50	top	2539	Cl 58.3	SO <sub>2</sub> 99.92
				mid	2218	100	99.90
				bot	6606	97.3	99.89
2	sand	CuSO <sub>4</sub>	25	top	1049	Cu 71.5	Cu 89.5
				mid	1253	89.2	89.7
				bot	1262	88.7	88.2
3	sand	CuSO <sub>4</sub>	50	top	2096	Cu 76.7	Cu 88.3
				mid	5791	94.9	97.9
				bot	8530	96.5	97.5
7	clay	NaOCl	25	top	20306	Cl 99.7	-
				mid	413	85.0	-
				bot	28	60.7	-
8	clay	NaOCl	50	top	20306	Cl 99.9	SO <sub>2</sub> 99.9
				mid	413	82.3	99.85
				bot	28	85.7	99.92
9	clay	CuSO <sub>4</sub>	25	top	8197	Cu 75.8	
				mid	2653	99.5	
				bot	86	76.7	
10	clay	CuSO <sub>4</sub>	50	top	8197	Cu 70.6	
				mid	2653	76.0	
				bot	86	76.8	

$\% \text{ Removal } 100 \times = \frac{(\text{concentration of contaminant in soil before treatment} - \text{concentration after treatment})}{\text{concentration of contaminant in soil before treatment}}$

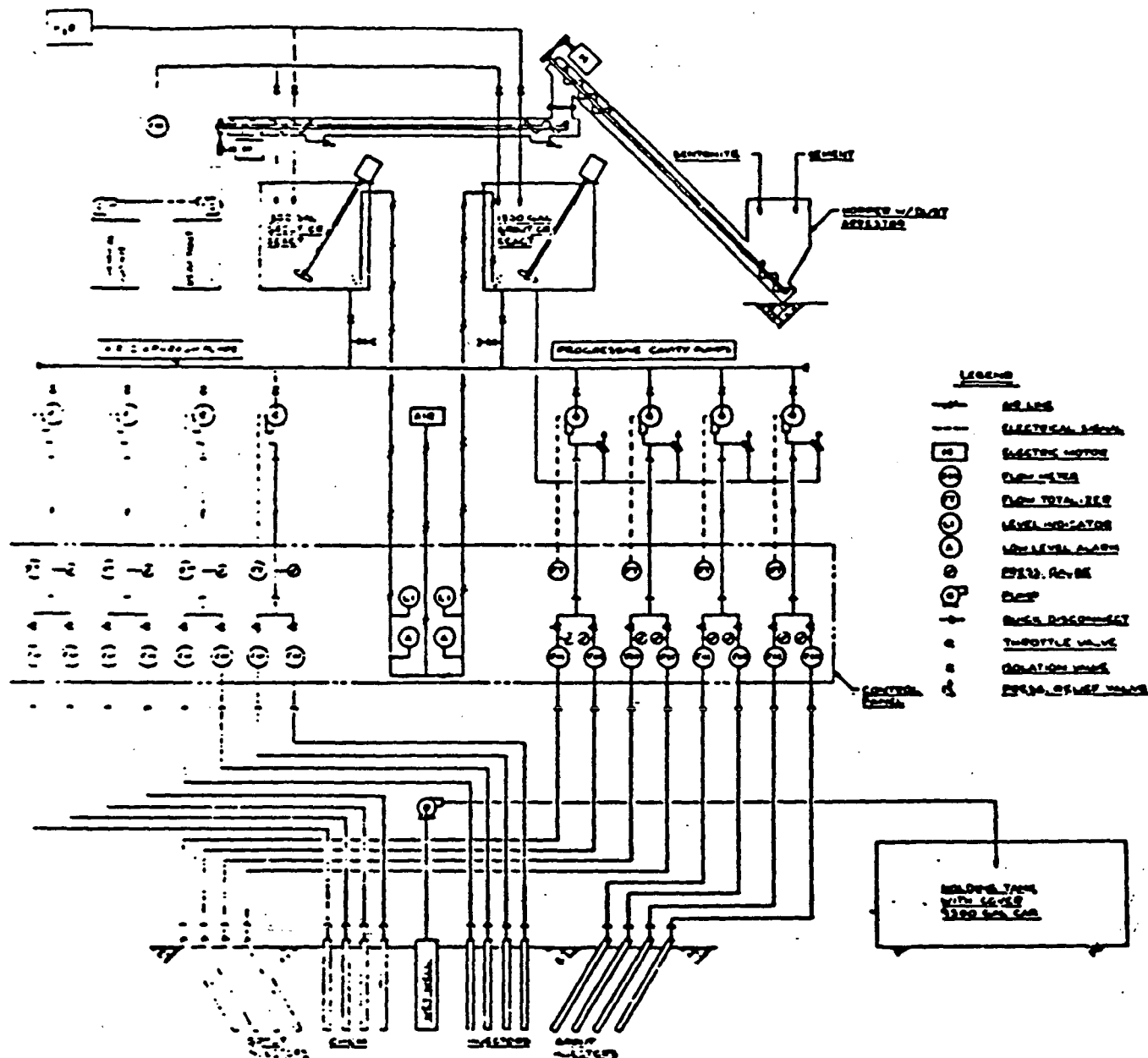


Figure 4: Process and Instrumentation Diagram of Prototype Unit

#### Design Limitations and Decision Matrix

The limitations of *in-situ* detoxification techniques either through surface treatment or direct injection of grout and chemicals must be understood before the prototype equipment is used. When a land spill occurs, alternative approaches should be evaluated and the most time and cost-effective approach for the specific situation chosen. In order to determine if *in-situ* detoxification is most efficient, a decision matrix will be prepared. This matrix will present an approach for evaluating the feasibility of grouting and chemical injection, as well as surface containment and treatment. Among the critical variables are type of chemical

spilled, interaction with the soil, the soil's "groutability" (permeability, void loading, geometry, water table level, etc.), soil volume contaminated, feasibility of excavation and availability of treatment supplies and manpower.

This equipment will not be applicable to all land spills. However, there are many situations in which it will be a feasible technique. The surface treatment approach may be desirable in many cases even if the spilled soil is to be removed and transported to a landfill. This pretreatment will protect equipment and may even allow redefinition of the removed soil as non-hazardous. Grouting in and of itself will be feasible even when direct chemical treatment is not possible. Construction of a grout layer will protect the

groundwater if excavation is incomplete or if rain rinses the area. Although grouting will be limited to relatively coarse grained sand and gravel materials, it is these soils that allow permeation of the contaminant through the soil structure and into the groundwater.

#### Design Changes

Several changes have been made in the initial design concept. Most significant is the addition of a surface treatment technique for fine grained soils. Polymerization was limited to a few possible materials and was determined to be too dangerous to implement in a field situation. The pilot tests indicated that it was critical to meter liquid flows individually so the original design which included a high capacity pump with extensive manifolding of injectors was changed to include a larger number of lower capacity pumps with much less manifolding.

It was also determined that the pumping rates for chemical injection should be relatively low to allow effective reaction. Therefore the overall time required for treatment will be longer than anticipated.

#### CONCLUSIONS

1. An in-place treatment technique has been shown to be an effective land spill cleanup on a laboratory and pilot scale basis.
2. Grouting technology appears to be an effective method to contain spills and thereby minimize potential groundwater contamination.
3. Where small grained soils (silt and clay) preclude the use of injection equipment, a surface treatment using a diluted reactant provides an efficient way to detoxify land spills of applicable hazardous materials.
4. In order to establish the most time and cost-effective method for land spill cleanup, the limitations of the in-place detoxification as well as specific spill variables must be considered.
5. A stepwise approach to containment by grout injection, followed by chemical treatment seems to provide the most flexible treatment system.

#### ACKNOWLEDGMENT

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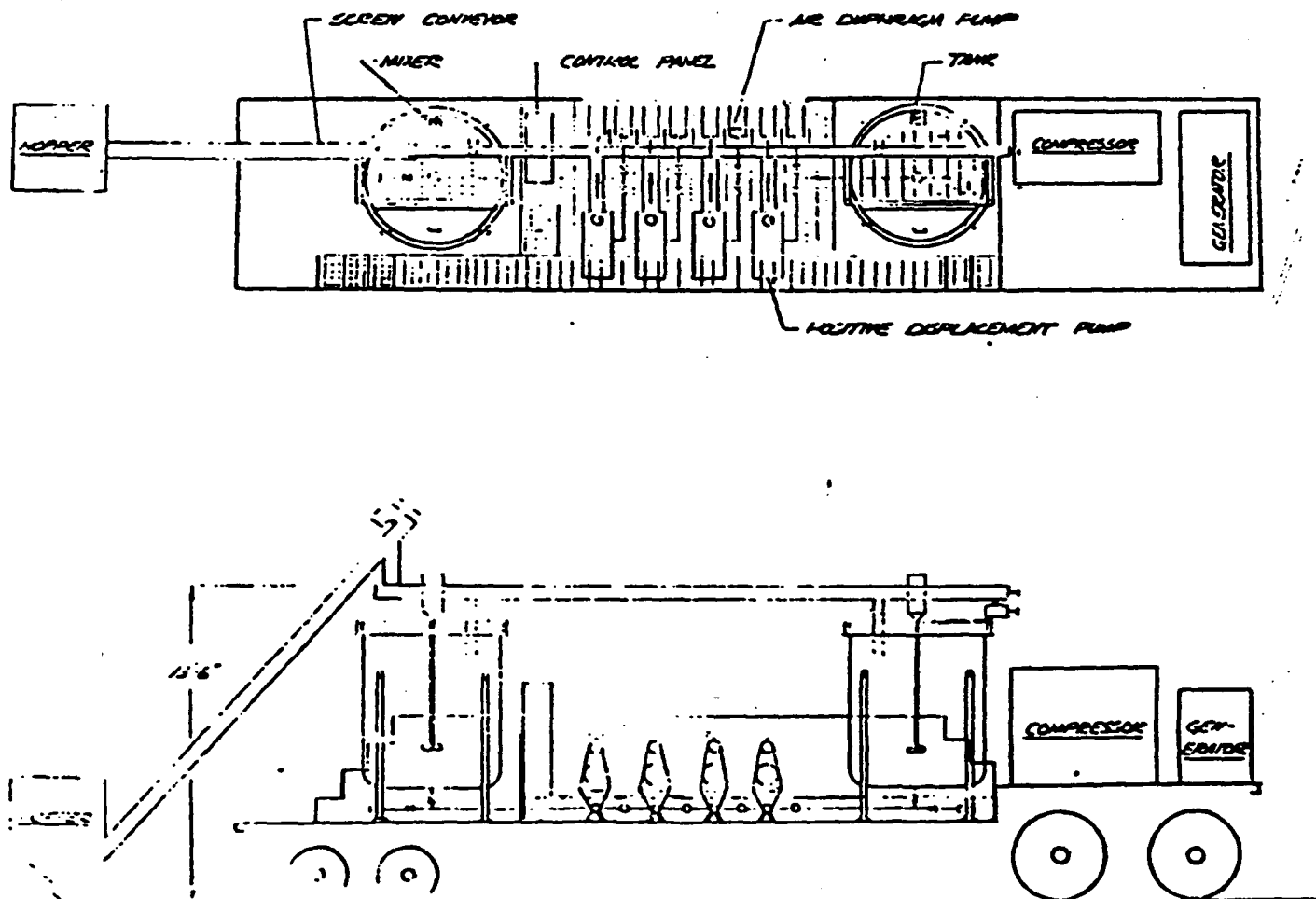


Figure 5: Preliminary Layout of Prototype Unit

# control of **HAZARDOUS MATERIAL SPILLS**

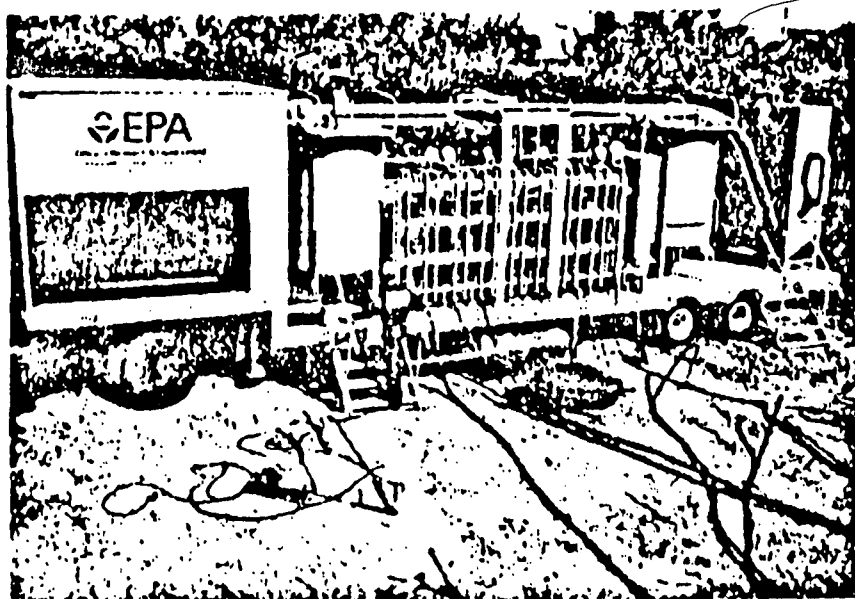
**Proceedings of the 1978 National Conference on  
CONTROL OF HAZARDOUS MATERIAL SPILLS**

**April 11-13, 1978  
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**Sponsored by:  
United States Environmental Protection Agency; United States  
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**In Participation with:  
Oil Spill Control Association of America**

## In-Situ Containment/Treatment System



EPA's Office of Research and Development (ORD) has recently completed construction of a Mobile In-Situ Containment/Treatment Unit designed for field use to detoxify soils which have been contaminated by hazardous materials from spills or uncontrolled hazardous waste sites. EPA develops such equipment to actively encourage the use of cost-effective, advanced technologies during cleanup operations. Once an item of hardware is complete, it is tested under field conditions. After testing, the plans, specifications and other information are made available publicly for the purpose of encouraging commercialization of the new technology. Numerous systems, including a mobile water treatment unit and a mobile laboratory, have been developed by ORD, were duplicated by the private sector, and are now available commercially.

When spills, or hazardous substance releases from waste sites, contaminate soils and threaten nearby surface water or groundwater, an effective method of treating the soil is needed. Excavation and hauling of contaminated soil to a secure landfill is one solution. However, this approach is not practical for those incidents where a large volume of soil is involved. An alternate commercially feasible approach is to flush the soil in place with water. ORD is developing an innovative, improved method for treating contaminated soils in place at reduced cost, in terms of dollars per pound of contaminant removed. The technique employs flushing with additives and detoxification by chemical reaction.

The mobile In Situ Containment/Treatment Unit, shown left, is mounted on a 13.1-m (43-ft) drop deck trailer and includes: a diesel electric generator, an air compressor, mixing tanks, hoses, a solids feed conveyor, pipe injectors, soil testing apparatus, and accessory items. In-situ containment is accomplished by direct injection of grouting material into the soil around the contaminated area in order to isolate the released chemicals. The chemicals are then treated in place by flushing, oxidation/reduction, neutralization or precipitation. Specially prepared solutions of wash water can be delivered into highly contaminated soil through 16 injectors. A vacuum well-point withdrawal system (not shown) creates an artificial hydraulic gradient which draws the wash solution from the injectors through the contaminated soil thereby collecting water-soluble contaminants in the solution. The withdrawal system has granular activated vapor-phase carbon packs for removal of organic vapors released during the withdrawal operation.

The collected chemically contaminated wash solution is processed through a mobile water treatment unit, where contaminants are removed. Fresh chemical additives are then introduced into the cleansed wash solution which is re-injected into the contaminated area. This process is continued until a point of diminishing returns is reached.

For further information, contact Mr. Frank J. Freestone or Mr. Richard P. Traver, Municipal Environmental Research Laboratory, Oil & Hazardous Materials Spills Branch, Edison, New Jersey 08837. Telephone numbers are: (201) 321-6632/6677 (Commercial); 340-6632/6677 (FTS).

## TREATMENT OF SOILS CONTAMINATED WITH HEAVY METALS

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### ABSTRACT

The U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory has initiated a program to evaluate in situ methods for mitigating or eliminating environmental damage from releases of toxic and other hazardous materials to the soils around uncontrolled hazardous waste disposal sites. As part of this program, various reagents suitable for the in situ washing of heavy metal contaminants from soil were tested at laboratory scale. The work was performed on a soil from an actual Superfund site near Seattle, WA. The soil contained five toxic heavy metals often found in hazardous waste site soils: cadmium, chromium, copper, lead, and nickel.

The tests demonstrated that sequential treatment of soil with ethylenediaminetetraacetic acid (EDTA), hydroxylamine hydrochloride, and citrate buffer was effective in removing metals from soil, and all were necessary for good cleanup. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the soil iron oxide-manganese oxide matrix, releasing bound metals, and also reduced insoluble chromates to chromium (II) and (III) forms; and the citrate removed the reduced chromium and additional acid-labile metals. The best removals observed were: cadmium, 98 percent; lead, 96 percent; copper, 73 percent; chromium, 52 percent; and nickel, 23 percent.

### INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) Hazardous Waste Engineering Research Laboratory (HWERL) initiated a program to develop in situ chemical methods for mitigating or eliminating environmental damage from releases of hazardous materials at chemical spill sites and around hazardous waste disposal sites. As part of this program, Science Applications International Corporation (SAIC), under

EPA Contract No. 68-03-3113, investigated chemical methods for in situ cleanup of heavy-metal-contaminated soil.

Toxic heavy metals are frequently found in soil at uncontrolled hazardous waste sites, including lead (15 percent of sites surveyed), chromium (11 percent), cadmium (8 percent), and copper (7 percent) (Ellis and Payne, 1983).

Based on these results, an optimum treatment sequence was designed. Then column tests of the optimum treatment sequence were conducted.

The column studies evaluated metal removal under gravity flow conditions, with analysis of soil and duplicate analysis of leachate after each treatment. A three-agent sequential extraction was tested using five pore volumes of the optimum concentration and pH for the EDTA solution to remove most metals, followed by hydroxylamine hydrochloride to reduce any hexavalent chromium to trivalent, and to reduce any soil iron or manganese oxides to release any bound metal. Citrate buffer was then used as a final acidic leaching agent. The same metal-contamin-

ated soil was used for all tests; all initial concentrations for each metal were the same (see Table 1).

Samples were analyzed for trace elements by atomic adsorption spectrophotometry (AAS) using flame or graphite furnace procedures. Analyses by the method of standard additions were routinely performed along with standard calibrations. When the two calibration curves deviated significantly, calculations of sample concentrations were based upon the standard addition calibration; when they were the same, a combination of the standard addition/standard calibration was used. Sample blanks and National Bureau of Standards (NBS) standards were analyzed in the same manner as the samples.

TABLE 1. SINGLE AGENT SHAKER TABLE EXTRACTION EFFICIENCIES

Soil Metals (ppm)	<u>Cd</u> 47	<u>Cr</u> 349	<u>Cu</u> 219	<u>Ni</u> 214	<u>Pb</u> 2,480
EDTA (0.1 M @ pH 6) % Extracted	114	24	62	14	106
Hydroxylamine hydrochloride (0.1 M in acetic acid) % Extracted	86	32	43	20	80
Citrate buffer (0.1 M @ pH 3) % Extracted	77	24	48	14.5	65
Pyrophosphate (0.1 M) % Extracted	5.4	9.6	29	2.9	9.7
DPTA (0.005 M in 0.1 M triethanolamine) % Extracted	59	2	48	2	67



Conventional remedial methods for sites containing heavy metals include excavation followed by land disposal and groundwater pumping and treatment. The use of excavation and land disposal is meeting with increased opposition not only because of high cost but also because the contaminated soil is simply transferred to another location. Also, pump and treatment methods are costly and are not effective for removing contaminants sorbed to the soil. In situ treatment of toxic metals in soil and groundwater offers a potentially cost-effective remedial alternative. However more research is needed before the in situ methods can be implemented in the field.

The objective of this project was to select the most promising in situ treatment method for metals and evaluate the method through laboratory studies. The study was limited to methods suitable for in situ treatment of cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and nickel (Ni). These metals are found frequently at hazardous waste sites and are among the most toxic. Methods that are effective with these metals might also be suitable for treating other heavy metals found at hazardous waste sites.

Potential in situ treatment methods for metals include methods that immobilize the metals in soil by means such as precipitation and methods that solubilize and remove the metals from the soil. Methods that solubilize and remove the metals offer an advantage over immobilization methods because the need for long-term monitoring is eliminated. Immobilization methods, on the other hand, simply reduce the concentration of dissolved species. The potential exists for resolubilization of the metals through subsequent natural chemical reactions; therefore, the site must be continually monitored.

Methods for mobilizing metals in soils involve the use of dilute weak acids, bases, or aqueous solutions of chelating agents. Considerable research on a laboratory scale has already been conducted on the use of chelating and other complexing agents for selectively removing metals from soil.

This research demonstrated different degrees of extractability of any given heavy metal from soil. The extractability has been described according to which type of extraction agent will remove the bound metal which corresponds to a specific soil-metal binding mechanism or the chemical state of the metal. For example, soluble heavy-metal salts are extractable with water; metals bound to the soil organic fraction are extractable with aqueous alkaline buffers such as tetrasodium pyrophosphate ("tetrapyrophosphate"); and metals occluded in the iron and manganese oxide fraction of the soil are released by reduction of the oxides with hydroxylamine hydrochloride. These techniques, if developed further, could be used for the cleanup of contaminated soil at hazardous waste sites.

### Laboratory Task Description

Laboratory studies were conducted to determine whether in situ cleanup of heavy-metal-contaminated soil by treatment with chelating solutions or acidic buffers was possible. The soil used in the studies was collected from the Western Processing, Inc. Superfund site, near Seattle, WA. Previous analysis of this soil (Repa, et al, 1984) had shown high levels of cadmium, chromium, copper, and lead (>10 ppm).

The laboratory task consisted of: (1) soil characterization; (2) laboratory equilibration (shaker table) experiments designed to evaluate treatment methods (i.e., single agent treatment vs sequential treatment with several agents) for metal removal; and (3) soil column tests to evaluate cleanup efficiency under gravity flow conditions.

Based on a review of the literature, the chelating agent ethylenediaminetetraacetic acid (EDTA), the reducing agent hydroxylamine hydrochloride, and the acidic citrate buffer were identified as suitable agents for testing. Shaker table equilibration studies were conducted in which various combinations of the above treatment agents (10:1 w/w agent solution: soil), either singly or in sequence, were shaken with the contaminated soil in a closed container on a vibrating platform.

## RESULTS AND DISCUSSION

### Soil Characterization

Soil permeability measured in the laboratory was approximately  $5 \times 10^{-5}$  cm/sec. The grain size distribution was determined by wet and dry sieve procedures and pipet analyses on organic-free soil after a hydrogen peroxide wash. Approximately 75 percent of the soil was in the silt and clay range. This probably caused the rather slow percolation rate. X-ray diffraction analysis showed alpha-quartz and feldspar to be the only measurable constituents of the soil. No measurable amounts of crystalline aluminum oxide forms were present. The total carbon content of the soil averaged  $16,400 \pm 709$  ppm by weight (1.64 percent). This Intermediate level of carbon corresponds to the phenols and other organic compounds found in the soil.

The cation exchange capacity (CEC) of the soil was also determined. The results were 13 and 8.2 milliequivalents per 100 g for bulk and organic-free soil, respectively. These results are quite low and indicate an absence of mineralogic clay in the soil. The pH and Eh measurements (made in triplicate) yielded an average soil pH of 7.39 and an Eh of +0.198 v (electron potential,  $pe = +7.01$ ), revealing a neutral, slightly oxidizing soil. The iron and manganese oxide mean concentrations were 15,000 and 291 ug/g, respectively. The carbonate results yielded an average value of 1.42 meq/g as bicarbonate.

The results of the determination of heavy metals of interest in Western Processing soil were as follows (in ug/g): cadmium (47), chromium (349), copper (219), iron (30,200), manganese (1,690), nickel (214), and lead (2,480). These values were compared with the concentrations of the metals in the treatment solution to assess percent removal of metals by the treatment.

### Shaker Table Studies

In the single shaker table extractions using EDTA at different concentrations and pH values, the 0.1 M solution was much more effective in metal removal than the 0.01 M solution. The pH trends, however, were not so clear cut. A pH of 6 was chosen as the optimum because it afforded slightly better chromium removal than that obtained at pH 7 or 8; EDTA is more ionized at pH 6. This pH and concentration combination was used in subsequent studies.

The results of the EDTA, hydroxylamine hydrochloride, acidic buffer, and diethylenetriamine pentaacetic acid (DTPA) single-method shaker table extractions (Table 1) showed that EDTA was the best single extraction agent for all metals. However, hydroxylamine hydrochloride was more effective at chromium extraction.

Results of the two-agent sequential extraction (Table 2) indicated that the EDTA was much more effective in removing metals than the weaker agents often used to characterize the mechanism of binding of metals to soils. Thus, weaker extraction techniques (magnesium chloride, potassium fluoride, acetate buffer, tetrapyrophosphate) can be eliminated if just an EDTA solution is used.

The results of the three-agent sequential extraction studies (Table 3) showed that, compared to bulk untreated soil, this extraction scheme removed nearly all the lead and cadmium, 73 percent of the copper, almost 52 percent of the chromium, and only 23 percent of the nickel. Overall, this scheme was shown to be better than three EDTA washes, better than switching the order of EDTA and hydroxylamine hydrochloride, and much better than simple water washes, in subsequent three-agent tests. However, the EDTA washing alone might be used with only a slight decrease in removal efficiency.

TABLE 2. TWO-AGENT SEQUENTIAL SHAKER TABLE EXTRACTION EFFICIENCIES

Soil Metals (ppm)	<u>Cd</u> 47	<u>Cr</u> 349	<u>Cu</u> 219	<u>Ni</u> 214	<u>Pb</u> 2,480
EDTA (0.1 M @ pH 6) % Extracted	83.6	24.4	77.6	10.8	84.6
Magnesium chloride (1 M) % Addnl. Extracted	1.02	0.11	2.22	1.47	0.29
EDTA (0.1 M @ pH 6) % Extracted	95.3	28.9	56.4	11.6	85.3
Potassium fluoride (0.5 M) % Addnl. Extracted	1.17	0.37	1.27	0.47	0.85
EDTA (0.1 M @ pH 6) % Extracted	119	24.3	76.3	10.7	117
Acetate buffer (1 M @ pH 5) % Addnl. Extracted	2.36	2.36	1.18	1.89	1.41
EDTA (0.1 M @ pH 6) % Extracted	75.3	24.2	59.6	9.72	98.2
Tetrapyrophosphate (0.1 M) % Addnl. Extracted	23.9	5.59	3.11	0.99	1.20

TABLE 3. CUMULATIVE SHAKER TABLE  
THREE-AGENT SEQUENTIAL EXTRACTION EFFICIENCIES (%)

Soil Metals (ppm)	<u>Cd</u> 47	<u>Cr</u> 349	<u>Cu</u> 219	<u>Ni</u> 214	<u>Pb</u> 2,480
1) EDTA (0.1 M @ pH 6)	87.2	24.6	63.0	13.8	87.1
2) Deionized water	92.5	27.5	67.4	15.4	92.6
3) Hydroxylamine hydro- chloride (0.1 M in acetic acid)	96.3	34.0	69.8	19.8	94.8
4) Deionized water	96.6	34.5	70.1	20.6	94.9
5) Citrate buffer (0.1 M @ pH 3) (=Total % Extracted)	98.4	51.9	73.0	23.0	96.4

### Column Studies

The results of the metals extraction achieved during column tests are shown in Table 4.

The pattern of removal for each metal was somewhat unique. Lead appeared to be removed easily by the EDTA; further removal occurred with citrate. Cadmium was removed by EDTA and also by hydroxylamine hydrochloride; removal was slightly improved with the other treatments. Copper was removed only by EDTA; the other treatment methods had little effect on removal. The data indicated a generally high extraction efficiency for EDTA. The analysis of metal remaining in soil versus pore volume and type of treatment indicated that lead and cadmium concentrations in soil decreased steadily from the beginning of treatment to the end. The pattern for the other metals was similar, but with slight differences, probably due to random sampling or analytical errors. Chromium appeared to exhibit a pattern of migration

from the top to the middle of the column, followed by rather ineffective removal. Nickel showed a similar trend. These latter results suggest that more pore volumes of each treatment solution (e.g., 10 rather than 5) would improve the removal, probably to the level of extraction efficiency achieved in the shaker table tests.

### CONCLUSIONS

The results of the shaker and soil column studies permit a number of conclusions about the potential feasibility of in situ cleanup of soil contaminated with heavy metals.

### The Cleanup Efficiency of the Soil Treatment Agents

The various treatment-agent tests showed that there are definite differences in efficiency of the agents that vary with the heavy metal.

TABLE 4. THREE-AGENT SEQUENTIAL EXTRACTION EFFICIENCIES:  
SOIL COLUMN TESTS

Soil Metals (ppm)	<u>Cd</u> 47	<u>Cr</u> 349	<u>Cu</u> 219	<u>Ni</u> 214	<u>Pb</u> 2,480
Water					
% Extracted by water	0.2	0	0	0	0.1
EDTA (0.1 M @ pH 6)					
% Extracted by agent	60.5	12.2	47.1	6.8	60.1
Hydroxylamine hydrochloride (0.1 M in acetic acid)					
% Extracted by agent	23.8	8.9	0.7	8.7	2.3
Citrate Ruffer (0.1 M @ pH 3)					
% Extracted by agent	3.6	12.2	0.2	4.8	8.8
Water Wash					
% Extracted by water	0.4	1.1	0.1	0.5	0.5
Total % Extracted:	88.5	34.4	48.1	20.8	71.8

The preliminary tests of single heavy-metal treatment agents provided the optimum concentration and optimum pH for EDTA treatment. The more concentrated solution, 0.1 M EDTA, is clearly more effective. A pH of 5 is probably as effective as pH 6, but either is more effective than pH 7 or above.

The two-agent tests demonstrated that weaker agents do not remove any of the metals of interest more efficiently than EDTA alone.

The three-agent tests demonstrated that EDTA, hydroxylamine hydrochloride, and citrate buffer are all necessary for good cleanup of the soil. The EDTA chelates and solubilizes all of the metals to some degree; the hydroxylamine hydrochloride probably reduces the iron oxide-manganese oxide matrix, releasing bound metals, and also reduces insoluble chromates to chromium (II) and (III) forms; and the citrate removes the reduced chromium and additional acid-labile metals. The chelating agent/reducing agent/acidic citrate buffer combination appears to be very effective in heavy-metal cleanup.

The three-agent test with just EDTA demonstrated that cleanup of cadmium and chromium is significantly better with the sequential EDTA/hydroxylamine/ citrate than with three treatments of EDTA alone. However, EDTA alone appears to be sufficient for removing the lead and copper; although the nickel removal was poor with EDTA alone, the treatment with all three agents showed no better removal.

The three-agent test with hydroxylamine hydrochloride first, followed by EDTA and then citrate, demonstrated that the use of a chelating agent following the reduction step does not improve the cleanup.

## Effects of the Soil Characteristics on the Cleanup Efficiency

The efficient cleanup of the heavy-metal contamination in the soil was probably facilitated by the low cation exchange capacity (CEC) of the soil. However, the presence of iron and manganese oxides apparently interferes with heavy metal removal by EDTA; reducing these oxides was necessary to remove all the cadmium.

## Feasibility Studies Using Shaker and Column Tests

The shaker studies were quick and effective screening tests for estimating treatment-agent efficiency. The column tests, although more difficult and time-consuming more closely represent the behaviour that might be expected if the agents were used for in situ cleanup of an actual contaminated site. The column tests model cleanup under gravity flow conditions through soil with a permeability somewhat similar to the native soil. If time had permitted longer soil column tests, extraction efficiencies would probably have been similar to the shaker table test results. Both the shaker and column tests are very useful for studying the feasibility of potential soil cleanup agents.

## REFERENCES

1. Ellis, W. D., J. R. Payne, and G. D. McNabb. 1985 Treatment of Contaminated Soils with Aqueous Surfactants. EPA/600/S2-85/129 U. S. Environmental Protection Agency.
2. Repa, E. W., E. F. Tokarski, and R. T. Eades. 1984. Draft Final Report. Evaluation of the Asphalt Cover at the Western Processing, Inc., Superfund Site. EPA Contract #68-03-3113. U.S. Environmental Protection Agency.

## STUDENT PAPER COMPETITION

To encourage student participation in the Association and to recognize outstanding research at New England colleges and universities, NEWPCA recently held its fourth annual student paper competition. Judges under the direction of Mr. William VanBlarcom reviewed a number of entries and selected four finalists who presented their papers at the January 28 session of the NEWPCA 1985 winter meeting. Based on the quality of the written papers and the oral presentations, judges selected Camille C. Connick as winner of the \$200 cash award. Other finalists, each of whom received a \$100 cash prize, were Robert C. Backman, Northeastern University (The Treatment of Dairy Wastewater by the Anaerobic Up-Flow Packed Bed Reactor); Akbar Johari, University of Rhode Island (A Pilot Study of the Responses of Powered and Granular Activated Carbon in the Removal of Shock Loadings of Synthetic Organics); and Eid Alkhatib, University of Rhode Island (Treatment of a Combined Petrochemical Industrial Waste Stream for Reuse).

Presented herein is Ms. Connick's winning entry. Copies of the other finalists' papers are available from NEWPCA.

## MITIGATION OF HEAVY METAL MIGRATION IN SOIL

BY CAMILLE C. CONNICK\*

### INTRODUCTION

The uncontrolled or accidental contamination of the environment with hazardous materials through chemical spills and hazardous waste site releases necessitated the enactment of the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) often called Superfund. The purpose of one Superfund program, the U.S. Environmental Protec-

tion Agency's (USEPA) Chemical Countermeasures Program (CCP), is to investigate in-situ chemical methods for mitigating or eliminating environmental damage from releases of toxic and other hazardous materials to the soils around uncontrolled hazardous waste disposal sites and from spills of hazardous chemicals to still or relatively slow moving surface water bodies. Because it is recognized that the environmental impact of hazardous material spills and releases can be worsened by adding chemicals indiscriminately, the CCP is intended to provide guidance and define appropriate treatment techniques.

This investigation of in-situ treatment of soils contaminated by heavy metals was performed as a joint research project with the USEPA and Northeastern University. The study involved the determination of adsorption isotherms for the heavy metals and specified soil, as well as the desorption behavior of the metal using water rinses, water and surfactant rinses, and water plus chelating agent rinses. The first phase consisted of shaker table agitation (equilibration) to determine maximum adsorption of metal to soil. The second phase involved the use of soil column studies to evaluate the maximum adsorption/desorption of the metal. A simulated spill of heavy metal-laden liquid for soil contamination was followed by successive treatment rinses under gravity flow conditions to determine removal efficiencies. Influent and effluent pH, metal content, permeability rates and variations, and chemical oxygen demand (COD) were monitored during the study to determine metal removal efficiencies and the occurrence of unanticipated reactions.

The results of this research and results from a similar study investigating the use of in-situ treatment of soil contaminated with hazardous organic constituents are to be used as the basis for development of pilot scale testing in a chemical additive treatment tank at USEPA's Oil and Hazardous Materials Spills Environmental Test Tank (OHMSETT) facility in Leonardo, NJ.

### BACKGROUND INFORMATION & LITERATURE REVIEW

The soil used in the chemical countermeasure study was selected based on its frequency of occurrence at Superfund sites in New Jersey and also its availability for excavation in ar

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uncontaminated condition. The soil selected for the research was Typic Hapludult of the Freehold Series. It is described as fine to coarse loamy, low clay content (< 15%) and a high content (> 15%) of fine, medium, and coarse sands, plus coarse fragments up to three inches. Only soil from the B horizon was intended to be used so as to attempt to model soil containing contaminant releases which are greater than two feet underground. Such releases usually affect large volumes of soil, making excavation and land treatment methods and equipment uneconomical and physically impractical.

The characteristics of soil have a tremendous effect on the efficiency of various treatment processes for contaminant removal. Grain size, specific gravity, density and water content characterizations determine available void volume, soil porosity, and permeability which directly affect both pollutant and treatment considerations. Buffering capacity and soil pH affect neutralization and possibly precipitation reactions resulting in enhanced or decreased water solubility of products. High organic soils (such as peat) have a higher affinity for non-polar organics, which can affect in-situ treatment with surfactants and/or solvents. A high cation exchange capacity (CEC) observed in some clays and fine silts can attenuate treatment of metals and metal salts. A high mineral content can affect neutralization and redox treatment of acid spills. In some cases, treatment of a caustic spill with acid might increase resolubilization of inherent metal species. Interfering reactions can result in a need for a greater volume of the treatment reagent, increasing wastewater treatment requirements.

A complete chemical and physical analysis of the soil was performed prior to the start of the studies by JRB Associates'. The mineralogical composition of Clarksburg soil was determined using X-ray diffraction studies. Quartz is the major phase, representing at least 98 percent of the total weight. No measurable amounts of clay minerals appeared in the sample which accounts for the relatively low CEC of 8.6 mg Na/100 grams. The organic carbon analysis showed only 0.12 percent.

The average permeability when compacted to a density of 107 lbs/cu ft was  $1.5 \times 10^{-3}$  cm/sec. The natural moisture content was 10 to 12 percent.

### *Metal Contaminants*

The heavy metals (Cd, Cu, Pb, Ni, Zn) selected for use in the research were chosen based on frequency of occurrence in soil at USEPA Region II Superfund sites and concern for toxicity to human health and the environment. The metals Cd, Cu, Pb, Ni and Zn were detected in soil at 4, 3, 7, 3 and 5 of 50 sites reviewed, respectively, at concentrations ranging from 2,000 to 30,000 ppm. The toxicity of these metals in such elevated concentrations is apparent when compared to the acceptable concentrations specified by USEPA water quality criteria and the reported Rat Oral LD<sub>50</sub> of these cations (Table 1).

Table 1. WATER QUALITY AND TOXICITY LIMITS

<u>Metal</u>	<u>USEPA Water Quality Criteria, ppm</u>	<u>Rat Oral LD<sub>50</sub> mg/kg</u>
Cd	0.01	88 (CdCl <sub>2</sub> )
Cu	1.	265 (CuCl <sub>2</sub> )
Pb	0.05	—
Ni	0.0134	105 (NiCl <sub>2</sub> )
Zn	5.	350 (ZnCl <sub>2</sub> )

### *Chemical Countermeasures*

A literature review was performed to investigate the available methods for in-situ treatment of contaminants. Three types of treatment were reported for either removing or fixing contaminants in soil including: use of surfactants to solubilize and flush contaminants; use of chemicals for in-situ metal precipitation; and use of chelating agents for metal extraction.

Surfactants were reported as being successful in the recovery of gasoline from soils and as having the ability to solubilize organic materials that were previously only solubilized in organic

solvents<sup>1</sup>. Several analyses were performed by JRB Associates<sup>1</sup> to determine the appropriate concentration of surfactant/water solution which would provide adequate pollutant extraction efficiency and yet not inhibit soil-column flow. A mixture of two non-ionic surfactants, one percent Adsee 799 (Whitco Chemicals) and one percent NP90 (Diamond Shamrock) in tap water was chosen as the chemical countermeasure to be tested for in-situ treatment. Both surfactants, Adsee 799 and NP90, are considered non-toxic. They are often used for treating farmland to enhance percolation of fertilizers and irrigation waters. The surfactants are biodegradable and the potential for excessive accumulation or hazardous effects is minimal, which further enhances their applicability for in-situ removal of organic contaminants. The high organic content of the surfactant allows one to monitor its concentration in soil leachate by performing analyses such as the COD determination of organic content.

The use of sodium sulfide for in-situ metal precipitation and the use of ethylenediaminetetracetic (EDTA), a chelating agent for metal extraction were reported as successful in fixing and removing heavy metal contaminants in soil. Chelating agents are compounds or ligands (generally organic) that coordinate or bond a metal ion in more than one position. This bonding of the metal ion, in most cases results in its deactivation. The metal is no longer able to react chemically and is, therefore, made less toxic<sup>2</sup>. Competition from hydrogen ions usually occurs at low pH levels. A decrease in pH always produces a shift towards disassociation of the complex ion (an increase in free metal concentration). Organic chelating agents may be divided into two classes, sequestrants and precipitates. Sequestrants form chelate complexes which are soluble in water; therefore, the compound still remains distributed throughout the water body although in a less toxic form.

