1 of 2

**Decontamination Systems Information
and Research Program**

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**Quarterly Technical Progress Report
for Period January 1 through March 31, 1993**

Work Performed Under
Contract No.: DE-FC21-92MC29467

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P. O. Box 880, Collins Ferry Road
Morgantown, West Virginia

By
National Research Center for Coal And Energy
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April 1993

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ADMINISTRATIVE SUMMARY

West Virginia University (WVU) and the U. S. DOE Morgantown Energy Technical Center (METC) entered into a Cooperative Agreement on August 29, 1992 entitled "Decontamination Systems Information and Research Programs" (DOE Instrument No. : DE-FC21-92MC29467). Stipulated within the Agreement is the requirement that WVU submit to METC a series of Technical Progress Reports on a quarterly basis. This report comprises the second Quarterly Technical Progress Report for Year 1 of the Agreement. This report reflects the progress and/or efforts performed on the six (6) technical projects encompassed by the Year 1 Agreement for the period of January 1 through March 31, 1993.

A. ADMINISTRATIVE ACTION

A Cooperative Agreement was entered into by formal signature on August 29, 1992 by METC and on October 5, 1992 by WVU. Six (6) projects were chosen from the Annual Research Plan for implementation; the remaining proposed projects were tabled for further consideration. The Scope of Work and Budgets for the six projects were reviewed and approved by METC in late October, 1992. NEPA documentation was submitted to METC on December 4, 1992 approval was received by WVU in mid-March, 1993. All projects are in effect with literature reviews being performed, instrumentation being ordered, apparatus being constructed, and experimentation being initiated. Limited experimentation was accomplished this quarter without the NEPA approval. A Management Plan was submitted to METC on February 3, 1992 and is currently under review and revision.

Two projects were submitted to METC for consideration as additional projects for Year 1. One project deals with a soil remediation problem at the Winfield Lock & Dam Works in the southern part of West Virginia. This proposal is currently under technical review by METC with indications implying that it may be added as an additional project in the next quarter.

The second project proposes an assessment of remediation technology dealing with extraction, storage and monitoring of wastes. An industrial partner, BDM, is being proposed. The project would also include the development of a chemical hygiene, environmental, and safety plan for the university to perform experimentation at a METC site. The proposal is currently under review at METC.

B. PROJECT VARIANCES, ACCOMPLISHMENTS AND PROBLEMS

Experimental work has commenced upon receipt of the NEPA approval. However, projects involving laboratory experimentation may have some delay in meeting their time lines due to alignment of work force, equipment and supply procurements.

MASTER
JP

Systematic Assessment of the State of Hazardous Waste Clean-up Technologies

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1.0 EXECUTIVE SUMMARY

It is estimated that over 3700 hazardous waste sites are under the jurisdiction of the Department of Energy (DOE). Over the next 30 years, the Department of Energy (DOE) is committed to bringing all its facilities into compliance with applicable Federal, State, and local environmental laws and regulations. To perform this clean-up effort in the most efficient manner at each site will require that DOE managers have access to all available information on pertinent technologies; i.e., to aid in maximum technology transfer. The purpose of this effort is to systematically develop a database of those currently available and emerging clean-up technologies.

The development of a database of those currently available and emerging clean-up technologies is to be done in several phases: 1) A systems approach, 2) data collection, and 3) software development. Although the project officially started October 1, 1992, our award did not arrive until December, 1992. Thus, our main effort in the first quarter was 1) the recruitment of graduate research assistants, 2) the organization of project responsibilities, and 3) the procurement of software. In the second quarter we have begun to Currently, we are in the process of an initial screening of DOE hazardous waste sites. This task should be completed within the next several weeks.

2.0 BACKGROUND

It is estimated that over 3700 hazardous waste sites are under the jurisdiction of the Department of Energy (DOE). These sites were primarily generated from 45 years worth of environmental pollution from the design and manufacture of nuclear materials and weapons, and contain numerous types of wastes including: 1) volatile, low-volatile and nonvolatile organics, 2) radionuclides (e.g., uranium, plutonium and cesium), 3) nonradioactive heavy metals (e.g., chromium, nickel, and lead), and 4) toxic chemicals. These contaminants affect several media including soils (saturated and unsaturated), groundwater, vegetation, and air. Numerous and diverse DOE hazardous waste sites can be enumerated from soils contaminated by organics such as trichloroethylene (TCE) and perchloroethylene (PCE) at the Savannah River site to biota and vegetation contaminated by radionuclides such as radiocesium and radiostrontium at the Oak Ridge site.

Over the next 30 years, the Department of Energy (DOE) is committed to bringing all its facilities into compliance with applicable Federal, State, and local environmental

laws and regulations. This clean-up task is quite complex involving numerous sites containing various radioactive, organic and inorganic contaminants. To perform this clean-up effort in the most efficient manner at each site will require that DOE managers have access to all available information on pertinent technologies; i.e., to aid in maximum technology transfer. The purpose of this effort is to systematically develop a database of those currently available and emerging clean-up technologies.

The construction of a database of clean-up technologies requires a systematic development of those steps necessary to achieve clean-up objectives. These steps and associated technology groupings are given in Figure 1.

Figure 1: Division of technologies based on primary steps necessary for clean-up

The initial step in assessing a potential hazardous waste site is the characterization and identification of the type and extent of the contamination. In this characterization step technologies are required both for in-situ and ex-situ assessment of contamination levels. Once site characterization is performed, the risks posed by the contamination must be assessed. This step necessitates the use of mathematical models to predict contaminant fate and subsequent impact on local populations.

Assuming that a risk exists, technologies must then be examined (or developed) to either extract the contaminant from the fostering media for treatment and/or disposal, treat the contaminant in-situ, or directly dispose of the contaminant. Furthermore, at each step in the clean-up process decisions regarding technology choices must be made within the existing political, economic, and social climate.

Using the conceptual approach given in Figure 1, a systematic assessment of available and emerging technologies in each area will be developed. This will be accomplished for each area by the development of a database of both current and emerging technologies. An example to illustrate the concept of such a database is given in Figure 2. In this simple example, the user of the database may be interested in investigating the available technologies for cleaning up a soil contaminated by dioxin (TCDD). In this case, information regarding soil extraction and treatment procedures is organized such that the user can extract pertinent clean-up information.

Figure 2: Conceptual view of database construction in which the arrows indicate one path explored for the clean-up of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

It is envisioned in the initial phase of development that a DOE manager via a computer terminal will have access to information in the database via a query system. This system will allow the user to access the different available technologies for each step in the clean-up process, and extract pertinent information on how to proceed and obtain more detailed information. A natural result of such a systematic assessment is the discovery of where clean-up capabilities are lacking. Thus, as the process proceeds, a database will be compiled of those clean-up processes that are in need of further research.

3.0 METHODOLOGY

The development of a database of hazardous waste technologies will be carried out in several phases:

Phase I: A systems approach. This phase involves a systematic development of the components to be included in the database. The approach will drive the development of the computer database. The following sub-tasks are to be performed:

1. An initial screening of DOE hazardous waste sites;
2. The development of a conceptual model to classify DOE hazardous waste problems;
3. An initial formulation of the structure (or fields) of the database.

Phase II: Data collection. In this phase a complete review of the current clean-up technologies will be done. This review will be driven by the database structure developed in phase I (sub-task 3), and will be accomplished through a comprehensive literature review, discussions with clean-up experts, and possible hazardous waste site visitations.

Phase III: Software development. In parallel with the data collection phase of this work, a computer based database is to be developed. This includes a data storage/retrieval system along with user friendly access software. Several main sub-tasks are to be performed including:

1. Development of a user friendly front end (i.e., user interface);
2. Development of the structure of the database;
3. Input of the technologies collected in the data collection phase;
4. Software verification and testing.