EDTA is a sequestering agent used in metal cleaning, preservation of canned fruits and vegetables, leather tanning, and in medical treatment of Zn, Fe, Ni, Pb, and Hg poisoning. EDTA is generally applied as a soluble sodium salt along with a buffer solution such as ammonia ammonium nitrate to maintain a pH of

9 to 10. Since the effectiveness of the chelating agent EDTA is pH dependent, the buffer solution was prepared so as to maintain a pH of 9 to 10 when subjected to the acidity of the soil system at the time of treatment and during the displacement of hydrogen ions as the EDTA reacted with the metal cations in the soil system<sup>3</sup>. A 0.144 M concentration of disodium EDTA was selected as the chemical countermeasure to be tested in this research along with the prescribed surfactant combination supplied by JRB Associates and tap water<sup>1</sup>.

### EXPERIMENTATION METHODS AND MATERIALS

The laboratory study conducted to evaluate the effectiveness of the chemical countermeasures included shaker table agitation and gravity flow soil column studies. To insure data accuracy replicate leachate samples were analyzed along with blank samples (non-contaminated soil mixed with deionized water) for each run during shaker table analysis and column tests. All glassware, plastic ware, columns, storage vials, and any instruments used in the study were acid cleaned (1+1 HNO<sub>3</sub>) and rinsed with deionized water where feasible. Control samples of metal contaminants were placed in shaker table bottles and a column to evaluate the extent of the cation adsorption onto the experimental apparatus throughout the course of the study.

#### Shaker Table Studies

Four different concentrations, as shown in Table 2, were prepared for each metal using a solution of the sulfide or acetate salt of the metal with deionized water. The selection of the metals

Table 2. METAL CONCENTRATIONS FOR SHAKER TABLE ADSORPTION STUDY

<u>Metal (Source Compound)</u>	<u>Concentrations, mg/l</u>			
Cadmium (Sulfate)	40,000	4,000	400	40
Copper (Sulfate)	2,000	200	20	2
Lead (Acetate)	20,000	2,000	200	20
Nickel (Sulfate)	20,000	2,000	200	20
Zinc (Sulfate)	30,000	3,000	300	30



concentrations was based on the review of the data on average contaminant concentrations found in Superfund sites. The purpose of various concentrations of the specified metals during the adsorption shaker analysis was to determine Freundlich and Langmuir isotherms which allow determinations of compound-specific soil/water partition coefficients.

Seven pyrex bottles for each of the specified concentrations of the five metals were agitated with 100 ml of the metal solution and 10 grams of the soil. Agitation time ranged from 15 minutes to 48 hours with samples removed at intervals of 15 min, 30 min, 1 hr, 3 hr, 6 hr, 12 hr, 24 hr and 48 hr for analysis. The shaker table was operated at 180 rpm throughout the analysis to insure complete mixing of the soil in the metal solution (Figure 1). pH values of the initial metal solution prior to mixture with the soil and pH of each liquid sample from the adsorption analysis were

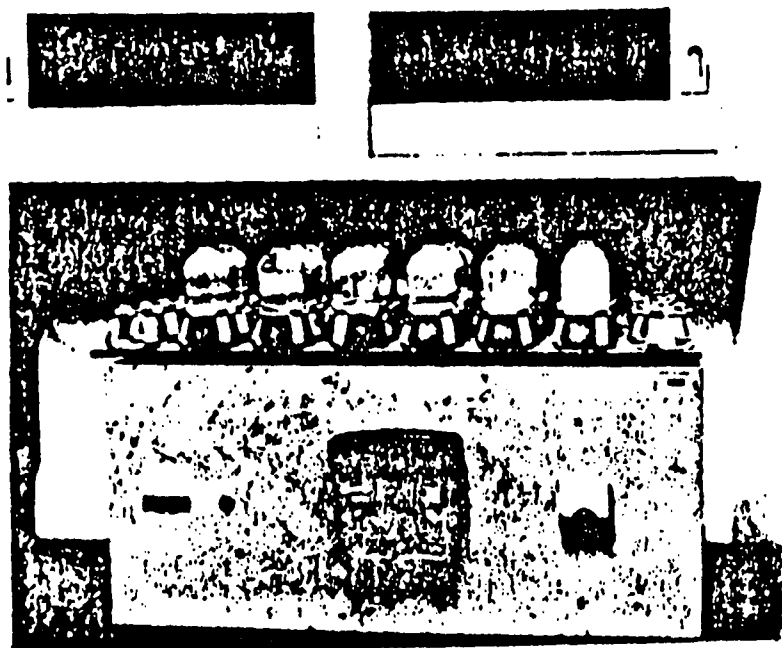


Figure 1. SHAKER TABLE ADSORPTION STUDY

recorded. Samples removed at the specified times for each metal and their respective concentrations were filtered using a Vacuum Pump Millipore Filter Apparatus and a 0.45-micron filter pad placed in a sample vial and acidified to a pH of 2 with 1+1 HNO<sub>3</sub>.

Soil samples from the 48-hour time interval for each metal and its respective concentrations were digested using the Nitric Acid Digestion Procedure (*Standard Methods*, 302D, 15th Ed.) The purpose of the digestion was to determine the maximum quantity adsorbed on the soil following the longest contact period. Metal content of each sample was determined using a Perkin Elmer 560 Atomic Absorption Spectrophotometer (AA). Data from the adsorption analysis using the shaker table were presented in the form of plots of percentage of contaminants in liquid samples versus time. These data were used to obtain the adsorptive capacity of the soil at a given contaminant concentration. Plots of concentration adsorbed per unit weight versus residual concentration were used to obtain adsorption isotherms.

#### Soil Column Studies

Column tests were conducted for each of the five metal contaminants and a mixture of Cd, Cu, Ni, and Zn to simulate field contamination and cleanup using the specified chemical countermeasures, under gravity flow conditions. The custom-fabricated soil columns used in this study were 32-inch (81.28-cm) long clear plexiglass cylinders with an inside diameter of 2.75 inches (6.985 cm). Both ends of the column were fitted with a plexiglass cap with 1-inch (2.54-cm) diameter holes. A 2.5-inch (6.35-cm) diameter, 0.25-inch thick perforated plastic disk was placed at the base of each column to prevent the loss of soil during the analysis. The caps were held in place with four nuts attached to support rods running from column top to column bottom. Teflon tubes connected to plastic fittings threaded into the end caps allowed the introduction of aqueous solutions and the collection of effluent samples. Tubes at the base of the columns were placed into one-liter plastic containers for the collection of effluent samples during column rinsing. An aqueous solution contaminant or treatment rinse was introduced at the top of each column in

premeasured aliquots in such a manner as to minimize the disturbance of the surface soil structure (Figure 2).

#### Column Packing

A plug of soil weighing 0.73 pounds (331 grams) was brought to the field moisture content of 11 to 12 percent and added to the column. It was packed in 2-inch (5.1-cm) lifts using a custom-made controlled-drop hammer compactor designed to fit inside the column (Figure 3.)

This procedure was repeated for a total of nine lifts per column to achieve a soil height of 18-inches (45.72-cm), a total volume of 106.9 cubic inches (1752.3 cc) and a total mass of 6.6 pounds (2979 grams). Records were maintained for each plug of soil that was added to each column. Soil weight, packing depth, number of taps required, and compaction data (from the pocket penetrometer) were monitored for uniformity. The columns were packed

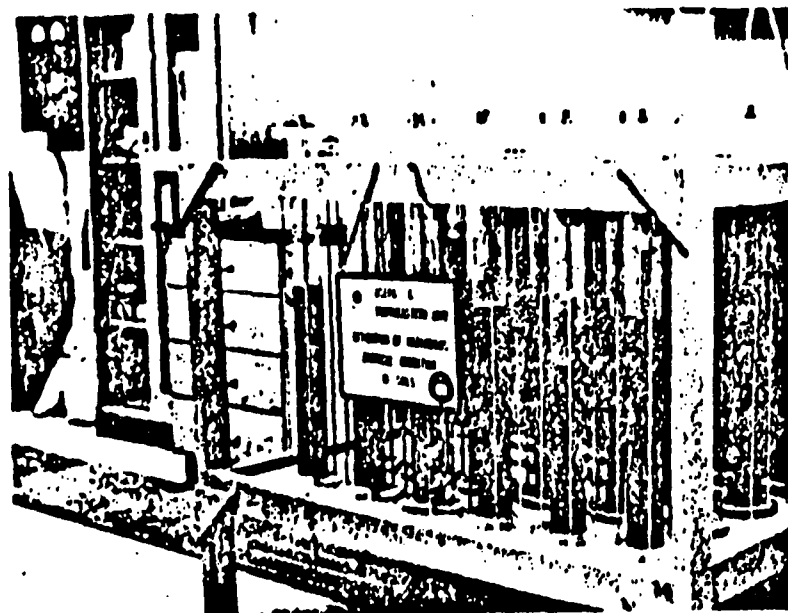


Figure 2. SOIL COLUMN APPARATUS

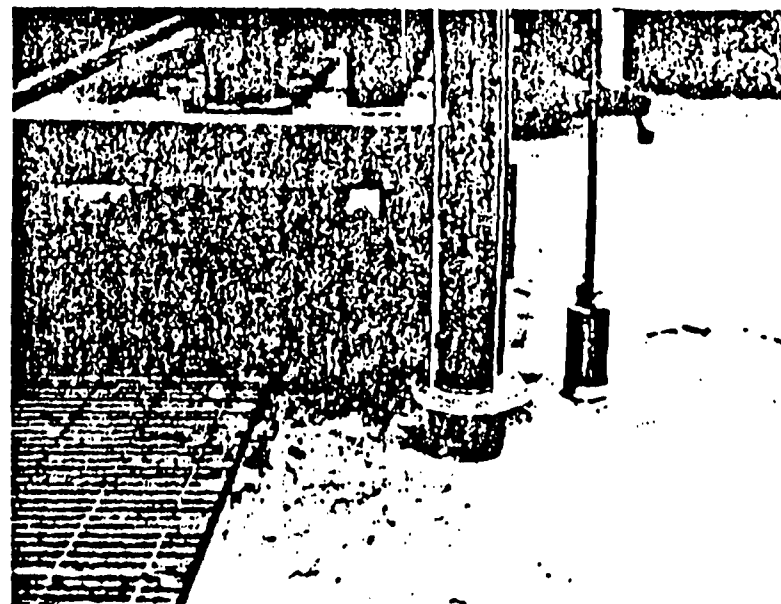


Figure 3. CONTROLLED-DROP HAMMER COMPACTOR

In this manner to achieve the desired density of 105 to 110 lbs/cf (1.68 to 1.76 gm/cc) to simulate original field conditions and the desired permeability rates of approximately  $1.6 \times 10^{-8}$  to  $1.0 \times 10^{-8}$  ft/sec ( $5 \times 10^{-4}$  to  $3 \times 10^{-4}$  cm/sec).

#### Determination of Quantity of Countermeasure

The treatment or cleanup of the contaminated soil was defined as the number of pore volumes of water or water and countermeasure needed to remove the desired amount of metal. Successful cleanup was defined as the removal of enough metal to produce a leachate from the columns which fell below EP toxicity criteria. EP Toxicity Concentrations for the heavy metals used in this study are presented in Table 3. EP toxicity values are 100 times the concentration permitted by drinking water standards.

The pore volume (quantity of water within the pores of a saturated soil sample) was calculated using the following equation:

$$pv = wv - sv$$

where  $p_v$  = pore volume (cc);  $w_v$  = whole volume of soil in column (cc); and  $s_v$  = solid volume of soil (cc) = (weight of soil added to column in grams)/(specific gravity in g/cc)<sup>3</sup>.

The determination of specific gravity of the soil was calculated following the procedure outlined in *Methods of Soil Analysis*<sup>4</sup> and ASTM D854-58. The pore volume of each of the packed columns was determined based on the above formula. The average pore volume of the 14 packed columns was 690 ml and for the remainder of the study this volume was used as the "treatment" pore volume.

Table 3. EP TOXICITY CONCENTRATIONS

<u>Metal</u>	<u>Concentration, mg/l</u>
Cadmium	1
Copper	100
Lead	5
Nickel	1.34
Zinc	500

#### Column Contamination

The concentration of contaminant used in the column analysis was chosen as the maximum concentration used in shaker table analysis. Two columns were contaminated with each metal. Two columns packed with soil were used as blanks. No metal was applied to these columns, but they did receive the treatment rinses applied to the contaminated columns.

Columns 1 to 10 received 1.915 liters of the metal contaminants. The tube at the base of the columns was closed off and the contaminant poured slowly into each column through the hole in the cap of each column. The columns were filled to the top with the metal solution which was allowed to saturate the soil for four days. Following this period of saturation, the metal contaminants were drained from the base of each column into a two-liter collection container. The columns were then allowed to air dry for two days to insure complete draining and simulate the

drying of a spill which might occur in the field. Samples of the drained contaminants (leachate) were analyzed for metal concentration using the atomic adsorption spectrophotometer (AA). The pH of the metal contaminant was recorded before and following its passage through the soil column. A soil sample was taken from the surface of each column and digested using the Nitric Acid Digestion Procedure (SM 302D).

#### Column Treatment and Cleanup

One column of each contaminant pair received only tap water rinses while its sister column received the chemical countermeasures, water plus surfactant (Rinse 2) and water plus chelating agent (Rinse 6). Columns receiving only tap water were rinsed 15 times in pore volume aliquots (690 ml). Columns which received the surfactant and EDTA solution received a total of eight rinses, one surfactant rinse, one EDTA rinse and six tap water rinses. Initial and final pH, metal content, and COD were recorded for each rinse.

#### RESULTS AND DISCUSSION

From the shaker table analysis, plots of adsorbance versus time were prepared for each concentration of each metal. Figure 1 shows an example of cadmium adsorption. From each plot, the final adsorbance was estimated and presented as total percent adsorbance and total mg metal adsorbed per gram of soil as well as the equivalent (m-moles) metal adsorbed per gram of soil (Table 4). The shaker table results were used to estimate a "minimum contact time between soil and contaminant to achieve a heavily contaminated soil and to determine if the time to reach equilibrium is a function of initial contaminating concentration. Data indicated that six hours of agitation achieved maximum adsorption values for the contaminant concentration tested, with a longer time needed for the lower concentrations. The shaker table data were also used to generate adsorption isotherms, a graphical presentation of the mass of metal adsorbed per gram of soil versus the residual metal contaminant concentration in the contact solution. Table 4 (showing the format of data generated for each metal

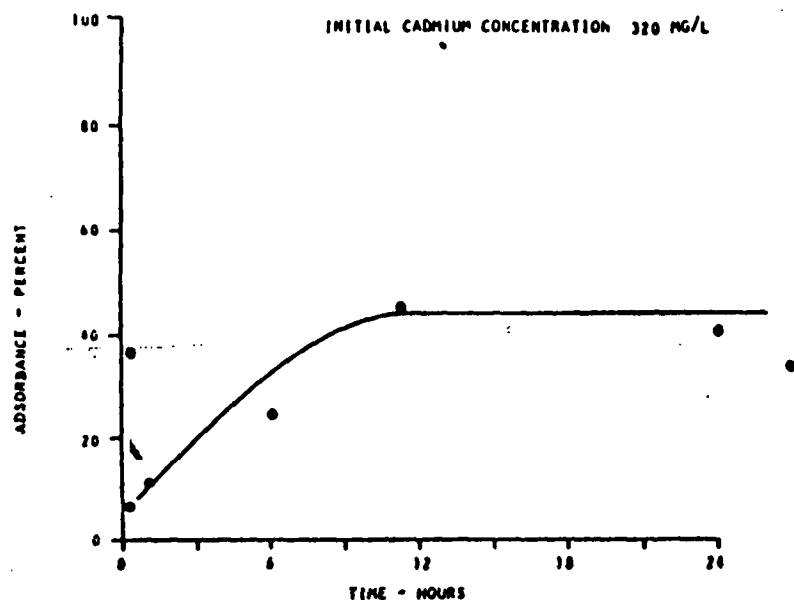


Figure 4. CADMIUM ADSORPTION  
— SHAKER TEST ANALYSIS

Table 4. SHAKER TEST RESULTS — CADMIUM ANALYSIS

A) 24 Hour Test — Liquid Sample Analysis

No	Initial Conc, mg/l	Final Conc, mg/l	Reduction Conc, mg/l	Adsorbance, mg/g	Adsorbance, percent
1	30000	26000	4000	40	13
2	2200	1300	900	9	41
3	320	176	145	1.45	45
4	25	12	13	0.13	52

B) Soil Sample Digestion Analysis

No	Initial Conc, mg/l	Digested Sample Conc, mg/l	Soil Sample Mass, g	Adsorbance, mg/g	Equiv Conc, Removed, mg/l	Equiv Conc, Remaining, mg/l	Adsorbance, percent
1A	30000	7000	3.423	133	13300	16700	44
2A	2200	160	3.567	2.33	233	1967	11
3A	320	150	3.041	2.46	246	74	23
4A	25	2.25	3.224	0.041	4.07	20.9	84

Table 4. SHAKER TEST RESULTS — CADMIUM ANALYSIS  
(CONTINUED)

C) Summary

No	Concentration Remaining, mg/l	Concentration Remaining, mM/l	Log-Conc Remaining, mM/l	Adsorbance, mg/g	Adsorbance, mM/l	Log Abs, mM/l
1	26000	231.3	2.36	40	0.356	-0.44
2	1300	11.6	1.06	9.0	0.080	-1.10
3	176	1.56	0.19	1.45	0.013	-1.89
4	12	0.107	-0.97	0.13	0.0012	-2.94
1A	16700	148.6	2.17	133	1.183	0.07
2A	1967	17.5	1.24	2.33	0.021	-1.68
3A	74	0.658	-0.181	2.46	0.022	-1.66
4A	21	0.187	-0.731	0.041	0.00038	-3.44

summarizes the data required for isotherm generation based on liquid sample analysis. Part B presents the results of the digested soil samples. Part C is a representation of data in Part A and B expressed in units necessary for plotting the two types of isotherms.

A comparison of the percent adsorption columns in Part A and Part B of the summary tables showed that the digested soil samples consistently varied from the corresponding liquid/leachate samples. The soil sample analysis consistently indicated a lower value for total metal adsorbed than did the filtrate analysis. An explanation for this trend is that the soil digestion process does not remove all the metal adsorbed; therefore, total adsorbance is underestimated by the soil sample analysis.

The isotherms developed were prepared using the Freundlich (Figure 5) and Langmuir equations (Figure 6). The Langmuir 'adsorption isotherm equation' can be derived from simple ion exchange considerations, assuming that only one type of adsorption site is involved and that only simple heavy-metal cations take part in the exchange reaction (1-site model). The Freundlich 'isotherm' equation can be interpreted as an approximate description of ion exchange involving one or more types of heavy metal cations and one or more types of adsorption sites (2-site model).

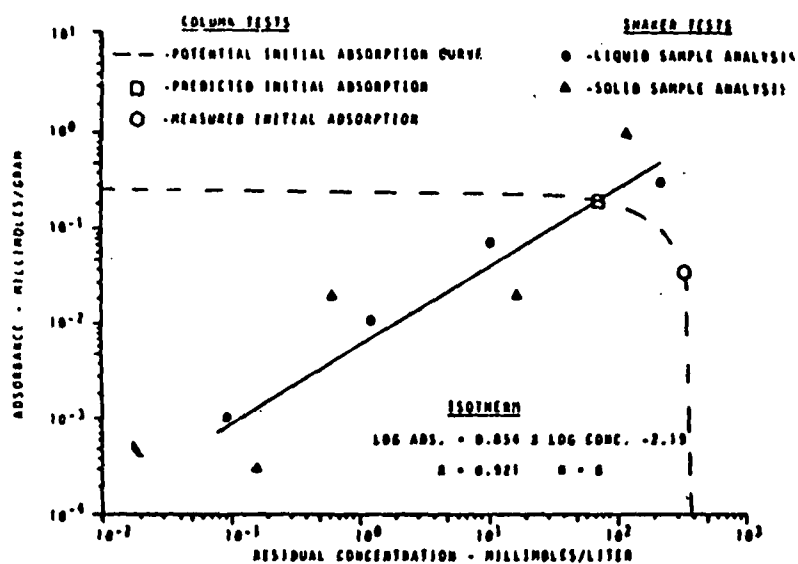


Figure 5. FREUNDLICH ISOTHERM - CADMIUM ADSORPTION

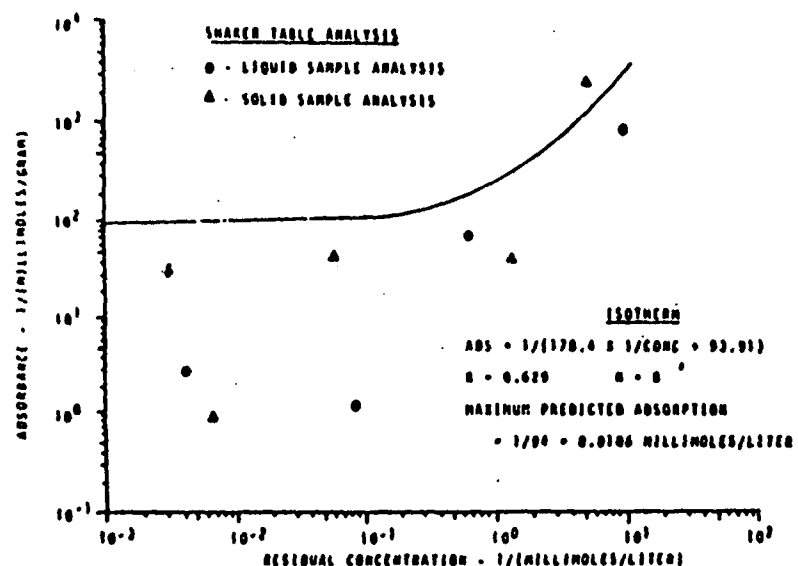


Figure 6. LANGMUIR ISOTHERM - CADMIUM ADSORPTION

From the plots and their corresponding correlation coefficients, it can be seen that for all five metals the Freundlich equation corresponds well with the adsorption data generated in the study of this soil and contaminant system. The Langmuir equation corresponds well only with data generated from the adsorption behavior of Pb, Ni, and Zn.

An explanation for the correlation of the data to the Langmuir equation for only Pb, Ni, and Zn is that these ions are not complexing in solution to the same degree as Cd and Cu and they are adsorbing to the soil based on the mono-layer theory with more uniform bonding strengths. Excessive complexing of Cd and Cu in solution would cause adsorption on the soil surface to be less uniform with varying strengths of attachment and, therefore, be more accurately described by the Freundlich theory. Support of this hypothesis is found in a study by B.E. Blom<sup>4</sup> which determined that in the presence of a relatively large excess of calcium or potassium the formation of  $\text{CdCl}^+$  enabled the Cd to be more easily bound to the soil system due to the preference of univalent ions over multivalent ions. The soil used by Blom was similar in type to the Typic Hapludult soil type used in this study, although the calcium content of the Typic Hapludult soil was not determined. It can be hypothesized (but not proven) that Cd was adsorbed as  $\text{CdCl}^+$  in this study. During AA analysis, the flame appeared red and yellow in color, indicating the presence of significant levels of calcium and sodium respectively, in the liquid sample.

Considering the theoretical aspects of the two isotherm types and the better agreement of the Freundlich equation to the data generated, the Freundlich isotherm was selected for use during soil column evaluation. The isotherm plots also contain a dotted line which represents a family of potential adsorbance versus residual concentration end points. The line was formed by selecting a series of arbitrary final concentrations and, using the change from the initial concentration, calculating the unique adsorbance that could occur. The predicted adsorbance of the metal in the column at the initial contaminant concentration applied is designated at the intersection of the isotherm line by the square.

symbol. The actual adsorbance measured for the metal by the soil column is designated by the hexagon symbol. The optimum contamination obtained in the columns was consistently lower than that obtained in shaker tests. This is due to the greater contaminant-to-soil ratio in the shaker test and also the improved soil-liquid contact achieved during the agitation process, as compared to the gravity flow conditions in the soil column.

Adsorption of the metal contaminants achieved by the soil column were: Cd, 0.083 mM/g; Cu, 0.023 mM/g; Pb, 0.030 mM/g; Ni, 0.073 mM/g; and Zn, 0.132 mM/g. These values are about 70 percent of the values predicted to be adsorbed based on the shaker test analysis.

#### Soil Treatment and Decontamination

Table 5 presents the percent removals of the metal contaminants by each treatment method. The tap/surfactant/EDTA 8-rinse treatment was more effective than the 15 tap water rinse in all cases except lead. An increase of metal concentration in the leachate following the application of the EDTA/buffer solution indicates that EDTA is responsible for the increased removals in these columns. Metal concentrations in surfactant leachate are equivalent or less than the concentrations in the leachate of the corresponding tap water rinse from its sister column, indicating that the surfactant was ineffective in desorbing heavy metals from soil systems. This is shown in Figures 7 and 8. The shape of the removal curves indicates the majority of the metal is removed in the first four to five rinses. The column receiving the EDTA

Table 5. TOTAL PERCENT METAL REMOVED

<i>Metal</i>	<i>Tap Water Only, 15 Rinses</i>	<i>Tap/Surfactant/EDTA, 8 Rinses</i>
Cd	87	100
Cu	44	82
Pb	74	63
Ni	87	94
Zn	88	93

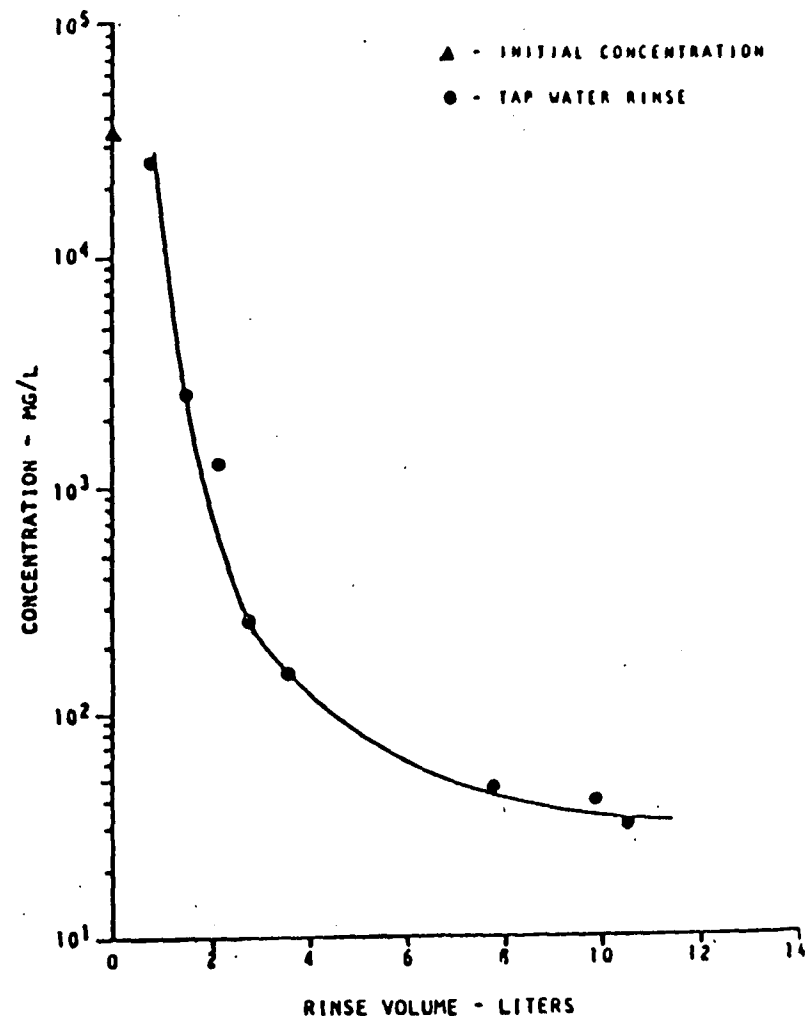


Figure 7. CADMIUM COLUMN TEST — WATER RINSE

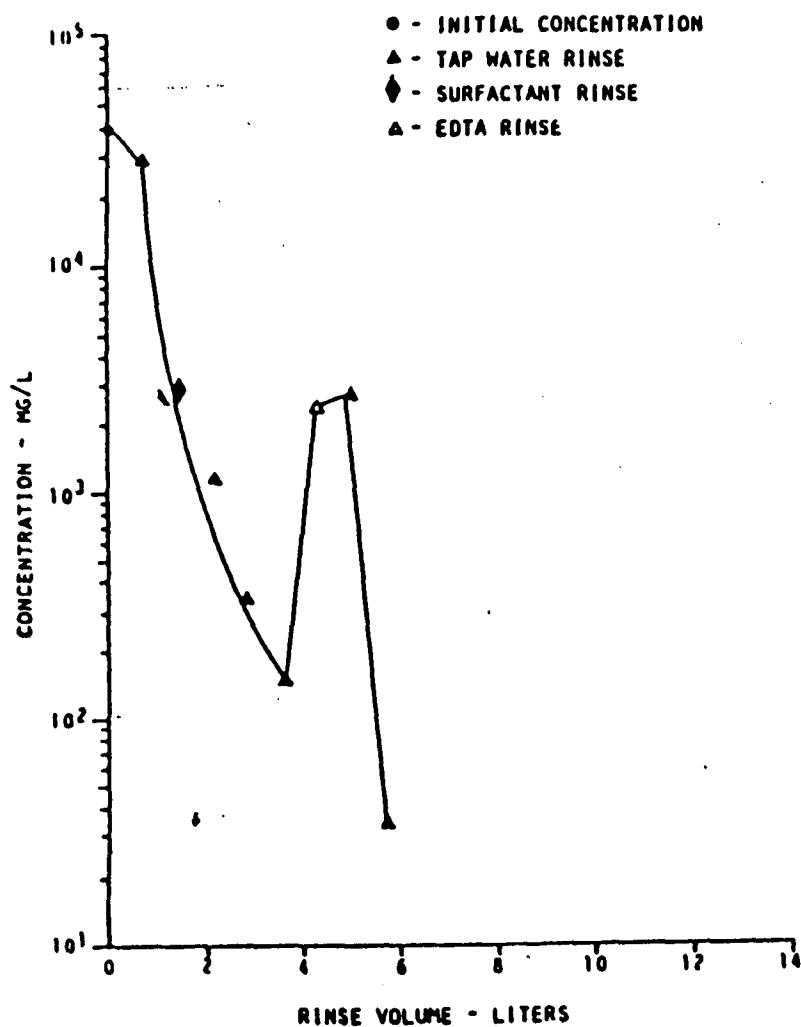


Figure 8. CADMIUM COLUMN TEST TAP WATER/SURFACTANT/EDTA RINSE

solution experienced a marked decrease in permeability. This indicates that the increase of the system pH due to the addition of the EDTA buffer mixture is causing the precipitation of the metals, presumably as hydroxides. (Precipitants were also observed in the leachate from the EDTA treated columns.)

EP Toxicity analysis performed in the soil following the treatment rinses indicated that five pore volumes of tap water (or tap water plus surfactant) were successful in reducing the metal content of the soil contaminated by zinc, copper and lead to within EP Toxicity limits, but only with the application of the EDTA/buffer rinse was the soil contaminated with cadmium and nickel reduced to levels within EP Toxicity limits. Using rain data for the area of the soil origin, the pore volume of rinse applied was equated to 0.34 years of rain.

### CONCLUSIONS

Results of this study indicate that in-situ treatment is a viable solution for the removal of metals Cd, Cu, Pb, Ni and Zn from contaminated soil. Care must be taken when extrapolating the results obtained in these tests to other situations as there are many variables which influence detoxification.

The use of the surfactant mixture as a rinse treatment for the removal of heavy metals proved ineffective in this soil system. The surfactant solution provided removal efficiencies comparable, but not superior to the tap water alone rinses.

EDTA proved effective in desorbing the metal cations from the soil system. The columns which received only eight treatment rinses, one of which included EDTA, indicated greater removals of contaminant than the columns which received 15 rinses of tap water alone. The use of EDTA appears to flush the metal from the soil as observed from the very high metal content of the EDTA rinse leachate in comparison to the previous tap water rinse leachate from the same column.

A decrease in the permeability of the column is observed when a large volume of treatment rinses is applied. This occurs in part

because the fines are washed to the base of the column where they accumulated and inhibit the flow. The application of the EDTA/buffer solution increases the system pH to 9 to 10 which induces the formation of precipitates within the column, further decreasing the column permeability and potentially clogging it.

Maximum adsorbance of the metal by the soil under shaker table analysis was obtained within the first three to six hours for contaminant concentrations greater than approximately 20,000 mg/l. The required contact time increased to six to twelve hours for contaminant concentrations between 20,000 mg/l and 20 mg/l. At contaminant concentrations less than 20 mg/l, the time to equilibrium was as long as 18 hours.

The Freundlich isotherm appeared to be applicable for the description of the adsorption behavior of all the soil/metal systems in this study. This implies that the adsorptive sites in the soil system are heterogeneous and a possible interaction among particles in the adsorbed phase may be occurring. The energy of this adsorption decreases logarithmically as the fraction of surface covered increases.

The Langmuir isotherm only successfully described the adsorptive behavior of Pb, Ni, and Zn. The Langmuir adsorption equation is derived from simple ion exchange considerations, assuming that only one type of adsorption site is involved and that only simple heavy metal cations take part in the exchange reaction. The fit of Pb, Ni and Zn adsorption results to the Langmuir equation may indicate that these ions are not complexing in solution to the same degree as Cd and Cu and that they are adsorbing to the soil based on the mono-layer theory with more uniform bonding strengths.

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# JOURNAL

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POLLUTION CONTROL ASSOCIATION





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
OFFICE OF RESEARCH AND DEVELOPMENT  
HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY  
CINCINNATI, OHIO 45268

REPLY TO:  
Releases Control Branch  
U.S. EPA  
Woodbridge Avenue  
Edison, New Jersey 08837

DATE: December 19, 1985

SUBJECT: Draft Research Project Plan: Removing Lead with EDTA Chelating Agent from Contaminated Soil at the Michael Battery Company, Bettendorf, Iowa

FROM: Richard P. Traver, Staff Engineer  
Releases Control Branch, LPCD, HWERL

A handwritten signature in black ink, appearing to read "Richard P. Traver", is written over the typed name and title.

TO: James R. MacDonald, Environmental Engineer  
Site Investigation Section, Emergency Planning  
and Response Branch, ESD - Region VII

THRU: Frank J. Freestone, Chief  
Technology Evaluation Staff, RCB, LPCD, HWERL

A handwritten signature in black ink, appearing to read "Frank J. Freestone", is written over the typed name and title.

This is in response to your request to Ira Wilder for an estimate to use the EPA Mobile Soils Washing System at an Immediate Removal Action at the former Michael Battery Company, Bettendorf, Iowa.

Attached is a Research Project Plan for your review and comment. The proposed project consists of the following four phases:

Phase I ..... Preliminary Laboratory Feasibility Study for Evaluating Potential Use of EDTA Chelating Agent for Removing Lead from Michael Battery Soil

Phase II ..... Laboratory Feasibility Study for Evaluating Removal of Chelated Lead from EDTA Solution, and Preliminary Process Design

Phase III ..... Full Scale Pilot Study

Phase IV ..... Field Demonstration

The objective of the proposed project is the development of operating protocols and cost estimating procedures that could be used by Region VII to engage the services of a commercial cleanup company or those of an existing EPA cleanup contractor. We are flexible regarding the extent to which this plan needs to be implemented and we stand ready to discuss any modifications you might suggest to suit your purposes.

DRAFT RESEARCH PROJECT PLAN

REMOVING LEAD WITH EDTA CHELATING AGENT FROM SOIL CONTAMINATED  
WITH LEAD IN BETTENDORF, IOWA

OPTION B: On-Site Treatment/Soil Washing

December 19, 1985

OBJECTIVE

The overall objective of this project is the development of engineering specifications, cost estimates, and operating protocols for use by Region VII to evaluate the alternative of soils washing for treatment of lead-contaminated soil, defined as Option B under the Region VII Action Memorandum of 8/28/85. If this alternative is subsequently implemented for a full-scale cleanup, the treatment of substantial quantities of contaminated material at the Michael Battery Company could be pursued under either a separate contract with a hazardous material cleanup company or under the appropriate EPA Emergency Response Cleanup Services contract.

SUMMARY AND LIMITATION OF SCOPE

The Hazardous Waste Engineering Research Laboratory's Releases Control Branch (RCB) in Edison, NJ, has been asked by EPA Region VII to evaluate the feasibility of removing lead from contaminated soils at the Michael Battery Company, located in Bettendorf, IA. Previous work by RCB and others<sup>1-7</sup> has shown that lead may be removed from some soils using EDTA as a chelating agent in an aqueous solution to solubilize the lead, with subsequent removal and concentration of the lead from solution. This Research Plan addresses a multi-phase engineering feasibility study only, and does not explore other aspects of the lead-in-soil problem at the Bettendorf Site such as: a detailed "extent of contamination" survey, or means of solving the contamination problem other than by processing the soils. It should be further noted that removal and treatment of contaminated soils may be limited to collected dust/soil from the main building, the approximate 535 cubic yards of soil from site drainage ditches, and the approximate 300 cubic yards from around the building.

BACKGROUND

1. Site Description - The information Pertaining to the Site Description is Basically a Summary of Information Provided in James R. McDonald's Draft Action Memo of 8/28/85.

The Michael Battery Company operated a battery manufacturing and recycling business in Bettendorf, Iowa, from October 1979 thru June 1983. Michael Battery Company leased the 0.6 acre site and a 5,000-square-foot metal building from the present deeded owner, Jesse Roofing and Painting Company. The site is located

in an industrial area of Bettendorf within the floodplain of the Mississippi River which is located approximately one half mile south. Surface run-off from the battery manufacturing operation has contaminated portions of the adjacent property.

The subsurface geologic characteristics are the bedrock, which is approximately 10-15 feet below the surface, and the 0-10 feet of unconsolidated sediments which are alluvial silts, clays and fine sands. The upper surface has received crushed limestone to level the surface and to serve as footings for the building. The hydrology in the area consists of the surface water, groundwater in the unconsolidated alluvial deposits, and the deep bedrock aquifer. The surface water and storm runoff is largely contained in the industrialized area around the site, and is eventually diverted to the Mississippi River. Local drainage from the Michael Battery Company site is to the south, over the adjacent Rogan Scales property, into a railroad ditch draining west. The runoff in the ditch ponds and percolates into the substrata. The Davenport Water Company has water intakes on the Mississippi River, 3.75 miles downstream from the site.

#### A. Quantity and Types of Substances Present

In February 1982, in response to a report of illegal dumping of sulfuric acid at the site, preliminary soil and surface water samples were collected. These preliminary samples identified heavy metal contamination of both soils and surface waters. Followup sampling conducted by EPA on July 8, 1982, detected lead concentrations in soil up to 5,200 ppm. In response to these sampling efforts, an expanded EPA field investigation was conducted in April 1984. On site monitoring wells were installed in June 1984. The results of the above investigations have indicated that significant lead contamination exists on site. The areas of lead contamination have been divided into four subareas: (1) metal building; (2) western drainageway; (3) sump area and eastern drainageway; and (4) storage areas around the building. The concentrations of lead and the volume of lead-contaminated soil/dust in each area are summarized below:

##### 1. Interior Dust/Soil Samples

Concentrations of lead in dirt and dust collected from inside the 5,000 square foot metal building, ranged from 4% to 5% for EPA samples collected in June, 1984, and from 17% to 33% for the National Institute of Occupational Safety and Health (NIOSH) samples collected in November, 1984. Dust has settled throughout the building on walls, roof and floors; with notable concentrations on the roof trusses and cross member supports for the walls and loft area. An estimate of the quantity of dust/soil that could be vacuumed from the building would be approximately ten 55-gallon drums.