4.0 RESULTS AND DISCUSSION

Although the project officially started October 1, 1992, our award did not arrive until December, 1992. Thus, our main effort in the first quarter was 1) the recruitment of graduate research assistants, 2) the organization of project responsibilities, and 3) the procurement of software. As of January, 1992 we have recruited several graduate students who will function both to aid in the collection of data (phase II) and to work on software development. We have also organized project responsibilities toward the collection of data. All faculty will be responsible for the collection of data on characterization, extraction, treatment and disposal technologies in their field of expertise. Such data will be reported to the P.I. for integration into the database. We have also selected and ordered database software for the project. We have selected

the relational database software FOX PRO 2.5 as our development package. This software will be run on an Intel 486 based computer.

In this quarter (January 1 to March 31) we have 1) began an initial screening of DOE hazardous waste sites, 2) developed a conceptual model to classify DOE hazardous waste problems, and 3) developed an initial formulation of the structure (or fields) of the database. An initial screening of DOE hazardous waste sites was initiated using the DOE Environmental Restoration and Waste Management Five Year Plan⁺. This report, however, gives only very general information on contaminated DOE sites. For example, information is given on the clean-up of volatile organics in saturated soils at the DOE's Savannah River site. The levels and extent of vcontamination are not given. We are in the process of searching for site specific data on the extent and level of contaminating at specific sites.

In order to identify remediation technologies applicable to specific DOE sites, we have developed a conceptual model to classify DOE hazardous waste problems. This entails first the development of a general classification of hazardous waste problems. This general classification is simply a division of contamination problems based on 1) the media in which the pollutant resides, and 2) the chemical characteristics of the pollutants. This division is illustrated by the matrix given in Figure 3 in which the bold boxes indicate a class of technologies used to remediate sites with the given pollutant/media characteristics. Thus, for each step in the remediation process (i.e., characterization, extraction, and treatment) there exists sets of potential technologies that can address the specific problems. The choice of this division was based on the behavior of pollutants in the environment. Pollutant behavior is driven by both its physical/chemical characteristics and the media in which it resides (i.e., pollutant fate and transport are driven by media pollutant interactions along with pollutant characteristics). These fate and transport characteristics will drive the potential technologies that will be applicable for remediation. For example, pollutants which reside in soils and are tightly bound, hydrophobic, and not susceptible to bioremediation (e.g., dioxins) can be remediated using similar approaches. In this case, this class of pollutants is typically excavated and treated ex-situ via thermal or chemical technologies for organics or possible immobilization for inorganics.

⁺ USDOE, 1991. Environmental Restoration and Waste Management Five Year Plan. DOE/S-0090P.

MEDIA	POLLUTANT CLASS		
	ORGANICS	INORGANICS	RADIONUCLIDES
SOIL			
GROUND WATER			
AIR			

Figure 3: Classification of technologies into groups used to address combinations of different pollutants with different media.

Within each pollutant class we have further grouped chemicals with similar physical and/or chemical characteristics; i.e., groups of chemicals which tend to have similar behavior in the environment. These groups are given in Table 1⁺⁺. In a similar fashion the media in which the pollutant resides can be subdivided based on its affect on pollutant behavior. In Table 2 we list several factors affecting pollutant behavior in soil, groundwater, and air (Note: this is not intended to be a complete list of factors). Thus, by developing classifications for both the pollutant and the respective media it resides in, we are reducing the subset of remediation technologies that need be explored for a particular circumstance.

For specific hazardous waste problems (i.e., pollutants in specific media) we envision candidate alternative remediation strategies. These alternative remediation technologies themselves can be categorized based on the processes used in remediation. We have categorized remediation technologies into four general classes¹: 1) physical/chemical, 2) thermal, 3) biological, and 4) immobilization. Within each technology class there exists several specific remediation technologies which can be applied at each stage of the remediation process (i.e., characterization, extraction, treatment and disposal). Physical/chemical technologies include such processes as dehalogenation, air stripping, and chemical sorption; thermal technologies include such processes as vitrification, incineration and fluidized bed combustion; biological technologies include aerobic and anaerobic decomposition; immobilization includes such processes as cement solidification and carbonate immobilization.

⁺⁺ EPA, 1989. Superfund Treatability Clearinghouse Abstracts. EPA/540/2-89/001.

Table 1
Grouping of Pollutants based on behavior in the environment.

Pollutant Class	Example
Halogenated non-polar aromatics	Chlorobenzene
PCB's, halogenated dioxins and furans	Tetrachlorodibenzo-p-dioxin
Halogenated phenols, cresols, amines, and other polar aromatics	Tetrachlorophenol
Halogenated aliphatic compounds	Vinyl chloride
Halogenated cyclic aliphatics, ethers, esters, and ketones	Toxaphene
Nitrated aromatic and aliphatic compounds	Trinitrotoluene
Heterocyclics and simple non-halogenated aromatics	Benzene
Polynuclear aromatics	Naphthalene
Other polar non-halogenated organic compounds	Methanol
Non-volatile metals	Iron
Volatile metals	Mercury
Other inorganics	Sulfate
Other organics	Methyl Propane
Radionuclides	Cs-137

Table 2
Division of media with several factors affecting pollutant behavior in the environment.

Media	Factor Affecting Transport
SOIL	Texture (%sand,%silt,%clay)
	Grain size distribution
	pH
	Hydraulic conductivity
	Organic content
	Moisture content
	Temperature
	Biota
	Bulk density
	Cation exchange capacity
GROUND WATER	Dissolved organic content
	Colloidal particals
	Dissolved oxygen content
	Temperature
	Biota
	pH
AIR	Pressure
	Temperature
	Humidity

Based on the classification schemes for pollutants, media, and remediation technologies described above, we have developed an initial structure for the database. This structure is illustrated in Figure 4. To date we have created the structure for five relational databases. These databases will contain specific information regarding pollutants and the alternative technologies available for remediation. In conjunction to these databases, a User interface, search routines and a report generator will be developed. The User interface will be used both in the data gathering phase in which the data is input in each database (i.e., the development of input screens) along with User interface during execution of search routines. The search routines will entail programs that generate a "best" match of site specific data on the pollutant and the media it resides in to potential remediation technologies. Finally, report generation routines will be developed to extract information from the database. We are currently in the data gathering phase of the project with only minimal development of screens for User input of information.

Figure 4: Components of database

Tables 3-7 show the initial structure (or fields) of the relational databases given in Figure 4. Tables 3-5 represent the structure used to collect data on specific inorganic, organic and radioactive pollutants. First, a classification of all pollutants is accomplished by the database represented by Table 3. The groups (i.e., field 2) are assigned based on the classification scheme developed previous (see Table 1). Tables 4-5 then tabulate specific data regarding each pollutant. This data gives information regarding the physical and chemical characteristics of each pollutant that are important for assessing pollutant behavior in different media. Such data includes a pollutants volatility, solubility, molecular weight, etc. Tables 6-7 give the organization for database construction of remediation technologies. Two databases of remediation technologies are to be constructed: 1) a general classification of technologies used to address contaminated sies (Table 6), and 2) a database of technologies already demonstrated at the laboratory, bench or field scale.