## 2. Western Drainage Samples

The western drainage from the Michael Battery Company site is directed south from the blacktop around the building, southwest across Rogan Scales property, flowing west in the drainage ditch to the southwest corner of the lot. Concentrations of lead in this drainageway varied from 65 ppm to 31,700 ppm and averaged over 4,000 ppm. Soil samples were collected to a depth of 12 inches; if subsequent soil sampling below the 12 inch depth reveals further lead contamination, quantities of soil to be processed could be dramatically increased. The length of the western drainage ditch is approximately 150 feet. The surface area of the surrounding contaminated drainage area is approximately 13,000 square feet. The estimated volume of contaminated soil, assuming an average depth of one foot, is 480 cubic yards.

## 3. Sump and Eastern Drainage Samples

Drainage from the sump at the loading bay at the east end of the building was pumped onto the shoulder of Devils Glen Road where it drained south to the drainage ditch beside the railroad and then drained west. Concentrations of lead in this eastern drainage varied from 94 ppm to 9,600 ppm and averaged 4,600 ppm.

The length of the Devils Glen Road shoulder from the sump to the drainage ditch south is approximately 150 feet. The surface area of the surrounding contaminated area is estimated to be 1,500 square feet. The estimated volume of contaminated soil, assuming an average depth of one foot, is 55 cubic yards.

## 4. Storage Areas Around the Building

The highest concentration of lead found (102,000 ppm) was located outside the backdoor where Michael Battery Company sorted lead. Other storage areas included an area north of the blacktop adjacent to the auto parts warehouse; concentrations range from 74 ppm to 5,300 ppm and average 1,000 ppm. A second storage area is located to the west of the blacktop area; concentrations range from 210 ppm to 2,300 ppm and average 770 ppm.

Sweeping of soil/dust from the asphalt surfaces would result in an estimated five 55-gallon drums of material. The unsurfaced area on the site with potential storage, not including the western drainage-way, is estimated at 8,000 square feet. The estimated soil volume assuming a one foot depth is 300 cubic yards.

## 5. Surface Water and Groundwater Analysis

Previous sampling efforts have documented moderate lead contamination of surface drainage waters (96 ppm). No significant groundwater contamination has been detected, however.

## REMEDIAL ACTION

Based on CDC advisories, a clean-up level of 1,000 ppm lead in soil is recommended. Soils which fail the E.P. Toxicity Test for lead, it is proposed, would be handled as hazardous waste and transported to a licensed hazardous waste site for disposal. Soils which do not fail the E.P. Toxicity Test, but which contain lead in concentrations above 1,000 ppm, would be disposed of at a state approved landfill.

Region VII's Remedial Action Plan calls for cleaning the interior of the building, including the roofing, trusses, walls and floor of all dirt/dust. This would be accomplished vacuuming with a High Efficiency Particulate Air (HEPA) filter followed by pressurized water and detergent wash. The use of a chelate solution of EDTA should be considered for the wash solution. This would allow for the collected wash solution to be treated and recycled. The concentrated lead would be either disposed of as a hazardous material, or could be sold to a metal refinery to be reprocessed.

Region VII has proposed three action options: Option A - Dig and Haul, Option B - Soils Washing, and Option C - On-Site Chemical Fixation and Capping. Options A and C are briefly summarized with a detailed explanation of Option B following.

### OPTION A - DIG & HAUL

Region VII's Option A calls for excavation and off-site disposal of soil and materials having lead concentrations in excess of 1,000 ppm. It is estimated that the volume of soil and lead dust would approach 900 cubic yards. It is presumed that 75% of this material (675 cubic yards) would not fail E.P. Toxicity criteria for lead ( $< 5$  mg/l in leachate) and would be suitable for disposal in a state approved landfill. The remaining material, approximately 225 cubic yards, is expected to fail the E.P. Toxicity Test and would be handled as a hazardous waste. Disposal of this material would be carried out at an approved Resource Conservation and Recovery Act (RCRA) disposal site. Cost estimates are approximately \$214 K if only a portion of the material must be disposed of at a RCRA approved site. If all material must be taken to a RCRA site, the cost estimate is \$463 K. It should be noted that this Option does not eliminate the contamination problem, but merely relocates it until such time that the RCRA site material would have to be treated.

#### OPTION C - ON-SITE CHEMICAL FIXATION & CAPPING

Region VII has proposed a commercial chemical fixation process for on-site encapsulation. This approach would stabilize the contaminated soil through a proprietary fixation process. The fixated soil would be replaced on-site and then covered with a clean soils cap.

- With the approximate 1125 cubic yards of material, the rough cost for on-site chemical fixation is \$100/cubic yard, or \$112 K. An additional estimated \$60 K would be needed to install a clean soil cover.

No laboratory analysis has been performed evaluating the effectiveness of chemical fixation with the site specific Bettendorf Soil. A thorough bench-scale study would be necessary in order to determine if the fixated soil would pass the E.P. Toxicity Test for lead. It is also uncertain if the site would be usable by the owners following the chemical fixation process.

#### OPTION B - SOILS "WASHING" USING EDTA

The soil decontamination process first used by RCB was at a lead-storage type battery reclamation site in Leeds, Alabama, in 1984, at the request of Region IV. This involved the use of a prototype "Soils Washing System" for application of 13% EDTA solution to lead contaminated soil. The lead-in-soil concentration was reduced from 50,000 to less than 100 ppm. EDTA or ethylenediaminetetraacetic acid, disodium or tetrasodium salt, is a commercially produced chelating agent that, in an aqueous solution, can complex with lead to produce a water soluble chelate. (See attached Project Summary and Fact Sheet for more detail on the design and operation of the EPA prototype Soils Washing System.)

Region V has subsequently evaluated various treatment processes for the cleanup of a battery reclamation site at Woodville, Wisconsin. After examining the ORD experience and conducting laboratory tests, Region V also chose washing with EDTA as the best approach. A pilot-scale system is now being implemented in the field for treatment of battery casings.

A literature search and laboratory study, performed by JRB Associates under the Hazardous Waste Engineering Research Laboratory's "Chemical Countermeasures Program," also established the use of EDTA as the likely technology for the removal of a variety of heavy metals from soils. The study noted that lead-in-soil washing with EDTA must be evaluated on a site-specific basis. An independent study conducted by Northeastern University, in cooperation with RCB, corroborated these findings.

A significant concern at this time is not knowing the percent of EDTA that can be regenerated for reuse. Chelate that cannot be regenerated causes a double expense: one, it must be replaced; and two, it must be disposed of in a safe manner. Apparently, iron blocks the regeneration process. In the Alabama work, iron is listed at 2,100 mg/kg and apparently, although not specifically noted, the EDTA regeneration was only 5% through sulfide precipitation. The iron content of the alluvial silts, clays and fine sand at the Bettendorf site is approximately 1-2% in the form of hematite, magnetite and ilmenite. Dr. Anderson of the Geology Department of Augustana College (across the river from Bettendorf) indicated that the Mississippi River received a "slug" of iron from Wisconsin in that area in the last ice age. If this is the case, there is, on the average, three times as much iron as there is lead. This would be expected to cause significant problems in regenerating the lead if the chelate can remove the iron from these mineral structures. For this reason, a thorough comparison on a laboratory scale basis needs to be run on both sulfide precipitation and electrodiagnosis as means for EDTA regeneration.

#### SCOPE OF WORK

The response activities proposed by RCB for dealing with the lead problem in Bettendorf consist of four phases. Phase I will be a laboratory feasibility study to determine if EDTA offers a reasonable chance of success for removing lead from the type of soil matrix present at the affected Michael Battery site. Phase II will also be a laboratory-scale engineering study geared to determine the optimum approach and conditions for removing chelated lead from solution and regenerating EDTA for recycling purposes. If these phases are successful, Phase III will be a full-scale pilot study involving approximately 100 drums of lead-contaminated soil being shipped to Edison, New Jersey, where the ORD Soils Washing System will be used to evaluate process performance, operating costs, and system capacity. Additionally, Phase III will provide for any necessary permit applications, including a delisting petition. Phase IV will be a field activation with the Soils Washing System at the Michael Battery site to demonstrate the field capability of the technology and to develop operating protocols for use by Region VII in acquiring contracted cleanup services, if so desired.

#### Phase I      Preliminary Laboratory Feasibility Study for Evaluating Potential Use of EDTA Chelating Agent for Removing Lead from Bettendorf Soil

The objective of Phase I is to establish the optimum concentration of EDTA in solution for lead removal and the percent lead reduction in the Bettendorf soil.



A 2-4 kg sample consisting of a homogeneous blend of "Michael Bettendorf Site Soil" contaminated with 2,000-330,000 ppm lead will be obtained by Region VII by compositing samples from several hot spots. Region VII will attempt to make this single composite sample as representative as practicable of the soils in the hot spots in terms of organic content, soil particle size, and potentially interfering elements such as Zn, Ba, Ti, Cr, and Fe.

It should be noted that this preliminary study is a single sample study only--the results must, therefore, be interpreted with great caution. Soil variability among the hot spots could easily be obscured in the blending process needed to obtain the single "representative" sample. Phase II will include samples from a greater number of locations such that an analysis of the variability of key parameters of the soils to be treated can be made.

The single sample will be "washed" with EDTA solution in the laboratory to determine the effectiveness of the EDTA chelating process. Ten gram (10g) soil portions will be agitated on a "shaker table" for 30 minutes with one hundred milliliter (100 ml) volumes of the following percentages of EDTA (disodium salt) in water:

0 (blank); 1.0; 2.5; 6.5; 13.0; and 25.0

Analyses will then be performed to determine the amount of lead removed by EDTA washing and lead remaining on treated soil.

An EP Toxicity Test (40 CFR 261.24) and a qualitative analysis for all metals present in the Bettendorf soil blend will also be performed to determine some of the soil's characteristics.

The QA/QC program for this Phase I study will have the single sample limitation as noted above, and will include the following:

- [a] The soil washing and analyses procedures will be performed in duplicate.
- [b] At least three replicate portions of the original Bettendorf soil blend will be analyzed to assure homogeneity.
- [c] "Lead in Soil" analyses will be performed using both X-Ray Fluorescence and Acid Digestion methods.
- [d] Analyses performance will be evaluated using "QA Audits" with primary emphasis on Performance Evaluation Audits.

A reduction of lead content in soil to approximately 1,000 ppm is currently considered successful for Phase I. If unsuccessful, due to the possible presence of interfering compounds (e.g., iron) that limit the performance of EDTA, a more intensive laboratory effort (not fully described in this Plan) may be necessary. This subsequent effort would seek to define alternative chelating agents or entirely different treatment processes. If successful and an adequate reduction of the soil lead level is achieved with EDTA, Phase II will be implemented.

It should be noted that some residual EDTA will remain on the treated soils along with residual lead (and probably other residual substances). There is a possibility that the residual EDTA could cause the residual lead to have a greater environmental mobility than that experienced by an equivalent concentration of lead prior to the treatment process, or the EDTA may, itself, pose some type of toxicity problem. While the reported LD<sub>50</sub> of EDTA is 2 g/kg (rats, orally), and toxicity does not appear to be an obvious problem, these aspects of the use of EDTA will be investigated on a preliminary level during this initial laboratory study phase. Assistance from other ORD offices may be needed for answers to these questions.

Time Frame ... 15-30 days from receipt of "representative" sample.

Cost ..... \$10,000 - \$15,000

Product ..... Letter report on the preliminary feasibility of EDTA extraction.

Phase II      Laboratory Feasibility Study for Evaluating Removal of Chelated Lead from EDTA Solution, and Preliminary Process Design

The objective of this phase is to establish the optimum treatment process for the recovery of lead and EDTA from the "soil wash" solution and to prepare preliminary engineering process specifications, a detailed cost estimate, a test plan, and a schedule for Phase III.

The EDTA recovery process used by ORD at Leeds, Alabama, reacted sodium sulfide with the EDTA-lead chelate to form a lead sulfide precipitate that was dewatered and disposed of at a smelter. Subsequent acidification of the remaining EDTA solution enabled substantial recycling of EDTA. An alternative treatment process for the removal of lead from solution is based on electrolytic reduction and may be potentially more cost-effective than the use of sodium sulfide. Evaluation of final disposal or reclamation of the EDTA (e.g., solidification for storage) will be pursued.

Additionally, further testing with a selected concentration of EDTA on several separate "representative" samples from hot spots (the inverse program of Phase I) will be performed to determine if variability of soil parameters will cause unacceptable treatment system performance changes among the various soils to be treated. Each soil sample will be analyzed for particle size, organic content, presence of other metals or other interfering compounds, and other parameters that could affect performance of either the EDTA extraction or the recycle of the EDTA. This testing will be performed with QA/QC similar to that in Phase I to assure reliability and reproducibility of data. The samples will be obtained through coordination with Region VII.

At this time, it will be necessary to assure that the soil samples received are reasonably representative of those expected in the field. Subsequent project elements (Phases III and IV) are considerably more expensive than these laboratory phases and rely heavily upon the precision and accuracy of the laboratory data.

Once an EDTA recovery process is identified, the necessary process equipment for executing the entire treatment (lead removal with EDTA recycle) at pilot scale (Phase III) must be identified and sources sought for needed equipment not now on hand (e.g., dewatering equipment for lead sludge or electrolytic lead removal cells).

Finally, a detailed cost estimate, testing protocol, including a Sampling and Analysis Plan and a Quality Assurance Project Plan, and schedule for Phase III will be prepared.

Time Frame ... 30-60 days from receipt of authorization to proceed.

Cost .....	Laboratory work:	\$10,000-\$15,000
	Detailed Engineering Planning:	\$50,000-\$135,000

Product ..... Letter report providing the results of Phase II and detailed planning information for Phase III as noted above.

### Phase III Full Scale Pilot Study

The objective of this phase is to obtain engineering information on the unit cost, capacity, personnel requirements, and treatment effectiveness of lead removal using EDTA in the EPA soils washing system, and to provide preliminary planning information for Phase IV.

The study will simulate a field activation using the full-scale prototypical equipment in Edison, New Jersey. Equipment needed for the treatment process but not currently on hand will be acquired or leased, whichever is more favorable. The buy/lease decision will be made during Phase II, such that the estimate for Phase III is as accurate as possible.

The tests will involve the following sequence of activities:

1. EPA and contractor personnel involved with the proposed tests will be provided with operator training, safety training, and medical monitoring as appropriate.
2. Equipment will be set up indoors in a suitable area where the testing can be conducted safely and in an environmentally suitable manner.
3. Initial process shakedown will be conducted using clean soils to assure that all elements of the process function properly individually and together. Such normal operating activities as determining pump capacities and flow balances among the various unit processes must be performed carefully and on clean material. During this activity, minor process adjustments will be made to assure appropriate system function in the absence of contaminants or treatment chemicals.
4. Clean soil of a type reasonably similar to the Bettendorf soil will be intentionally contaminated with lead known to be in similar form and concentration as the lead from the Michael Battery site and controlled-condition tests will be performed, first at laboratory scale, then at pilot scale to assure that the treatment process is operating properly. (This is done to reduce the amount of Bettendorf soil that must be transported to Edison for the shakedown portion of the tests as opposed to the portion of the tests intended for data gathering.) This activity will assure that the treatment chemistry is operating properly and that such steps as EDTA addition, addition of other treatment agents, and/or removal/recycle of the EDTA are functioning properly.
5. Approximately 100 - 200 (55 gal.) drums of lead-contaminated soil will be obtained from Region VII and used in a set of tests (probably three or four "runs") designed to provide capacity and performance information. The samples contained in the drums must be "representative" to the satisfaction of the EPA Office of Solid Waste such that the data resulting from the treatment test can be submitted in a delisting petition, as noted below. Variables for the test will include soil feed rates, EDTA concentration, recycle system data, and other system operating parameters. Measurements will include initial lead concentration, final lead concentration, lead concentration in produced sludge, feed rates, EDTA recycle effectiveness (EDTA use rate), and other chemical use rates. Also, the number and training levels of the personnel needed for operating the process will be determined. The goal of these tests is to identify the most cost-effective treatment conditions, requiring the minimum personnel, at the greatest possible capacity.

6. After the tests, remaining soil must be disposed of. Some soils, by design, will not have been adequately treated and may have to be recycled to reach the design treatment level. There is always an outside possibility that all of the soil will fall short of the treatment goal. These soils will be either transported back to Bettendorf or sent to a hazardous waste disposal facility. Specific arrangements for the disposition of untreated/inadequately treated soils must be made and agreed to by all principals prior to the transportation of the contaminated soils from Bettendorf to Edison, and should be addressed in the Plan for Phase III prepared during Phase II.
7. The equipment and test area must be decontaminated and the decontaminating solutions disposed of in a suitable manner as noted above for the soils.
8. The test equipment must be disassembled and returned to storage or prepared for shipment to the field.

Concurrent with these tests, necessary permitting documentation associated with Phase IV (and also appropriate to a full field activation using the same process) will be prepared. As noted above, this will include State and Federal requirements and will probably include a delisting petition. Data from the pilot-scale tests will be used in the delisting petition to demonstrate that the treated soil is "nonhazardous" to the satisfaction of OSW.

Additionally, during and following these tests, preliminary planning will be conducted for a field activation using the EPA prototype Soils Washing System. This planning will include all of the necessary logistical elements and preparations for operating the system in the field for an extended period. However, because this planning is a significant effort, a detailed plan will not be conducted until authorization to proceed with Phase IV is received.

Time Frame ... 3-6 Months from authorization to proceed

Cost ..... \$300,000 - \$700,000

Product ..... Interim report providing data, detailed estimates and preliminary plans for Phase IV

Note: This interim report will contain sufficient data for the specification of a field operation by sources other than ORD. Therefore, Phase IV is designed  
• to be an optional phase.

#### Phase IV     Field Demonstration

The objective of this phase will be to determine field-related variations to the unit costs, lead removal performance and system reliability determined during the pilot scale tests in Phase III. The resulting information from this phase would be used by Region VII to specify contracted cleanup efforts using commercially available equipment and personnel.

Pilot scale tests conducted during Phase III will be done under carefully controlled conditions at Edison, NJ, with a maximum of nearby shop and logistical support to help overcome unanticipated difficulties. Running changes can be made relatively easily and cheaply because of the availability of extra personnel when needed and a strong base of equipment testing capabilities. Field operations, by comparison, require substantial advance planning to assure that the operation proceeds smoothly from mobilization through startup and into reliable continuous operations. Omissions or errors in the planning process, as well as uncontrollable variations such as severe weather, quickly translate into lost time and extra costs. Field tests are, therefore, expensive, demand the most from advance planning and preparations, and require contingencies in the planning process relative to both time and costs. However, once these advance planning activities have been completed, the equipment has been set up and is operating smoothly, continuing field operations are not especially difficult.

RCB has had twelve years of field experience with operations utilizing complex cleanup equipment for hazardous material spills and waste sites. These experiences have highlighted the need for careful, sequential advance planning and adequate shakedown and testing prior to committing to expensive field activities.

This phase would proceed in approximately the following manner:

- o Meet with Region VII to define goals, objectives, financing arrangements, operating location(s) permitting responsibilities; division of activities between ORD and Region VII (e.g., Region would handle legal and public affairs, ORD would execute technical aspects of project; Regional analytical support could be very helpful if available; authority to access site critical). Note that operating location may or may not be on the site to be cleaned up--depending upon many factors.
- o Define with Region VII a project management plan, including roles and responsibilities of Regional, ORD, and contractor individuals on the project. Define lines of communication and patterns of routine reporting. This is critical!
- o Define with Region VII a desirable scope of operation, e.g., materials to be treated during demonstration, duration of operation, operating period per day (8, 10, 12, or 24 hours).
- o Define with Region VII means to excavate and transport (if needed) contaminated soils to treatment site and treated soils from treatment site to point of origin.

- o Define with State of Iowa, as needed, permitting requirements and responsibilities. (This will be done preliminarily during Phase III but must be continued during Phase IV.)
- o Prepare detailed site-installation design(s), with provision for security, power, wastewater discharge, water supply, storage of equipment and chemicals, personnel support trailers or other quarters, etc.
- o Prepare detailed logistical support list of all necessary equipment to be taken to the field, including spare parts and necessary tools and troubleshooting apparatus.
- o Arrange for necessary analytical support, either through the Region, a local laboratory, or an on-site mobile laboratory, as appropriate. Prepare a detailed Sampling and Analysis Plan and a Quality Assurance Project Plan.
- o Arrange for suitable ultimate disposal (hazardous landfill, smelter) of concentrated lead products.
- o Arrange for chemical and other expendable supplies.
- o Prepare detailed project plans, including schedule and budget, with arrangements for routine reporting to compare planned progress and expenditures against actual progress and expenditures, and management "checkpoints."
- o Mobilize operating crews, with appropriate safety, environmental, and operator training (may be subcontractor personnel, particularly if 24 hr/day, 7 day/week operations are needed and multiple crews with rotation are used). Conduct training on equipment set up at Edison or at Bettendorf.
- o Mobilize equipment including all necessary arrangements for transportation, setup, and on-site shakedown.
- o Execute operation, in accordance with detailed operating plans.
- o Demobilize and decontaminate equipment and restore operating site(s) to a condition suitable to owners (criteria for suitability to be agreed to prior to mobilizing personnel and equipment at site). Return equipment to Edison and perform restoration maintenance, as needed.

The scope of this Phase can be highly variable. It is desirable to clean up a small site or sites to demonstrate the suitability of the process; however, it is not desirable to use the ORD equipment for extended operations for the purpose of cleaning up many sites. The most appropriate scope will involve a short proof-of-technology demonstration to obtain specifications and cost estimates such that the actual cleanup involving many "hot spots" could be executed by a cleanup contractor.

Time Frame ... Planning & preparations: 1-6 months (depending on permits)

Field Demonstration: 30-90 days of operations (including some "down time" for maintenance, etc.)

Report: Draft delivered 90 days after completion of field operation; final report to management after additional 90 days.

Cost ..... \$500,000 - \$2,000,000: (depending on hours/day of operation and degree of acceleration of the schedule)

Products ..... Final Report, consolidating the work of all phases, and providing specifications, cost estimates, and activity schedules suitable for use by Region VII in procuring contracted services for a full-scale cleanup using EDTA-extraction technology.

Technical paper, providing synopsis of Final Report.



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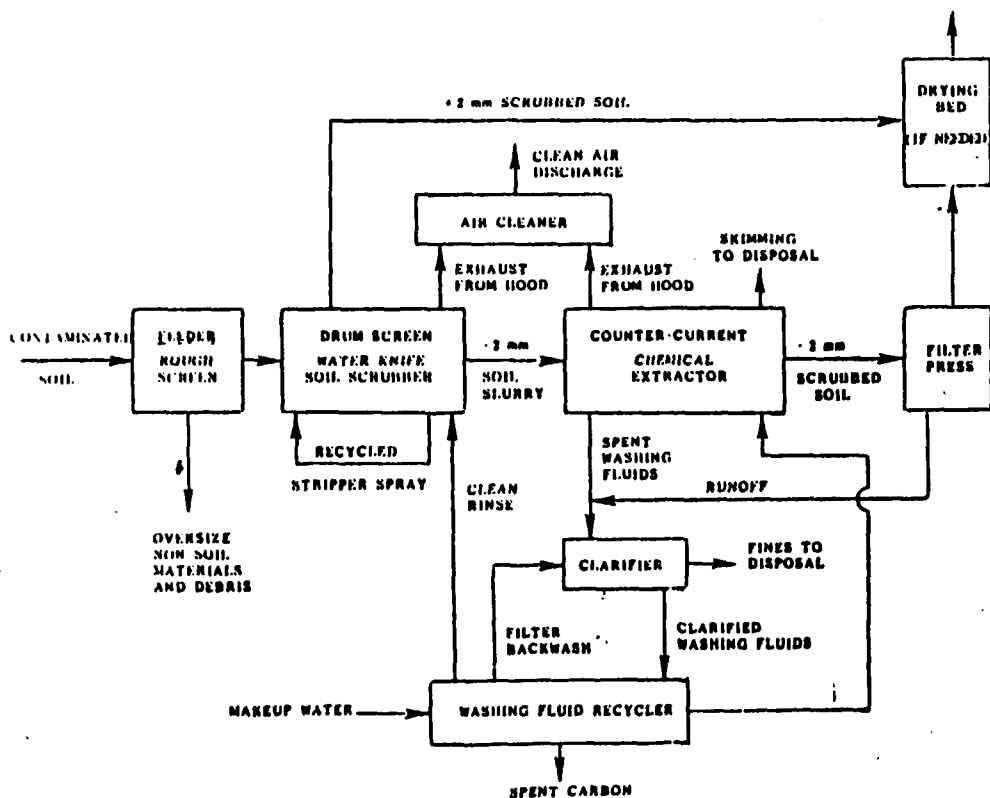
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## Mobile System For Extracting Spilled Hazardous Materials From Soil

The Hazardous Waste Engineering Research Laboratory, Releases Control Branch at Edison, NJ, has recently developed a mobile system for extracting spilled hazardous materials from soils at cleanup sites.

Landborne spills of hazardous materials that percolate through the soil pose a serious threat to groundwater.

Effective response to such incidents should include the means for removing the contaminants and restoring the soil to its original condition. Currently practiced techniques, such as excavation with transfer to land fill or flushing with water *in situ*, are beset with difficulties - large land area and volume of materials involved. An innovative *In Situ* Containment/Treatment System has been developed to treat contaminated soils. However, it is not suitable for all soils and/or all chemicals.



PROCESS FLOW SCHEME FOR SOIL SCRUBBER

The mobile treatment (see illustration) has been designed for water extraction of a broad range of hazardous materials from spill-contaminated soils. The system will: (1) treat excavated contaminated soils, (2) return the treated soil to the site, (3) separate the extracted hazardous materials from the washing fluid for further processing and/or disposal, and (4) decontaminate process fluids before recirculation, or final disposal. A prototype system has been developed utilizing conventional equipment for screening, size reduction, washing, and dewatering of the soils. The washing fluid - water - may contain additives, such as acids, alkalies, detergents, and selected organic solvents to enhance soil decontamination. The nominal processing rate will be 3.2-m<sup>3</sup> (4-yd<sup>3</sup>) of contaminated soil per hour when the soil particles are primarily less than 2-mm in size and up to 14.4-m<sup>3</sup> (18-yd<sup>3</sup>) per hour for soil of larger average particle size.

For further information contact Frank J. Freestone or Richard P. Traver, Hazardous Waste Engineering Research Laboratory, Releases Control Branch, Edison, NJ. Telephone numbers are: (201) 321-6632/6677 (commercial) or 340-6632/6677 (FTS).

## Project Summary

# Mobile System for Extracting Spilled Hazardous Materials from Excavated Soils

Robert Scholz and Joseph Milanowski

A technique was evaluated for the scrubbing or cleansing of excavated soils contaminated by spilled or released hazardous substances. Laboratory tests were conducted with three separate pollutants (phenol, arsenic trioxide, and polychlorinated biphenyls [PCB's]) and two soils of significantly different character (sand/gravel/silt/clay and organic loam).

The tests show that scrubbing of excavated soil on site is an efficient approach for freeing soils of certain contaminants but that the effectiveness depends on the washing fluid (water + additives) and on the soil composition and particle-size distribution. Based on the test results, a full-scale, field-use, prototype system was designed, engineered, fabricated, assembled, and briefly tested under conditions where large ( $>2.5$  cm) objects were removed by a bar screen. The unit is now ready for field demonstrations.

The system includes two major soil scrubbing components: a water-knife stripping and soaking unit of novel design for disintegrating the soil fabric (matrix) and solubilizing the contaminant from the larger particles ( $>2$  mm) and an existing, but re-engineered, four-stage countercurrent extractor for freeing the contaminants from smaller particles ( $<2$  mm). The processing rate of the system is 2.3 to 3.8  $\text{m}^3/\text{hr}$  (4 to 5  $\text{yd}^3/\text{hr}$ ), though the water-knife unit (used alone) can process 11.6 to 13.5  $\text{m}^3/\text{hr}$  (15 to 18  $\text{yd}^3/\text{hr}$ ). The complete system requires auxiliary equipment, such as the EPA-ORD physical/chemical treatment trailer, to process the wastewater for

recycling; under some circumstances, provision must be made to confine and treat released gases and mists. Treatment residues consist of skimmings from froth flotation, fine particles discharged with the used washing fluids, and spent carbon. The principal limiting constraint on the treatability of soils is clay content (high weight-percent), since breaking down and efficiently treating consolidated clays is impractical or not economically attractive. Most inorganic compounds, almost all water soluble or readily oxidizable organic chemicals, and some partially miscible-in-water organics can be treated with water or water plus an additive.

During limited laboratory extraction tests, phenol was very efficiently removed from both organic and inorganic soils, whereas PCB and arsenic clung more tenaciously to the soils and were released less readily into the washing fluids. The extent to which the system has practical, cost-effective utility in a particular situation cannot be determined until preliminary, bench-scale lab work has been performed and acceptable limits of residual concentrations in the washed soil are adopted. Laboratory tests show that soil scrubbing has the capability of vastly speeding up the release of chemicals from soils, a process that occurs very slowly under natural leaching conditions.

Note that this system requires excavation of the soil, which can subsequently be replaced or transported to a low-grade landfill. In situ washing of contaminated soil, a process in which the contaminated area is isolated for

example, by grouting, and then water-flushed with removal of the wash water at a well-point is an alternative. The overall efficiency of the soil washing system is greater than that currently being achieved by in situ methods.

Based on the laboratory program, a series of steps (water-knife size reduction; soaking; countercurrent extraction; hydrocyclone separation; and waste fluid treatment for reuse) was selected as the most suitable process sequence for the prototype system. The system was constructed for the U.S. (EPA) and is now being subjected to field evaluation. However, soils rich in humus, organic detritus, and vegetative matter can present special problems in the extraction of certain hazardous substances, which may not partition between the solid and fluid phases to a practical and necessary extent.

*This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

The leaching of hazardous materials from contaminated soils into groundwater is recognized as a potential threat to the Nation's drinking water supplies. Such situations occur as the result of accidental spills of hazardous substances and from releases at the many uncontrolled hazardous waste disposal sites now known to exist across the country. Current removal/remedial technology is largely limited to the excavation and transfer of such soils to suitably sealed or lined landfills where uncontrolled leaching cannot occur.

Onsite treatment can be a more cost-effective solution to the problem. In some research projects, contaminated soils have been isolated by injected grout, trenched slurry walls, steel piling, etc., and then subjected to in situ leaching. The effectiveness of such a process is limited by, among many factors, the permeability of the soil in its undisturbed state. Economic and effectiveness factors cannot be generalized but are situation-specific.

An alternative process is needed for those situations in which permeability or other factors prevent effective in-situ leaching and where landfilling is too costly. The proposed technology — the

subject of the current effort — consists of excavation, onsite but above-ground treatment of the contaminated soil, and return of the treated soil to its original site. Excavation of the soil from its natural state opens a number of options for improved separation of contaminants through better (high energy) mixing and the potential for using different solvents. Such cleanups can also be carried out more quickly than they could by the leaching of a more or less compact natural soil (cost factors not being considered). This engineering approach has also made it possible, or more convenient, to incorporate any control devices that may be needed to reduce emissions of particulates or fumes into the air column and/or to treat the contaminated wastewaters generated during the processing.

The purpose of this project was to carry out appropriate laboratory studies and to develop, design, and construct a full-scale system capable of treating a wide range of contaminated soils. The existing system will be useful for the correction of long-standing (remedial) contamination problems (waste disposal sites), as well as for the emergency cleanup of spills and for the prompt removal of released wastes.

## Discussion

To meet the objectives of the program, specific criteria were identified for the solvent, the soils, the pollutants, and the process.

To be suitable for field use in such a process, the solvent or extracting fluid should have the following characteristics:

1. A favorable separation coefficient for extraction.
2. Low volatility under ambient conditions (to reduce air contamination effects).
3. Low toxicity (since traces of extractant may remain in the cleansed soil).
4. Safety and relative ease of handling in the field.
5. Recoverability for reuse.

The selected solvent must be able to separate the contaminant from the soil, preferably using a minimum volume of solvent so that the equipment can be kept compact. In addition, the solvent must be readily separable from the soil fines to

allow return of the decontaminated soil to the site and to permit treatment and reuse of the solvent. High volatility in the solvent can contribute to unacceptable losses and can, when coupled with flammability, exacerbate health and safety risks for the workers.

Following a brief evaluation and screening of potential solvents (including organics), consideration of all the above-cited factors clearly indicated that water was suitable as the primary target solvent. The use of additives such as acids or bases, oxidizing or reducing agents, or wetting agents was judged to be a reasonable approach for enhancing removal efficiency. Though certain organic solvents can meet most of the solvent criteria and may have definite advantages in specific cases, a decision was made early in the project to limit the investigation to water-based systems.

The range of soils that is encountered in a cleanup situation is very broad, encompassing fine, highly cohesive clays, sandy soils, silts, soils high in organic matter, etc. Though processes can be devised to handle any or all of these materials, certain contaminated soils do not require exhaustive extraction and others do not lend themselves to an extractive process. The organic content of a soil can affect the ease of size reduction and the efficiency of extraction. The pH of a soil can affect the extraction efficiency for a particular contaminant. When the soils and contaminants have cationic or anionic qualities, ion exchange (partition factors cannot be neglected).

For purposes of this investigation, two soils were selected as suitable representatives of many that might be encountered. These were a granular (sandy), essentially cohesionless inorganic soil (containing some fine sand and about 20% clay) and a highly organic (18.4%, mostly as peat and humus) commercial topsoil.

Though spill situations and waste disposal sites may differ in many ways (such as the portion of a contaminant that is tightly bound to the soil versus the amount loosely associated in the voids), plans for the test program emphasized the spill situation by using freshly prepared mixtures of soil plus contaminant. Funding was insufficient to support work with aged or weathered contaminated soils that are more representative of dumpsites.

The actual process for the planned system must include excavation and transfer to the processing equipment, screening to remove large (>2.5 cm)

objects, size reduction to maximize soil-solvent contact, extractive treatment, separation of contaminated solvent from (relatively) decontaminated soil particles, and return of the soil (either "as is" or after drying) to the excavation.

Excavation can be readily handled by conventional earthmoving and construction machinery. Size reduction of soils can be accomplished with various, commercially available equipment, including rotary scrubbers, log washers, attrition scrubbers, and high intensity water-knives. The properties of each were considered, and the water-knife was chosen as the most versatile unit; it was also suitable for both disintegrating clay-like lumps and for scrubbing the loosely held contaminant from the resulting smaller ( $>2$  mm) components.

For the decontamination process to be effective with a wide range of water-insoluble and tightly held contaminants on small particles ( $>2$  mm), follow-on multi-stage extraction was judged to be necessary. The use of countercurrent extraction allows several stages of extraction with minimum solvent use. Clearly, the final system also requires equipment to separate fines from the solvent, both between extraction stages and after the last stage. Gravity separators, clarifiers, and filters were generally inappropriate for the planned system; hydrocyclones were selected for evaluation.

The three hazardous contaminants selected for testing were phenol, arsenic trioxide, and PCB's. These were chosen because of the frequency with which they are encountered in spills and the range of physical and chemical characteristics they offer. Laboratory tests were carried out to assess the effects of different water-based solvents and different processing conditions on these three chemicals mixed with the two soil types noted earlier. The results of these studies were then used to design the full-scale prototype.

## Equipment Evaluation

### Size Reduction and Extraction

A series of tests was conducted with the water-knives, first using a local, available, uncontaminated soil sample. Numerous approaches to exposing the soil to the water-knife jets were tried and abandoned (refer to the full report). Only when the soil was contained in a truncated, cone-shaped, tilted rotary-screen drum (2-mm mesh openings) was the desired lump breaking obtained. The

first tests were performed in an 18-in. trash basket (top ID = 15 in.; bottom ID = 12 in.) in which 50% of the bottom sidewall (up to 8 in.) was cut away in four sections that were overlain with various mesh screens. (The device was re-engineered for the actual testing.) In the bench apparatus, approximately two-thirds of the soil was washed out through the screen within the first 2 min of treatment with 4.5 L/min (1.2 gal/min) of water at a pressure of 4.9 kg/cm<sup>2</sup> (70 psi) and a drum speed of 10 to 20 rpm. Further experiments indicated that a three step sequence was needed to achieve the best decontamination:

1. Low-pressure wash,
2. Soaking, followed by stripping, and
3. Low-pressure fresh-water wash.

### Liquid-Solid Separation

To study the separation of soil fines from water, a full-sized hydrocyclone (227 L/min) was used with different inflow rates (and pressures) and different concentrations of both soils. Though the results of these tests show that the hydrocyclone is suitable for each soil, they also indicate that the solids were better concentrated in the underflow from the inorganic soil. With both soils, the overflow contained a small but significant amount of fines (0.7% to 3.7%), which would require additional separation. Passing this overflow through the hydrocyclone in a second treatment was not notably effective in removing these fine solids.

Because the hydrocyclone was too large for routine use in the laboratory study of contaminant removal from soil, simply gravity settling in a beaker was evaluated and found to represent a good simulation of the separation achievable with the hydrocyclone.

### Extraction Tests

Tests were carried out with the three chemicals (all three were not used in all experiments) to establish the following:

- a) probable loading on a soil column,
- b) distribution on particles of different sizes, and
- c) effect of extraction with different solvents on particles of different sizes.

## Column Loading Studies

A stock solution of the contaminant equal in volume to the void space in the column was added to a 15.2-cm (6.0-in.) column of soil (various moistures and densities) and allowed to drain for 24 hr. The contaminant remaining in the column was calculated on a dry weight basis, based on the amount of fluid that drained from the column. Modified gas chromatographic and atomic absorption methods (described more fully in the report) were used. Results obtained with the three materials are shown in Table 1. Note the heavy loading of phenol, which represents the situation that might exist shortly after a spillage onto soil.

### Distribution Tests

Different procedures were used with phenol and with arsenic trioxide to evaluate their distribution on particles of different sizes. For phenol, dry soils were first size-classified with a sonic fractionation device. Each fraction was then wetted with a stock solution of phenol. After 18 hr, the fractions were rinsed with water and analyzed. For arsenic, the soil from the column dosing tests was dried, size fractionated, and then analyzed. High recoveries (based on analyses) were achieved in both cases.

With phenol, these tests indicated that approximately 90% of the contaminant was absorbed (or retained interstitially) on the larger particles (0.6 to 2 mm<sup>φ</sup>) of the organic soil. These somewhat unexpected results also appear to be a consequence of nonuniform distribution of organics in the different particle-size fractions. Tests confirmed that the fine particles contained predominantly organic degradation products rather than plant tissues, which remained primarily with the larger particles. Such differences may make it necessary, in some cases, to presoak the soil for efficient extraction.

Unexpected results were also obtained when testing the distribution of phenol on the inorganic soil. The relatively low adsorption by the finer particles was attributed to differences in internal porosity and chemical composition between the large and small particles rather than the proportionately greater surface area (calculated on a weight basis) of the fine particles.

The results obtained with arsenic trioxide on the organic soil were similar to those obtained with phenol. With the

<sup>φ</sup> Nominal sizes are given for screens.

inorganic soil, however, the arsenic compound exhibited the normally expected relationship between particle size (i.e., surface area) and amount adsorbed. That is to say, because of the greater surface-to-mass ratio, more adsorption occurs per unit weight of fines.

PCB's were not tested to any great extent because of their low solubility and the hazards involved in working with them. Time and funding constraints also influenced this decision to curtail PCB studies.

### Water-Knife Stripping Tests

Contaminated soil samples were subjected to 1 min of stripping by the water knife to remove particles smaller than 2 mm. Residual contaminants on the remaining (larger than 2 mm) particles were then determined. The results (Table 2) show the value of additional washing or extraction, at least for phenol and arsenic trioxide.

### Chemical Extraction Tests

Since water is not the optimum extractant for all contaminants tested, and since most of the contaminants will be absorbed by and adsorbed on the smaller (<2 mm) particles, a series of tests with the following aqueous solutions was conducted to determine whether extraction efficiency could be improved:

- water + sulfuric acid to pH 1
- water + sodium hydroxide to pH 11
- water + 7.5% sodium bisulfate
- water + 5.0% sodium hypochlorite
- water + 1.0% TWEEN 80
- water + 1.0% MYRJ 52
- water + 5.0% methanol

For the inorganic soils contaminated with phenol, all extractions were highly efficient, with removals greater than 87%. Only for the organic soil could the difference between solvents be considered significant, with the sodium hydroxide solution being the most effective solvent. A portion of the data presented in the report is summarized in Table 3. The relative and actual importance of the residual contaminant on the soil should not be ignored, nor should the fraction of solvent remaining in the soil (not shown in Table 3). When the residual level of contamination is

Table 1. Maximum Column Loadings

Contaminant	Organic Soil (mg/g soil)	Inorganic Soil (mg/g soil)
Phenol	453.2	48.3
Arsenic trioxide	5.0*	0.75*
PCB	25.6	3.0

\*As arsenic (As).

Table 2. Effect of Washing on Large Particles\*

Soil	Test Time (min)	% Removal		
		Phenol	As <sub>2</sub> O <sub>3</sub>	PCB
Inorganic	15	97.9	28.9	21.4
	30	98.2	52.1	50.0
	60	98.8	42.2	21.4
	120	99.1	52.1	28.6
Organic	15	60.7	47.7	
	30	79.2	55.8	
	60	86.0	54.0	
	120	91.6	59.0	

\*2 to 12.7 mm

Table 3. Solvent Extraction: Representative Single-Washing Tests\*

Contaminant	Soil**	Solvent	Initial Soil Dose (mg/g dry soil)	% Removal	Supernatant Concentration (mg/L)	Residual Soil Concentration mg/g
Phenol	I	Water	48	98.6	1,190	0.68
	O	Water	452	77.8	17,600	100.4
		NaOH (pH 11)		88.4	20,000	52.5
As <sub>2</sub> O <sub>3</sub>	I	Water	0.75	42.7	16	0.43
		H <sub>2</sub> SO <sub>4</sub> (pH 1)		85.3	32	0.11
	O	Water	5	75.0	375	1.25
		H <sub>2</sub> SO <sub>4</sub> (pH 1)		85.0	425	0.75
PCB	I	Water	3	24.6	72	2.66
		1% Tween 80		37.5	110	1.88
	O	Water	26	48.3	418	13.2
		1% Tween 80		23.8	366	19.5

\* Extractant to dry solids 10:1 (w/w).

\*\* I = inorganic; O = organic.

sufficiently low, the treated soil may no longer require disposal as a hazardous material, e.g., in a safe landfill.

Samples of phenol-contaminated organic and inorganic soils were also subjected to multiple extractions. These tests demonstrated that continued removal of phenol did occur, even when the extractant was recovered solvent (water) from a previous stage and already contained phenol. Residual phenol concentrations of 30 mg/kg (0.03 mg/g)

of soil were achieved after four countercurrent extractions of the inorganic soil.

### Prototype Design and Construction

The process sequence for full-scale treatment (Figure 1) was finalized, based on the laboratory experiments. The sequence includes initial removal of oversized chunks (>2.5 cm), water-knife

scrubbing to deconsolidate the remaining soil matrix and to strip any contaminant loosely absorbed on the solids ( $>2$  mm) or held in the void spaces of the soil, and four-stage, countercurrent extraction coupled with hydrocyclone separation after each extraction stage to separate the solids ( $<2$  mm) from the liquid. Froth flotation is used to give maximum mixing of extractant and soil in each stage. The overhead extract (mostly sorbent) from the first stage extractor hydrocyclone contains the highest level of dissolved (or dispersed) contaminants and fines. This extract must be clarified and then treated (possibly with activated carbon) before it is recycled.

Note that: chunks ( $> 2.5$  cm) are not normally processable in the system except for moderate washing on a bar screen\*; the 2.5-cm to 2-mm as well as the  $<2$ -mm fraction, will be used to fill in the excavation; all processing fluids must be appropriately treated. All dust and vapor emissions should be ducted to an air cleaner or scrubber before discharge.

The basic system was constructed according to the design shown in Figure 1.

The water-knife unit (rotary drum-screen scrubber) consists of a tilt-skip loader and hopper feed from which the soil moves into a tiltable 19-m (21-ft) long by 1.4-m (4.5-ft) ID cylinder fitted with end pieces, water-knives, and a rotating mechanism (Figures 2, 3, and 4).

Soil is metered from the tilt-skip reservoir hopper at rates up to 18 yd<sup>3</sup>/hr onto a manually washed bar screen where  $>2.5$ -cm (1-in.) chunks are rejected. The solids then pass into the tilted drum-screen scrubber where it is subjected to first-stage water-knife stripping, water soaking, and finally second-stage water-knife stripping using fresh or partially recycled water. The first section of the scrubber cylinder is 1.3-m (4-ft) long and is fabricated from 2-mm mesh (HYCOR Contra-Shear screen) and equipped with internal water-knives. Solids then move into the 5-m (15 ft) soak cylinder that is fitted with a baffle plate that has a 0.5-m (22-in.) center opening through which solids pass into a 0.7-m (2-ft) long screened, water-knife rinse zone. Fines ( $<2$  mm) pass through the screens, as does the wash water. The coarse particles are voided at the end of

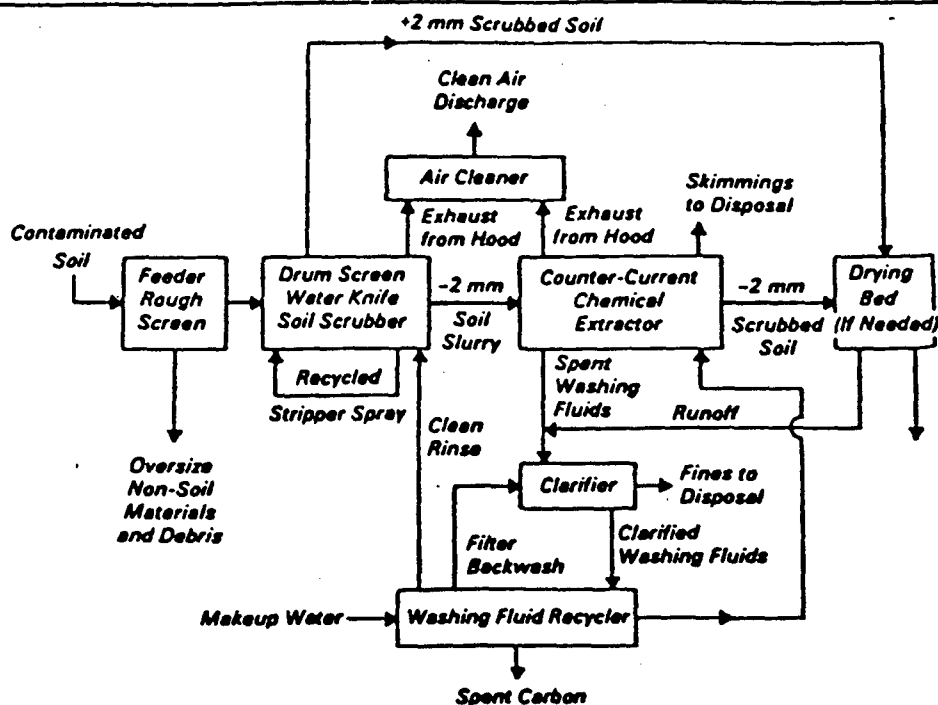


Figure 1. Process flow scheme for soil scrubber.

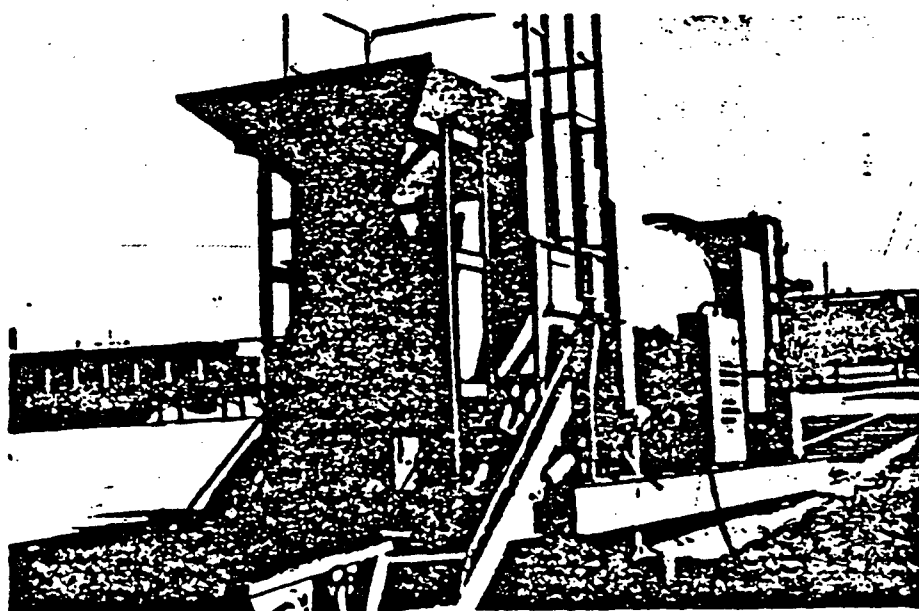


Figure 2. Fully constructed rotary drum screen scrubber.

the drum. The unit can be backflushed as needed. The screens resist buildup of fines (blinding). The actual arrangement of the water-knives and other details of construction are given in the project report.

From the water-knife and soaker unit, the slurry ( $<2$ -mm particles) is pumped to the countercurrent extractor. The four-stage countercurrent extraction unit (Figures 5 and 6) has been modified from the so-called EPA beach sand froth

\* There are two bar screens. The soil is hoist-raised on a 7.5- or 8-cm (3- or 2-in.) upper screen in the skip-hopper from which large or nondisintegrable chunks are raked off. Washed chunks that pass the upper screens are rejected and removed at the second (lower) bar screen ( $<2.5$  cm [1 in.]).

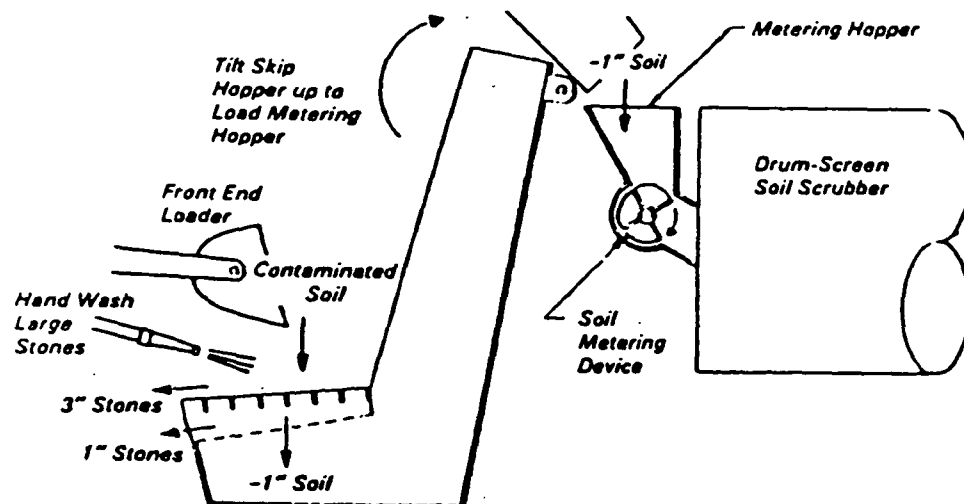
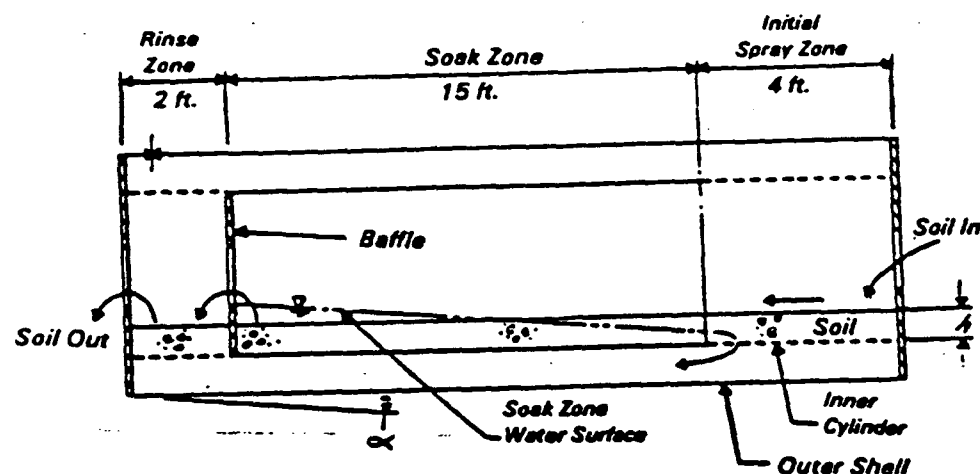
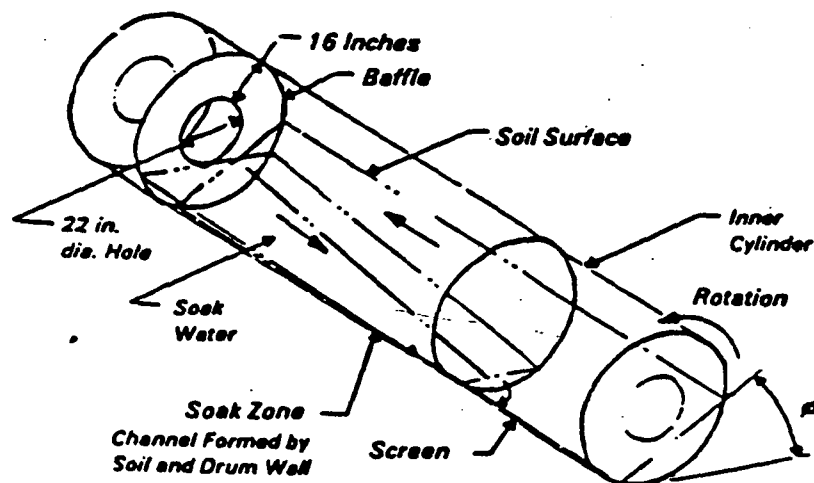


Figure 3. Soil loading and metering system (cross sectional side view).



A. Drum cross section



B. Drum Isometric

Figure 4. Soak zone description.

flotation unit.\* Basically, the washing chamber was partitioned into four sections (3-ft long X 4-ft wide X 5-ft deep), each of which has an aerator agitator and a hydrocyclone with pumps and piping. Flow of solids (<2mm) and fluid is countercurrent with clear water being introduced at the fourth (discharge) chamber (Figure 6). The extraction unit has an on-board diesel generator; the water-knife unit requires external power. The underflow (solids-rich) slurry from the fourth hydrocyclone is discharged to a drying bed.

To achieve mobility, the water-knife unit is skid-mounted for transport by semi-trailer; the countercurrent extractor is integrally attached to a separate semi-trailer. Refer to Figures 2 and 5 for details. Calculations indicate that the total system has a throughput range of 2.3 to 3.8 m<sup>3</sup>/hr (3-5 yd<sup>3</sup>/hr), but that the water-knife unit alone can process 11.5 to 13.5 m<sup>3</sup>/hr (15 to 18 yd<sup>3</sup>/hr).

## Conclusions

The following conclusions can be drawn from the work carried out during this program and the knowledge gained during that effort:

1. Spill-contaminated soils can be excavated and treated onsite using extraction with water or aqueous solutions for many pollutants that are frequently encountered in such situations.
2. A system capable of decontaminating 2.3 to 3.8 m<sup>3</sup>/hr (3-5 yd<sup>3</sup>/hr) of soil has been designed and constructed and it is now available for field testing by EPA.
3. Water-knives function as a compact, efficient, and economical means of achieving effective contact between contaminated soil particles and extractant.
4. Countercurrent extraction is an effective process for removing certain adsorbed contaminants from soils and, for the size of equipment needed, hydrocyclones are preferred devices for separating the extracted solids from the extractant.

\*Gerth D. Guntz, Restoration of Beaches Contaminated by Oil, EPA-R2-72-045 (Washington, D.C.: US EPA, 1972).



5. Laboratory experiments demonstrate that soil characteristics (particle size, distribution, organic content, pH, ion-exchange properties, etc.) are important factors in the removal or retention of contaminants.
6. In addition to the actual percentage of the contaminant removed, the allowable level of pollutant remaining in the soil is an important factor in determining when adequate decontamination has been achieved since the final, residual concentration affects the options available for disposal of the cleansed solids.

## Recommendations

Based on the observations made during this investigation, several suggestions are offered for future work.

1. Laboratory screening tests should be performed on a wider range of typical compounds and mixtures encountered in hazardous substance spill and release situations to ensure that appropriately high levels of decontamination can be achieved with this process.
2. The results of this study apply primarily to spill situations. Contaminated soils found at waste disposal sites may exhibit different extraction characteristics because of the extended soil/contaminant contact time and of weathering and in situ reactions. Studies are needed to establish whether and to what extent such changes affect the decontamination process.
3. Other extractant solutions should be evaluated to determine whether the efficiency of the process can be improved without damaging the equipment or increasing the hazards to which the workers are exposed.
4. A wider range of soils should be examined to determine what changes in the system are practical to better cleanse soils with characteristics (e.g., greater cohesiveness and adsorptive properties of clay- or silt-rich soils) that differ significantly from those of the soils already tested.

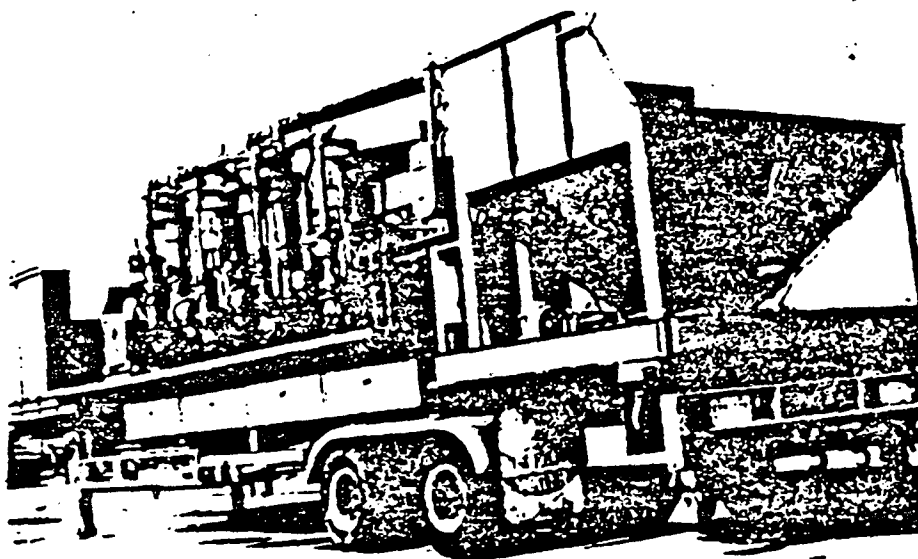


Figure 5. EPA Froth Flotation System (beach cleaner) modified as a countercurrent chemical extractor for soil scrubbing.

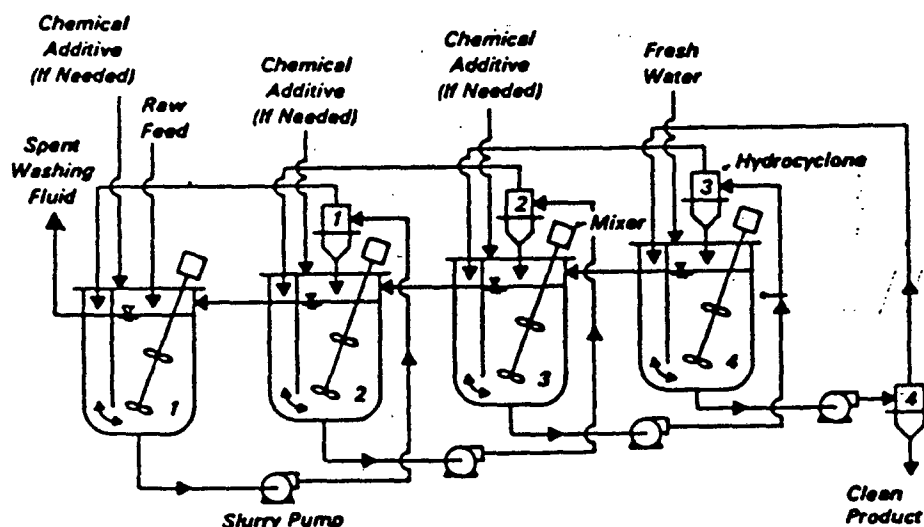


Figure 6. Process flow scheme for soil scrubber.

The full report was submitted in fulfillment of Contract No. 68-03-2696 by Rexnord, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

*Robert Scholz and Joseph Milanowski are with Rexnord Inc., Milwaukee, WI 53214*

*John E. Brugger is the EPA Project Officer (see below).*

*The complete report, entitled "Mobile System for Extracting Spilled Hazardous Materials from Excavated Soils," (Order No. PB 84-123 637; Cost: \$11.50, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Municipal Environmental Research Laboratory—Cincinnati*

*U.S. Environmental Protection Agency*

*Edison, NJ 08837*

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## *Project Summary*

# Guidelines for the Use of Chemicals in Removing Hazardous Substance Discharges

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This project was undertaken to develop guidelines for the use of various chemical and biological agents to mitigate discharges of hazardous substances. Eight categories of mitigating agents are discussed along with their potential uses in removing hazardous substances discharged on land and in waterways. The agents are classified as follows: mass transfer media, absorbing agents, thickening and gelling agents, biological treatment agents, dispersing agents, precipitating agents, neutralizing agents, and oxidizing agents. Each of these classes is developed in terms of the agents' general properties, their use in spill scenarios, environmental effects, possible toxic side effects, and recommended uses.

A matrix of countermeasures has been developed that refers to various classes of mitigating agents recommended for treatment of hazardous substances involved in spills in or near a watercourse. The matrix includes a list of hazardous chemicals, the corresponding U.S. Environmental Protection Agency (EPA) toxicity classification, and the physical properties of the chemical.

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*documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The 1972 Water Pollution Control Act Amendments gave the U.S. Environmental Protection Agency (EPA) responsibility for removing spilled hazardous substances from the environment. EPA was also made responsible for developing criteria to be used for designating substances as hazardous. Of the two criteria developed, the first involves the potential toxic effect of a substance on the biosphere. The second criterion considers the probability of spills based on annual production, methods of transporting, storage, physical-chemical properties, and past history. Based on these criteria, a proposed list of hazardous substances was published in the Federal Register (Vol. 40, No. 250) on December 30, 1975.

The responsibility EPA bears for hazardous material spills raises many questions about removing discharged hazardous substances effectively. Many parameters are involved in deciding how to counteract a hazardous substance spill, and which countermeasure (if any) to use. The guidelines developed by this study for mitigating hazardous material discharges are to be used by EPA in the future to expand and revise

Annex X of the National Oil and Hazardous Substance Pollution Contingency Plan, 40CFR1510, so that it includes specific reference to chemical use for spills of hazardous substances. The guidelines also establish a method for determining the circumstances under which a particular mitigating agent can be used and those under which the use of chemicals and other additives is harmful to the environment.

## Results

### Use and Effects of Mitigating Agents

Study results are outlined in Table 1, which summarizes the recommended uses for each class of agent and the possible toxic side effects associated with their use. The eight categories of mitigating agents are as follows: mass transfer media, absorbing agents, gelling and thickening agents, biological treatment agents, dispersing agents, precipitating agents, neutralizing agents, and oxidizing agents. The recommended uses, effectiveness, and possible toxic effects of these agents are discussed here briefly.

Note that the effectiveness of a mitigating agent depends largely on the specific spill situation. The amount of agent needed to counteract a hazardous substance discharge is dictated by many factors, including the size of the watercourse, the conditions of flow, and the possible long-term toxic effects of

irretrievable contaminated agents and byproducts.

### Mass Transfer Media—

Agents within this category include activated charcoal and ion exchange resins. Available evidence indicates that activated charcoal and ion exchange resins introduced in moderate amounts to the aquatic environment will not in themselves be toxic. But the desorption of a hazardous chemical from such mass transfer media in natural surface water and the potential persistence of these toxic organic compounds in the aquatic environment must be considered in any decision to use irretrievable mass transfer agents. We can safely assume that if those toxic compounds can be removed from the environment by biological processes, they can also be removed if bound to a mass transfer medium. We can also assume that the total toxic effect of those biodegradable materials can be reduced if mass transfer agents can be used to minimize acute toxicity.

Irretrievable mass transfer media should be considered acceptable for treating the class of materials that is biodegradable under all conditions.

### Absorbing Agents—

The use of absorbing agents is generally limited to spills of oil and petroleum products. Natural agents such as straw, sawdust, etc., are routinely used in such cleanups. A

variety of synthetic absorbents are available for mitigating both hydrophobic and hydrophilic chemicals. These absorbents are nontoxic and do not present a hazard to the environment in an uncontaminated state, but desorption of the spilled material from both natural and synthetic absorbents can be significant. For this reason, the use of absorbing agents is recommended only in those situations in which the sorbent can be removed from the environment.

### Thickening and Gelling Agents—

Mitigating agents in this category are actually special types of absorbents used to immobilize the spilled material to prevent further spread into the environment and to condition the spill for mechanical removal. We recommend that these agents be used on land spills of all liquid materials on which they are effective. Certain agents should be considered appropriate for treatment of water spills of insoluble organics that float. Thickening or gelling agents should not be used on water spills of materials that sink or mix into the water column.

### Biological Treatment Agents—

Biological agents have been shown to be effective in mitigating spills of oil and oil-derived products. Several limitations, however, exist to the use of these agents in the treatment of spilled organic materials.

Table 1. Mitigation Summary

Mitigation Category	Possible Toxic Effect(s)	Recommended Uses
Mass transfer media	Desorption of hazardous substance - chronic toxicity.	Biodegradable substances.
Absorbing agents	Desorption of hazardous substance - chronic toxicity, increased biological oxygen demand.	All land spills. Insoluble organics that float, provided absorbent can be removed from the environment.
Thickening and gelling agents	No known toxic effects.	All land spills. Insoluble organics that float.
Biological treatment	Ecological imbalance. Toxicity of degradation products.	Biodegradable substances. Spills that are easily contained and monitored.
Dispersing agents	Increase in toxicity resulting from dispersed substances. Toxicity of degradation product of added agent.	Biodegradable substances.
Precipitating agents	Toxic effect of insoluble metal salts.	Removal of metal ions from solution.
Neutralizing agents	Toxicity resulting from change in pH from natural conditions. Toxic metal ion byproduct.	All spills involving acids or bases.
Oxidizing agents	Toxic intermediate reaction products. Oxidation of natural organic materials - ecological imbalance.	Limited to detoxification of hazardous substances in closed system to allow control of reaction.

Considerable time is required by the biological degradation process, which makes it necessary to contain and isolate the spilled material from the environment before treatment. The bacterial culture must also be given sufficient nutrients and maintained in an environment that will encourage adequate growth. A culture maintenance program must therefore be initiated. Finally, no agent should be introduced into the environment if it will cause any significant change to the ecological balance of the treated waterway. Biological agents should be considered appropriate for treating spills of materials that are biodegradable, but only when conditions allow the contaminated environment to be contained for sufficient time to permit detoxification. Other types of mitigating agents should be used whenever possible.

#### **Dispersing Agents—**

Dispersing agents can be used to (1) increase the rate of biodegradation of spilled material, (2) protect aquatic fowl by removal of oil or other organics from surface water, (3) minimize fire hazards by dispersing hazardous material into the water column, and (4) prevent shoreline contamination. Some dispersants are toxic, however, and care must be exercised to prevent unnecessary harm to aquatic life.

#### **Precipitating Agents—**

Precipitation is a valid mitigating technique for removing toxic metal ions from solution. The technique generally requires the addition of either hydroxide or sulfide ions at elevated pH levels.

Hydroxide ions will re-enter the water column when the pH returns to neutral, creating the possibility of a long-term environmental hazard. Sulfide precipitation is thus recommended. At toxic concentrations of heavy metal ions, an insoluble metal sulfide will form and reduce toxicity rapidly. The precipitate is insoluble enough to reduce re-entry of metal ions into the environment to a nontoxic level. Further study will be necessary, however, to determine the long-term effect of metal salts on the water system.

A byproduct of sulfide precipitation is toxic hydrogen sulfide gas. To inhibit hydrogen sulfide formation, the sodium sulfide precipitating solution should be stabilized with sodium hydroxide.

#### **Neutralizing Agents—**

Neutralization is an acceptable method of treating all spills of acids and bases,

provided some method for monitoring pH is available. Treatment should be accomplished on land whenever possible to prevent the spilled material from entering aquifers or surface water. Toxicity associated with pH change from normal values once the spill has entered a waterway is critical, in which case neutralization of the spill becomes the primary method of treatment.

Toxicity reduction is coupled with the return of normal pH values regardless of the neutralizing agent; however, care must be taken to select an agent that produces the least toxic byproducts. All other considerations being equal, weak acids and bases should be selected to neutralize a spill in preference to strong acids and bases. This policy will minimize the potential for overtreatment. The use of solid agents should also be avoided when possible.

Where the monitoring system is not accurate enough to ensure treatment to the exact pH desired, it is better to undertreat than to risk overtreatment. pH values between 6 and 9 are recommended.

#### **Oxidizing Agents—**

Oxidizing agents are toxic to most organisms at relatively low concentrations. The reactions are difficult to control and seldom go to completion, thus leaving toxic intermediate reaction products. The use of oxidizing agents should be limited to land or water spills that are completely contained. Furthermore, these agents should be used only as a last resort.

#### **Countermeasure Matrix**

A comprehensive list of the various types of mitigating agents and their potential uses has been generated in matrix format (Table 2). This countermeasure matrix refers to classes of agents recommended for treating hazardous substances involved in spills in or near waterways. The matrix is a comprehensive list of hazardous chemicals, the EPA toxicity classification for each, and the density and the physical form of the pure hazardous substance. Each chemical is also assigned a physical/chemical/dispersal (P/C/D) factor, which has a range from 0.1 to 1.0 and is "...based on the solubility, density, volatility, and associated propensity for dispersal in water of each hazardous substance." 40CFR60002, December 30, 1975. The remainder of the matrix specifies which categories of countermeasures are effective for

controlling hazardous substances discharged on the ground or in a waterway.

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Table 2. Hazardous Substance/Countermeasure Matrix

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Acetaldehyde	C	0.783	L	M	#				#			#	#		
Acetic acid	C	1.049	L	M	#				#			#	#		
Acetic anhydride	C	1.083	L	SF	#				#			#	#		
Acetone															
Acrylonitrile	C	0.90	L	SF	#							#	#		
Acetyl bromide	D	1.52	L	SS	#				#			#	#		
Acetyl chloride	D	1.11	L	SS	#							#	#		
Acrolein	A	0.839	L	SF	#							#	#		
Acrylonitrile	C	0.907	L	SF	#							#	#		
Adiponitrile	D	0.96	L	SF	#							#	#		
Adiponitrile	A	1.66	S	SS	#							#	#		
Adiponitrile															
Allyl alcohol	B	0.854	L	M	#							#	#		
Allyl chloride	C	0.9	L	NF	#							#	#		
Aluminum															
fluoride	D	2.68	S	P	#							#	#		
Aluminum sulfate	D	1.63	S	P	#							#	#		
Ammonia	C	0.60	L	SF	#							#	#		
Ammonium acetate	D	1.073	S	SM	#							#	#		
Ammonium															
benzoate	D	1.26	S	SS	#							#	#		
Ammonium															
bicarbonate	D	1.50	S	SS	#							#	#		
Ammonium															
bichromate	D	2.18	S	SS	#							#	#		
Ammonium															
bisulfide	D	1.21	S	SS	#							#	#		
Ammonium															
bisulfate	D	—	S	SS	#							#	#		
Ammonium															
bromide	D	2.43	S	SS	#							#	#		
Ammonium															
carbonate	D	—	S	SS	#							#	#		
Ammonium															
carbonate	S	—	S	SM	#							#	#		
Ammonium															
chloride	D	1.53	S	SS	#							#	#		
Ammonium															
chromate	D	1.91	S	SS	#							#	#		
Ammonium															
citrate	D	—	S	SS	#							#	#		
Ammonium															
fluoride	D	1.88	S	SS	#							#	#		
Ammonium															
fluoride	D	1.31	S	SM	#							#	#		
Ammonium															
hydroxide	C	0.9	S/L	M	#							#	#		
Ammonium															
hypophosphite	D	—	S	SS	#							#	#		
Ammonium															
iodide	D	2.56	S	SM	#							#	#		
Ammonium															
nitrate	D	1.66	S	SM	#							#	#		
Ammonium															
acetate	D	1.80	S	SS	#							#	#		
Ammonium															
perchlorate	D	—	S	SS	#							#	#		
Ammonium															
persulfate	D	1.90	S	SS	#							#	#		
Ammonium															
silicofluoride	C	2.01	S	SS	#							#	#		
Ammonium															
sulfamate	D	—	S	SM	#							#	#		
Ammonium															
sulfide	D	1.02	S	SS	#							#	#		
Ammonium															
sulfate	D	1.41	S	SS	#							#	#		
Ammonium															
tartrate	D	1.61	S	SS	#							#	#		
Ammonium															
thiocyanate	D	1.31	S	SM	#							#	#		
Ammonium															
thiosulfate	D	—	S	SM	#							#	#		
Ammonium															
acetate	C	0.88	L	SP	#							#	#		
Ammonium															
perchlorate	C	1.022	L	SS	#							#	#		
Ammonium															
perchlorate	C	2.34	S	P	#							#	#		
Ammonium															
perchlorate	C	2.90	S	P	#							#	#		
Ammonium															
potassium tartrate	C	2.6	S	P	#							#	#		
Ammonium															
tribromide	C	4.14	S	P	#							#	#		
Ammonium															
tribromide	C	3.14	S	P	#							#	#		
Ammonium															
tribromide	C	4.30	S	P	#							#	#		

Table 2. (continued).

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Antimony trioxide	C	5.2	S	P											
Arsenic acid	C	2-2.5	S	P											
Arsenic disulfide	C	3.4	S	IS											
Arsenic pentoxide	B	4.08	S	P											
Arsenic trichloride	C	2.16	S	P											
Arsenic trioxide	B	3.89	S	P											
Arsenic trisulfide	B	3.43	S	IS											
Barium cyanide	A	—	S	SS											
Benzene	C	0.879	L	MF											
Benzoic acid	D	1.266	S	SS											
Benzonitrile	C	1.01	L	SS											
Benzoyl chloride	D	1.20	L	SS											
Benzyl chloride	D	1.08	L	IS											
Beryllium chloride	D	1.90	S	P											
Beryllium fluoride	C	1.99	S	P											
Beryllium nitrate	C	1.66	S	P											
Buryl acetate	C	0.89	L	SF											
Butylenes	C	0.74	L	M											
Butyric acid	D	1.00	L	M											
Cadmium acetate	A	2.01	S	SS											
Cadmium bromide	A	5.19	S	P											
Cadmium chloride	A	4.06	S	P											
Calcium arsenate	C	3.0	S	IS											
Calcium arsenite	C	—	S	SS											
Calcium carbide	D	2.2	S	P											
Calcium chromate	D	2.89	S	SS											
Calcium cyanide	A	—	S	SS											
Calcium dodecylbenzenesulfonate	B	—	S	SS											
Calcium hydroxide	D	2.804	S	SS											
Calcium hypochlorite	A	2.36	S	SM											
Calcium oxide	D	2.40	S	SM											
Caplan	A	1.5	S	SS											
Carbaryl	B	—	S	SS											
Carbon disulfide	C	1.26	L	SS											
Chlorane	A	1.89	L	IS											
Chlorine	A	2.2	L	SF											
Chlorobenzene	B	1.1	L	IS											
Chloroform	B	1.5	L/G	IS											
Chlorosulfonic acid	C	1.8	L	SS											
Chromic acetate	D	—	S	SS											
Chromic acid	D	2.7	L	SM											
Chromic sulfate	D	1.7	S	SS											
Chromous chloride	D	2.67	S	IS											
Chromyl chloride	D	1.91	S	SS											
Cobaltous bromide	C	2.47	S	P											
Cobaltous fluoride	C	4.46	S	P											
Cobaltous formate	C	2.13	S	P											
Cobaltous sulfamate	C	—	S	P											
Coumaphos	A	—	S	SS											
Cresol	B	1.0	S	SS											
Cupric acetate	B	1.8	S	P											
Cupric arsenate	B	—	S	IS											
Cupric chloride	B	3.39	S	P											
Cupric formate	B	1.63	S	P											
Cupric glycinate	B	—	S	P											
Cupric lactate	B	—	S	P											
Cupric nitrate	B	2.32	S	P											
Cupric oxalate	B	—	S	IS											

Table 2. (continued)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agents		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Cupric subacetate	B	1.9	S	P	x	x				x					
Cupric sulfate	B	2.28	S	P	x	x				x					
Cupric sulfate ammoniated	B	—	S	P	x	x				x					
Cupric tartrate	B	—	S	IS	x	x				x					
Cuprous bromide	B	4.72	S	IS	x	x	x			x					
Cyanogen chloride	A	1.186	G	SS	x	x									
Cyclohexane	C	0.779	L	INF	x										
2,4-D acid	B	0.82	—	IS							x	x	x		x
2,4-D esters	B	—	—	IS									x		
Calceon	B	1.38	L	SS	x							x	x		
DOT	A	—	S	IS	x							x	x		
Diazinon	A	1.116	L	IS	x							x	x		
Dicamba	C	—	S	SS	x								x		
Dichlorobenzil	C	—	S	SS	x								x		
Dichloro	A	—	S	SS	x							x	x		
Dichlorous	A	—	L	SS	x								x		
Dieldrin	A	1.78	S	SS	x								x		
Diethylamine	C	0.71	L	SF	x						x	x	x		x
Dimethylamine	C	0.69	L	SF	x						x	x	x		x
Dinitrobenzene	C	1.54	L	SS	x						x	x	x		x
Dinitrophenol	B	1.68	L	SS	x						x	x	x		x
Diquat	C	—	S	SS	x								x		
Disulfoton	A	1.14	L	SS	x								x		
Duron	B	—	S	SS								x	x		
Dodecylbenzene-sulfonic acid	B	—	L	SS	x						x	x	x		x
Dursban	B	—	—	SS	x								x		
Endosulfan	A	—	S	SS	x								x		
Endrin	A	—	S	IS	x								x		
Ethion	A	1.22	L	SS	x							x	x		
Ethylbenzene	C	0.868	L	INF	x						x	x	x		x
Ethylene diamine	C	0.95	L	SF	x							x	x		x
EDTA	D	—	S	IS	x						x		x		x
Ferric ammonium citrate	C	—	S	P	x		x			x					
Ferric ammonium oxalate	C	—	S	P	x		x			x					
Ferric chloride	C	2.89	S	P	x		x			x					
Ferric fluoride	C	3.52	S	P	x		x			x					
Ferric nitrate	C	1.68	S	P	x		x			x					
Ferric sulfate	C	2.0	S	P	x		x			x					
Ferrous ammonium sulfate	C	1.87	S	P	x		x			x					
Ferrous chloride	C	1.93	S	P	x		x			x					
Ferrous sulfate	C	1.839	S	P	x		x			x					
Formaldehyde	C	0.815	L	M	x					x		x	x		x
Formic acid	C	1.22	L	M	x				x			x	x		x
Fumaric acid	D	1.635	L	SS	x				x			x	x		x
Furfural	C	1.15	L	SS	x						x	x	x		x
Guthion	A	1.44	L	IS	x							x	x		
Heptachlor	A	1.58	S	IS	x								x		
Hydrochloric acid	D	1.00	L	SS	x		x		x			x	x		
Hydrofluoric acid	D	1.15	L	M	x		x		x			x	x		
Hydrogen cyanide	A	0.70	L/G	M	x		x		x			x	x		
Hydroxylamine	D	1.23	S	SS	x							x	x		
Isoprene	C	0.681	L	INF	x						x	x	x		x
Isopropylamine dodecylbenzene sulfonate	B	0.90	L	SS	x						x	x	x		x
Kelthane	C	—	—	IS	x								x		
Lead acetate	D	2.25	S	P	x		x			x					
Lead arsenate	D	7.8	S	IS	x		x			x					
Lead chloride	D	5.85	S	P	x		x			x					
Lead fluoride	D	—	S	P	x		x			x					
Lead fluoride •	C	8.2	S	IS	x		x			x					
Lead hydride	D	6.16	S	IS	x		x			x					
Lead nitrate	D	4.53	S	P	x		x			x					
Lead stearate	D	1.4	S	P	x		x			x					
Lead sulfate	D	6.2	S	IS	x		x			x					
Lead sulfide	C	7.1	S	IS	x		x			x					
Lead tetracetate	D	2.23	S	P	x		x			x					
Lead thiocyanate	D	3.8	S	IS	x		x			x					
Lead thiosulfate	D	5.18	S	IS	x		x			x					
Lead tungstate	D	8.24	S	IS	x		x			x					
Lindane	A	1.87	S	SS	x										