Table 3
Division of Pollutants into Classes

Field	Field Name	Description
1	NUM	Pollutant class number (e.g., P01,P02, etc.)
2	GROUP	Name of Pollutant Class identified by NUM
3	CLASS	General class: organic/inorganic/radionuclide
4	POLLUTANT	Specific pollutant

Table 4
Physical and chemical data for specific inorganic and radioactive pollutants

Field	Field Name	Description
1	POLLUTANT	Specific pollutant
2	NUM	Pollutant class number (e.g., P01,P02, etc.)
3	REDOX_NUM	Oxidation number
4	BOIL_PT	Boiling point (C ⁰)
5	MELT_PT	Melting point (C ⁰)
6	DENSITY	Density of pollutant (g/ml)
7	SOLUBILITY	Solubility of pollutant (g/100 ml)
8	DIFFUSION	Diffusion coefficient (Cm ² /sec)
9	GIBBS	Standard state free energy (kcal/g-mole)
10	VAPOR_PRESS	Vapor pressure (atm)
11	HENRY_CON	Henry's law constant (atm-m ³ /mole)
12	HALF_LIFE	Half life for radionuclide (year)
13	DAUGHTER	Daughter produced by decay of radionuclide
14	BIO_EFFECT	Description of biological effect of pollutant

Table 5
Physical and chemical data for specific organic pollutants

Field	Field Name	Description
1	POLLUTANT	Specific pollutant
2	NUM	Pollutant class number (e.g., P01,P02, etc.)
3	MOL_WT	Molecular weight (g/mole)
4	BOIL_PT	Boiling point (C ⁰)
5	MELT_PT	Melting point (C ⁰)
6	DENSITY	Density of pollutant (g/ml)
7	SOLUBILITY	Solubility of pollutant (g/100 ml)
8	DIFFUSION	Diffusion coefficient (Cm ² /sec)
9	GIBBS	Standard state free energy (kcal/g-mole)
10	VAPOR_PRESS	Vapor pressure (atm)
11	HENRY_CON	Henry's law constant (atm-m ³ /mole)
12	LOG_OCT_H2	Log of octanol to water partition coefficient
13	PHOTODEG	Ability of organic to photo degrade (Yes/No)
14	BIODEGRAD	Ability of organic to biodegrade (Yes/No)
15	BIO_AGENTS	Specific biological agents found to degrade
16	POLAR	Is organic polar (Yes/No)
17	BIO_EFFECT	Description of biological effect of pollutant

Table 6
Classification of Technologies used to remediate contaminated sites

Field	Field Name	Description
1	REMED_PHAS	Phase of remediation: Characterization/Extraction/Treatment/Disposal
2	TECH_GROUP	Technology group: Physical- Chemical/Biological/Thermal/Immobilization
3	PROCESS	Specific process used under TECH_GROUP
4	MEDIA	Process Media: Soil/Ground water/ Air
5	CONTAM_GRP	Pollutant class number (e.g., P01,P02, etc.)
6	REF	References in which technology is described

Table 7
Compilation of technologies that have been demonstrated at laboratory, bench or field scale

Field	Field Name	Description
1	TECHNOLOGY	Title of technology
2	DEVELOPER	Developer of technology
3	MEDIA	Process Media: Soil/Ground water/ Air
4	DOMAIN	Remediation domain: In-situ/Ex-situ
5	SCALE	Scale of application: Lab/Bench/Field
6	DESCRIPTION	Description of technology
7	APP_WASTE	General class of applicable waste
8	SPEC_WASTE	Specific waste in which technology is applied
9	WAST_CLASS	Pollutant class number (e.g., P01,P02, etc.)
10	TECH_GROUP	Technology group: Physical-Chemical/Biological/Thermal/Immobilization
11	PROCESS	Specific process used under TECH_GROUP
12	SITE	Site description (if any)
13	STATUS	Status of work
14	CONTACTS	Specific persons to contact
15	DOCUMENTS	Publications of work
16	COST	Cost data
17	REF	Reference in which information was obtained

5.0 CONCLUSION

The resources necessary for the development of a computer database of hazardous waste technologies have been assembled. In this quarter, we have systematically developed the structure of the database. This structure was driven by the necessity to relate the physical and chemical data of specific hazardous waste sites to specific remediation technologies. We have created the databases (i.e., developed the fields) using Microsoft FOXPRO. We are in the data collection phase of the project. To date, we have entered into the database 296 specific pollutants, and 58 classes of technologies. At this time we are in the process of obtaining specific data on the pollutants entered (i.e., filling out Tables 5 and 6), and obtaining more information regarding specific technology classes (i.e., filling out Table 7). We have also begun entering data on technology demonstrations on the laboratory, bench and field scale.

Site Remediation Technologies: Drain-Enhanced Soil Flushing for Organic Contaminants Removal

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ABSTRACT

The effectiveness of the soil flushing process is limited by the extent with which the contaminant is extracted from the soil and solubilized in the flushing solution, and the ease with which the flushing solution moves through the contaminated soil. Generally, for fine grained soils, both the extraction of the contaminant from the soil and movement of flushing solution are less than that observed for large grained soils (i.e., sands). Thus, soil flushing is not always effective for remediating contaminated aquifers and the use of "pump and treat systems" on extremely long term basis is often required.

Prefabricated Vertical Drains (PVD) can be used to shorten the drainage path of the flow and therefore expedite the soil flushing process. Because the installation process is relatively simple and inexpensive, fluid extraction using this process can prove to be practical and cost-effective. Compared to conventional well fields and drains, the use of PV drains would expedite the contaminant recovery and reduce both labor and material costs.

Work to be conducted in this research investigates major parameters affecting the efficiency of contaminant extraction using PV drains. A single polycyclic aromatic hydrocarbon (PAH), in this case naphthalene ($C_{10}H_8$), is chosen as the study contaminant. Analysis to be conducted include naphthalene (by GC method 8100, USEPA, SW-846), and total organic carbon or chemical oxygen demand. The testing program include column and batch studies to estimate appropriate environmental and engineering parameters for the soils, contaminants, and surfactants under consideration. In addition, several pilot scale systems (Contaminant Recovery Cells, CRC) in which the recovery efficiency of the PV drains will be evaluated.

Preliminary laboratory work was conducted to evaluate the proper mix of the soil to be used in the testing program. Compaction tests according to ASTM 698D and permeability tests according to ASTM D5084 were conducted using blends of kaolinite and Ottawa sand. The blends consisted of 80/20 percent by dry weight sand to kaolinite. The average coefficient of permeability varied with the moisture content of the samples and was estimated to be on the order of 1×10^{-5} to 1×10^{-4} cm/sec. Based on the results of these experiments the blend to be used in the experiment will range from 80/20 to 70/30 sand to kaolinite.

Literature review was conducted to investigate the existing theories dealing with applications of PVD and their applicability to the soil type to be used in the project. A contact was established with the NILEX corporation, one of the largest installers of the PVD in the U.S. Discussion is underway regarding their possible involvement in the project as an industrial partners. In addition, acrylic material for construction of the column and the recovery cells was received and a prototype recovery cell was constructed. The construction of four test columns is underway. The Gas Chromograph (GC) for conducting analysis including naphthalene by GC method 8100, USEPA SW-846 has been ordered and delivery date is around the end of May. Details of the soil extraction method are presented.

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1.0 INTRODUCTION

Recently, the United States Environmental Protection Agency (USEPA) evaluated the progress of 112 sites where groundwater extraction was an integral part of containment and/or restoration activities (USEPA 1989a,b,c). The majority of the 112 sites were contaminated with organic compounds. The type and concentration of these organic compounds were found to be extremely diverse. In general, chemicals such as TCE, creosote, and PCBs have been reported as contaminants of concern (USEPA 1989d). In addition to the variety of contaminants and concentrations that prevail at these sites, wide variations in soil type, geological formation, and hydrogeologic conditions exist. A "typical" contaminated soil is difficult to define and remediation measures are usually developed on a site-specific basis.

There are a number of approaches to remediation that are used at contaminated sites. Examples are in-situ bioremediation, vacuum or air stripping, immobilization, and soil washing/flushing. In the case of in-situ bioremediation, organic compound(s) are biochemically degraded within the contaminated subsurface. Air or steam stripping are feasible if the Henry's Law constant of the organic compound(s) is greater than 3×10^{-3} atm/m³ mol. In the case of immobilization techniques, contaminants are tightly bounded within a solid matrix that minimizes their migration. Solidification, stabilization, and vitrification are the principal immobilization techniques. Contrary to immobilization, the soil washing/flushing approach promotes contaminant solubilization and migration in the liquid phase so that the contaminants can be easily flushed from the soil matrix. Soil washing refers to ex-situ remediation of soils whereas soil flushing refers to in-situ extraction of contaminants (i.e., pump and treat technology). Considering all remediation approaches, only soil flushing and stripping remove contaminant(s) from the contaminated zone without excavating the soil. Of these two, soil flushing is the process of investigation in this research proposal.