Table 2: (continued)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Mode			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Lithium															
Lithium acetate	D	2.34	S	SM	x	x	x			x					
Lithium chromate	D	—	S	SM	x	x	x								
Maleic anhydride	A	1.23	L	SS											
Maleic acid	D	1.69	S	SS	x				x		x				x
Maleic anhydride	D	0.934	S	SS	x				x		x				x
Mercuric acetate	A	3.26	S	P	x	x				x					
Mercuric cyanide	A	4.08	S	P	x	x	x			x					
Mercuric nitrate	A	4.3	S	P	x	x				x					
Mercuric sulfate	A	6.47	S	P	x	x				x					
Mercuric thiocyanate	A	—	S	IS	x	x	x			x					
Mercurous nitrate	A	4.79	S	P	x	x				x					
Methoxychlor	A	1.41	S	IS	x										
Methyl mercaptan	B	0.87	L/G	MP	x										x
Methyl methacrylate	D	0.936	L	MP	x										x
Methyl parathion	B	1.268	L	IS	x										
Menthylol	A	—	L	M	x										
Monomethylamine	C	1.01	—	M	x										x
Monomethylamine	C	—	—	SS	x										x
Nalad	A	—	S/L	IS	x										
Naphthalene	B	1.162	S	IS	x										
Naphthoic acid	A	1.4	S	SS	x										
Nickel ammonium sulfate	D	1.82	S	P	x	x				x					
Nickel chloride	D	3.66	S	P	x	x				x					
Nickel formate	C	2.16	S	P	x	x				x					
Nickel hydrosulfide	C	4.36	S	IS	x	x				x					
Nickel nitrate	D	2.06	S	P	x	x				x					
Nickel sulfide	D	1.948	S	P	x	x				x					
Nitric acid	C	1.502	L	M	x				x						
Nitrobenzene	D	1.19	L	SS	x										
Nitrogen dioxide	C	1.448	L/G	IS	x										
Nitroethanol	B	1.4	L	SS	x										x
Parformaldehyde	C	1.46	S	SS	x										x
Parathion	A	1.26	L	IS	x										
Parachlorophenol	A	1.076	S	IS	x										
Phenol	B	1.071	S	SS	x		x								
Phenol	D	1.292	O/L	SS	x										x
Phosphoric acid	D	1.834	L	M	x				x						
Phosphorus	A	1.8-2.7	S	IS	x										
Phosphorus oxychloride	D	1.67	L	SS	x	x									
Phosphorus pentasulfide	C	2.03	S	SS	x										
Phosphorus trichloride	D	1.574	S	SS	x	x	x								
Polychlorinated biphenyls	A	—	S	IS	x										
Potassium arsenate	C	2.67	S	P	x		x								
Potassium arsenite	C	—	S	P	x		x								
Potassium															
Potassium acetate	D	2.69	S	SS	x		x								
Potassium chromate	D	2.73	S	SS	x		x								
Potassium cyanide	A	1.62	S	SS	x		x								
Potassium hydroxide	C	2.04	S	SM	x				x						
Potassium															
permanganate	B	2.7	S	SS	x		x								
Propionic acid	D	0.993	L	M	x				x						x
Propionic anhydride	D	1.013	L	M	x				x						x
Propyl alcohol	D	0.8	L	M	x										x
Pyrethrin	C	—	L	SS	x										
Quaroline	A	1.09	L	SS	x										x
Resorcinol	B	1.27	S	SS	x										
Selenium oxide	C	3.964	S	SS	x	x				x					
Sodium	C	0.971	S	SS	x										
Sodium arsenate	C	1.76	S	SS	x		x								
Sodium arsenite	C	1.67	S	SS	x		x								
Sodium bisulfate	D	2.52	S	SM	x	x									
Sodium bisulfide	D	2.08	S	SS	x		x			x					
Sodium bisulfite	D	1.48	S	SS	x		x								
Sodium chromate	D	1.463	S	SS	x		x								
Sodium cyanide	A	1.48	S	SS	x		x								
Sodium dodecylbenzene sulfonate	B	—	S	SS	x		x								x
Sodium fluoride	D	2.78	S	SS	x		x			x					
Sodium hydrosulfide	D	—	S	SS	x		x								
Sodium hydroxide	C	2.13	L	SS	x				x						

Table 2. (continued)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Sodium hypochlorite	A	—	S	SM	x		x								
Sodium methylate	C	2.4	S	SS	x		x				x		x		x
Sodium nitrite	B	2.17	S	SS	x										
Sodium phosphate monobasic	D	2.04	S	SS	x										
Sodium phosphate dibasic	D	2.06	S	SM	x										
Sodium phosphate tribasic	D	1.6	S	SS											
Sodium selenite	C	1.63	S	SS			x								
Sodium sulfide	C	1.854	S	SS	x		x			x				x	
Stannous fluoride	D	2.79	S	SS		x	x			x					
Strontium chromate	D	—	S	IS	x	x	x			x					
Styrene	C	1.36	S	SS	x								x		x
Sulfuric acid	C	0.909	L	MF	x							x	x		x
Sulfur monochloride	C	1.834	L	M	x							x	x		
	D	1.69	S	SS	x				x						
2,3,5-T acid	A	—	S	IS									x		
2,4,5-T esters	A	—	S	IS									x		
TDE	A	—	S	IS	x								x		
Tetraethyl lead	A	1.659	L	IS	x								x		
Tetraethyl pyrophosphate	B	1.2	L	M	x								x		
Toulene	C	0.86	L	MF	x						x		x		x
Toxaphene	A	1.66	L	IS	x								x		
Trichloron	B	1.73	S	SS	x								x		
Trichlorophenol	A	1.1	L	IS	x								x		
Triethanolamine															
dodecylbenzene sulfonate	B	—	L	SS	x								x		
Triethylamine	C	1.13	L	SF	x						x		x		x
Trimethylamine	C	0.66	L	SF	x						x		x		x
Uranium peroxide	D	2.8	S	IS	x		x								
Uranyl acetate	D	2.89	S	P	x		x								
Uranyl nitrate	D	2.80	S	P	x		x								
Uranyl sulfate	D	3.28	S	P	x		x								
Vanadium pentoxide	C	3.36	S	P	x		x								
Vanadyl sulfate	C	—	S	P	x		x								
Vinyl acetate	C	0.94	S	SF	x						x		x		x
Xylene	C	0.86	L	MF	x								x		x
Xylol	C	1.02	L	SS	x								x		
Zactron	C	—	—	SS	x										
Zinc acetate	C	1.738	S	P	x		x								
Zinc arsenic															
chloride	C	1.80	S	P	x		x								
Zinc bichromate	C	—	S	P	x		x								
Zinc borate	C	3.64	S	P	x		x								
Zinc bromide	C	4.22	S	P	x		x								
Zinc carbonate	C	4.42	S	IS	x		x								
Zinc chloride	C	2.907	S	P	x		x								
Zinc cyanide	A	1.86	S	IS	x		x								
Zinc fluoride	C	4.84	S	P	x		x								
Zinc formate	C	2.21	S	P	x		x								
Zinc hydrosulfide	C	—	S	P	x		x								
Zinc nitrate	C	2.07	S	P	x		x								
Zinc phenyl sulfonate	C	—	S	P	x		x								
Zinc phosphide	C	4.86	S	IS	x		x								
Zinc potassium chromate	C	—	S	IS	x		x								
Zinc silicofluoride	C	2.1	S	P	x		x								
Zinc sulfate	C	3.64	S	P	x		x								
Zinc sulfate monohydrate	C	3.28	S	P	x		x								
Zirconium acetate	D	—	S	P	x		x								
Zirconium nitrate	D	—	S	P	x		x								
Zirconium oxychloride	D	—	S	P	x		x								
Zirconium potassium fluoride	D	—	S	P	x		x								
Zirconium sulfate	D	3.22	S	P	x		x								
Zirconium tetrachloride	D	2.8	S	P	x		x								

*C. K. Akers, R. J. Pilie, and J. G. Michalovic are with Claspan Corporation, Buffalo, NY 14221.*

*Joseph P. Lafornera is the EPA Project Officer (see below).*

*The complete report, entitled "Guidelines for the Use of Chemicals in Removing Hazardous Substance Discharges," (Order No. PB 82-107 483; Cost: \$9.50, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*For information contact John E. Brugger at:*

*Oil and Hazardous Materials Spills Branch*

*Municipal Environmental Research Laboratory—Cincinnati*

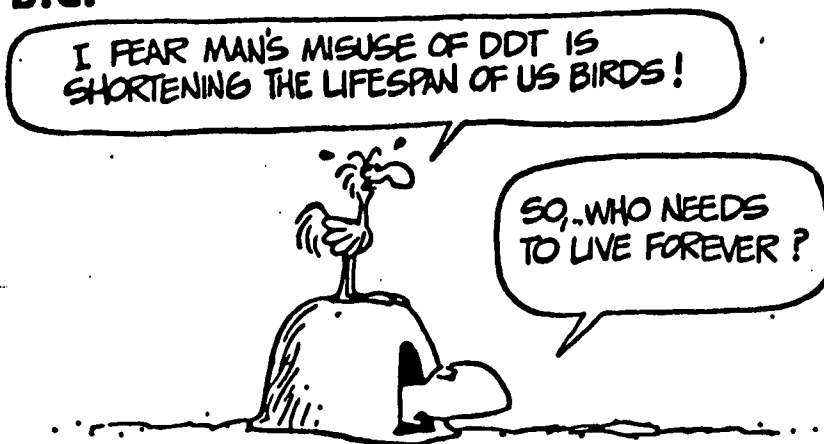
*U.S. Environmental Protection Agency*

*Edison, NJ 08837*

# WIZARD OF ID

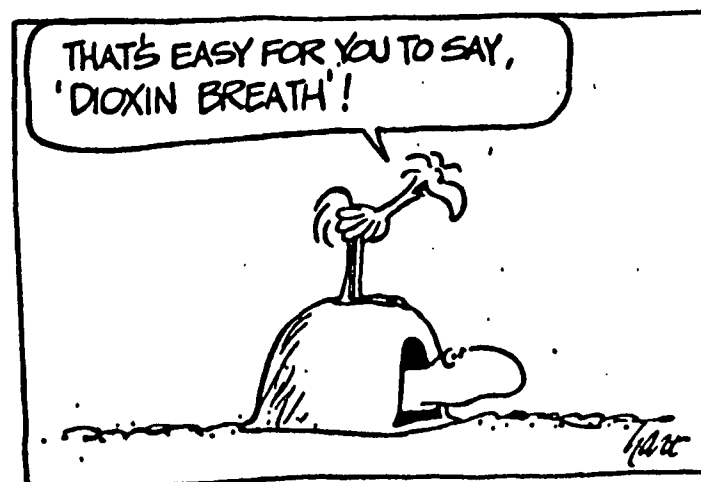


B.C.



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**RCRA / CERCLA  
ALTERNATIVE TREATMENT  
TECHNOLOGY SEMINARS**

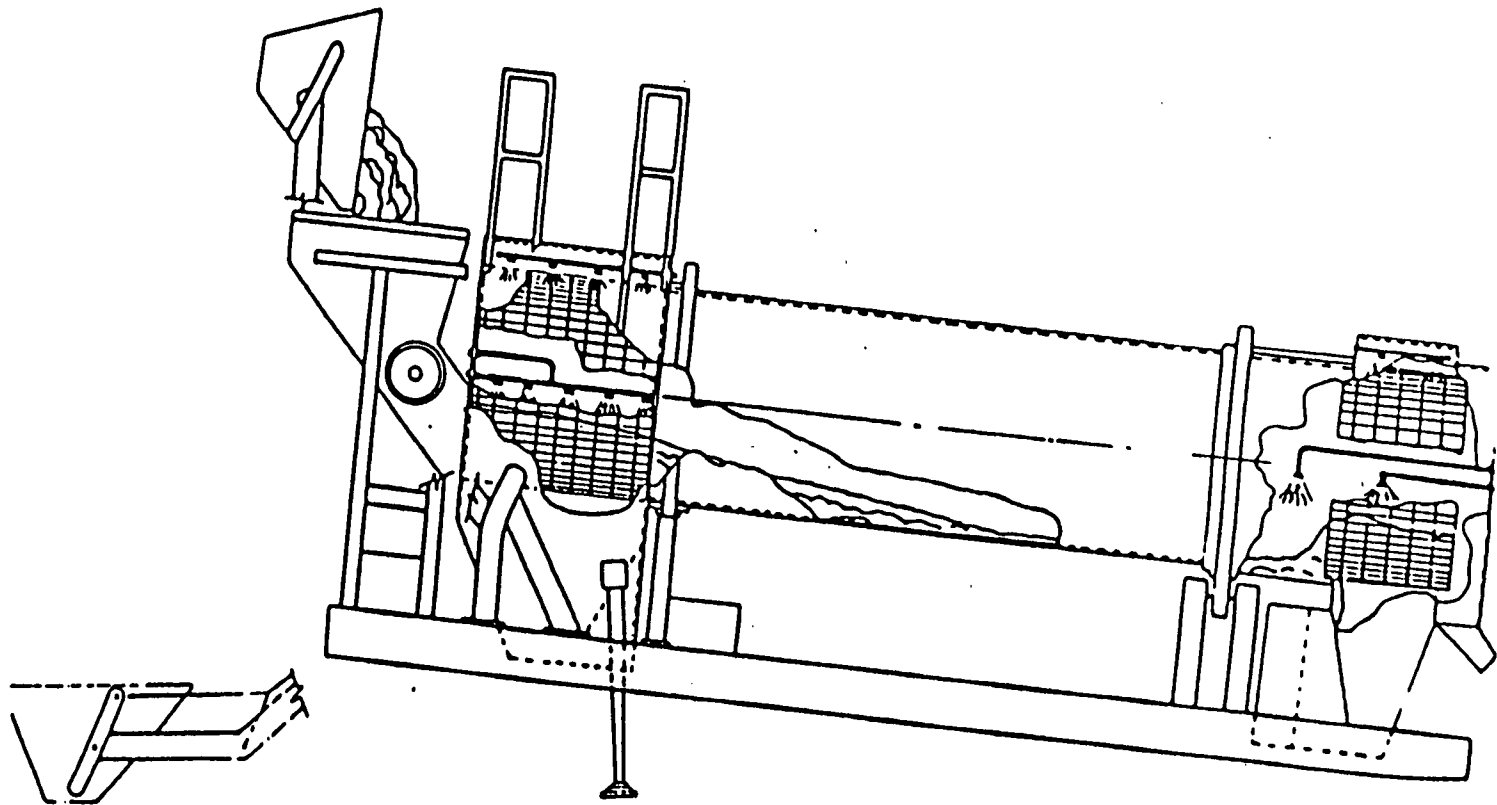
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**SOIL WASHING OF LEAD  
CONTAMINATED SOIL**

**EPA Mobile Soils Washer**

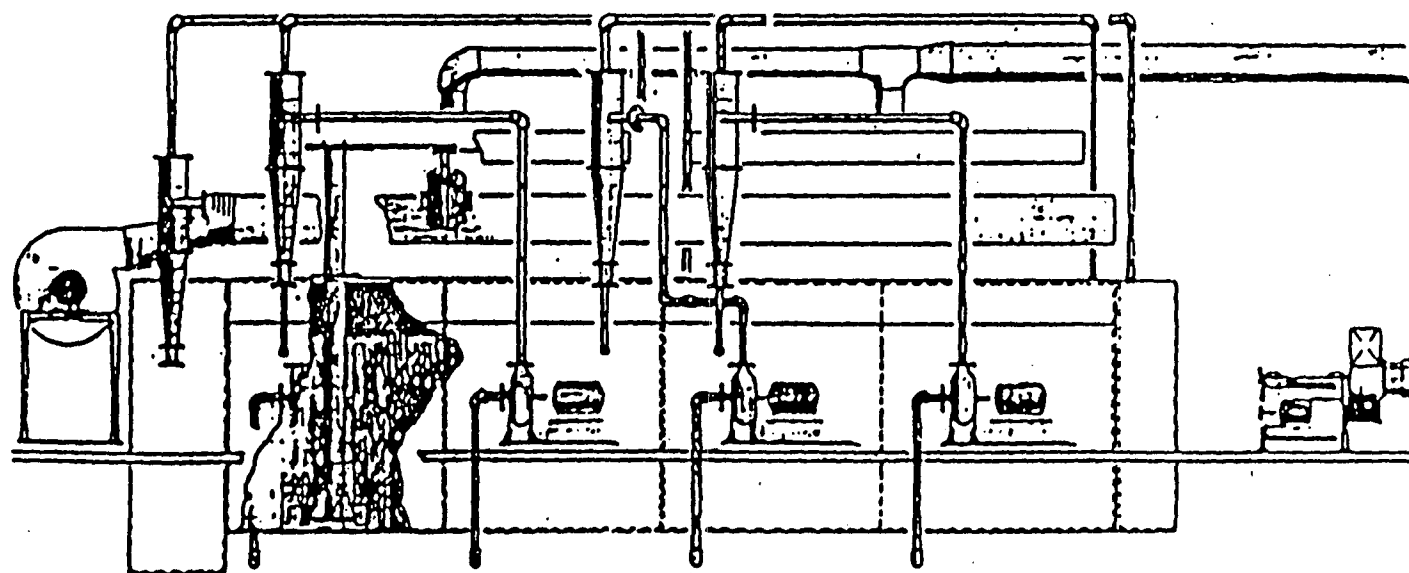
**Leeds, Al.**

## DRUM WASHER UNIT

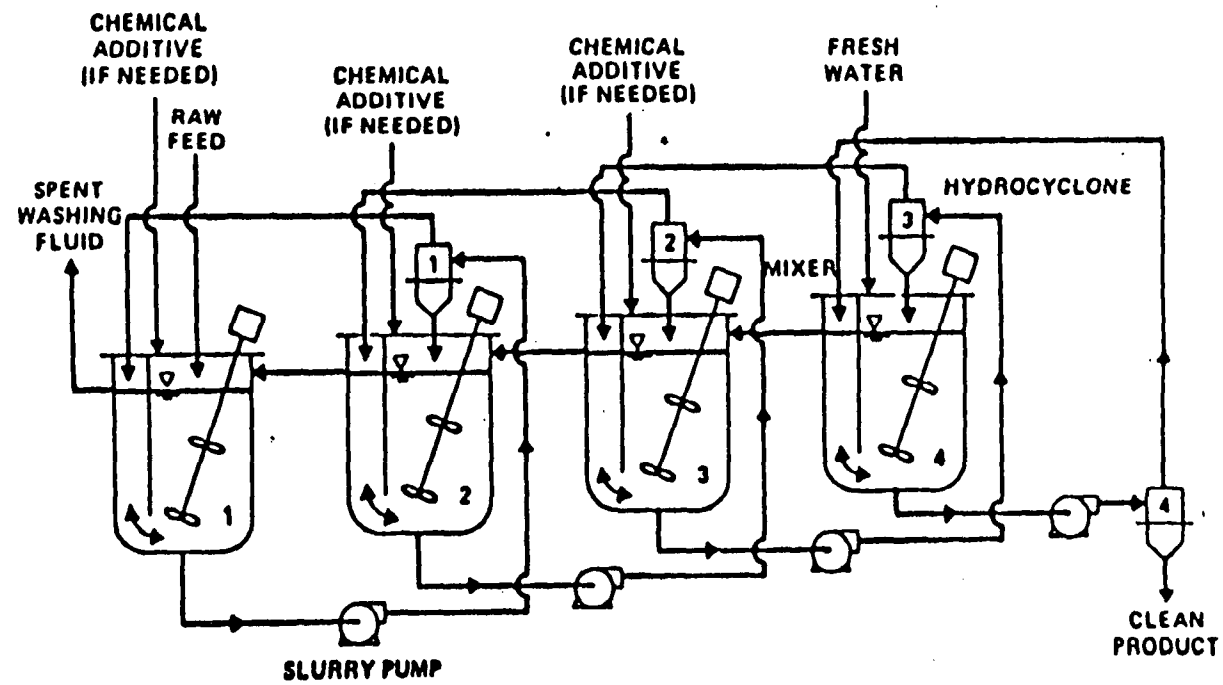


# MOBILE SOILS WASHER

Counter-Current Extraction Unit

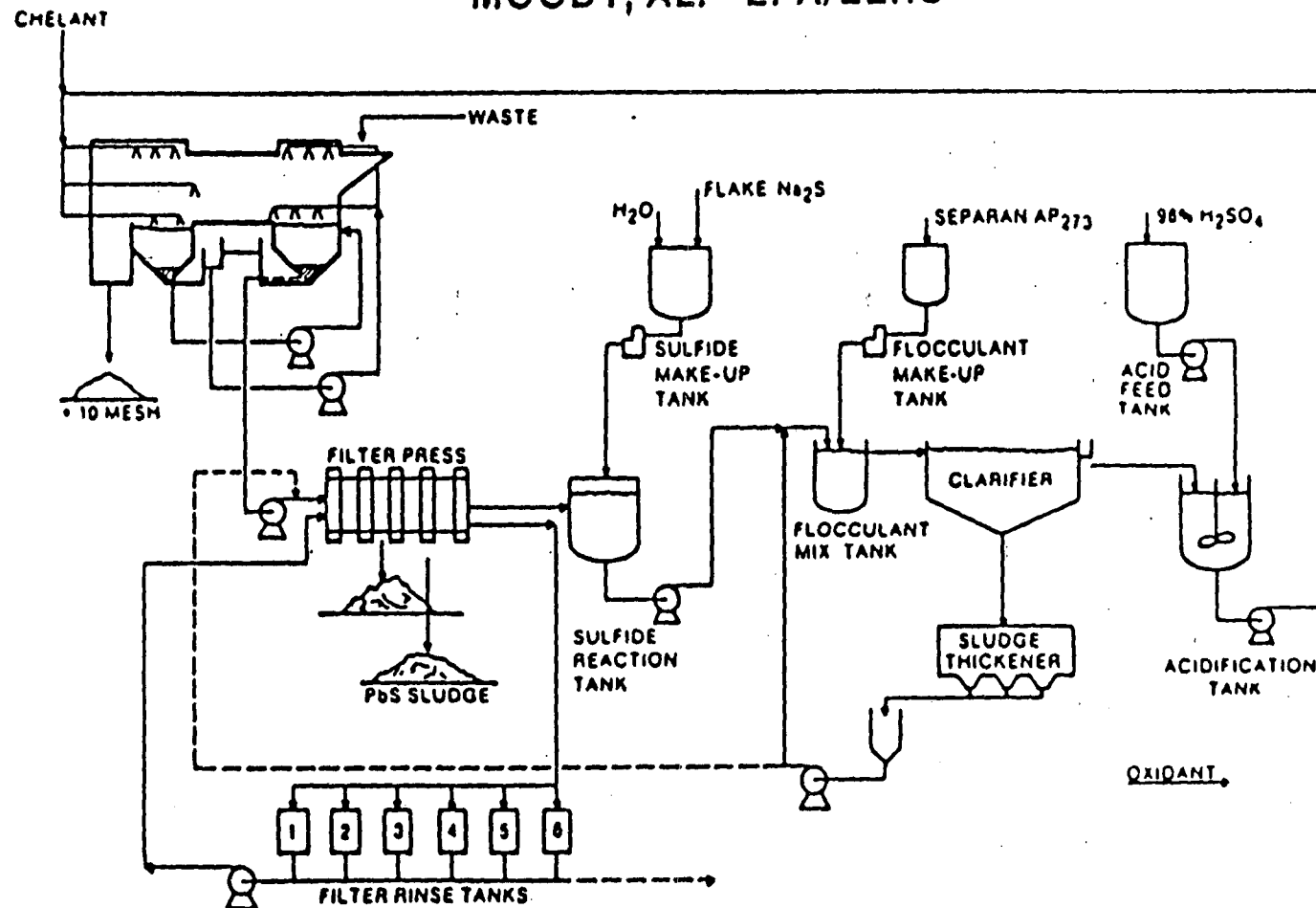


## PROCESS FLOW SCHEME FOR COUNTERCURRENT EXTRACTOR





# PROCESS FLOW DIAGRAM AND SAMPLE POINT LOCATIONS - BATTERY WASTE TREATMENT SYSTEM MOODY, AL. - EPA/EERU



# LEAD REMOVAL

LEEDS, ALABAMA

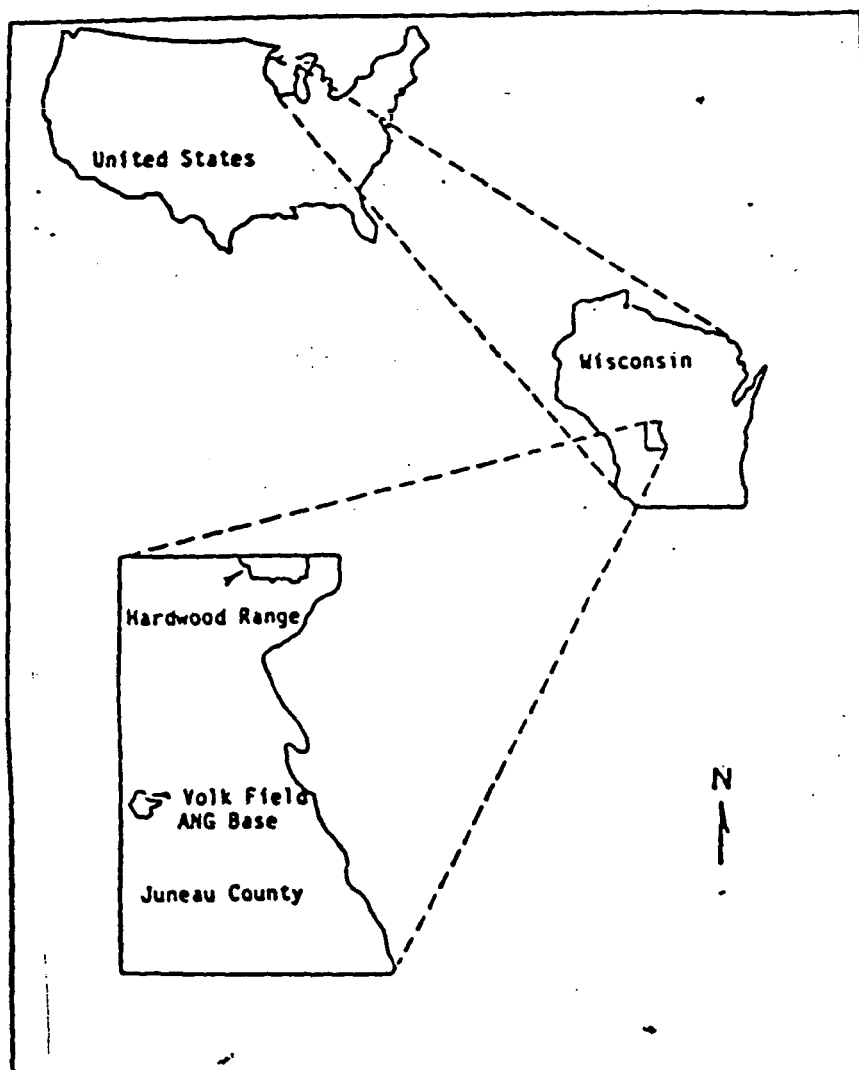
MATERIAL	LEAD (mg/l)	E.P. TOXICITY (mg/l)
ILCO FEED	47,000	88
+ 2mm DISCHARGE	3,050	60
- 2mm DISCHARGE	1,300	49

# IN-SITU WASHING OF JP-4 AND SOLVENTS

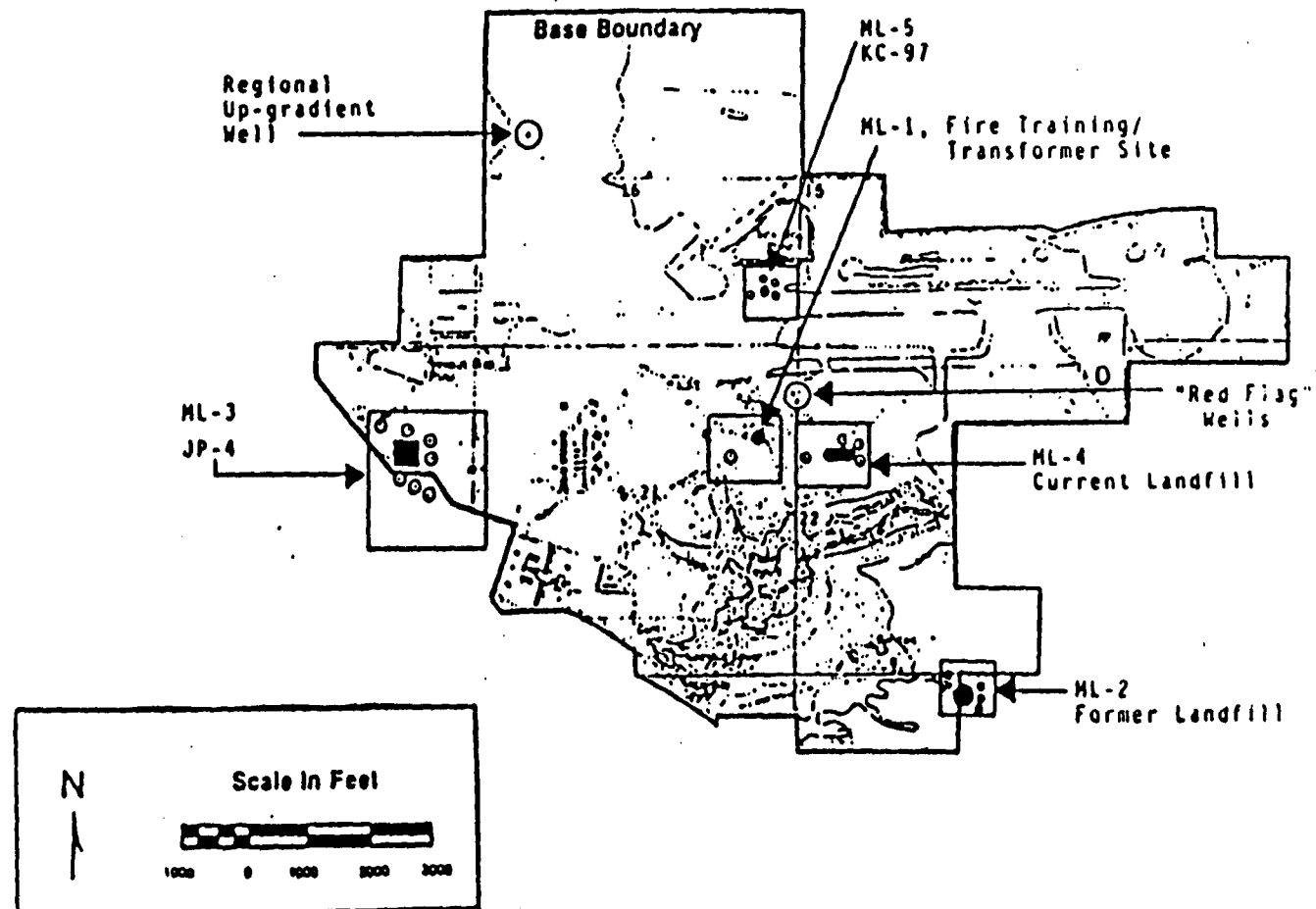
Volk Air National Guard Field  
Camp Douglas, WI

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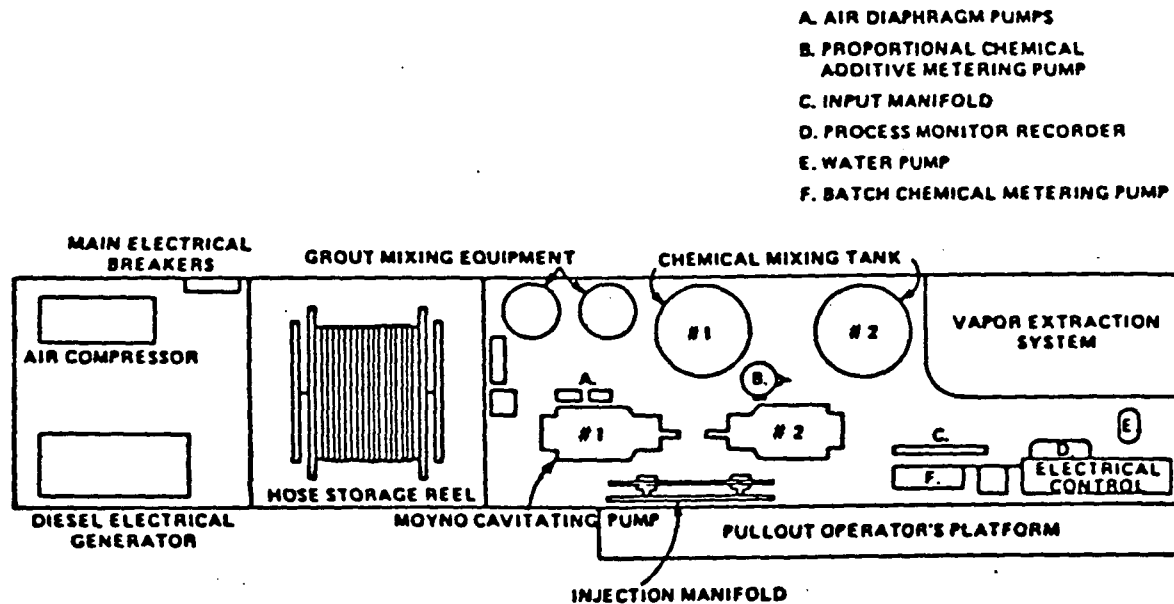
LOCATION OF VOLK FIELD ANG BASE AND HARDWOOD RANGE



LOCATIONS OF THE PROPOSED AREAS AT VOLK FIELD TO BE  
INVESTIGATED DURING PHASE II



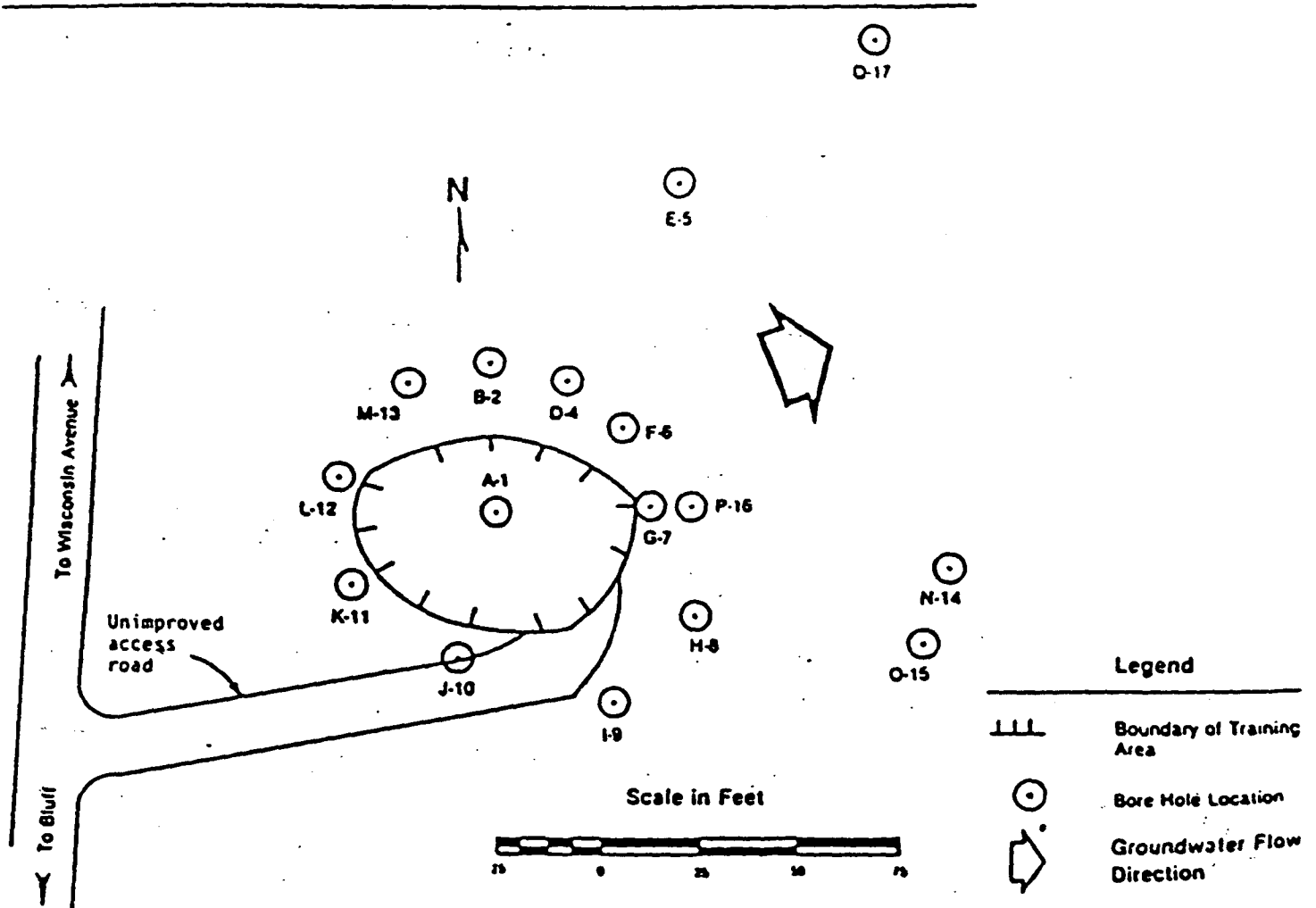
## LAYOUT OF THE IN SITU CONTAINMENT/ TREATMENT UNIT (ISCTU)



## VOLK FIELD EVALUATION CRITERIA

- Reduction
  - Total Organic Carbon
  - Volatiles
  - Oil And Grease
  - Chemical Oxygen Demand
  - Biological/Chemical Oxygen Demand

Locations of Existing Groundwater Monitoring Bore Holes at the  
Fire Department Training Area.



## DESCRIPTION OF VOLK ANG FIRE TRAINING PIT

- Diameter: 75 Feet
- Depth (To Water Table): 12 Feet
- Surface Area: 4,400 Sq. Feet
- Volume Of Soil: 53,000-Cu. Feet



## FACT SHEET

United States  
Environmental Protection  
Agency

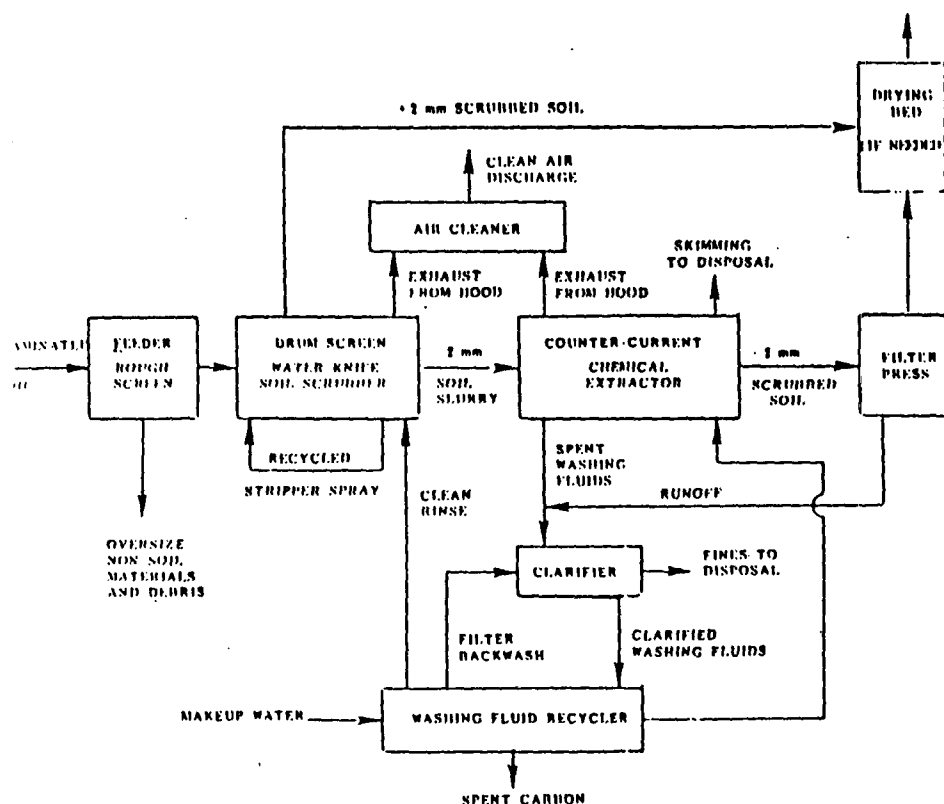
September, 1985

### Mobile System For Extracting Spilled Hazardous Materials From Soil

The Hazardous Waste Engineering Research Laboratory, Releases Control Branch at Edison, NJ, has recently developed a mobile system for extracting spilled hazardous materials from soils at cleanup sites.