The effectiveness of the soil flushing process is limited by the extent that the contaminant is extracted from the soil and solubilized in the flushing solution, and the ease with which the flushing solution moves through the contaminated soil. Generally, for fine grained soils, both the extraction of the contaminant from the soil and movement of flushing solution are less than that observed for large grained soils (i.e., sands). Thus, soil flushing is not always effective for remediating contaminated aquifers and the use of "pump and treat systems" on extremely long term basis is often required.

The improvement of flushing solution movement in low permeability soils (10^{-4} to 10^{-7} cm/s) is the subject of this research proposal. Specifically, the use of Prefabricated Vertical Drains (PVD), also referred to as wick drains, to decrease the flow path and travel time between flushing solution injection and extraction points will be investigated. The development of improved flushing agents (e.g., surfactants) is not within the scope of this proposal. Rather, several flushing agents will be selected based on literature and manufacturers' information and their effectiveness in extracting contaminants from soils will be evaluated in the laboratory. The most effective extracting agent(s) will then be employed to demonstrate the feasibility of using PV drains to improve the soil flushing process.

A cresote contaminated site has been selected as the object of remediation. The chemical composition of cresote is approximately 85 percent polycyclic aromatic hydrocarbons (PAHs), 10 percent phenolic compounds and 5 percent others (N, S, and O heterocyclic compounds). Thus, a single PAH will be used as the study contaminant. Naphthalene will be used as the study contaminants.

In summary, the proposed research has as its objective the completion of the following three phases of study:

Phase 1: Quantifying the parameters that govern the release and transport of PAHs by and through the subsurface.

Phase 2: Development of a predictive mathematical model to simulate full-scale operation of PV drain-enhanced soil flushing systems.

Phase 3: Operation of a mesoscale pilot facility to investigate the performance of the PV drain-enhanced soil flushing technique and to calibrate the predictive model.

Specific tasks for each phase of the research program are discussed in the Investigative Approach section of this proposal.

2.0 BACKGROUND

In this section background information on the conventional soil flushing system, the use of PV drains to improve liquid movement in the subsurface, and how PV drains will be used to improve the soil flushing system, will be presented. Because the focus of this research is on improving the movement and extraction of the flushing solution through the contaminated zone, the literature review will focus on liquid and mass transport in the subsurface. However, a brief discussion on PAH contaminated sites, and the fate of PAHs in the subsurface (adsorption, desorption, biodegradation, and volatilization) is included.

2.1 Soil Flushing as a Remediation Technique

In soil washing/flushing water is the primary washing fluid; chemical additives are carried by the water to promote contaminant solubilization. Non-ionic and ionic surfactants, acids, and solvents are examples of chemical additives. While soil flushing is the focus of this research, much information can be gained by examining the effectiveness of chemical additives in extracting soil-bound contaminants in the soil washing process. Soil washing refers to the ex-situ remediation of soils, whereas soil flushing refers to the in-situ extraction of contaminants. Use of these two methods has been limited. However, of these two methods, there has been a greater amount of study conducted on soil washing systems, especially in Europe (USEPA, 1988a).

The conventional soil flushing process involves a number of steps. Each step must be considered separately when assessing the overall effectiveness. The four steps are:

- 1) contaminant solubilization by the wash fluid (surfactant),
- 2) extraction of the solubilized contaminants from the subsurface,
- 3) treatment of the spent flushing water, and,
- 4) disposal/reuse of the treatment residuals.

A general schematic of the first two steps, which defines the scope of this proposed investigation, is shown in Figure 1 (Holden et al. 1989). Conditions adversely affecting the success of soil flushing process are listed in Table 1. Hydrogeologic conditions of the contaminated area are extremely important to the success of the soil flushing process. USEPA (1988b) reported that soil flushing has been used at five Superfund sites for the removal of organics. The permeability of the soils at these sites was relatively high. Currently, the soil flushing option is difficult to implement at sites with low permeabilities.

Table 1. Characteristics Affecting the Soil Flushing Process

Characteristics	Reason for Potential Impact
Unfavorable Waste Characteristics Mixed waste types Variable Waste Composition	Washing solution difficult to formulate Frequent formulation of washing solution
Unfavorable Soil Characteristics Variable soil conditions Low permeability High soil humic content Soil-solvent interactions	Inconsistent flushing Movement of flushing solution hampered Desorption difficult Desorption inhibition
Unfavorable Flushing Solution Characteristics Difficult recovery of washing solution Poor treatability of washing solution Toxicity of washing solution Reduction of soil permeability	High costs Replacement of washing solution Health risks Flushing chemicals reduce porosity.

Source: Technology Screening Guide for Treatment of CERCLA Soils and Sludges, U.S. EPA, 1988.

2.2 PV Drains and Subsurface Liquid Movement

Prefabricated vertical (PV) drains, also referred to as wick or strip drains, were originally developed as a substitute for the commonly used sand drains. They have been used extensively in the past for the expedient drainage and consolidation of low permeability soils under surface

surcharge. The design of prefabricated vertical drains varies according to a specific application. Key parameters usually addressed in the design include:

1. Equivalent diameter of the drain which dictates the size of the inflow surface; and,
2. Discharge capacity of the drain .

As described by Anon (1988) PV drains consist of porous geotextiles wrapped around a plastic drainage core 3 to 4 inches wide and one quarter to 3/8 of an inch thick. PV drains are usually spaced in a manner to allow the dissipation of pore pressure generated due to the application of surcharge or hydraulic stresses on the system. They provide a conduit for flow under the induced hydraulic gradient. Typically they are arranged in a triangular or square grid pattern with 3 to 12 feet spacing. Installation rates reported in the literature are on the order of 1-3 feet per second excluding equipment mobilization and set-up time. Figure 2 illustrates the installation process of a typical PV drain configuration in a field situation.

The use of synthetic PV drains has evolved to many applications and several case studies were reported in literature. A theoretical study pertaining to the design and application of vertical drainage systems was conducted by Guido (1986). Recommendations for the selection of design spacing for band-shaped PV drains were examined. A comprehensive research program was carried out by New York State Department of Transportation (Suits et al 1986) to estimate the effectiveness of several types of PV drains. This research program included laboratory and field testing. Results indicated the suitability of using PV drains to accelerate the drainage of a given soil profile.

A successful implementation of PV drains was presented by Mattox (1987). In this project, construction of a 21.7 ft high embankment over weak marsh deposits in Mobile, Alabama, was accomplished through the use of geogrid reinforcing and PV drains. Installation of PV drains was necessary to reduce the time required for settlement of the embankment through accelerated drainage of the subsurface profile. Estimated savings due to the use of the innovative drainage technology was on the order of \$600,000. In another application, Thacker et al (1988) presented a case in which PV drains were used in the construction of a coal refuse impoundment to allow complete pore pressure dissipation. Field measurements with pneumatic piezometers indicated that the use of PV drains in the drainage scheme was successful. The coal refuse impoundment met prudent engineering criteria with regard to stability even though a large portion of the dam was being built over hydraulically filled fine coal refuse. In a similar application, Saye et al (1988) presented a case in which PV drains, installed at spacing ranging from 3 feet to 5.5 feet, were used in order to facilitate drainage and strength gain of soft highly plastic clay deposited in a cutoff oxbow of the Missouri River.

In general, research work conducted to quantify the performance of the PV drains is mostly directed toward the drainage potential to accelerate the consolidation process, or compression of a soil profile due to expulsion of water. No research specifically addressed the quantity of flow being collected using a PV drainage scheme. Furthermore, no research was conducted to

address the potential of using a PVD drainage scheme for the removal of pollutant substances from subsurface soils.

However, some research was conducted on the retrieval of tracers in agricultural applications through the use of subsurface drains. Everts and Kanwar (1990) presented the results of a study in which potassium bromide and calcium nitrate were used as tracers in sprinkler irrigation water. These tracers were applied to a field plot drained with a single subsurface drain line during two irrigations. Drain outflow was measured, and water samples were collected from drain discharge and analyzed for Nitrate (NO_3^-) and Bromide (Br^-) content. Results indicated that, transported on a mass basis, 24% and 12% of the bromide and 20% and 9% of the nitrate reach the drain, respectively, during the two sprinkler irrigations. Although not directly related to the scope of the proposed work, the results of this study indicates the promising potential of using subsurface drains for collecting subsurface pollutants.

In summary, PV drains shorten the drainage path of the flow and therefore would expedite the soil flushing process. Compared to conventional well fields and drains, the use of PV drains would reduce both labor and material costs. Because the installation process is relatively simple and inexpensive, fluid extraction using this process can prove to be practical and cost-effective. Figure 3 schematically shows a possible arrangement for the use of PVD system for recovery of subsurface pollutants in the field.

2.2.1 Theory of Liquid Retrieval Using PVD

Analysis techniques for performance evaluation of the PVD focus on the ability to induce consolidation and therefore accelerate the rate of settlement at a given site with soft clay soils. However, the use of PVD for this project is to improve the soil washing process through the efficient retrieval of subsurface liquid in fine grained soils that may contain appreciable amount of cohesionless material. As shown in Figure 4, the installed PVD has a zone of influence with a radius r_{eq} . The governing differential equation for the solute transport assuming full saturation and no decay:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (D_r r \frac{\partial C}{\partial r}) + D_z \frac{\partial^2 C}{\partial z^2} - \frac{1}{r} \left(\frac{\partial}{\partial r} \left(\frac{r v_r C}{n} \right) \right) - \frac{1}{n} \frac{\partial}{\partial z} (v_z C) - \left(\frac{1}{n} \frac{\partial}{\partial z} \left(\frac{r v_r C}{n} \right) \right) - \frac{\partial}{\partial t} \left(\frac{\rho_b K_d C}{n} \right) \quad (1)$$

where:

C = concentration

r = equivalent radius

D_r and D_z = coefficient of vertical and radial dispersion: $f(v_r$ and $v_z)$

v_r and v_z = radial velocity and vertical velocity

k_d = equilibrium distribution coefficient

ρ_b = bulk density

n = porosity of soil

Solution of the above equation is obtained by imposing the proper boundary conditions and defining the physical and engineering properties of the soil.

The movement of the subsurface liquid can be induced using applied surface surcharge or injection and vacuum system. The theoretical model to estimate the maximum discharge (q_{max}) to be recovered from the PVD in clay under surface surcharge is as follows:

$$q_{max} = \pi r_{eq}^2 \frac{dU}{d\epsilon} L \epsilon \quad (2)$$

$$U = 1 - \exp\left(-\frac{2T_R}{f(n)}\right) \quad (3)$$

$$T_R = \frac{C_r}{r_{eq}^2} \cdot t \quad (4)$$

$$F(n) = \frac{n^2}{(n^2 - 1)} \ln(n) - \frac{3n^2 - 1}{4n^2} \quad (5)$$

where:

U = average degree of consolidation
 ϵ = strain due to consolidation
 C_r = coefficient of radial consolidation
 $n = r_{eq}/r_{st}$

Modeling of the vacuum system can be achieved using the theory of wells. This effort is currently underway and is a part of the ongoing literature review.

2.3 Examples of PAH Contaminated Sites

There are over 2000 wood preserving sites in the United States requiring remediation with over 50 of these sites on the National Priority List (NPL), Stinson et al. (1991). The MacGillis and Gibbs Superfund site in New Brighton, Minnesota, is heavily contaminated with cresote, pentachlorophenol, and fuel oil. PAH concentrations as high as 407 mg/kg have been reported (Stinson et al. 1991). PAH concentrations of 2,800, 240, and 10 mg/kg for peat, soils, and sediments, respectively, have been reported at the Pine Street Canal Superfund site in Burlington, Vermont, (Weir and McLane 1991). Christiansen et al. (1991) reported PAH concentration exceeding 1900 mg/kg at an undisclosed Texas site. PAH concentrations exceeding 3,000 mg/kg and 20,000 mg/kg have been reported at the Bayou Bonfouca (Slidell, Louisiana)

and the Jennison-Wright (Granite City, Illinois) sites, respectively, as stated by Halloran et al. 1991. In examining contaminated sites, a wide variety of PAHs (and other organic contaminants) are present in widely ranging concentrations. Thus, remediation research must address diverse conditions. However, because the main focus of this research project is the improvement of the liquid movement phenomenon of the soil flushing process, relatively simple PAHs (e.g., naphthalene) will be chosen as the study organics. It is tacitly assumed that the PV drain-enhanced soil flushing method will improve the efficiency of the pump and treat process regardless of the specific organic contaminant(s).

2.4 Use of Surfactants to Remove Soil-Bound Organics

Surfactant molecules have both a polar (hydrophilic) and nonpolar (hydrophobic) segment and thus they accumulate at polar-nonpolar interfaces. Above a certain concentration surfactants will form micelles (aggregates). The polar end of the molecule in the micelles is presented to the aqueous phase. The nonpolar end of the surfactant molecule faces inward, away from water molecules. The interior of the surfactant micelles is nonpolar and thus can solubilize nonpolar compounds that are sorbed onto soil particles. A large number of commercial surfactants that are environmentally safe and relatively inexpensive are available. Surfactant types can be categorized as ionic (anionic, cationic), nonionic, and amphoteric. Examples of surfactants and their characteristics are presented in Table 2 (USEPA 1985).

Table 2. Surfactant Types

Anionic	Cationic	Non-ionic	Amphoterics
Carboxylic acid salts	Long chain amines	Alcohol ethoxylates	pH sensitive
Sulfonic acid salts	Quaternary ammonium salts	Polyoxyethylenated alkylphenols	pH insensitive

The use of surfactants was first investigated by the Texas Research Institute (1979, 1985) as a method of recovering gasoline. Ellis et al. (1985) investigated the use of nonionic surfactants for removal of PCBs, chlorinated phenols, and petroleum hydrocarbons from soils. At surfactant concentrations of 1.5 percent (by volume) over 90 percent of the contaminants were removed from the soil. The use of surfactants increased removal by an order of magnitude over that observed for a water-only flush. A possible drawback to using nonionic surfactants in the soil flushing process is the difficulty encountered in separating the surfactant from the contaminated groundwater and subsequent surfactant reuse. Nash (1987) investigated surfactant enhanced soil flushing at the lab and field-scale using soil from the Volk Air National Guard Base, Wisconsin. Significant removal of organics in the lab-scale systems was reported. However, organic removal in the field-scale systems was less than that observed in the laboratory. The decrease in organic removal was attributed to the surfactant not penetrating the soil.

Liu et al. (1991) investigated the solubilization of several PAHs (anthracene, phenanthrene, and pyrene) by nonionic and anionic surfactants. Nonionic surfactants octyl- and nonyl-phenylethoxylates (9 to 12 ethoxylate units) were the most effective. A 1 percent (by volume) surfactant dosage was required to achieve 70-90 percent solubilization. Fountain and Hodge (1992) reported that several surfactants were able to increase the solubility of common chlorinated organics (e.g., perchloroethylene (PCE)) by several order of magnitudes. They also reported that, for PCE, several surfactants lowered interfacial tension between water and PCE to less than 1 dyne/cm causing downward vertical movement of the PCE. Thus, proper selection of surfactant mixtures is required if spreading of the contaminant downwards towards uncontaminated soils is to be minimized.