Landborne spills of hazardous materials that percolate through the soil pose a serious threat to groundwater.

Effective response to such incidents should include the means for removing the contaminants and restoring the soil to its original condition. Currently practiced techniques, such as excavation with transfer to land fill or flushing with water *in situ*, are beset with difficulties - large land area and volume of materials involved. An innovative *In Situ* Containment/Treatment System has been developed to treat contaminated soils. However, it is not suitable for all soils and/or all chemicals.



The mobile treatment (see illustration) has been designed for water extraction of a broad range of hazardous materials from spill-contaminated soils. The system will: (1) treat excavated contaminated soils, (2) return the treated soil to the site, (3) separate the extracted hazardous materials from the washing fluid for further processing and/or disposal, and (4) decontaminate process fluids before recirculation, or final disposal. A prototype system has been developed utilizing conventional equipment for screening, size reduction, washing, and dewatering of the soils. The washing fluid - water - may contain additives, such as acids, alkalies, detergents, and selected organic solvents to enhance soil decontamination. The nominal processing rate will be 3.2-m<sup>3</sup> (4-yd<sup>3</sup>) of contaminated soil per hour when the soil particles are primarily less than 2-mm in size and up to 14.4-m<sup>3</sup> (18-yd<sup>3</sup>) per hour for soil of larger average particle size.

For further information contact Frank J. Freestone or Richard P. Traver, Hazardous Waste Engineering Research Laboratory, Releases Control Branch, Edison, NJ. Telephone numbers are: (201) 321-6632/6677 (commercial) or 340-6632/6677 (FTS).

## CALVIN AND HOBBS





## **ESTIMATED TIME REQUIRED FOR VOLK IN-SITU WASHING**

- ◆ Recommended Application Rate  
3 Inches Per Day
  - ◆ 3 Inches Applied On Surface  
Fills 10 Inches Of Soil Column
  - ◆ 14.4 Days Per Pore Volume Or  
144 Days Washing To Achieve  
80% Removal
- 

## **MASS BALANCE**

What Goes In...  
... Must Come Out.

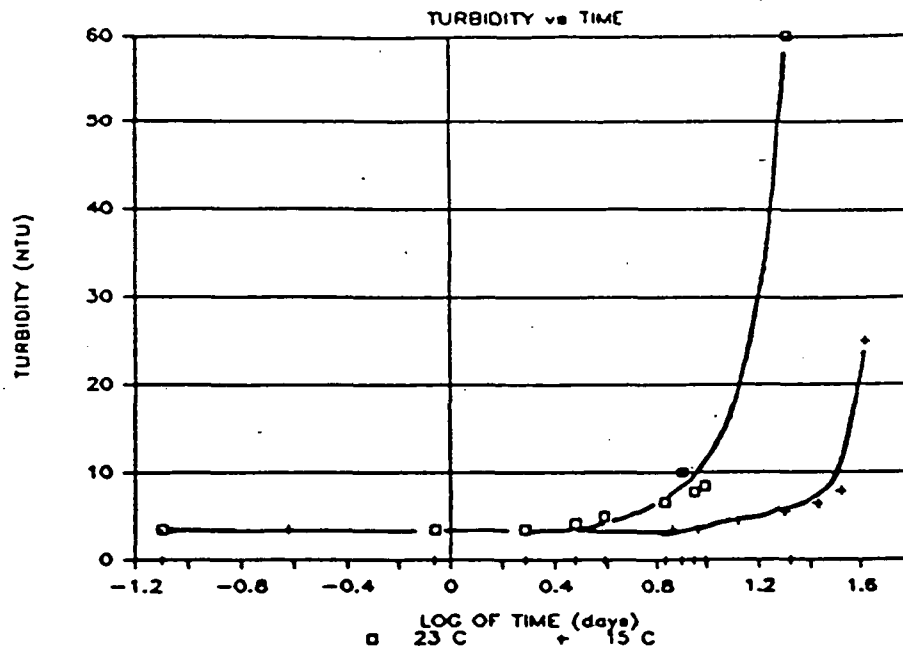
**SURFACTANT QUANTITIES REQUIRED  
TO REMOVE CONTAMINANTS AT  
VOLK ANG**

- ◆ 1.5% Surfactant Solution Required
  - ◆ Ten Pore Volumes Used In Pilot Lab Study To Achieve 80% Removal
  - ◆ One Pore Volume At Volk Fire Training Pit = 16,000 Cubic Feet
- 

**SURFACTANT QUANTITIES REQUIRED  
AT VOLK ANG (Continued)**

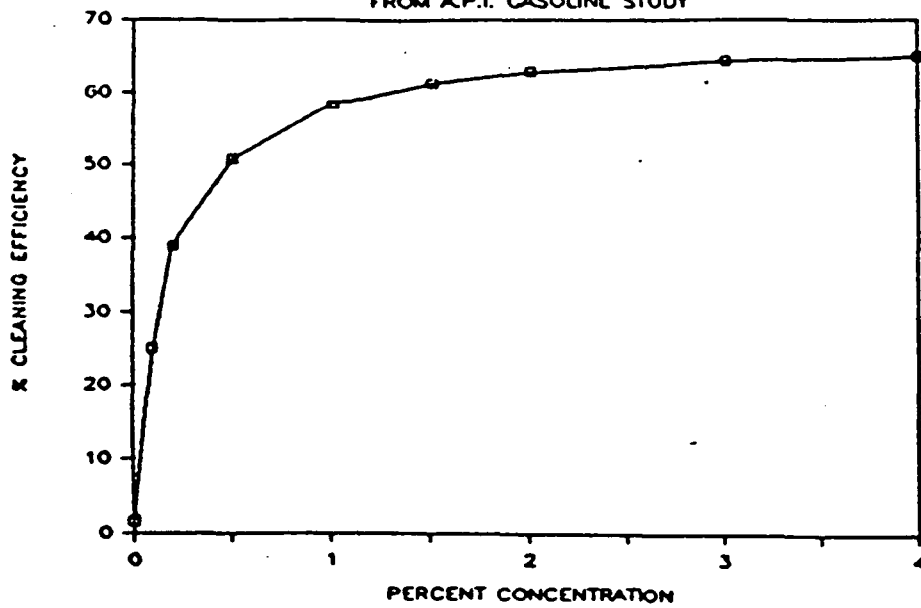
- ◆ 10 Pore Volumes = 9,984,000 lbs.
- ◆  $9,984,000 \text{ lbs.} \times .015 = 150,000 \text{ lbs.}$   
Of Surfactant

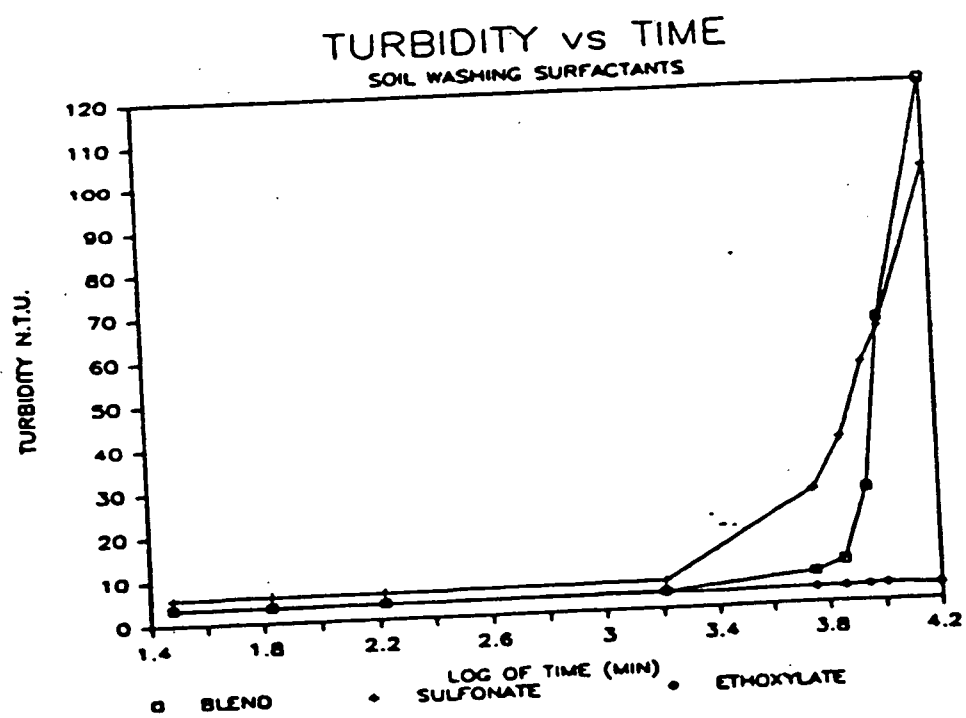
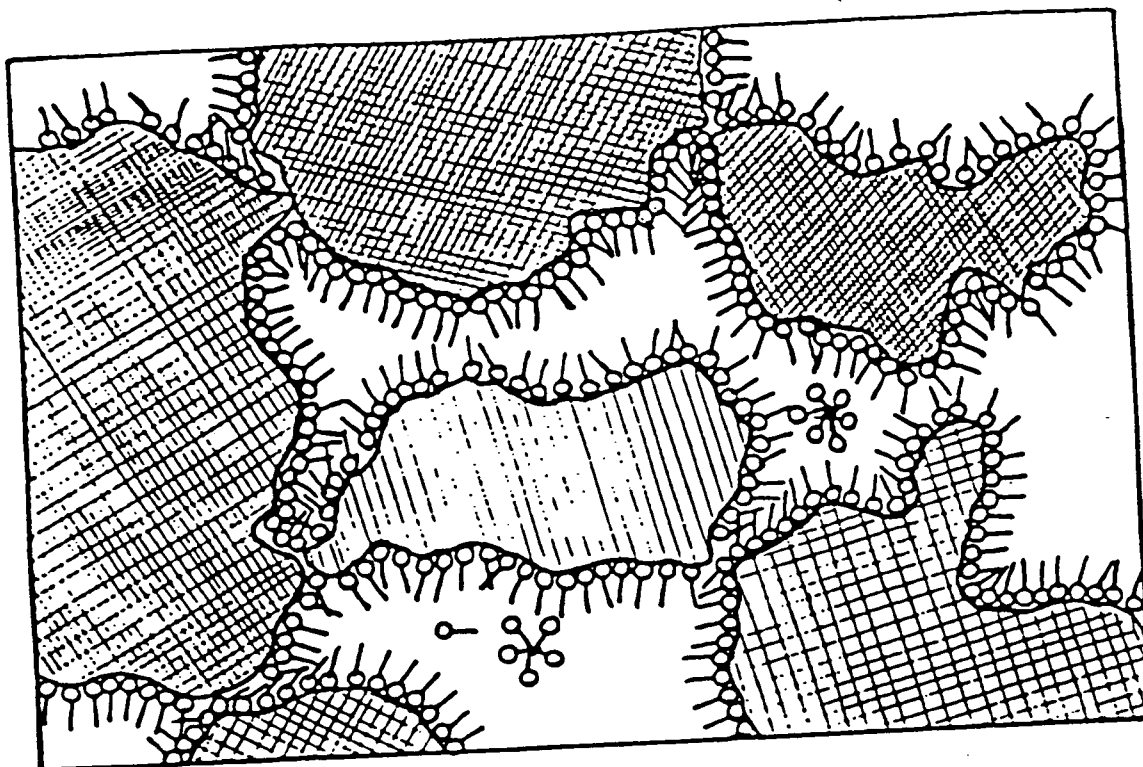
# TEMPERATURE EFFECT



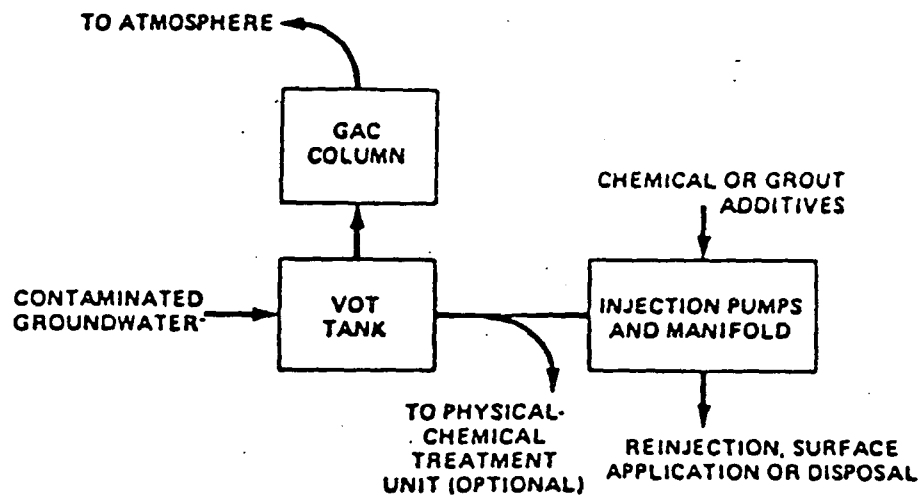
# HOW MUCH SURFACTANT?

FROM A.P.I. GASOLINE STUDY





## FLOW DIAGRAM FOR ISCTU



## WATER TREATMENT PROCESSES AT VOLK ANG

- ◆ Lime Precipitation
- ◆ Clarification
- ◆ Aeration

## **CONTAMINATION LEVELS AT VOLK ANG**

Soil:

Oil & Grease 500.-25,000 mg/kg

Groundwater:

Volatiles 10-20 mg/l

TOC 100-700 mg/l

---

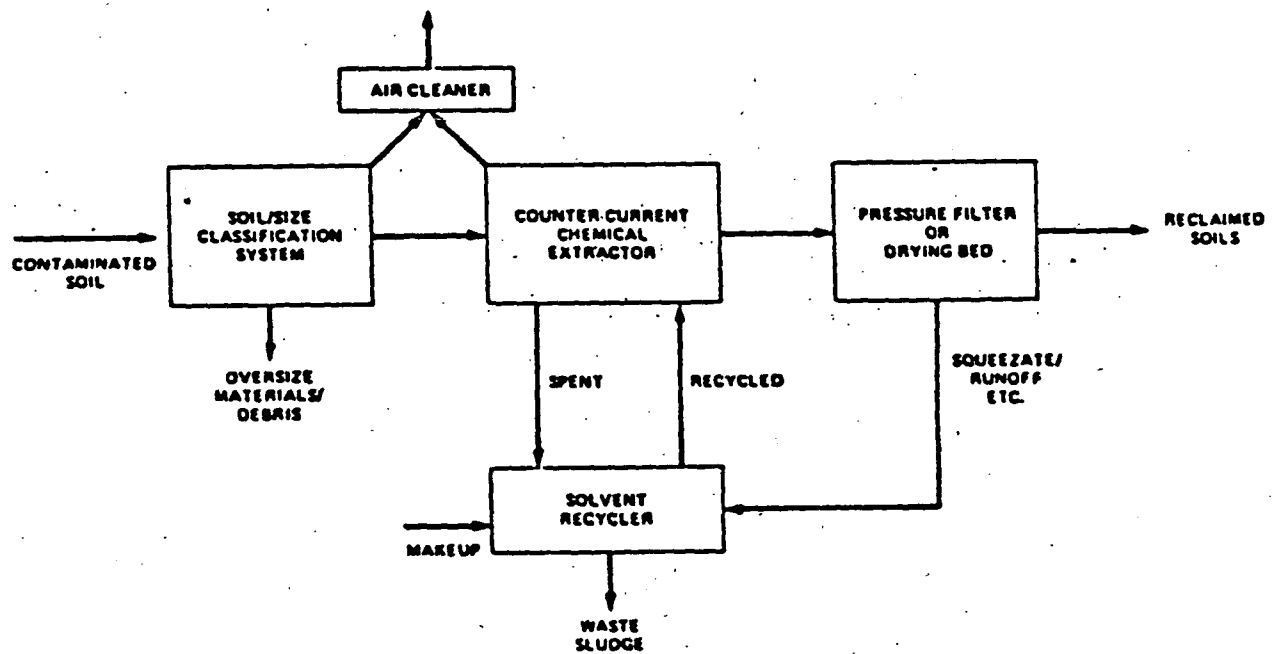
## **AMOUNT OF CONTAMINATION AT VOLK ANG FIRE TRAINING PIT**

- Estimated 52,000 Gallons "Unburnt"  
After 35 Years Of Operation
  - Remaining Contamination Averages  
0.2%, Equivalent To 1,700 Gallons
- 

## **SOIL TREATMENT AT VOLK FIELD**

- In-situ Washing
  - Water
  - Surfactants
  - Treated/Contaminated  
Groundwater

# SIMPLIFIED PROCESS FLOW DIAGRAM SOIL SCRUBBER



EPA Report Number  
November 1987

ROUGH DRAFT  
INTERIM REPORT  
INVESTIGATION OF FEEDSTOCK PREPARATION AND HANDLING  
FOR MOBILE ON-SITE TREATMENT TECHNOLOGIES

by

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Leonardo, New Jersey 07737

68-03-3450  
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Richard P. Traver, P.E.  
Releases Control Branch  
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HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
CINCINNATI, OHIO 45268



## SECTION 1

### BACKGROUND

Under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), the current National Contingency Plan (NCP) that implements it, and SARA (1986) requirements, response actions at hazardous waste sites must reduce the threat of uncontrolled wastes into the environment. In the 1984 Resource Conservation and Recovery Act (RCRA) Amendments, Congress clearly showed its intent to minimize the volume of solid waste disposal in landfills. This policy would mandate a major change in the current practices at CERCLA sites of removing the hazardous waste material and burying it elsewhere without any prior treatment.

The policy of the Office of Solid Waste and Emergency Response (OSWER), responsible for implementing the 1984 HSWA requirements, is to discourage the excavation and reburial "disposal" philosophy of CERCLA waste and debris, and to encourage technologies to eliminate or reduce the hazardous character of the waste materials. On-site treatment technologies that destroy or reduce contaminant levels achieve more positive control than containment techniques. Off-site disposal to engineered and protected landfills will only be allowed in the future when no destruction technology is available, or for "pretreated" soil and debris materials complying with Best Demonstrated Available Treatment (BDAT) levels as promulgated under the impending 1988 Land Ban legislation. In addition, as landfill disposal becomes more expensive and as hazardous waste transportation is more stringently regulated, on-site waste destruction or volumetric

reduction technologies will be far more desirable--if they are technologically feasible, environmentally safe, and economically viable.

In order to destroy or reduce the hazardous character of any contaminated material, the treatment technology selected must receive a "feedstock" with a predetermined range of physical/chemical characteristics to ensure reliable treatment efficiencies and cost effectiveness. The types of contaminated materials normally identified and discussed in remedial investigation/feasibility study (RI/FS) reports are primarily materials such as soils, sludges, and liquids. The debris component is not addressed unless the primary contaminated matrix is a mixture of materials (i.e., building demolition debris or sanitary landfill type wastes, such as household trash and garbage).

The land disposal rules, which are scheduled to be enacted in November 1988, will address feedstock and site debris as well as contaminated soil under the Land Ban legislation.

Following the review of numerous Records of Decision (RODs) and RI/FS's, there is a lack of historical site-specific data quantifying and qualifying Superfund debris. Few, if any RODs or RI/FS's factor in the operational considerations of handling, segregating, sizing, site excavation, and feedstock delivery to various recommended mobile on-site technologies such as biological degradation, chemical treatment (K-Peg), solidification/stabilization, incineration, low temperature thermal desorption, and physical treatment (soils washing). It is critical that an engineering and economic evaluation of the types of debris and their impacts on these technologies be

performed, if any form of on-site treatment is ever to be successfully executed. The current HWERL work assignment addresses these issues. The objectives of the work assignment are to:

- Categorize Superfund-related solids, sludges, sediments, and debris according to excavation, handling, and separation problems. Data will be provided on frequency of problem occurrences.
- Provide a written summary on the state-of-the-art isolation/separation technologies of debris from feedstock-excavated soils, sediments, and sludges.
- Identify specific handling areas for a detailed engineering analysis of feedstock preparation for the following six candidate on-site treatment technologies:
  - Incineration
  - Low temperature desorption
  - Chemical treatment (K-Peg)
  - Solidification/stabilization
  - Physical treatment (soils washing)
  - Biological degradation
- Provide recommendations for future research needed on technologies that have a high probability of success and that are applicable to frequently occurring debris-handling problems.

## SECTION 2

### CONCLUSIONS

Debris is anything that cannot be handled by the treatment process. In general, any material larger than the 1/4 to 6-inch range presented in Table 1 would be considered debris for all six technologies being reviewed. Decontamination of debris is not always possible because of its material nature (absorption of the contaminant), or because the contaminant should not be diluted, as in the case of dioxin. Debris cannot always be subjected to analytical testing to determine its hazard classification or its level of cleanliness. Debris is only currently categorized by the participating regulatory agencies as to its hazardous or nonhazardous status, and handled on a case-by-case basis. Disposal is currently based on the type of debris, quantity, contaminant involved, and local/regional regulatory concerns.

## SECTION 3

### RECOMMENDATIONS

#### RECOMMENDATIONS FOR PROPOSED RULEMAKING

1. Classify material as debris based on the size requirements of the recommended technology.
2. Segregate debris for decontamination, recycling and reuse, incineration, treatment, or land disposal.
3. Treat each site debris situation on a case-by-case basis with the disposal determination made by the local regulatory authority (i.e., county, state, or EPA region).

#### RECOMMENDATIONS FOR IMMEDIATE RESEARCH NEEDS

1. Modify reporting and site investigations under RI/FS programs to quantify and qualify the forms and amounts of debris as presented in Appendix A on both a percent weight and volume basis.
2. Conduct an engineering review and evaluation of existing applicable vendor technologies for segregation of soil and debris for further processing and feedstock preparation.

3. Conduct a pilot evaluation of selected feedstock processing equipment utilizing a standardized nonhazardous debris matrix as presented in Appendix A.
4. Preparation of a guidance document for use by EPA Remedial Project Managers, On-scene Coordinators, contractors, and emergency response personnel identifying mobile and transport separation equipment, sources, costs (lease/purchase, operation and maintenance), debris applications, and anticipated performance.

## SECTION 4

### DEBRIS DEFINITION

The six on-site technologies under review include: incineration, low temperature desorption, chemical treatment (K-Peg), solidification/stabilization, physical treatment (soils washing), and biological degradation. Each technology requires that the feedstock material (soil and debris) be delivered with predetermined consistencies so that the selected treatment "hardware" can function and perform reliably in order to efficiently and cost-effectively destroy or reduce the contaminants of interest. To accomplish this task, the contaminated material, which may be in the form of soil, sludge, liquid, or debris, must be prepared by either of the following means:

- Physical preprocessing of oversize material (e.g., crushing, shredding, screening, separation, dewatering, etc.).
- Chemical preconditioning, such as neutralization or reduction/oxidation.

Debris can be defined as oversize materials that cannot be handled by the selected treatment hardware, and may, in fact, damage the processing equipment.

The types of debris and contaminated materials found at Superfund sites vary considerably and range in size from clay-sized particles to large contaminated tanks and buildings. Debris can be grouped into the following nine general categories:

- Cloth
- Glass
- Metals (ferrous/nonferrous)
- Paper
- Plastic
- Rubber
- Wood
- Construction/demolition materials (e.g., concrete, brick, asphalt)
- Electronic/electrical devices

The nine categories of debris were determined by interviews with various EPA Regional Superfund Site Managers; EPA Environmental Response Team members; EPA, TAT, REM, FIT consultants; and the EPA HWERL Technical Project Managers for various treatment technologies. A detailed breakdown of specific items found in each debris category is located in Appendix A.

Along with the wide range in the types of debris, the quantities of debris at sites also vary considerably. It has been "unofficially" reported through interviews, that the debris at sites varies on a volumetric basis from less than 1 percent to greater than 80 percent. This is attributed to sites where demolition debris or sanitary landfill wastes have been co-disposed with hazardous materials.

A preliminary assessment of each of the six on-site treatment technologies was conducted to determine the maximum size of debris and material that could be allowed to undergo the treatment process. The maximum debris size for each technology based on this preliminary assessment is indicated in Table 1.



TABLE 1. MAXIMUM DEBRIS SIZE/TECHNOLOGY

Maximum debris size	Technology
1-2 inches	Biological degradation
1 inch	Chemical treatment (K-Peg)
6 inches	Incineration
1/4 inch	Low temperature desorption
2 inches	Physical treatment (soil washing)
6 inches	Solidification/stabilization

Debris larger than the maximum allowable size must be segregated from the feedstock material and handled separately. This oversized material must then be either treated separately or reduced in size to allow the debris to be refed to the treatment equipment.

In addition to debris removal, feedstock preparation may also include other preparatory steps for the treatment process to be effective. Feedstock requirements will vary with each technology and contaminant under consideration. The types of other feedstock factors that must be identified and evaluated when considering one of the six technologies include:

- Contaminant concentrations
- pH adjustment
- Moisture content
- Oxidation/reduction status
- Temperature range
- Salt concentrations
- Any special requirements

The range of contaminant concentrations found in the waste to be treated must be known to prevent "shock" loading of the treatment process and also to ensure that the technology treatment process can handle the contaminant concentrations identified. Biological degradation is adversely affected by "shock" loading of toxics. Dechlorination (K-Peg) treatment processes become noncost effective when contaminant concentrations exceed high levels of certain contaminants because of excessive sodium requirements.

pH adjustment of the wastes may be necessary to reduce corrosion potential; air impacts in incinerators and to ensure proper growth of microorganisms in the biological degradation process.

Moisture content also affects certain treatment technologies because excess moisture can adversely affect reaction rates and energy input requirements.

The temperature of the waste is an important factor in rotary kiln incineration because of the potential for thermal shock due to the moisture content and low temperature of the waste.

Salt concentrations in the waste under consideration affect biological degradation processes and immobilization/fixation treatment. Excessive salts retard or prevent biological growth, and, in the case of fixation technologies, salts interfere with the setting and curing times of cement.

Each treatment technology may have other special handling requirements for various wastes, and these need to be identified in a detailed engineering analysis of each technology.

## SECTION 5

### CURRENT DEBRIS HANDLING PRACTICES

The preliminary information collected on debris indicates that the current handling procedures at hazardous waste sites range from "elaborate separation and recycling" to "no separation." Processed material and debris are then handled in one of the following ways:

- Sent to a secure landfill for ultimate disposal.
- Decontaminated to levels allowing disposal in a municipal landfill.
- Treated material used for construction foundation bedding.
- Recycled/reclaimed as a recoverable resource.
- Delisted to a nonhazardous status.

Current debris handling practices have been determined by:

- Technology feedstock requirement.
- Type of contamination.
- Type of debris (size, shape, phase, form, Btu, and recycle value).

- Quantity of debris (percent volume or weight).
- "Clean-up" standards or target levels (Federal, state, local, private).
- Potential for decontamination of the debris.

A list of the types of debris and their handling history at 29 Superfund sites is shown in Table 2.

TABLE 2. DEBRIS HANDLING AT SUPERFUND SITES

Site name	Contact	EPA region	Major contaminant	Recommended clean-up alternative	Debris types	Debris handling
1. Kane & Lombard	Charles Kufs	III	Organics, metals	Incineration Soil washing Containment In-situ vitrification (ISV)	Concrete Rocks Metals	Presorting and shredding
2. Ambler Asbestos	Frank Finger	III	Asbestos, CaCO <sub>3</sub>	ISV Containment Capping Off-site land disposal	None reported	
3. Myers Property	Victor Velez	II	Organics, metals	Solidification/stabilization Biological degradation Soil washing Off-site land disposal (untreated waste)	Pebbles Boulders Wood Bolts	
4. Fried Industries	Victor Velez	II	Organics	Biological degradation Low temperature thermal stripping Incineration Soil washing	Drums	
5. Roebling Steel	George Anastos	II	Metals, organics, asbestos	FS not done; RI in progress Partial emergency removal action	Tires Shredded rubber Shredded plastic Concrete  Baghouse dust Buildings and metals Wire, cables	
6. L.A. Clark	Ralph Shapot	III	Organics	High temperature thermal stripping Metals, cyanides	Solidification/stabilization Biological degradation (in-situ) Soil washing Containment	Railroad ties Rails, wood Concrete, rocks

TABLE 2. (CONTINUED)

Site name	Contact	EPA region	Major contaminant	Recommended clean-up alternative	Debris types	Debris handling
7. Morgantown	Ralph Shapot	III	Organics, metals	Capping Incineration	Tires Refrigerators Wood Concrete Cloth	Separation
8. Southern MD	Jay Motwani	III	Organics, dioxins	Biological degradation Incineration Soil washing ISV activated	Railroad ties Rails, wood Concrete, rocks	
9. Cryochem	R. Purcell	III	Organics	Work plan stage	No debris	
10. Shaffer	—	III	PCBs	Methanol extraction	Tires Large stones	Vibratory screen-set aside
11. Montgomery Bros.	T. Massey	III	Organics	Off-site disposal	Drums Residential trash	Off-site disposal
12. Bridgeport Oil	D. Lynch	II	Oil Water	Incinerate lagoon contents	Wood, drums Tanks Buildings	Clean tanks
13 Swissvale	J. Downey	III	Dioxins, PCBs	Off-site disposal in secure land-fill and recycling	Buildings Metals Drums	Dioxins to secure land-fill; steel decontaminated and recycled to steel mill
15 Allied-Hopkins	—	5	Toxaphene, DDT, xylene	Incineration Off-site disposal	Railroad ties Rails Concrete pad Blocks	Rails decontaminated for re-use Railroad ties, concrete to secure land-fill

TABLE 2. (CONTINUED)

Site name	Contact	EPA region	Major contaminant	Recommended clean-up alternative	Debris types	Debris handling
16. Baird & McGuire	Ms. Sanderson	I	Cresote, dioxins	Incineration Off-site disposal	Tanks Wood buildings Masonry	Metal-recycled Wood-shredded and incinerated Masonry-Off-site disposal
17. Metaltec/ Aerosystems, NJ	M. Rusin	II	TCE	Heat treatment Rotary dryer	No debris Large stones	Screening of stones/rocks
18. Syncon	E. Finnerty	II	Pesticides PCBs, metals	Off-site disposal On-site capping	Buildings Tanks Piping, heat-coils	Buildings and tanks-decontam- inated for future use Piping, etc., -Off-site disposal
19. Delaware City	G. Chodwick	III	PVC, TCE	Off-site disposal Reuse of recoverable product	No debris	Reuse of recoverable product
20. Drake Chemical	T. Legel	III	Organics and inor- ganics	Off-site disposal	Furniture Piping	Off-site disposal
21. Coleman Evans	C. Teeppen	IV	PCP	Incineration	Miscellaneous	Separation with shredding and recycling of metals
22. Hollingsworth	E. Zimmermon	IV	TCE, metals	Vacuum extraction	None	
23. MowGray Engineering	J. Trudeau	IV	PCBs	Solidification	None	
24. Sapp Battery	E. Moore	IV	Lead, cadmium	Solidification	Battery cases	Crushing

TABLE 2. (CONTINUED)

Site name	Contact	EPA region	Major contaminant	Recommended clean-up alternative	Debris types	Debris handling
25. LaSalle Electrical	B. Cattiche	V	PCBs	Incineration	Roots, sticks, stones	Screening
26. Metamora Landfill	J. Tanaka	V	VOCs, metals	Incineration		
27. Geneva Industries	D. Williams	VI	VOCs, PCBs, PAHs	Off-site disposal	Tanks Prefabricated buildings Cracking tower Houses	Off-site disposal
28. United Creosoting	D. Williams	VI	PCPs, PAHs	On-going investigation		Clean Wipe samples Recycle
29. Denver/ROBCO	J. Brink	VIII	Radiation	Off-site disposal Wood	Miscellaneous masonry	Separation of materials



## SECTION 6

### DEBRIS DECONTAMINATION

Once contaminated debris has been separated from the hazardous waste material undergoing treatment, it must either be disposed of in a secure landfill, stored for future approved treatment (i.e., dioxin-contaminated material) or decontaminated. The determination that debris is contaminated is generally an assumption that is made with little or no analytical testing. In some instances monitoring devices such as an Hnu organic vapor analyzer or a geiger counter are utilized to determine if a particular object is contaminated with volatile organic compounds or is radioactive.

Decontamination of debris is possible for contaminants that are water soluble and can be washed, rinsed, or are removed when the associated contaminated soil is cleaned off. Insoluble and inorganic (heavy metal)-contaminated fine soil material can sometimes be successfully separated from debris by high pressure washing or vibratory separation, allowing the oversized material to be safely disposed of. Some contaminants, such as dioxin, are not generally considered for decontamination and are designated for interim storage, awaiting either incineration or alternate approved treatment.

Impervious debris, such as steel, brass, or copper, is generally decontaminated and recycled, when possible.

In most instances debris cannot be subjected to current or proposed testing procedures (EP toxicity (extraction procedure toxicity testing), TWA (total waste analysis), and TCLP (toxic contaminant leaching potential)) to determine if it is hazardous due to the type, form, and surface areas involved. Such determinations are generally made by the participating regulatory parties at the regional, state, and local levels.

Debris that is determined to be nonhazardous can be disposed of as industrial or municipal trash in a sanitary landfill. Debris that is deemed hazardous by the regulatory parties involved must then be incinerated, decontaminated, or otherwise disposed of in a secure landfill.

## SECTION 7

### DEBRIS HANDLING EQUIPMENT

Oversize material removal, disaggregation, and material sorting can be accomplished by physical preprocessing. The specific type of preprocessing required is dependent on the technology under consideration and the contaminant involved. Oversize material removal and debris sorting is generally accomplished by vibrating or static screens. Magnetic separation and flotation separation are also utilized in conjunction with the required screens to obtain a feedstock with a predetermined consistency.

Grizzlies and hammermills are used to remove a small amount of oversized material from fines. Shredders are used for size reduction.

A list of preprocessing equipment vendors was assembled and is included in Appendix B. The applicability of several specific types of preprocessing equipment should be considered when completing the detailed engineering analysis of the feedstock preparation and handling for the six mobile on-site technologies.

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## APPENDIX A

### DEBRIS IDENTIFICATION

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#### Cloth

- Rags
- Tarps
- Mattresses

#### Paper

- Books
- Magazines
- Newspaper
- Cardboard
- Packing

#### Glass

- Bottles
- (white, brown, green  
clear, blue)
- Windows

#### Plastic

- Buckets
- Pesticide  
containers
- Six-pack  
retainer rings
- Thin plastic  
sheets
- Plastic bags
- Battery cases

#### Ferrous Metals

- Cast iron
- Tin cans
- Slag

#### Rubber

- Tires
- Hoses
- Insulation
- Battery cases

#### Nonferrous Metals

- Stainless steel
- Aluminum
- Brass
- Copper
- Slag

#### Wood

- Stumps and  
leaves
- Furniture
- Pallets
- Plywood
- Railroad ties

#### Metal Objects

- Autos/vehicles
- 55-gallon drums/containers
- Refrigerators
- Tanks/gas cylinders
- Pipes
- Nails
- Nuts and bolts
- Wire and cable
- Railroad rails
- Structural steel

#### Electronic/Electrical

- Televisions
  - Transformers
  - Capacitors
  - Radios
-

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Construction Debris

- Bricks
  - Concrete blocks
  - Asphalt
  - Stones and rocks
  - Reinforced concrete pipe
  - Wood
  - Steel beams
  - Asbestos insulation and roofing/siding shingles
  - Fiberglass insulation
  - Fiberglass tanks
-

SUPERFUND STANDARD ANALYTICAL REFERENCE MATRIX PREPARATION  
AND RESULTS OF PHYSICAL SOILS WASHING EXPERIMENTS

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ABSTRACT

In response to the RCRA Hazardous and Solid Waste Amendments of 1984 prohibiting the continued land disposal of untreated hazardous wastes, the EPA has instituted a research program for establishing best demonstrated and available technologies for RCRA and Superfund wastes. Under Phase I of EPA's Superfund research program, several projects were initiated under which a surrogate soil containing a wide range of chemical contaminants was prepared for use in bench-scale and pilot-scale performance evaluations of five different treatment technologies. This paper covers one of the projects in which the surrogate test soil was developed and bench-scale soil washing treatability studies were completed. This work was conducted by PEI Associates under EPA Contract No. 68-03-3413 during 1987. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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## INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 prohibit the continued land disposal of untreated hazardous wastes beyond specified dates. The statute requires the U.S. Environmental Protection Agency (EPA) to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short-term and long-term threats to human health and the environment are minimized." The legislation sets forth a series of deadlines beyond which further disposal of particular waste types is prohibited if the Agency has not set treatment standards under Section 3004(m) or determined, based on a case-specific petition, that no further migration of hazardous constituents will occur for as long as the wastes remain hazardous.

In addition to addressing future land disposal of specific listed wastes, the RCRA land disposal restrictions also address the disposal of soil and debris from CERCLA site response actions. Sections 3004(d)(3) and (e)(3) of RCRA state that the soil/debris waste material resulting from a Superfund-financed response action or an enforcement authority response action implemented under Sections 104 and 106 of CERCLA, respectively, will not be subject to the land ban until November 8, 1988.

Because Superfund soil/debris waste often differs significantly from other types of hazardous waste, the EPA is developing specific RCRA Section 3004(m) standards or levels applying to the treatment of these wastes. These standards will be developed through the evaluation of best demonstrated and available technologies (BDAT). In the future, Superfund wastes in compliance with these regulations may be deposited in land disposal units; wastes exceeding these levels will be banned from land disposal unless a variance is issued.

In early 1987, EPA's Hazardous Waste Engineering Research Laboratory, at the request of the Office of Solid Waste, initiated a research program to evaluate various treatment technologies for contaminated soil and debris from Superfund sites. Under Phase I of this research program, which was conducted from April to November 1987, a surrogate soil containing a wide range of chemical contaminants typically occurring at Superfund sites was prepared for use across the board in the bench-scale or pilot-scale performance evaluations of five available treatment technologies: 1) soil washing, 2) chemical treatment (KPEG), 3) thermal desorption, 4) incineration, and 5) stabilization/fixation. This report covers those segments of Phase I related to development of the surrogate soil and experimental bench-scale tests on the potential effectiveness of physical soil washing as a treatment technology.

## PROCEDURES

### SARM PREPARATION

The surrogate soil is referred to throughout the text as SARM, an acronym for Synthetic Analytical Reference Matrix. More than 30,000 pounds of clean (uncontaminated) SARM was prepared after considerable research into the types of soils found at Superfund sites nationwide. The final composition selected

consisted of 30 percent by volume clay (a mixture of montmorillinite and kaolinite), 25 percent silt, 20 percent sand, 20 percent topsoil, and 5 percent gravel. The components were air-dried to minimize moisture and then mixed together in two 15,000-lb batches in a standard truck-mounted 6-yd<sup>3</sup> cement/concrete mixer.

A prescribed list of chemicals found to be widely and frequently occurring at Superfund sites was then added to the clean SARM in a series of smaller-scale mixing operations utilizing a 15-ft<sup>3</sup> mortar mixer. The organic chemicals added included ethyl benzene, 1,2-dichloroethane, tetrachloroethylene, acetone, chlorobenzene, styrene, xylene, anthracene, pentachlorophenol, and bis(2-ethylhexyl) phthalate. Salts or oxides of the following metals were also added: lead, zinc, cadmium, arsenic, copper, chromium, and nickel. Because concentrations of contaminants in soils vary widely, four different SARM formulas containing either high or low levels of organics and metals were prepared for use in subsequent treatability tests using the five technologies named. Table 1 presents the target contaminant concentration of the four SARMS prepared. Reserves of each SARM were also packaged and archived for future use. The archived samples are being stored at EPA's R&D facility in Edison, New Jersey.

#### PHYSICAL SOIL WASHING EXPERIMENTS

As part of the performance evaluation of soil washing as a potential treatment candidate, samples of each SARM were physically washed in a series of bench-scale experiments designed to simulate the EPA-developed Mobile Soils Washing System (MSWS). This system can extract certain contaminants from soils, which reduces the volume of the contaminated portion of the soils. The MSWS is expected to be an economic alternative to the current practice of hauling contaminated soils offsite to a landfill and replacing the excavated volume with fresh soils.

Specifically, this project was designed to simulate the drum screen washer segment of the MSWS as described by J.S. Shum in the Operation and Maintenance Manual(1). This segment of the MSWS separates the +2 mm soil fraction from the -2 mm soil fraction (fines) by use of a rotary drum screen. A high-pressure water knife operates at the head of the system to break up soil lumps and strip the contaminants off the soil particles. Both the design of the MSWS and the design of the bench-scale experiments to simulate the MSWS for cleanup of the SARMS samples are based on the following assumptions, which underlie the volume reduction approach of physical soils washing:

1. A significant fraction of the contaminants are attached to the silt, humus, and clay particles.
2. The silt and clay are attached to the sand and gravel by physical processes (primarily compaction/adhesion).
3. Physical washing of the sand/gravel/rock fraction will effectively remove the fine sand, silt, and clay-sized (less than 0.25 mm) materials from the coarse material.

TABLE 1. TARGET CONTAMINANT CONCENTRATIONS FOR SARMS  
(mg/kg)

Analyte	SARM I (High organic, low metal)	SARM II (Low organic, low metal)	SARM III (Low organic, high metal)	SARM IV (High organic, high metal)
<u>Volatiles</u>				
Acetone	6,800	680	680	6,800
Chlorobenzene	400	40	40	400
1,2-Dichloroethane	600	60	60	600
Ethylbenzene	3,200	320	320	3,200
Styrène	1,000	100	100	1,000
Tetrachloroethylene	600	60	60	600
Xylene	8,200	820	820	8,200
<u>Semivolatiles</u>				
Anthracene	6,500	650	650	6,500
Bis(2-ethylhexyl) phthalate	2,500	250	250	2,500
Pentachlorophenol	1,000	100	100	1,000
<u>Inorganics</u>				
Arsenic	10	10	500	500
Cadmium	20	20	1,000	1,000
Chromium	30	30	1,500	1,500
Copper	190	190	9,500	9,500
Lead	280	280	14,000	14,000
Nickel	20	20	1,000	1,000
Zinc	450	450	22,500	22,500

4. The contaminants will be removed to the same extent that the silt and clay are separated (i.e., increasing the efficiency of the washing process will directly increase the removal efficiency for the majority of the contaminant mix).

These assumptions were tested by evaluating different wash solutions in bench-scale shaker-table experiments. The wash solutions chosen for evaluation included 1) a chelant solution (tetrasodium salt of EDTA, Dow Chemical Versene 100<sup>R</sup>), and 2) an anionic surfactant solution (phosphated formulation from Procter and Gamble, Institutional Formula Tide<sup>R</sup>). Different pH and temperature conditions were evaluated for the wash solutions. Organic solvents and oxidizing agents were considered, but were found not to be viable soil-washing solutions because of material handling problems associated with these compounds, especially when used in a field situation. Following the shaker-table wash, the soil was wet-sieved to separate the fines from the coarse material. Although the EPA MSWS only separates the soil into +2 mm and -2 mm size fractions, three size fractions (+2 mm, 250  $\mu$ m to 2 mm, and -250  $\mu$ m) were investigated in this study to determine if an intermediate size fraction (medium to fine sand) could be cleaned effectively, thereby increasing the volume reduction potential. For determination of the effectiveness of the soil-washing techniques in reducing the volume of contaminated material, each of the resulting soil fractions was subsequently analyzed for total organics and metals by standard Gas Chromatography Mass Spectrometry (GC/MS) and Inductively Coupled Plasma (ICP) techniques (SW-846, 3rd ed.) and for leachable constituents by Toxicity Characteristic Leaching Procedures (TCLP).

## RESULTS

### SARM PREPARATION

Results of physical tests conducted on the clean SARM are summarized in Table 2. These test results indicate that the synthetic soil is characteristic of a slightly alkaline sandy loam with moderate clay and organic content and a relatively high cation exchange capacity. Such a soil, when contaminated, should present a reasonable challenge to any applied treatment technology.

Chemical analyses of samples of the four SARMS were conducted before treatment to verify contaminant levels and moisture content. Table 3 contains the average concentrations obtained for each analyte in each of the four SARMS. All numbers reported by each laboratory conducting the analyses (five separate analytical laboratories performed these analyses) were included in calculating the averages.

If the target contaminant levels (Table 1) are compared to the actual levels found (Table 3), the recovery efficiencies obtained are the highest and most consistent for the metals, followed by the volatiles and the semivolatiles. Generally, the SARMS containing the higher concentrations of volatiles and semivolatiles showed better correlation between the target and the actual contaminant levels. The results for the lower organic contaminated SARMS (SARM II and III) seem to indicate either that a greater portion (relative to the high organic SARMS) of the indicator organics added to the soil were lost through one or more routes (e.g., volatilization, adsorption), or alternatively, that the lower concentrations of the organics were more difficult to reliably detect and quantitate.

TABLE 2. PHYSICAL CHARACTERISTICS OF CLEAN SARM

	Average <sup>a</sup>	Range
Cation exchange capacity, meq/100 g	132.7 (10)	77.5 to 155
Total organic carbon, %	3.2 (6)	2.7 to 3.9
pH	8.5 (6)	8.0 to 9.0
Grain size distribution, weight %		
Gravel (>4.75 mm)	3 (6)	2 to 4
Sand (4.75 mm - 0.075 mm)	56 (6)	54 to 58
Silt (0.074 mm to 0.005 mm)	28 (6)	27 to 30
Clay (<0.005 mm)	12 (6)	11 to 14

<sup>a</sup> Values in parentheses indicate number of samples analyzed.



TABLE 3. ANALYTICAL PROFILE OF SARMS: AVERAGE CONCENTRATION  
FOUND UPON ANALYSIS<sup>a</sup>  
(mg/kg)

Analyte	SARM I (High organic, low metal)	SARM II (Low organic, low metal)	SARM III (Low organic, high metal)	SARM IV (High organic, high metal)
<u>Volatiles</u>				
Acetone	4,353 (9)	356 (8)	358 (2)	8,030 (2)
Chlorobenzene	316 (9)	13 (6)	11 (2)	330 (2)
1,2-Dichloroethane	354 (9)	7 (8)	5 (2)	490 (2)
Ethylbenzene	3,329 (9)	123 (8)	144 (2)	2,708 (2)
Styrene	707 (9)	42 (8)	32 (2)	630 (2)
Tetrachloroethylene	408 (9)	19 (8)	20 (2)	902 (2)
Xylene	5,555 (9)	210 (8)	325 (2)	5,576 (2)
<u>Semivolatiles</u>				
Anthracene	5,361 (9)	353 (7)	181 (3)	1,920 (3)
Bis(2-ethylhexyl) phthalate	1,958 (9)	117 (7)	114 (3)	646 (3)
Pentachlorophenol	254 (9)	22 (7)	30 (3)	80 (3)
<u>Metals</u>				
Arsenic	18 (10)	17 (7)	652 (4)	500 (4)
Cadmium	22 (8)	29 (6)	2,260 (2)	3,631 (2)
Chromium	24 (8)	28 (6)	1,207 (4)	1,314 (4)
Copper	231 (10)	257 (8)	9,082 (4)	10,503 (4)
Lead	236 (10)	303 (8)	14,318 (4)	14,748 (4)
Nickel	32 (10)	38 (8)	1,489 (4)	1,479 (4)
Zinc	484 (8)	642 (6)	31,871 (4)	27,060 (4)
<u>Moisture, %</u>	20 (7)	11 (7)	19 (3)	26 (2)

<sup>a</sup> Values in parentheses indicate number of samples analyzed.

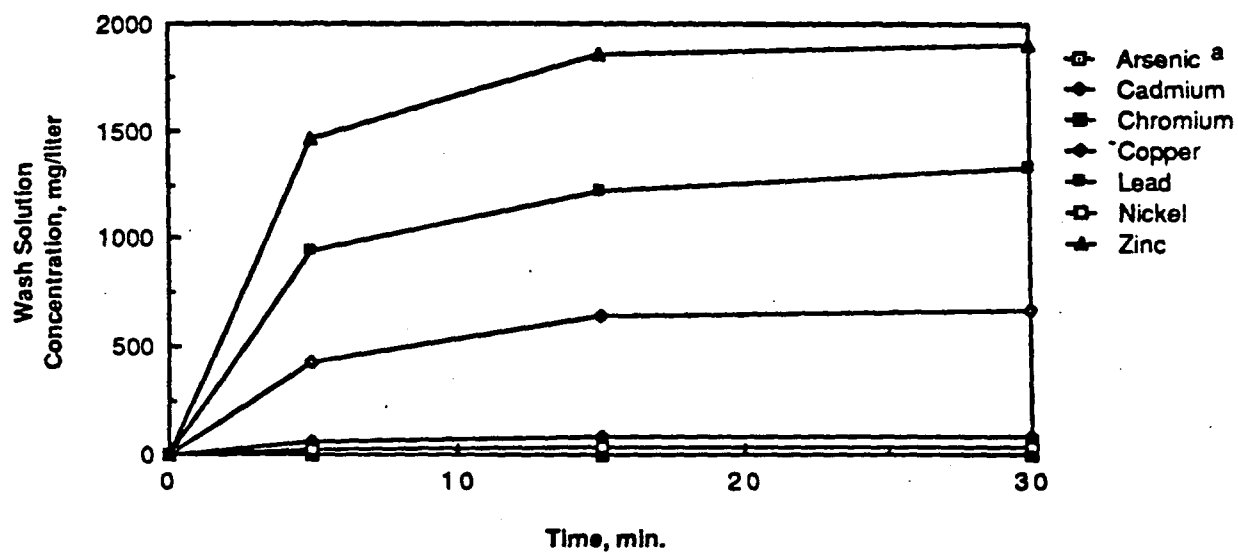
## PHYSICAL SOIL WASHING EXPERIMENTS

During the initial phase of these experiments, pH and temperature variations were evaluated as well as different chelant and surfactant concentrations. Experiments were also run to determine the optimum reaction time for both the chelant and surfactant solutions. In all cases, a 10:1 wash solution-to-soil ratio was utilized. Temperature ranges from 78° to 120°F were found to have little effect on the contaminant reduction efficiencies. Adjustment of the pH of the surfactant solution from 5.0 to 12.0 resulted in no appreciable change in the organic contaminant removal efficiencies. Also, reducing the pH of the chelant solution from its natural pH of 12 to 8.0 produced no additional metal removal.

Reaction times of 5, 15 and 30 minutes were evaluated in a series of trial tests for the chelant and surfactant solutions in order to select the optimum reaction time for all subsequent testing. Figures 1 and 2 present the reaction time results for a 1:1 molar ratio (moles of tetrasodium EDTA to moles of total metals present in the SARM) chelant wash of metals from SARM III, and for a 0.1 percent (by weight) surfactant wash of organics from SARM I, respectively. The concentrations used for evaluation of the reaction times were the lowest concentrations of both chelant and surfactant chosen for overall evaluation in this study. As shown in Figure 1, no significant additional metal chelation occurred for SARM III after 15 minutes for any of the six metals. Therefore, a 15-minute reaction time was chosen for all of the subsequent chelant wash tests. As shown in Figure 2, no similar completion of reaction was evident for the organic contaminants (as total organic halogens); their concentration in the wash water continued to increase over the entire 30-minute interval. Therefore, 30 minutes was chosen as the reaction time for all subsequent surfactant washes. Longer reaction times were not evaluated because reaction times in excess of 30 minutes are typically too costly in scale-up operations.

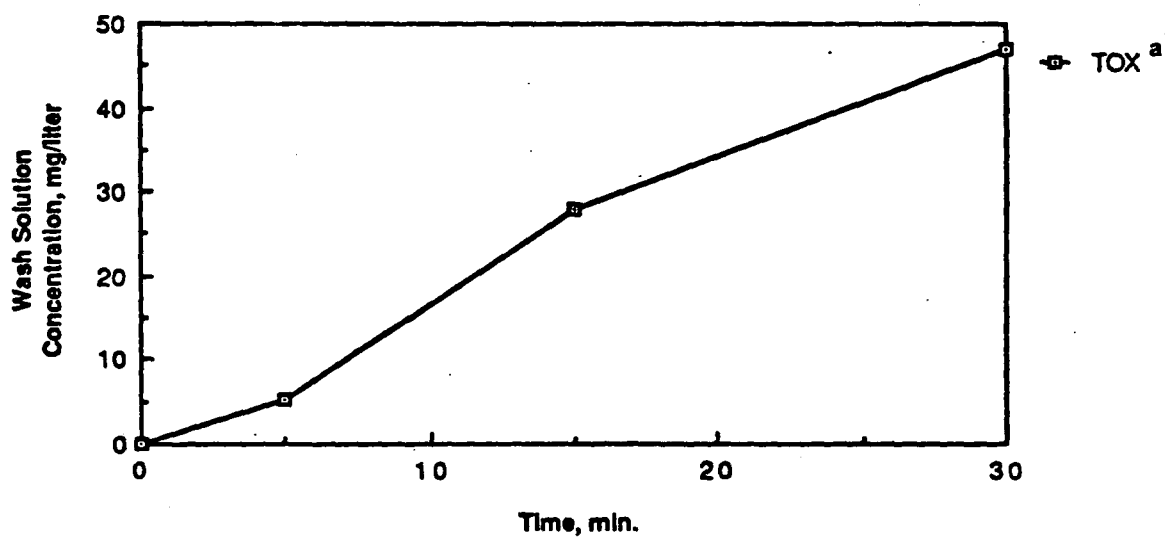
Next, surfactant concentrations of 1.5, 0.5, and 0.1 percent (by weight) were evaluated in a series of 30-minute washing tests of SARM I to determine the optimum organic contaminant removal efficiency achievable. The tests showed that the 0.1 percent solution was least effective, and that the 1.5 percent and 0.5 percent concentrations were essentially equal; the results obtained for the 1.5 percent solution did not indicate sufficient additional contaminant reduction over the 0.5 percent solution to justify the higher surfactant concentration. Thus the 0.5 percent surfactant solution was chosen as the optimum wash concentration for subsequent organics removal tests. Two molar ratios (moles of tetrasodium EDTA to total moles of metals present in the higher metal SARM-SARM III) were evaluated for metals removal—1:1 and 3:1. The 3:1 EDTA molar ratio solution exhibited consistently higher removal efficiencies for the metals, particularly in the middle soil fraction (250  $\mu$ m to 2 mm); therefore it was chosen for further study in all subsequent metal removal tests.

During the second phase of these experiments, the optimum conditions for reducing organic and metal contamination (as determined in the initial phase of the soil experiments and discussed in the preceding paragraphs) were applied to all four SARMs and compared with a baseline plain water wash for each SARM. Tables 4 through 7 present the results of these final washings. In



<sup>a</sup> Arsenic and nickel overlap in this figure.

Figure 1. Reaction time - 1:1 molar chelant wash, SARM III



<sup>a</sup> Total organic halogens

Figure 2. Reaction time - 0.1% surfactant wash, SARM I

TABLE 4. SOIL WASHING RESULTS: SARM I (HIGH ORGANICS, LOW METALS)  
(ppm)

Contaminant	Initial concentration <sup>a</sup>	Water wash			0.5% Surfactant wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Volatile organics							
Acetone	4,353	10	20	140	22	8.0	50
Chlorobenzene	316	0.028	0.28	160	0.30	1.0	31
1,2-Dichloroethane	354	<0.023	0.18	24	0.15	0.32	6.0
Ethyl benzene	3,329	0.13	1.4	2300	2.3	8.5	680
Styrene	707	ND <sup>b</sup>	ND	400	<0.17	ND	96
Tetrachloroethylene	408	0.009	0.12	250	0.20	0.81	49
Xylene	5,555	0.38	3.2	1800	4.0	14	820
Total volatile organic reduction		>99.9%	99.8%	66.2%	>99.8%	99.8%	88.5%
Semivolatile organics							
Anthracene	5,361	6.5	3200	1400	3.3	2500	2700
Bis(2-ethylhexyl) phthalate	1,958	4.0	92	1600	<6.1	100	1600
Pentachlorophenol	254	66	26	53	8.4	4.6	ND
Total semivolatile organic reduction		98.9%	56.2%	59.7%	>99.8%	65.6%	43.2%
Inorganics							
Arsenic	18	3.0	5.2	18.6	4.5	5.8	19.1
Cadmium	22	7.3	11.3	28.8	6.9	11.0	26.2
Chromium	24	1.5	2.6	43.4	3.0	3.0	46.8
Copper	231	10.6	30.5	387	11.8	34.6	384
Lead	236	11.1	28.8	402	10.1	40.1	420
Nickel	32	3.2	7.8	35.1	5.1	6.8	31.6
Zinc	484	44.8	106	726	47.9	101	647
Total metal reduction		92.2	81.6	NR <sup>c</sup>	91.5	80.7	NR

<sup>a</sup> From Table 3.

<sup>b</sup> ND = not detected.

<sup>c</sup> NR = no reduction in overall contamination.

TABLE 5. SOIL WASHING RESULTS: SARM II (LOW ORGANICS, LOW METALS)  
(ppm)

Contaminant	Initial concentration <sup>a</sup>	Water wash			3:1 Molar chelant wash			0.5% Surfactant wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Volatile organics										
Acetone	356	0.50	0.31	0.50	0.58	1.2	2.7	0.46	0.75	1.8
Chlorobenzene	13	0.002	0.013	<0.23	<0.004	0.006	0.020	0.002	0.002	ND
1,2-Dichloroethane	7	ND	<0.004	ND	ND	0.003	0.003	ND	0.004	ND
Ethyl benzene	123	0.014	0.082	0.14	0.005	0.058	0.13	0.009	0.015	0.62
Styrene	42	0.016	0.13	0.25	<0.006	0.066	0.12	0.010	<0.013	0.28
Tetrachloroethylene	19	ND	<0.004	<0.22	ND	<0.004	0.009	ND	ND	<0.30
Xylene	210	0.040	0.31	0.52	0.021	0.20	0.44	0.028	0.040	1.3
Total volatile organic reduction		99.9%	>99.9%	>99.8%	>99.9%	>99.8%	99.6%	99.9%	>99.9%	>99.4%
Semivolatile organics										
Anthracene	353	3.2	180	830	8.8	210	660	1.6	120	700
Bis(2-ethylhexyl) phthalate	117	27	46	370	40	44	260	28	32	160
Pentachlorophenol	22	ND	6.8	4.6	ND	5.1	ND	2.4	7.8	ND
Total semivolatile organic reduction		93.9%	52.7%	NR <sup>c</sup>	90.1%	47.3%	NR	93.5%	67.5%	NR
Inorganics										
Arsenic	17	2.5	4.2	24.8	3.9	4.4	12.6	3.0	3.6	27.8
Cadmium	29	6.0	10.2	55.6	2.0	4.0	7.5	4.8	9.4	37.7
Chromium	28	<0.88	4.0	90.4	1.6	3.4	69.7	2.7	3.5	56.6
Copper	257	5.0	25.4	652	8.2	15.6	238	9.0	28.6	478
Lead	303	4.0	69.0	710	6.2	12.6	110	8.5	31.8	511
Nickel	38	4.0	7.2	68.6	4.2	7.0	43.0	3.2	6.8	41.8
Zinc	642	21.0	107	1380	28.3	63.6	546	25.8	112	906
Total metal reduction		>96.7%	82.7%	NR	95.9%	91.6%	21.9%	95.7%	85.1%	NR

<sup>a</sup> From Table 3.

<sup>b</sup> ND = not detected.

<sup>c</sup> NR = no reduction in overall contamination.

TABLE 6. SOIL WASHING RESULTS: SARM III (HIGH ORGANICS, LOW METALS)  
(ppm)

Contaminant	Initial concentration <sup>a</sup>	Water wash			3:1 Molar chelant wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Volatile organics							
Acetone	358	0.74	1.7	16	0.96	2.6	3.3
Chlorobenzene	11	0.008	0.16	1.6	0.011	0.23	1.2
1,2-Dichloroethane	5	<0.004	0.024	0.084	0.002	0.034	<0.050
Ethyl benzene	144	0.040	1.3	34	0.054	2.0	20
Styrene	32	0.026	<0.30	6.4	ND <sup>b</sup>	0.55	3.0
Tetrachloroethylene	20	0.002	0.16	3.0	0.006	0.23	2.2
Xylene	325	0.10	2.6	58	0.091	3.6	31
Total volatile organic reduction		>99.9%	>99.3%	86.7%	99.9%	99.0%	>93.2%
Semivolatile organics							
Anthracene	181	<5.6	480	1,800	1.7	540	1,800
Bis(2-ethylhexyl) phthalate	114	2.2	7.4	1,100	3.4	9.4	790
Pentachlorophenol	30	9.2	40	59	<6.6	13	<96
Total semivolatile organic reduction		>94.8%	NR <sup>c</sup>	NR	96.4%	NR	NR
Inorganics							
Arsenic	652	54.6	102	1,160	36.6	51.0	243
Cadmium	2,260	372	276	746	290	116	110
Chromium	1,207	3.8	14.8	2,590	3.2	9.2	1940
Copper	9,082	68.4	264	20,800	38.6	104	2250
Lead	14,318	122	491	30,600	98.1	171	1470
Nickel	1,489	18.6	42.2	1,570	17.5	28.2	472
Zinc	31,871	558	1010	48,200	500	519	6760
Total metal reduction		98.0%	96.4%	NR	98.4%	98.4%	78.2%

<sup>a</sup> From Table 3.

<sup>b</sup> ND = not detected.

<sup>c</sup> NR = no reduction in overall contamination.

TABLE 7. SOIL WASHING RESULTS: SARM IV (HIGH ORGANICS, HIGH METALS)  
(ppm)

Contaminant	Initial concentration <sup>a</sup>	Water wash			3:1 Molar chelant wash			0.5% Surfactant wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Volatile organics										
Acetone	8,030	5.8	5.8	120	16	21	180	14	15	53
Chlorobenzene	328	0.020	1.5	68	0.012	1.4	99	0.076	0.94	22
1,2-Dichloroethane	490	0.028	<0.34	<8.6	<0.004	<0.54	40	0.10	<0.30	4.4
Ethyl benzene	2,708	0.080	15	2,000	0.051	12	1000	0.52	7.4	300
Styrene	630	ND <sup>b</sup>	<2.8	150	<0.026	ND	200	0.17	ND	54
Tetrachloroethylene	902	<0.017	2.3	120	0.006	1.4	170	0.048	1.1	45
Xylene	5,576	0.18	25	3,200	0.11	23	1700	0.86	26	460
Total volatile organic reduction		>99.9%	>99.7%	>69.6%	>99.9%	>99.7%	81.8%	99.9%	>99.7%	95.0%
Semivolatile organics										
Anthracene	1,920	28	2700	5,200	40	1700	3300	2.4	1800	5,800
Bis(2-ethylhexyl) phthalate	646	5.8	34	3,100	9.6	70	2800	<5.6	26	1,500
Pentachlorophenol	80	23	39	360	8.4	22	<180	38	42	100
Total semivolatile organic reduction		97.8%	NR <sup>c</sup>	NR	97.8%	32.3%	NR	>98.3%	29.4%	NR
Inorganics										
Arsenic	500	126	110	924	63.4	91.7	180	30	110	538
Cadmium	3,631	348	286	643	279	210	107	308	336	739
Chromium	1,314	7.7	29.0	2,180	6.4	29.8	1480	5.9	32.5	1,500
Copper	10,503	148	467	18,400	80.6	332	1990	63.1	446	11,100
Lead	14,748	168	1260	23,900	103	272	1360	68.4	818	15,000
Nickel	1,479	29.8	56.4	1,240	19.4	70.7	284	14	62.9	618
Zinc	27,060	873	3320	36,200	558	4730	5160	462	3040	25,400
Total metal reduction		97.1%	90.7%	NR	98.1%	90.3%	82.2%	98.4%	91.8%	7.3%

<sup>a</sup> From Table 3.

<sup>b</sup> ND = not detected.

<sup>c</sup> NR = no reduction in overall contamination.

general, the cleaning results of the water wash, the 3:1 molar chelant wash, and 0.5 percent surfactant wash for the +2 mm soil fraction did not differ significantly. As hypothesized, the silt and clay particles appeared to be attached to the sand and gravel primarily by physical processes such as compaction and adhesion. These physical attractions are often related to the age of the soil and the contact time between the contaminants and soil particles. Because the SARM was a freshly prepared soil that had not been compacted, weathered, and aged, the physical forces of attraction are believed to have been relatively weak, a condition more typical of a spill site soil than an older soil found at an abandoned CERCLA site. Consequently, the water wash was as effective in cleaning the +2 mm soil fraction as the water-plus-additive solutions were.

Removal of contaminants from the medium-grained fraction (250  $\mu$ m to 2 mm) appears to entail both physical and chemical processes. By nature, this middle soil fraction, which is composed of medium to fine sand, does not absorb contaminants to the degree that clays and silts do. It has more surface area, however, and should be somewhat harder to clean than the coarse +2 mm fraction. A comparison of the water wash with the 3:1 molar chelant wash showed that the chelant wash reduced the residual concentration of metals in the medium soil size class for each SARM subjected to the chelant wash (SARM II, III, and IV). This trend is especially apparent in the data for SARM II (Table 5) where the total residual metal reduction increased from 82.7 percent for the water wash to 91.6 percent after the chelant wash. The organics show less variation among experimental runs in this soil size class. For the most part, water was as effective as the surfactant wash for reducing the level of organic contamination. The one anomaly was anthracene, which showed very high concentrations in the medium soil class. The anthracene evidently was not fully dissolved before it was added to the SARM; flakes of what was believed to be anthracene were observed on the 250  $\mu$ m screen during the washing experiments.

Reduction of contaminants appears to be affected more by the use of different wash solutions in the fine soil fraction (less than 250  $\mu$ m) than in the other soil fractions. Contaminants are typically bound by both chemical and physical processes in fine soil fraction. As shown in Tables 5 through 7, the chelant wash significantly reduced metal contamination in the fine soil fraction. This reduction is particularly evident in Tables 6 and 7, which present the results for the SARMS initially high in metal content. Although the spent wash water was not analyzed, it can be assumed that the chelant effectively mobilized the metals into solution. Similarly, the surfactant wash significantly reduced the volatile organic contamination in the fine soil fraction, as evidenced by the results shown in Tables 4 and 7 for the high-organic-content SARMS. Again, the wash water was not analyzed; however, it can be assumed that the surfactant successfully mobilized the organics into solution.

The trends indicated by the results of the TCLP analysis were similar to those shown in Tables 4 through 7. In general, reduction efficiencies ranging from 93 to 99 percent were obtained in the TCLP analysis of volatile organics, semi-volatile organics, and metals for the top two soil fractions (+2 mm and 2 mm to 250  $\mu$ m). Most of the TCLP contaminants present in the +2 mm soil fractions dropped below the proposed regulatory limit given in the Federal Register, Volume 51, No. 114, June 13, 1986. In the SARMS containing lower levels of



metals (specifically SARM I and II), the middle soil fraction (2 mm to 250  $\mu$ m) also exhibited concentrations below the proposed TCLP levels.

## CONCLUSIONS AND RECOMMENDATIONS

### SARM PREPARATION

The preparation of a standard synthetic surrogate soil with physical characteristics and contaminant levels representative of a wide range of conditions typically found at Superfund sites was successfully completed. The surrogate or SARM was subsequently utilized in evaluating the relative effectiveness of five selected treatment technologies (physical soil washing, chemical treatment, stabilization, low temperature thermal desorption, and incineration), and a soil treatability data base has now been established.

Further studies comparing the treatability results that were obtained with the SARM to results from similarly designed studies using actual site soils are needed to further supplement the data base. Also, future studies in which the SARM is used to evaluate the relative effectiveness of other proposed treatment technologies at Superfund sites would be valuable.

### PHYSICAL SOIL WASHING EXPERIMENTS

The soil washing results from this study appear to support the basic assumptions underlying the volume-reduction approach to site remediation--that a significant fraction of the contaminants in contaminated soils are attached to the smaller sized particles or fines (i.e., silt, humus, and clay) and that the coarse material can be cleaned and returned to the site by physically washing and separating it from the fines. The data indicate that water alone can efficiently remove a significant portion of the contamination from the +2 mm soil fraction. Contaminant removal from the middle (2 mm to 250  $\mu$ m) soil fraction and the fine (<250  $\mu$ m) soil fraction, however, can be generally enhanced by chelant and surfactant solutions. Addition of a chelant to the wash solution can improve metal reduction efficiencies for both the medium and small particle size fractions. Addition of a surfactant to the wash solution can lead to higher organic removals (compared with the water wash) from the fine particles. In general, water appears to be more effective in mobilizing the organics into solution than in mobilizing the metals.

In the preliminary bench-scale experiments, it was determined that the SARM was approximately 13 percent (by weight) coarse material (i.e., >2 mm), 29 percent medium-grained material (250  $\mu$ m to 2 mm), and 58 percent fines (<250  $\mu$ m). Therefore, the data presented in Tables 4 through 7 indicate achievement of at least a 13 percent weight reduction of contaminated material with a water wash alone. Addition of a chelant solution resulted in a 42 percent reduction by weight of the metal-contaminated SARM, and use of the chelant and surfactant solutions resulted in lower metal and organic contamination, respectively, in the fine particles.

The mix of contaminants in Superfund soils often lends itself to an extraction or washing treatment technology such as that demonstrated in this study. Although promising results have already been achieved at the pilot scale at a number of lead-contaminated Superfund sites, additional research is needed to demonstrate the cost-effectiveness of soil washing for full-scale

treatment of a wide range of metal- and organic-contaminated soils. Specifically, most of the research conducted to date has involved demonstration of the operation of various pieces of equipment for pretreatment and extraction of the contaminants from the soil and for post-treatment of the extractant. The effective separation of the wash solution from the soil, the recycling of the regenerated wash solution, and the concentration/destruction of the contaminants, however, have not been demonstrated at a large-scale pilot facility(2). The following is a listing of areas in which future work is needed with respect to the development of soil washing as a full-scale, viable treatment option for Superfund soils:

1. Laboratory feasibility studies for evaluating removal of contaminants from the wash water.
2. Laboratory-scale physical soil washing studies using actual Superfund soils containing a mix of metal and organic contamination. (The first study of this type is currently funded and should begin in the spring of 1988.)
3. Evaluation of sequential wash solutions for reducing combined organic and metal contamination.
4. Additional pilot-scale studies on the use of the EPA Mobile Soil Washing System.
5. Bench-scale feasibility studies evaluating stabilization/solidification effectiveness as a treatment train option for the concentrated fines remaining after soil washing.
6. Evaluation of feed stock preparation methods for the EPA Mobile Soil Washing System.

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## RESULTS OF TREATMENT EVALUATIONS OF CONTAMINATED SOILS

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## INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 prohibit the continued land disposal of untreated hazardous wastes beyond specified dates. The statute requires the U.S. Environmental Protection Agency (EPA) to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short-term and long-term threats to human health and the environment are minimized." The legislation sets forth a series of deadlines beyond which further disposal of untreated wastes is prohibited. Specifically, Sections 3004(d)(3) and (e)(3) require solid/debris waste material resulting from a Superfund-financed response action or an enforcement authority response action implemented under Sections 104 and 106 of CERCLA,\*\* respectively, to become subject to the land ban on November 8, 1988.

In response to this mandate, the EPA Office of Solid Waste and Emergency Response (OSWER) is developing standards for the treatment of these wastes. These standards will establish treatment levels through the evaluation of readily available treatment technologies. In the future, Superfund wastes meeting these levels or standards may be deposited in land disposal units; otherwise, they will be banned from land disposal unless a variance is issued. EPA's Office of Research and Development has initiated a research program to

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\*\* Comprehensive Environmental Response, Compensation, and Liability Act

identify and evaluate readily available treatment technologies for contaminated Superfund soils.

Under Phase I of EPA's research program, which was conducted from April to November 1987, a surrogate soil containing a wide range of chemical contaminants typically occurring at Superfund sites was prepared and subjected to bench- or pilot-scale performance evaluations using the following treatment technologies: 1) physical separation/volume reduction (soil washing), 2) chemical treatment (specifically, KPEG), 3) thermal desorption, 4) incineration, and 5) stabilization/fixation. This report covers the formulation and development of the surrogate soil; it also highlights the results of the five treatment evaluations. It is worth noting that virtually all of the analytical data underlying this research were developed using EPA-SW846 methods. Detailed project reports covering the findings of each study are available through EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati (see acknowledgments for contact names).

#### PREPARATION OF SURROGATE SOIL (SARM)

SARM, an acronym for synthetic analytical reference matrix, is the term used throughout this text to refer to the synthetic soil. The decision to use a synthetic soil was driven by several factors. First, RCRA permit regulations restricting off-site treatment of hazardous wastes, such as contamination Superfund site soils, limited the planned research program. Second, there was a strong desire for the test soil to be broadly representative of a wide range of soils and contaminants, and it was felt that no single site soil could adequately satisfy this need. Third, large quantities of a homogeneous test material were needed for the research program, particularly for incineration, which was to be evaluated using pilot-scale equipment (requiring thousands of pounds of feed stock). Fourth, it was important to have contaminants present in the soil at sufficient levels to determine at least 99 percent reduction efficiencies. Fifth, the contaminants had to include both metals and organics, and the organics had to include compounds representing a wide variety of structural types (e.g., both chlorinated and nonchlorinated aliphatics and aromatics, volatiles and semivolatiles, etc.). Sixth, the soil with its mix of contaminants had to present a reasonable challenge to the technologies of interest.

The basic formula for the SARM soil was determined from an extensive review of 86 Records of Decision (ROD's) and a parallel independent study of the composition of eastern U.S. soils. The recommendations of both sets of data came to almost the same conclusion: 30 percent by volume of clay (montmorillonite and kaolinite), 25 percent silt, 20 percent sand, 20 percent top soil, and 5 percent gravel. These components were assembled, air-dried, and mixed together in two 15,000-lb batches in a standard truck-mounted cement mixer.

Also, as part of the background work, the ROD's were studied to determine the occurrence, frequency, and concentration of more than 1000 contaminants found on Superfund sites. The objective of this effort was to identify contaminant groups, and indicator chemicals for those groups, that were most representative of CERCLA wastes.

The three basic contaminant groups identified as being frequently found in Superfund site soil and debris were volatile organics, semivolatile organics, and metals. The selection of specific compounds to serve as representative analytes for each contaminant group was based on an analysis of specific site contaminants and their occurrence, as well as the physical and chemical properties of each compound, including:

- Molecular structure
- Vapor pressure
- Heat of vaporization
- Heat of combustion
- Solubility
- Henry's Law constant
- Partition coefficient
- Soil adsorption coefficient

Health effects and toxicity were also taken into account during the selection process.

As a result of this research effort, a list of target contaminant compounds was developed that represented the most frequently occurring hazardous compounds at Superfund sites, and that also provided a challenging test matrix for all five treatment technologies. The final list of chemical contaminants chosen for the SARM studies is as follows:

Volatile organics

Ethylbenzene  
Xylene  
1,2-Dichloroethane  
Tetrachloroethylene  
Acetone  
Chlorobenzene  
Styrene

Metals

Lead  
Zinc  
Cadmium  
Arsenic  
Copper  
Chromium  
Nickel

Semivolatile organics

Anthracene  
Pentachlorophenol  
Bis(2-ethylhexyl)phthalate

The final step in this research process was to examine the levels at which these chemicals have been found at Superfund sites and to select concentrations that would be representative of contaminated soils and debris. The EPA compiled average and maximum concentrations of each selected chemical and calculated the percentage of each compound within its group. From these data, target contaminant concentrations were devised for formulating four different SARM preparations:

SARM 1: High levels of organics (20,800 ppm volatiles plus 10,000 ppm semivolatiles) and low levels of metals (1,000 ppm total metals).

- SARM 2: Low levels of organics (2,080 ppm volatiles plus 1,000 ppm semi-volatiles) and low levels of metals (1,000 ppm total metals).
- SARM 3: Low levels of organics (2,080 ppm volatiles plus 1,000 ppm semi-volatiles) and high levels of metals (50,000 ppm total metals).
- SARM 4: High levels of organics (20,800 ppm volatiles plus 10,000 ppm semivolatiles) and high levels of metals (50,000 ppm total metals).

Table I presents the selected target levels for each of the contaminants in each of the four SARM's.

More than 28,000 pounds of SARM samples were prepared through a series of small-scale mixing operations utilizing commercial stocks of chemicals, the clean SARM soil, and a 15-ft<sup>3</sup> mortar mixer. Batches of each SARM were prepared in 500-lb quantities sufficient to meet the needs of each treatment technology. Only a few pounds of each SARM was necessary for most of the technologies because they were conducted at bench scale; however, incineration was evaluated at pilot scale, and therefore required thousands of pounds of SARM to serve as feed stock for the testing. More than 200 lb of each SARM was also reserved, packaged, and archived for future use. The archived samples are currently being stored at EPA's R&D facility in Edison, New Jersey, and are available to serve as standard test material for future treatability studies.

A number of chemical and physical analyses of the basic SARM soil and the four spiked SARM formulas have been conducted to verify their composition prior to treatability testing. Results of the physical and chemical analyses are compiled in Tables II through IV. Toxicity characteristic leaching procedure (TCLP) data were also generated during the study, but space limitations prevent their being presented here. These data can be found in the individual EPA project reports.

## METHODOLOGY AND RESULTS OF TREATMENT EVALUATIONS

### Physical Separation/Volume Reduction (Soil Washing)

As part of the performance evaluation of this technology, samples of each SARM were physically treated in a series of bench-scale washing experiments designed to simulate the EPA-developed pilot-scale Mobile Soils Washing System (MSWS). This system physically separates contaminated fines from coarse soil material, which effectively reduces the volume of the contaminated portion of the soils. The MSWS is expected to be an economic alternative to the current practice of hauling contaminated soils offsite to a landfill and replacing the excavated volume with fresh soils. The use of a soil washing system also performs the task of feedstock preparation for other subsequent treatment technologies by prescreening the soil into a "smooth" homogenous feed.