Dworkin et al. (1988) and Kuhn and Piotek (1989) reported favorably on the use of soil flushing for wood preserving contaminated sites. The relationship between the amount of contaminant that is solubilized and the surfactant concentration is approximately linear provided that the surfactant concentration is above the "critical" micelle concentration (CMC) as described by Gannon et al. 1989. At surfactant concentrations below the CMC contaminant solubilization does not occur. Gannon et al. (1989) reported that the CMC may be substantially reduced by the presence of a hydrophobic contaminant. However, Liu et al. (1991) reported that the solubilization of several soil-bound PAHs occurred at surfactant concentrations that were larger than the "clean-water" CMC.

In summary, a great deal of research on the development and use of surfactants to remove organic compounds from soils has been conducted. Based on results from lab-scale studies as well as full scale remediation systems, the use of surfactants in the remediation of contaminated soils appears to be promising. As mentioned previously, the focus of this research is not the development of improved surfactants but rather the improvement of the movement of the flushing solution through the contaminated zone. Thus, surfactants, such as those presented in Table 2, will be selected based on literature and manufacturers' information. Their effectiveness in extracting contaminants from soils will be determined in the laboratory and the most effective and environmentally safe agents(s) will then be employed in the demonstration of the PV drains enhanced soil flushing process.

2.5 PAH Adsorption and Desorption, Degradation, and Volatilization

The fate of contaminants in the subsurface is influenced by the extent with which the contaminant adsorbs and desorbs, degrades, and volatilizes. Each of these topics will be discussed separately. The majority of the review focuses on adsorption and desorption because during the conduct of the proposed research, steps will be taken to minimize degradation and volatilization.

2.5.1 Adsorption and Desorption

PAHs, the study contaminant, readily accumulates on soil particles. The concentration of the soil-bound contaminant can be related to the solution concentration through a number of

isotherms (Freundlich, Langmuir, and B.E.T). In this study it is assumed that the soil has been contaminated thus, adsorption of the PAH will not be examined to a large extent. However, the adsorption of the surfactant-PAH onto clean soil will be investigated. It is conceivable that the contaminated flushing solution will pass through areas of the subsurface that are not contaminated and thus, it is possible that re-adsorption can occur. Desorption or solubilization of the contaminant from the soil in the presence of surfactants will be studied.

2.5.2 Biodegradation

A large number of organic compounds are subject to biochemical degradation. Biological treatment of contaminated sites has been named as the remediation technique in about 15 percent of the Records of Decision (ROD) (Christiansen et al. 1991). Naphthalene, the simplest PAH, is considered relatively degradable with a BOD5/COD ratio of < 0.2 (USEPA 1985). Christiansen et al. (1991), reported that the half-lives of total and carcinogenic PAHs in a soil-sludge slurry reactor were between 16 and 88 days. Weir and McLane (1991) reported that PAHs of low molecular weight (e.g., naphthalene and 2-methylnaphthalene) were biodegradable in soils, but higher weight PAHs were not. Berg et al. (1991) demonstrated that the composting of PAH contaminated soils was a viable treatment alternative. Total PAH soil concentration was decreased from approximately 300 mg/kg to less than 50 mg/kg in 14 weeks. Thus, it is apparent that PAHs, especially those with lower molecular weights, are susceptible to biochemical degradation. Measures to deter or account for biodegradation in laboratory experiments will be implemented.

2.5.3 Volatilization

PAHs are classified as semivolatile and generally have a Henry's constant lower than 10^{-4} atm/m³ mol. Organic compounds having a Henry's constant greater than 3×10^{-3} atm/m³ mol are candidates for air stripping (Holden et al. 1989). While volatilization of PAHs is possible, transfer of the contaminant to the gas phase is not an efficient process. However, during the conduct of this research, the loss of PAHs from the soil via volatilization will be accounted for by using a controlled experiments environment.

3.0 METHODOLOGY

The proposed research plan is the first phase of five year plan during which the major parameters affecting the efficiency of contaminant extraction using PV drains will be quantified, pilot scale study is performed and the project can move to field implementation. The current phase program consists of column and batch studies to determine appropriate environmental and engineering parameters for the soils, contaminants, and surfactants under consideration. These experiments will be conducted during year one along with several pilot scale systems (Contaminant Recovery Cells, CRC) in which the recovery efficiency (hydraulic only) of the PV drains will be evaluated for uncontaminated soils.

3.1 Laboratory Testing

During the first year of the project, laboratory studies will be conducted to ascertain fundamental parameters of the soils, contaminant and surfactants. In addition, fundamental parameters of the recovery system will be evaluated. Preliminary laboratory work was conducted to evaluate the proper mix of the soil to be used in the testing program. Compaction tests according to ASTM 698D and permeability tests according to ASTM D5084 were conducted using blends of kaolinite and Ottawa sand to select the appropriate soil mix for use in the experiments.

3.1.1 Batch Isotherms

Batch isotherm studies will be performed in order to evaluate the effectiveness of surfactants for contaminant removal from soil surfaces. A suite of tests will be performed resulting in a matrix consisting of surfactant type and concentration, and soil contact time versus percent of contaminant removed from the soil. This information will lead to the selection of a surfactant for application in the column studies and in the contaminant recovery cells. Soils will be contaminated with Naphthalene by dissolving Naphthalene in Methanol, mixing the solution with soil, and allowing Methanol to evaporate. The initial soil/Naphthalene concentration will then be determined.

As previously mentioned, surfactants will be selected based on literature and manufacturer's data. Equilibrium isotherms will be estimated for the adsorption of Naphthalene on the three soils to be considered. Also, re-adsorption of Naphthalene, in the presence of the "short-listed" surfactant, by the clean soil will be assessed.

3.1.2 Column Studies

A series of column studies will be conducted, first on clean soil and then on contaminated soil. Clean soil studies will be used to obtain permeability characteristics of the soil types both for water and for surfactants as permeating liquids. The studies on contaminated soil columns will be used to ascertain the effectiveness of the surfactant in removing contaminants under a flow type situation and estimate the dispersion/advection characteristics of the system. Only the most promising surfactants according to the batch tests will be investigated. At this stage of the research and based on limited preliminary testing, sample preparation for the columns study will proceed as follows:

1. Samples will be prepared from a mixture of 80% ottawa sand and 20% kaolinite.
2. An initial sieve analysis will be conducted as a baseline to check the final integrity of the soil upon completion of a test.

3. Compaction will be done at a water content of approximately 9% to achieve a permeability of 1×10^{-5} cm/sec.

4. The present plan is that the samples will be compacted in the columns by a laboratory fabricated proctor hammer. In order to conserve the compactive energy applied in a standard compaction, a hammer has been constructed that will duplicate the compaction effort on the column scale. The hammer consists of a 703 gram hammer enshrouded by a thin walled aluminum casing. The hammer will fall a distance of 12.5 inches for 20 blows per lift. Ten lifts will be used to compact the column. An alternative plan is to use column with 4 inch diameter and follow the standard proctor method for compaction with the samples prepared directly inside the columns.

5. The bottom as well as the top of the column will be protected from any discharge of the soil by use of filter paper.

6. Flow tests conducted with the uncontaminated soil will have a duration necessary to provide discharge of 2-3 pore volumes of water.

At the conclusion of the flow tests, the sample will be dissected into four parts. Each part will be examined for the following: water content, saturation, voids ratio, porosity, and dry unit weight. A sieve analysis will be the final characteristic looked at. Equating the results of this analysis with the initial sieve analysis will determine if the above outlined preparation alters the soil distribution. A sketch of the column that is currently being used in preliminary testing is shown in Figure 5.