Specifically, this project was designed to simulate the drum-screen washer segment of the MSWS. This segment separates the  $\geq 2$ -mm soil fraction (coarse material) from the  $\leq 2$ -mm soil fraction (fines) by use of a rotary drum screen. A high-pressure water knife operates at the head of the system

TABLE I. TARGET CONTAMINANT CONCENTRATIONS FOR SARMS.  
(mg/kg)

Analyte	SARM I	SARM II	SARM III	SARM IV
	(High organic, low metal)	(Low organic, low metal)	(Low organic, high metal)	(High organic, high metal)
<u>Volatiles</u>				
Acetone	6,800	680	680	6,800
Chlorobenzene	400	40	40	400
1,2-Dichloroethane	600	60	60	600
Ethylbenzene	3,200	320	320	3,200
Styrene	1,000	100	100	1,000
Tetrachloroethylene	600	60	60	600
Xylene	8,200	820	820	8,200
<u>Semivolatiles</u>				
Anthracene	6,500	650	650	6,500
Bis(2-ethylhexyl) phthalate	2,500	250	250	2,500
Pentachlorophenol	1,000	100	100	1,000
<u>Inorganics</u>				
Arsenic	10	10	500	500
Cadmium	20	20	1,000	1,000
Chromium	30	30	1,500	1,500
Copper	190	190	9,500	9,500
Lead	280	280	14,000	14,000
Nickel	20	20	1,000	1,000
Zinc	450	450	22,500	22,500

TABLE II. Results of Clean Soil Matrix Analyses.<sup>a</sup>

Sample Batch	Sample and Batch Numbers										Average
	1 1	2 2	3 2	4 1	5 1	6 2	7 2	8 1	9 1	10 2	
Cation exchange capacity, meq 100/g	117.5	152.5	150	150	77.5	150	155	80	147.5	147.5	133
TOC, %	3.2	3.9	3.0	3.8	2.8	2.7	- <sup>b</sup>	-	-	-	3.2
pH, S.U.	8.0	9.0	8.5	8.5	9.0	8.0					8.5
Grain size distribution, %											
Gravel	3	2	4	3	2	3	-	-	-	-	3
Sand	55	57	58	54	56	57	-	-	-	-	56
Silt	29	30	27	30	28	27	-	-	-	-	28
Clay	13	11	11	13	14	13	-	-	-	-	12

<sup>a</sup> The clean SARM was also analyzed for all contaminants on the Hazardous Substances List to determine background contamination, if any. Organic analyses showed no volatile or semivolatile compounds at the micrograms/kilogram level; metals analyses showed appreciable quantities of iron, potassium, aluminum, calcium, and magnesium (as would be expected), but no substantial amounts of the more toxic metals (e.g., chrome, nickel, lead, zinc). In other words, the clean SARM was found to be free of anthropogenic contamination.

<sup>b</sup> A dash indicates that the sample was not analyzed for this parameter.



TABLE III. MOISTURE CONTENT OF SPIKED SARMS<sup>a</sup>  
(percentage)

Laboratory	SARM-I	SARM-II	SARM-III	SARM-IV	Method
IT Corp. (thermal desorption for PEI)	16.9	6.0 <sup>b</sup>	--	--	Oven-dried
Hittman-Ebasco (stabilization for Acurex)	31.4	8.6 <sup>b</sup>	19.3	22.1	Oven-dried
Radian Corp. (incineration for PEI)	17.1	16.0 <sup>c</sup>	--	--	Oven-dried
	16.1	17.8 <sup>c</sup>	--	--	Oven-dried
	16.1	17.6 <sup>c</sup>	--	--	Oven-dried
EPA - Edison (soil washing for PEI)	22.9	7.2 <sup>b</sup>	20.6	30.1	Oven-dried
	19.6	6.2 <sup>b</sup>	18.6	--	Dean Stark distillation
Analytical Enter- prises (KPEG for Wright State)	--	--	--	--	
Average (all values)	20.0	11.3 <sup>b</sup> 7.0 <sup>b</sup> 17.1 <sup>c</sup>	19.5	26.1	

<sup>a</sup> Values obtained by the oven-drying method (ASTM D2216) are expressed as percent total moisture (i.e., water plus volatile organics); values obtained by Dean Stark distillation Method (ASTM D95) represent percent water only.

<sup>b</sup> These values are for aliquots taken only from Batch 1 of SARM-II, to which only a small amount of water was added. See footnote C.

<sup>c</sup> These values are for subsequent batches of SARM-II, which were prepared with a higher water content, similar to that added to other SARMS.

TABLE IV. ANALYTICAL PROFILE OF SPIKED SARM'S:  
AVERAGE CONCENTRATIONS FOUND UPON TOTAL WASTE ANALYSIS<sup>a</sup>  
(mg/kg)

Analyte	SARM I (High organic, low metal)	SARM II (Low organic, low metal)	SARM III (Low organic, high metal)	SARM IV (High organic, high metal)
<u>Volatiles</u>				
Acetone	4,353 (9)	356 (8)	358 (2)	8,030 (2)
Chlorobenzene	316 (9)	13 (6)	11 (2)	330 (2)
1,2-Dichloroethane	354 (9)	7 (8)	5 (2)	490 (2)
Ethylbenzene	3,329 (9)	123 (8)	144 (2)	2,708 (2)
Styrene	707 (9)	42 (8)	32 (2)	630 (2)
Tetrachloroethylene	408 (9)	19 (8)	20 (2)	902 (2)
Xylene	5,555 (9)	210 (8)	325 (2)	5,576 (2)
<u>Semivolatiles</u>				
Anthracene	5,361 (9)	353 (7)	181 (3)	1,920 (3)
Bis(2-ethylhexyl) phthalate	1,958 (9)	117 (7)	114 (3)	646 (3)
Pentachlorophenol	254 (9)	22 (7)	30 (3)	80 (3)
<u>Inorganics</u>				
Arsenic	18 (10)	17 (7)	652 (4)	500 (4)
Cadmium	22 (8)	29 (6)	2,260 (2)	3,631 (2)
Chromium	24 (8)	28 (6)	1,207 (4)	1,314 (4)
Copper	231 (10)	257 (8)	9,082 (4)	10,503 (4)
Lead	236 (10)	303 (8)	14,318 (4)	14,748 (4)
Nickel	32 (10)	38 (8)	1,489 (4)	1,479 (4)
Zinc	484 (8)	642 (6)	31,871 (4)	27,060 (4)
Moisture, %	20 (7)	11 (7)	19 (3)	26 (2)

<sup>a</sup> Values in parentheses indicate number of samples analyzed.

to break up soil lumps and strip the contaminants off the soil particles. Both the design of the pilot-scale MSWS and the design of the bench-scale experiments to simulate the MSWS for cleanup of the SARMS samples are based on a set of assumptions that underlie the volume-reduction approach of treating contaminated soil, i.e.:

- 1) A significant fraction of the contaminants are either physically or chemically bound to the silt, humus, and clay particles.
- 2) The silt and clay are attached to the sand and gravel by physical processes (primarily compaction/adhesion).
- 3) Physical washing of the sand/gravel/rock fraction will effectively remove the fine sand, silt, and clay-sized (less than 0.2 mm) materials from the coarse material.
- 4) The contaminants will be removed to the same extent that the silt and clay are separated from the sand/gravel/rock fraction (i.e., increasing the efficiency of the washing process will directly increase the removal efficiency for the majority of the contaminant mix).

These assumptions were tested by evaluating different wash solutions in a series of bench-scale shaker-table experiments. Two wash solutions were chosen for evaluation: 1) a chelant solution (tetrasodium salt of EDTA, Dow Chemical Versene 100<sup>R</sup>), and 2) an anionic surfactant solution (phosphated formulation from Procter & Gamble, Institutional Formula Tide<sup>R</sup>). Organic solvents and oxidizing agents were considered, but were found unacceptable because of material-handling problems associated with these compounds, especially when used in a field situation. Following shaker-table washing, each SARM soil was wet-sieved to separate the fines from the coarse material. Although the EPA MSWS only separates the soil into >2-mm and <2-mm size fractions, three size fractions (>2-mm, 250- $\mu$ m to 2-mm, and <250- $\mu$ m) were investigated in this study to determine if the middle fraction (medium to fine sand) could be cleaned effectively and thereby increase the potential volume reduction. For determination of the effectiveness of the soil-washing techniques in reducing the volume of contaminated material, each individual treated size fraction was analyzed for residual total organics and metals by standard gas chromatography/mass spectrometry (GC/MS) and inductively coupled plasma (ICP) techniques (SW-846, 3rd ed.), and for leachable constituents by toxicity characteristic leaching procedures (TCLP, Federal Register Vol. 51, No. 114, June 13, 1986).

The soil-washing experiments were conducted in two phases. During the initial phase, pH and temperature variations were evaluated as well as different wash concentrations of chelant and surfactant. Experiments were also run to determine the optimum reaction time for both the chelant and surfactant solutions. Temperature ranges from 78° to 120°F had little effect on the contaminant reduction efficiencies. The pH of the surfactant solution was adjusted from 5.0 to 12.0 with no appreciable change in the organic contaminant removal efficiencies. A reduction of the pH of the chelant solution to 8.0 produced no additional metal removal (ambient pH of the chelant solution was 12.0).

The optimum chelant concentration was determined to be a 3:1 molar ratio of tetrasodium EDTA to total contaminant metals present in the SARM. A surfactant solution of 0.5 percent (by weight) proved to be most effective in removing the organic contaminants. Reaction times of 15 minutes for the chelant solution and 30 minutes for the surfactant solution were determined to be optimum for allowing sufficient contact between the solution and soil matrix.

During the second phase of these experiments, the optimum conditions for reducing organic and metal contamination (as determined in the initial phase of the soil experiments and discussed in the preceding paragraphs) were applied to all four SARM's and compared with a baseline tap-water wash for each SARM. Tables V through VII show an approximation of the effectiveness of various treatment solutions (wash solutions) by presenting the overall removal efficiencies observed for each size fraction and contaminant group. These efficiencies, which are expressed as percentage reductions, were developed by dividing the residual contaminant concentration in each size fraction by the initial concentration in the whole soil. Although this comparison is admittedly imprecise, it is nevertheless useful for demonstrating trends and relationships between soil fractions, contaminant types, and waste solutions. The discussion that follows examines the data according to the results achieved for each soil size fraction.

The data underlying Tables V through VII clearly showed the tendency for contaminants to accumulate or concentrate in the smaller size fractions (i.e., to bind to the clay and silt). For nearly all of the contaminants, the concentration increased as the size fraction decreased. This finding is consistent with the findings of earlier soil-washing tests.<sup>1,2,3</sup>

For the >2-mm soil fraction (see Table V), the water wash, the 3:1 molar chelant wash, and 0.5 percent surfactant wash were all about equally effective. In all cases, overall contaminant removal efficiencies by group exceeded 90 percent, and volatile removals as a whole exceeded 99 percent across the board. Semivolatile removals ranged from 90 to 99+ percent, and metals from 92 to 98 percent. Individual contaminant removal efficiencies within groups varied somewhat. These variations are probably due to physical properties associated with each contaminant (such as water solubility, volatility, polarity, etc.), as well as physical properties of the soil (e.g., cation exchange capacity, surface area) and the wash solution itself (pH, temperature, chelant, surfactant concentration, contact time, etc.). These excellent results are believed to be closely related to the "freshness" of the soil. It has been hypothesized that the physical processes of compaction and adhesion were not highly operative in the SARM soils, which allowed the loosely attached silt and clay particles to be easily separated from the larger sand and gravel fractions. These physical attractions tend to be more operative in older soils, and are especially noticeable in soils that have experienced long periods of weathering and contact time between contaminants and soil particles. Because the SARM was a freshly prepared synthetic mixture, the forces of compaction and adhesion at the time of treatment were probably weak, a condition more typical of a recent spill-site soil than an older soil found at an abandoned CERCLA site. Consequently, in these studies, the water

Table V. Soil Washing Effectiveness (greater than 2-mm size<sup>a</sup> fraction), overall percentage reduction by contaminant group.

	SARM I (high organics, low metals)		SARM II (low organics, low metals)			SARM III (low organics, high metals)		SARM IV (high organics, high metals)		
	Water	Surfactant	Water	Surfactant	Chelant	Water	Chelant	Water	Surfactant	Chelant
Volatiles	>99.9	>99.8	99.9	99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9
Semivolatiles	98.9	>99.8	93.9	93.5	90.1	>94.8	96.4	97.8	>98.3	97.8
Inorganics	92.2	91.5	>96.7	95.7	95.9	98.0	98.4	97.1	98.4	98.1

<sup>a</sup> Total waste analysis.

Table VI. Soil Washing Effectiveness (250- $\mu$ m to 2-mm size<sup>a</sup> fraction), overall percentage reduction by contaminant group.

	SARM I		SARM II			SARM III		SARM IV		
	Water	Surfactant	Water	Surfactant	Chelant	Water	Chelant	Water	Surfactant	Chelant
Volatiles	99.8	99.8	>99.9	>99.8	>99.9	>99.3	99.0	>99.7	>99.7	>99.7
Semivolatiles	56.2	65.6	52.7	47.3	67.5	0	0	0	29.4	32.3
Metals	81.6	80.7	>82.7	91.6	85.1	96.4	98.4	90.7	91.8	90.3

<sup>a</sup> Total waste analysis.

Table VII. Soil Washing Effectiveness (less than 250- $\mu$ m size<sup>a</sup> fraction), overall percentage reduction by contaminant group.

	SARM I		SARM II			SARM III		SARM IV		
	Water	Surfactant	Water	Surfactant	Chelant	Water	Chelant	Water	Surfactant	Chelant
Volatiles	66.2	88.0	>99.8	>99.4	99.6	86.7	>93.2	>69.6	95.0	81.8
Semivolatiles	59.7	43.2	0	0	0	0	0	0	0	0
Metals	0	0	0	0	21.9	0	78.2	0	7.3	82.2

<sup>a</sup> Total waste analysis.

wash proved to be as effective in cleaning the  $\geq 2$ -mm soil fraction as the water-plus-additive solutions.

Contaminant removals from the 250- $\mu$ m to 2-mm size fraction are summarized in Table VI. Overall, the data show that the volatiles also were efficiently removed from this soil category at levels exceeding 99 percent by all wash solutions. These results are similar to those seen in the  $> 2$ -mm fraction. Semivolatile removal efficiencies dropped off compared with results for the  $\geq 2$ -mm size fraction (see Table V). Also, semivolatile removal efficiencies for SARM's III and IV were markedly lower than for SARM's I and II. Metal removal efficiencies were also somewhat lower across the board for this size fraction compared with the  $\geq 2$ -mm fraction. The trend toward reduced removal efficiencies for the semivolatiles and metals is not surprising, as this size fraction has more surface area than the  $\geq 2$ -mm fraction, and also some small amount of silt and clay particles; therefore, it has a higher potential to adsorb and retain more contamination than the larger  $\geq 2$ -mm fraction.

For the fine soil fraction ( $< 250 \mu$ m) washing with any of the solutions effectively removed the volatiles; conversely, none of the solutions were found to be consistently effective in removing the semivolatiles from this size fraction of the SARM's. Removal of metallic contaminants definitely appeared to be enhanced somewhat by the use of the chelant. As shown in Table VII, the chelant wash was much more effective than with the water wash or the surfactant wash in reducing metal contamination in the fine soil fraction.

In summary, the results support the basic assumptions underlying the volume-reduction approach to soil decontamination; that is, a significant fraction of the contaminants are attached to the fines (silt, humus, and clay), and the coarse material (sand and gravel) can be cleaned by physical separation from the fines. The data indicate that 1) water alone can efficiently remove a significant portion of both the organic and inorganic contamination from the  $\geq 2$ -mm soil fraction, and 2) the addition of a chelant can enhance metals removals from the middle (2 mm to 250  $\mu$ m) and fine ( $< 250 \mu$ m) soil fractions.

#### Chemical Dechlorination/KPEG

Chemical dechlorination was examined as a treatment technology because it had already been successfully demonstrated at laboratory scale with PCB- and dioxin-contaminated soils and sludges, and was viewed as a promising treatment technology for development to pilot scale and possibly full scale. The KPEG dechlorination process involves the application of a potassium hydroxide-polyethylene glycol reagent to contaminated soil at elevated temperatures for a period of 2 to 4 hours, after which the reagent is decanted and recovered and the soil is rinsed and neutralized. The reagent strips one or more chlorine atoms from the PCB or dioxin molecule, forming an inorganic chloride salt and a derivative of the PCB or dioxin, which, in theory, should be less toxic than the original contaminant.

Each of the four SARM's was evaluated in this study. Although the SARM's did not contain any PCB's or dioxins, other chlorinated species were present, and there was interest in learning whether these compounds could be dechlorinated. There was also interest in learning whether the process would exhibit any removal effectiveness on the other organic and inorganic contaminants in the test soils.

Testing was conducted in either 500-ml or 2-liter glass reaction vessels mounted within temperature-controlled heating mantles. In each test, either 125 or 500 g of SARM were treated with KPEG reagent at 100°C for 2 hours. During the reaction period, the contents of the glass reaction vessel were continually stirred at 100 rpm with a Teflon-coated stainless steel stirring rod. The system was also continually purged with nitrogen, and the off-gases were filtered through a Tenax/XAD-2/carbon trap system. The contents of the traps were subsequently analyzed to establish material balances and to determine which compounds had been destroyed versus those which had simply been volatilized. At the end of the 2-hour reaction period, the reagent was separated from the soil by centrifugation and decantation. The soil was then neutralized by an acid rinse followed by a plain water rinse. All rinse solutions, soil residues, and the spent reagent were analyzed for the target SARM contaminants.

Overall results of the KPEG tests are given in Table VIII. The analyses show that the KPEG process was very effective in removing the volatiles from all four SARM's. Removal rates for all volatiles exceeded 90 percent in all tests, and most often ranged from 98 to 99+ percent. Although material balances were generally poor, the data strongly indicated that most of the volatiles were unaffected chemically by the treatment and were removed strictly

Table VIII. KPEG effectiveness on SARM's - overall percentage reduction by contaminant group.<sup>a</sup>

	SARM I		SARM II		SARM III		SARM IV	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
Volatiles (all)	99.9	98.3	98.2	96.3	99.5	97.5	99.9	98.1
Semivolatiles								
Anthracene	91.3	96.3	75.6	-10	-490	-1246	96.0	97.0
Pentachlorophenol	98.1	97.7	91.9	94.5	99.6	99.0	95.8	95.4
Inorganics (all)	44.5	-	39.4	-	49.4	-	29.3	-

<sup>a</sup> As measured by total waste analysis. A negative percent reduction results when chemical analysis of a treated residue yields a higher contaminant concentration than the untreated material.

by volatilization processes. Notable exceptions to this were 1,2-dichloroethane and tetrachloroethylene, which appeared to have been completely destroyed by the process.

Semivolatile results are available for only anthracene and pentachlorophenol. In the case of pentachlorophenol, the data indicate it was removed from the soil at efficiency levels ranging from 92 to 99 percent; however, the mass balance data indicate that it was not dechlorinated by the KPEG reagent. Anthracene also was not destroyed. Removal efficiency data for the compound are somewhat equivocal; in the tests utilizing SARM's I and IV, which had starting concentrations of anthracene of 4000+ ppm, it was found to be efficiently removed (i.e., removal rates ranged from 91 to 97 percent). In tests involving SARM's II and III, which had much lower anthracene levels (i.e., less than 250 ppm), no removal was observed. This may be due to analytical limitations associated with recovering anthracene at these levels in soils.

The KPEG process had only a limited effect on removing the inorganic contaminants from the SARM's. Overall removal rates ranged from 29 to 49 percent.

#### Low-Temperature Thermal Desorption

The purpose of this research was to investigate the capability of a laboratory-scale low-temperature thermal desorption technology for removing volatile and semivolatile contaminants from the SARM's. The laboratory testing program consisted of 15 separate bench-scale tests (10 in a tray furnace and 5 in a tube furnace). Only SARM's I and II were tested at 150°, 350°, and 550°F for 30 minutes to determine the effect of each temperature on removal of the contaminants. The tray furnace was used as a baseline technology to determine the overall effectiveness of thermal desorption in removing contaminants from the soil. The tube furnace was used to provide additional data on the concentration of contaminants in the off-gas in an attempt to establish a material balance.

The first series of 10 tests involved the use of the tray furnace in which SARM's I and II were each tested once at 150° and 350°F (four tests) and three times each at 550°F (six tests). The second series of five tests involved the use of the tube furnace to evaluate the nature of the off-gas (desorbed volatiles) generated during thermal treatment. One tube furnace test was run at 150° and 350°F and three tube furnace tests were run at 550°F using only SARM I. For the tray furnace, the bed of soil that was heated represented the entire sample that was analyzed. For the tube furnace, all of the off-gas was collected as one sample, and the remaining soil residue was collected as a second sample.

Table IX shows the overall results for the tray tests for SARM's I and II. The studies showed that volatiles were efficiently removed from the soil by at least 95 percent at all temperatures. Semivolatiles were removed less efficiently than the volatiles at 150° and 350°F, but removals tended to increase with temperature and approached the 90 percent efficiency range when



550°F was applied. The apparent increase in metal concentrations in the residues (as indicated in the negative reduction values) may be an artifact in the data, due to moisture losses during heating; because the SARM's contained 6 to 17 percent moisture before treatment (see Table III), the losses tended to produce a higher metal-to-soil ratio (i.e., concentration) in the treated residual, which results in an apparent (but unreal) increase in metal content. A second factor that may have contributed to the change in concentration of the metals may have been a change in the matrix's ability to retain metals after heating.

Table IX. Low temperature desorption - overall percent reduction of contaminants by group at various test temperatures using tray furnace and 30-minute residence time.<sup>a</sup>

	SARM I			SARM II		
	150°F	350°F	550°F	150°F	350°F	550°F
Volatiles	97.8	99.8	99.8	98.3	95.9	96.0
Semivolatiles	-5.3	41.6	93.6	11.7	74.8	86.3
Metals	-9.3	-12.1	-15.1	5.1	10.2	-7.3

<sup>a</sup> As measured by total waste analysis. A negative percent reduction results when chemical analysis of a treated residue yields a higher contaminant concentration than the untreated material.

In terms of total actual residual concentrations, the following statements can be made (refer to Table IV for initial concentrations prior to treatment):

SARM I:

- ° At 350° and 550°F, all volatiles except acetone were reduced to less than 1 mg/kg in the treated residue; acetone residuals on the order of 100 ppm remained, even at the highest temperature.
- ° For the semivolatiles anthracene and BEHP, residuals remained well above 1000 mg/kg at the 150° and 350°F temperatures, but were reduced to less than 20 mg/kg at 550°F. Pentachlorophenol residuals remained high at the 150° and 350°F temperatures and were only reduced to levels on the order of 100 ppm at the 550°F temperature.

SARM II:

- ° As with SARM I, at 350° and 550°F, all volatiles except acetone were reduced to less than 1 mg/kg; acetone residuals on the order of 100 mg/kg remained, even at the 550°F temperature.
- ° All semivolatiles were reduced to less than 100 mg/kg at 350°F and to less than 10 mg/kg at 550°F.

Overall, the 150°F temperature was considered ineffective under the reaction conditions tested.

#### High-Temperature Incineration

In this segment of the test program, a series of pilot-scale test burns was conducted with SARM's I and II only. The testing was conducted at the John Zink testing facility in Tulsa, Oklahoma, in a rotary kiln incineration system using a nominal feed rate of 1000 lb/h. More than 12,000 pounds of each SARM soil was prepared for the tests so that three 4-hour test burn runs (for a total of six test burn runs) could be conducted on each SARM. Approximately 1 week prior to startup of the test burns, the soils were delivered to John Zink in forty-eight 55-gallon steel drums, each containing 500 to 600 lb of SARM I or SARM II.

Two runs per day were conducted over the 3-day period of September 16 through 18, 1987. Runs 1, 2, and 3 were conducted with SARM I (high organics, low metals), and Runs 4, 5, and 6 were conducted with SARM II (low organics, low metals). Equipment operations were normal throughout each run.

The process operating data collected during each test show that the temperatures and feed rates achieved were reasonably close to the goals (i.e., 1800°F in the kiln, 2000°F in the secondary combustion chambers, and a nominal feed rate goal of 1000 lb/h). Excess air was maintained at about 3 percent in the kiln and about 5 percent in the secondary chamber during both tests. Emissions of O<sub>2</sub>, CO<sub>2</sub>, and CO were steady throughout; and CO remained at less than 10 ppm at all times except for a few brief excursions of 45 to 90 ppm, which lasted from 1 to 5 minutes. A total of 13,932 lb of SARM I and 13,460 lb of SARM II were incinerated over a course of 3 days that involved 29 hours 22 minutes of testing.

Table X presents the results of chemical analyses (total waste analyses) of the bottom ash (i.e., SARM residue) samples collected during each test run. Samples analyzed for semivolatiles and metals were collected as composites over the course of each test; samples analyzed for volatiles were collected as discrete samples at the beginning, middle, and end of each run and composited at the time of analysis.

The volatile compounds styrene, tetrachloroethylene, and chlorobenzene, and the semivolatile compounds anthracene and pentachlorophenol were not detected in any of the ash samples. Measureable quantities of ethylbenzene and xylene were found in the ash of both SARM's, and 1,2-dichloroethane was found in the ash of SARM II, but the amounts were small (in the low parts-per-billion range) and typically at levels within 2 to 3 times the method detection limit. Acetone was found in the ash samples of all runs for both SARM's at significant levels ranging from 190 to 790 µg/kg; these levels are 24 to 99 times higher than the method detection level (8 µg/kg).

On the average, the concentrations of acetone and phthalate found in the ash of SARM I are similar to those found in the ash of SARM II, even though

Table X. Total Waste Analysis for SARM ash.

Parameter	Method detection limit	SARM I			SARM II		
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
<u>VOLATILES, <math>\mu\text{g/kg}</math></u>							
Ethylbenzene	7.0	ND <sup>a</sup>	19	ND	8	ND	13
Xylene	5.0	ND	34	ND	11	6	20
Tetrachloroethylene	4.0	ND	ND	ND	ND	ND	ND
Chlorobenzene	6.0	ND	ND	ND	ND	ND	ND
Acetone	8.0	440	420	630	190	210	790
1,2-Dichloroethane	3.0	ND	ND	ND	ND	5	10
Styrene	3.0	ND	ND	ND	ND	ND	ND
<u>SEMIVOLATILES, <math>\mu\text{g/kg}</math></u>							
Anthracene	37	ND	ND	ND	ND	ND	ND
Bis(2-ethylhexyl) phthalate	63	1600	540	740	950	710	1300
Pentachlorophenol	370	ND	ND	ND	ND	ND	ND
<u>METALS, <math>\text{mg/kg}</math></u>							
Lead	4.2	56	98	107	146	75	88
Zinc	0.12	217	227	250	252	199	237
Cadmium	0.12	<0.2	<0.2	<0.2	0.2	<0.2	<0.2
Arsenic	0.04	38	36	44	46	39	37
Copper	0.42	111	132	159	125	106	162
Nickel	0.30	12	15	11	12	9.1	12
Chromium	0.30	10	14	12	12	7	10
<u>VOLATILE PICs, <math>\mu\text{g/kg}</math></u>							
2-Butanone	25	35	ND	ND	14 <sup>b</sup>	ND	ND
Methylene chloride	2.8	2.9	5.4	4.2	ND	ND	ND
2-Chloroethylvinyl ether	5.0	70	ND	ND	ND	ND	ND

<sup>a</sup> ND = Not detected.<sup>b</sup> Estimated value; less than method detection limit.

the input waste feed levels for these compounds were roughly 10 times higher in SARM I than in SARM II. This suggests sample contamination or carryover, and the data for these compounds should be interpreted with caution. Significant quantities of phthalate were also found in several of the method blanks, and phthalates are known to be commonly encountered contaminants in sample analysis.

The metals data for the ash samples were also interesting. Prior to the testing, most of the metals concentrations in the ash were expected to be elevated compared with those in the waste feed because of the combined effects of the retention of metals in the ash and the losses of water and organics from the feed during the incineration process. Cadmium levels in the ash, however, were expected to be low as a result of volatilization of the metal in the kiln at the high operating temperature of 1800°F. As expected, cadmium levels in the ash were quite low, at least 99.9 percent lower than the waste feed levels. Surprisingly, all of the other heavy metal levels were also lower in the ash (e.g., on the order of 50 to 80 percent lower) than in the waste feed, which indicates significant volatilization or perhaps slagging or condensation onto the kiln refractory. On the other hand, arsenic levels in the ash were more than double those in the feed across the board.

The test burns successfully met all the RCRA emission requirements for hazardous waste incineration. Stack samples collected during the SARM I and II test burns revealed the following:

- ° Particulate concentrations corrected to 7 percent O<sub>2</sub> were below the RCRA allowable limit of 0.08 gr/dscf for each SARM type.
- ° Measured HCl emission rates in pounds per hour were considerably less than the RCRA allowable rate of 4.0 lb/h for each SARM type.
- ° The average stack gas concentration of CO was less than 23 ppm during each test.
- ° The destruction and removal efficiency (DRE) performance standard of 99.99 percent was achieved for all of the volatile compounds for each SARM. The DRE data for the semivolatiles show that anthracene was effectively destroyed, as the amount in each emission was less than the method detection limit, and the resulting DRE's were greater than 99.99 percent. The DRE data for bis(2-ethylhexyl)phthalate showed that only three of six sample runs met the 99.99 percent criteria. Sample contamination (background level) problems may have been responsible for the poor DRE's in the other three runs.

#### SOLIDIFICATION/STABILIZATION

This project evaluated the performance of solidification as a means of treating the SARM soils. Tests were conducted on all four SARM's using three commonly used solidification agents or binders: portland cement (Type 1), lime kiln dust, and a 50:50 mixture by weight of lime and fly ash. At 7, 14,

21, and 28 days after the SARM's and binders were mixed, samples of the solidified material were subjected to unconfined compressibility strength (UCS) testing. Samples that achieved a UCS minimally greater than 50 psi or that showed the highest UCS below 50 psi after 14 and 28 days were subjected to total waste and TCLP analyses.

Results of the testing showed that the UCS tended to increase with time as the samples cured. Portland cement produced the strongest, hardest, and most consistent product, followed by kiln dust and lime/fly ash. The lime/fly ash samples required several weeks of curing before they finally set. The amount of moisture in the SARM's seemed to be an important factor in solidifying the soils. Offgassing of volatile compounds from the stabilized samples occurred during mixing and continued throughout the curing period.

Table XI presents an overall summary of the 28-day samples when analyzed for TCLP and TWA. The percentage reduction values in this table represent the total amount of contaminants found in the untreated soil samples (or TCLP extract) less the total amount of contaminant found in the stabilized sample (or TCLP extract) divided by the amount in the untreated soil (or TCLP extract) x 100 percent. The data have been adjusted to account for changes in soil volume and contaminant concentration caused by the addition of the binders.

The results fail to indicate either dramatic or consistent treatment efficiencies. Volatiles in the SARM's were reduced, but the reductions are attributed to volatilization losses (offgassing) during mixing and curing rather than binding within the stabilized matrix. Metals were less prevalent in the treated sample TWA and TCLP extracts, which indicates reduced mobility after stabilization/solidification. The percent reductions seldom exceeded 90 percent, however, and generally tended to range from 0 to 20 percent to 60 to 75 percent. Overall, kiln dust and lime/fly ash produced the best contaminant-reduction results.

#### SUMMARY AND CONCLUSIONS

The research program produced a valuable and interesting new data base outlining the kinds of results that can be achieved by treating a synthetic contaminated soil at bench and pilot scale. This paper only highlights key portions of the data base; it is by no means complete. Detailed reports covering the complete findings of each study are available through EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati (see Acknowledgments).

Preparation of the SARM's is viewed as a particularly valuable segment of the research because this had never before been attempted on such a large (volumetric) scale. Methods of mixing both the basic clean soil and the contaminated material were developed and found to produce a quality product with good homogeneity. This allowed each of the treatment technologies to operate with a high degree of assurance that the starting materials were essentially identical from one test to another.

Table XI. Summary of Effectiveness of Stabilization/Solidification Agents  
After 28-Day Cure  
(% Reduction)<sup>a</sup>

	SARM I			SARM II			SARM III			SARM IV		
	PC <sup>b</sup>	KD <sup>c</sup>	L/FA <sup>d</sup>	PC	KD	L/FA	PC	KD	L/FA	PC	KD	L/FA
TCLP												
Volatiles	73.9	97.6	75.8	42.2	82.0	88.0	68.3	>93.6	90.3	-45	77.5	73.7
Semivolatiles	67.2	>98.8	>96.5	>53.8	>68.5	>72.8	-47.0	82.2	54.8	-139	57.2	88.6
Inorganics	>82.1	>75.0	>92.3	>83.0	>71.2	>92.1	99.4	83.7	54.3	85.3	66.4	68.3
TWA												
Volatiles	-	98.5	83.7	86.9	99.7	97.0	76.9	98.1	92.0	58.5	95.3	83.4
Semivolatiles	-	87.7	80.2	33.1	38.0	27.5	-101	-37.5	-32.2	24.2	28.3	47.9
Inorganics	-	43.8	56.6	-13.6	9.7	28.1	28.5	73.2	82.3	32.3	60.5	73.9

<sup>a</sup> A negative percent reduction results when analysis of the treated residual (or extract of a treated residual) yields a higher contaminant concentration than the untreated material.

<sup>b</sup> PC = Portland cement.

<sup>c</sup> KD = Kiln dust.

<sup>d</sup> LFA = Lime/fly ash.

A rank-order summary of the effectiveness of each treatment technology on the four SARM's, is presented in Table XII. The thermal technologies effectively reduced the organic fractions (>99.6%) when measured by TWA. The chemical treatment (KPEG) operated on the semivolatile fraction with greater than 90 percent reduction effectiveness. Greater than 98 percent of the volatile organic compounds were removed, but this was likely due to volatilization during the test runs. Soil washing was the best metals reduction technique across all the SARM's, averaging 93 percent. Soils washing was also very effective in reducing the semivolatile compounds (averaging about 87%) and the volatiles (99%). Stabilization generally ranked behind the other technologies, as expected, since it does not remove metals, but immobilizes them. For stabilization, TCLP is a better measure of treatment effectiveness than TWA.

Phase II of the CERCLA Research Program was initiated in 1988 and is continuing. Soils from actual Superfund sites have been collected and are being tested for treatment effectiveness using the same bench-scale procedures as in Phase I. Results, which are expected to be available in late 1988, will be compared with those produced on the SARM's.

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<u>Project</u>	<u>Contractor</u>	<u>EPA contract</u>	<u>EPA Project Officer</u>
SARM preparation	PEI Associates, Inc. Cincinnati, Ohio	68-03-3413 Work Assign- ment 0-7	Richard P. Traver
Physical soil washing	PEI Associates, Inc. Cincinnati, Ohio	68-03-3413 Work Assign- ment 0-7	Richard P. Traver
Dechlorination/ KPEG	Wright State Univer- sity Dayton, Ohio (subcon- tractor to PEI Asso- ciates)	68-03-3413 Work Assign- ment 0-6	Charles J. Rogers
Thermal desorp- tion	IT Corporation Knoxville, Tennessee (subcontractor to PEI Associates)	68-03-3389 Work Assign- ment 0-5)	Robert C. Thurnau

Table XII. Overall BDAT Phase I treatment efficiency summary.<sup>a</sup>

SARM I (high organics, low metals)	Percent reduc- tion	SARM II (low organics, low metals)	Percent reduc- tion	SARM III (low organics, high metals)	Percent reduc- tion	SARM IV (high organics, low metals)	Percent reduc- tion
<u>VOLATILES</u>							
Incineration	>99.99	Incineration	>99.98	Soils washing + 2 mm water	>99.9	Chemical treatment KPEG No. 1	99.98
Soils washing + 2 mm water	>99.99	Soils washing - all frac- tions - water	>99.9	Soils washing + 2 mm chelate	99.9	Soils washing + 2 mm water	>99.9
Chemical treatment KPEG No. 1	99.96	Soils washing - all frac- tions - chelate	>99.7	Chemical treatment KPEG No. 1	99.5	Soils washing + 2 mm chelate	>99.9
Soils washing + 2 mm surfac- tant	99.82	Soils washing - all frac- tions - surfactant	99.7	Soils washing 2mm to 250 $\mu$ m water	99.3	Soils washing + 2 mm surfactant	>99.9
Soils washing 2 mm to 250 $\mu$ m surfactant	99.82	Solidification - kiln dust 28 days	99.7	Soils washing 2mm to 250 $\mu$ m chelate	99.0	Soils washing 2 mm to 250 $\mu$ m surfactant	>99.7
Soils washing 2 mm to 250 $\mu$ m water	99.8	Low temperature thermal desorb at 150°F	98.70	Solidification - kiln dust - 28 days	98.1	Soils washing 2 mm to 250 $\mu$ m chelate	>99.7
Low temperature thermal desorb at 350°F	99.79	Chemical treatment KPEG test No. 1	98.2	Chemical treatment KPEG No. 2	97.6	Soils washing 2 mm to 250 $\mu$ m water	>99.7
Low temperature thermal desorb at 550°F	99.78	Solidification - lime/fly ash	97.0	Soils washing <250 $\mu$ m chelate	98.2	Chemical treatment KPEG No. 2	98.1
Solidification - kiln dust - 28 days	98.5	Chemical treatment - KPEG No. 2	96.3	Solidification lime/fly ash - 28 days	92.0	Solidification kiln dust - 28 days	95.3
Chemical treatment KPEG No. 2	98.3	Low temperature thermal at 500°F	96.17	Soils washing <250 $\mu$ m water	86.7	Soils washing <250 $\mu$ m chelate	81.8
<u>SEMIVOLATILES</u>							
Incineration	>99.98	Incineration	>99.87	Chemical treatment KPEG No. 1	99.6	Soils washing + 2 mm sur- factant	>98.3
Soils washing + 2 mm sur- factant	>99.8	Soils washing + 2 mm water	93.9	Chemical treatment KPEG No. 2	99.0	Soils washing + 2 mm chelate	97.8
Soils washing + 2 mm water	>98.9	Soils washing + 2 mm sur- factant	93.5	Soils washing + 2 mm chelate	>96.4	Chemical treatment KPEG No. 2	96.2
Chemical treatment KPEG No. 2	97.0	Soils washing + 2 mm chelate	90.1	Soils washing + 2 mm water	>94.8	Chemical Treatment KPEG No. 1	92.9

(continued)



Table XII (continued)

SARM I (high organics, low metals)	Percent reduc- tion	SARM II (low organics, low metals)	Percent reduc- tion	SARM III (low organics, high metals)	Percent reduc- tion	SARM IV (high organics, low metals)	Percent reduc- tion
Chemical treatment KPEG No. 1	95.6	Low temperature thermal desorb at 350°F	88.73			Solidification lime/fly ash - 28 days	47.9
Low temperature thermal desorb at 250°F	94.6	Chemical treatment KPEG Test No. 1	83.8			Soils washing 2 mm to 250 µm chelate	32.3
Soils washing 2 mm to 250 µm surfactant	82.3	Soils washing 2 mm to 250 µm surfactant	67.5			Soils washing 2 mm to 250 µm surfactant	39.4
Solidification lime/fly ash surfactant	80.2	Soils washing 2 mm to 250 µm water	22.7			Solidification kiln dust - 28 days	28.3
Solidification kiln dust	80.2	Soils washing 2 mm to 250 µm chelate	47.3				
Soils washing <250 µm water	59.7	Chemical treatment KPEG No. 2	42.3				
<u>METALS</u>							
Soils washing + 2 mm water	92.2	Soils washing + 2 mm water	>96.7	Soils washing 2 mm to 250 µm chelate	98.4	Soils washing + 2 mm sur- factant	98.4
Soils washing + 2 mm surfac- tant	91.5	Soils washing + 2 mm chelate	95.9	Soils washing 2 mm to 250 µm chelate	98.4	Soils washing + 2 mm chelate	98.1
Soils washing 2 mm to 250 µm water	81.6	Soils washing + 2 mm sur- factant	95.7	Soils washing 2 mm to 250 µm water	98.0	Soils washing + 2 mm water	97.1
Soils washing 2 mm to 250 µm surfactant	75.5	Soils washing 2 mm to 250 µm chelate	91.6	Soils washing 2 mm to 250 µm water	96.4	Soils washing 2 mm to 250 µm surfactant	91.8
Solidification lime/fly ash - 28 days	56.6	Soils washing 2 mm to 250 µm surfactant	85.1	Solidification lime/fly ash	82.3	Soils washing 2 mm to 250 µm water	90.7
Solidification kiln dust - 28 days	40.2	Soils washing 2 mm to 250 µm water	82.7	Soils washing <250 µm chelate	78.2	Solidification lime/fly ash	73.9
Incineration	38.7	Incineration	64.3	Solidification kiln dust - 28 days	73.2	Solidification kiln dust	60.5
		Chemical treatment KPEG No. 1	39.4	Chemical treatment No. 1	49.4		

<sup>a</sup> Based on total waste analyses.

<u>Project</u>	<u>Contractor</u>	<u>EPA contract</u>	<u>EPA Project Officer</u>
Incineration	PEI Associates, Inc. Cincinnati, Ohio	68-03-3389 Work Assign- ment 0-7	Robert C. Thurnau
Stabilization	Acurex Corporation Durham, North Carolina	68-03-3241 Work Assign- ment 2-18	Edwin F. Barth

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