3.1.3 Contaminant Recovery Cells

Three contaminant recovery cells (CRC's) will be constructed and used to assess the efficiency of the PV drain contaminant recovery system. The CRC's include a central section (0.67m X 0.67m X 1.0m - length/thickness/depth of soil) which will be filled with soil. An upstream reservoir will supply a base inflow into the soil while the downstream reservoir will collect the base outflow. The reservoirs will be used to pre-saturate the soil and to apply a constant base flow during water and contaminant recovery tests. For contaminant recovery purposes, PV drains will be installed into the soil. In order to quantify recovery efficiency, single and multiple drains will be used. Two systems of fluid recovery will be evaluated. These include applying a vacuum to the drains and applying a stress on the surface of the soil. Both systems provide a driving force for fluid transport from the soil.

A list of the CRC's and associated test parameters is given in Table 3. Drain efficiencies for the removal of fluids from the soils will be quantified. The time required for construction and preparation of the cells including saturation of the soils is expected to be on the order of two to three months. Contaminant recovery is expected to last for approximately two months for each recovery mode. Thus, CRC tests are expected to require 6 to 8 months to complete.

Table 3. Contaminant Recovery Cells and Operating Parameters

CELL No.	% SAND/ KAOLINITE	No. DRAINS	CONTAMINANT RECOVERY	
			VACUUM (psi) 10	APPLIED PRESSURE (psi) 2 - 10
1	80/20 to 70/30	1	It is estimated that each recovery step will require 2-3 months	
2	80/20 to 70/30	2		
3	80/20 to 70/30	MULTIP		

One of the CRC is constructed to date. Figure 6 shows a picture of the cell. Integrity testing in underway to confirm that the cell is leak-proof and select appropriate lining material to minimize leakage potential. Three more cells, similar to the one shown in the photograph are under construction

3.1.4 Procedure for Soil Extraction

The extractor procedure outlined below is based on EPA Method 3540 Soxhlet Extraction. Due to financial considerations and the scope of this project, minor alterations have been made to accommodate the University laboratory.

Materials:

Soxhlet Extractor: 37mm ID, with 250ml boiling flask and Allihn condenser (the cooling fluid will be the laboratory supplied cold water).

Kuderna-Danish Apparatus:

Concentrator Tube: 10ml graduated, with ground glass stopper.

Evaporator Flask: 250ml

Snyder Column: Three ball macro.

Boiling Chips: PTFE, 10/40 mesh.

Water Bath: Temp controlled bath under hood.

Paper Thimbles: 33mm x 80mm cellulose.

Reagents:

Distilled Water: Laboratory supplied.

Sodium Sulfate: Granular Anhydrous.

Methylene Chloride: Pesticide grade.

Methanol: Pesticide grade.

Methods:

1. Mix 10g of sample with 10g of anhydrous Sodium Sulfate and place in the extractor thimble.
2. Place 175ml of Methylene Chloride into a 250ml boiling flask with boiling chips and attach to the Soxhlet extractor.
3. Attach an Allihn condenser to the extractor and install the cold water lines to the hose barbs.
4. Heat the solvent and allow to extract for 16 hrs.
5. After the extract has cooled, place the remaining solvent into a Kuderna-Danish (K-D) concentrator.
6. Prewet the Snyder column with approx. 1ml of Methylene Chloride.
7. Place the concentrator in a water bath and allow the extract to evaporate until the volume left is 1ml. The temperature should be adjusted so this takes 15 min.
8. Remove the K-D concentrator from the bath and allow to cool.
9. Adjust the volume if necessary with Methylene Chloride to 2ml.

4.0 RESULTS AND BENEFITS EXPECTED

The blends consisted of 80/20 percent by dry weight sand to kaolinite. The average coefficient of permeability varied with the moisture content of the samples and was estimated to be on the order of 1×10^{-5} to 1×10^{-4} cm/sec. Figure 7 shows the variation of the dry unit weight and coefficient of permeability with moisture content. Based on the results of these experiments the blend to be used in the experiment will range from 80/20 to 70/30 sand to kaolinite.

While major strides in the hazardous waste management field have been made in minimizing the risks associated with the disposal of wastes being generated, hundreds of inactive and/or abandoned hazardous waste sites exist that require remediation. The required remediation approach varies from site to site, depending on the hazardous constituents and site conditions present. The proposed study is an initial step in what will be a continuing effort to develop an in situ method, namely PV drain-enhanced soil flushing, to remove PAHs and other organic compounds from the contaminated subsurface. Because there is little or no experience with using PV drains as part of the soil flushing process, the proposed study will provide fundamental and basic information on performance characteristics of the DESF process as a mean of removing contaminants from sites containing fine grained soils.

5.0 CONCLUSIONS

In summary, the proposed work is progressing on budget and on time. More laboratory tests are planned to estimate the physical and engineering properties of the test soil including Atterberg Limits, grain size distribution and compressibility characteristics.

In parallel, supplies were ordered for the construction of the columns and the recovery cells. Literature review was conducted to investigate the existing theories dealing with applications of PVD and their applicability to the soil type to be used in the project. A contact was established with the NILEX corporation, one of the largest installers of the PVD in the U.S. Discussion is underway regarding their possible involvement in the project as an industrial partners. In addition, acrylic material for construction of the column and the recovery cells was received and a prototype recovery cell was constructed. The construction of four test columns is underway. The HP Series II Gas Chromatograph with single flame ionization detector (GC) for conducting analysis including naphthalene by GC method 8100, USEPA SW-846 has been ordered and delivery date is around the end of May. A research team visited the Miles company for observing the performance of the EPA 8100 protocol. It is envisioned that this protocol with slight modification can be successfully adopted for this project.

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Site Remediation Technologies: In Situ Bio-remediation of Organic Contaminants

**Quarterly Technical Progress Report
for Period January 1 through March 31, 1993**

Work Performed Under
Contract No.: DE-FC21-92MC29467

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April 1993

**SITE REMEDIATION TECHNOLOGIES
IN SITU BIOREMEDIATION OF ORGANIC CONTAMINANTS**

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ABSTRACT

In-situ bioremediation offers a number of advantages over other processes for destruction of organics in groundwater. Advantages include the potential for complete or near complete destruction of contaminants in place, avoidance of transfer of the contaminants to another medium, less risk of health hazards due to human exposure and cost-effectiveness. The objective of this research is to evaluate and optimize the ability of methanogenic and other selected bacteria for biotransformation of TCE and other volatile organic compounds (VOC's) found at DOE sites. A five-phase workplan is presented which involves the systematic manipulation of environmental conditions to enhance the rate and extent of biodegradation of the candidate VOC's.

A literature review (Phase 1 of the workplan) was conducted this quarter to aid in guiding the research activities. Based on the review, it was decided to concentrate the research on bioremediation of chlorinated aliphatic solvents such as TCE and PCE. This class of compounds is one of the most common in contaminated groundwaters and one of the most difficult to remediate. Current understanding of the metabolic pathways utilized by methanotrophic and methanogenic bacteria for degradation of volatile chlorinated solvents suggests that the efficiency of bioremediation could be improved if the sybiotic relationship between the two were encouraged. The methanotrophs have an obligate requirement for methane, which is complimented by the methane production of methanogenic organisms. Exploration of sequential anaerobic and aerobic metabolism and the cometabolic pathway used by methane monooxygenase for halogenated VOC degradation appears to be a promising direction for enhancing the efficiency and attractiveness of in-situ bioremediation.

While a number of field-determined factors may limit the application of in-situ bioremediation, a review of a number of actual field studies which have been completed or are currently underway showed that it is possible in many cases to overcome difficult site conditions and to stimulate the growth of desired organisms for degradation of chlorinated solvents achieving significant levels of removal.

During next quarter, Phase 2 studies will be carried out to evaluate the optimum concentration of growth enhancing agents in both liquid and soil cultures. If time permits, Phase 3 (column studies) and Phase 5 (combination of methanotrophic and methanogenic sequential growth) will also be initiated.

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1.0 INTRODUCTION

A variety of toxic organic contaminants are found at DOE sites including fuel hydrocarbons, polychlorinated biphenyls (PCB's) and volatile organic solvents such as trichloroethylene (TCE), perchloroethylene, and carbon tetrachloride. These compounds may occur as single contaminants, but are often found in conjunction with heavy metals or in mixed wastes containing radioactive components.

In-situ bioremediation has a number of advantages for destruction of organic contaminants in groundwater. Other processes such as sorption and volatilization do not destroy contaminants, but rather just concentrate them or transfer them to another medium. Abiotic (chemical) transformation is not normally cost-effective in groundwaters and may even result in production of more toxic chemical species.

Clean-up methods often involve soil flushing to mobilize the contaminants for transport to the surface for treatment. However, because many organic contaminants sorb to soils, they are not readily leached from the soils often leaving toxic residuals in place even after flushing. Furthermore, bringing the contaminants to the surface increases the risk of health hazards due to human exposure. There is increasing recognition that bacteria are present and active in the subsurface and that *in situ* biotransformation offers a potentially more effective and economical method of contaminant destruction.

2.0 PURPOSE

The purpose of the research is to evaluate and optimize the ability of methanotrophic and other selected bacteria for biotransformation of TCE and other volatile organic compounds (VOC's) found at DOE sites. The approach outlined involves the systematic manipulation of environmental conditions in the subsurface for the purpose of enhancing the rate and extent of biodegradation of candidate (VOC's). This approach takes advantage of the ubiquity of methanotrophic bacteria and introduction of non-native organisms should not be necessary. Also, only relatively benign enhancing compounds will be added in non-toxic concentrations. In addition, it is envisioned to take advantage of the natural symbiotic relationship between the methanogenic and methanotrophic bacteria to aid in biotransformation.

3.0 BACKGROUND

A number of exciting developments are occurring in the field of environmental biotechnology (engineering applications of microbial ecology). For example, while trace concentrations of some organic contaminants cannot support microbial growth as the sole electron donor, they can still be biotransformed by engineering the system so that the microbial population obtains the majority of its energy and carbon from a different compound that serves as the primary substrate. This is sometimes referred to as *secondary utilization*. There are also many organic contaminants that are biotransformed in the environment for which no microorganisms have been found which are able to use them as sole carbon source. This is a special case of secondary metabolism often termed *cometabolism*. Cometabolism has been

defined (Dalton, 1982) as the "transformation of a non-growth substrate in the obligate presence of a growth substrate or another transformable compound". As an example, halogenated methanes, ethanes, and ethylenes are poor growth substrates for bacterial growth but may be degraded by methanotrophs growing aerobically on methane (Henson et al., 1988).

4.0 METHODOLOGY

The principal focus of the investigation is to develop methods which will enhance bacterial metabolism of organic contaminants in sub-surface environments in order to increase the rate and extent of biodegradation. The methodology is presented in five phases below, however it is anticipated that modifications will be made to the workplan as the work progresses.

Phase 1: Literature Review

As noted above, it is planned that the work will focus on the use of methanotrophs for in-situ VOC destruction. However, a complete review of the bioremediation literature will be carried out whether other classes of organisms also appear attractive and the research plan may be modified. The information gained from the literature review will be utilized both in this project and in the systematic study (METC/MC-1).

Phase 2: Batch Studies to Evaluate Optimum Concentration of Growth Enhancing Agents in Both Liquid and Soil Cultures

In order to enhance microbial activity, a variety of chemical compounds will be investigated for addition to areas of sub-surface VOC contamination. However, some of the compounds to be investigated are toxic in high concentrations (for example hydrogen peroxide). Thus, the maximum allowable and optimum concentrations of each of the candidate enhancing compounds will be evaluated. Several different methanotrophic species will be tested to determine if one is significantly more hardy than others. Liquid cultures of bacteria containing various concentrations of the test compound will be monitored for the rate of growth to determine the optimum concentration to promote growth and the concentration at which inhibition occurs.

These experiments will only offer a first approximation of the optimum concentrations because liquid cultures do not closely mimic the conditions found in sub-surface soils. Thus, additional experiments will involve inoculating soil samples containing various concentrations of test compounds (peroxide, acetate, formate, EDTA, etc.). Several methods will be evaluated to monitor cell growth such as the rate of oxygen or methane uptake, measurement of CO₂ production, microscopic cell counting, or isolation and quantification of DNA. In this way, we will be able to determine the maximum non-toxic concentration of potential biodegradation enhancing compounds.

Phase 3: Column Studies to Evaluate the Rate and Extent of Degradation of Candidate VOC's

At this stage, the work will begin to examine the effect of promising compounds on the actual rate and extent of degradation of TCE. This work will be performed using glass columns containing soil, TCE, and methanotrophic bacteria. The columns will be flushed with a slow stream of methane to provide a source of carbon. A control column using nitrogen gas will also be examined to insure that the gas is not volatilizing the TCE.

To test the ability of hydrogen peroxide to serve as a source of oxygen, the gas phase will contain little or no oxygen, and a dilute solution of hydrogen peroxide will be added, either as a steady stream or in periodic aliquots. At various times, samples will be taken and analyzed for TCE and bacterial growth. In this way, the relationship between rate of growth, and rate of TCE oxidation, as a function of peroxide concentration may be determined. Similar experiments will be performed for other compounds such as formate, formaldehyde, and EDTA.

Phase 4: Comparison of TCE Biotransformation by Particulate and Soluble Methane Monooxygenase

Some species of methanotrophic bacteria are able to express two distinct forms of methane monooxygenase: a soluble form (sMMO) located in the cytosol, or a particulate form (pMMO) located in the cell membrane. Only one of the two forms is expressed at any given time, with the amount of available copper serving as the metabolic switch controlling expression. The sMMO is expressed only when the amount of available copper is extremely low, and this is enhanced by excess iron, a necessary cofactor of sMMO. Thus it appears that in most subsurface environments, the membrane-bound form of MMO will be expressed. Indirect evidence suggests that sMMO is the more effective form for degradation of TCE and other VOC's. Thus, by reducing the amount of available copper in the environment, it may be possible to enhance expression of sMMO, and thereby increase the rate of contaminant degradation. Various metal chelators will be used to reduce the level of available copper to evaluate the potential benefit of sMMO expression.

Phase 5: Investigation of the Utilization of the Symbiotic Relationship Between Methanogenic and Methanotrophic Bacteria for VOC Degradation Without Addition of Exogenous Methane

In order to investigate the possibility of enhancing the symbiotic relationship between methanogenic and methanotrophic bacteria, a two-part column will be used. The lower section will contain acetate and an inoculum of methanotrophic bacteria; the upper portion will contain TCE and the methanotrophs. In this way, methane produced by methanogenesis will provide the carbon source for the methanotrophic bacteria. No exogenous methane will be added, with either peroxide or air serving as the source of oxygen. The amount of oxygen added will be critical, since the methanogens are strict anaerobes. Thus the goal will be determination of the amount of oxygen needed to optimize methanotroph growth and TCE degradation without inhibiting methanogenesis. This will closely mimic the actual sub-surface

conditions, with both an anaerobic zone where methane can be generated, and an aerobic zone where it can be oxidized and support growth of methanotrophs.

5.0 RESULTS AND DISCUSSION

This major task undertaken this quarter was completion of the Literature Review (Phase 1-Methodology) which will serve to provide a background which will guide the research plan. The Literature Review is presented in Section 5.1 below. Based on the Literature Review and the work plan as originally proposed (see Methodology), the research plan for next quarter is presented in Section 5.2. It should be noted that the NEPA Review was completed allowing experimental work to begin after notification on March 16, 1993.

5.1 Literature Review

IN-SITU BIOREMEDIATION OF CHLORINATED SOLVENTS

5.1.1 Introduction

It is estimated (Russel, et. al, 1992) that hazardous waste remediation and site restoration costs in the United States may approach \$1.7 trillion over the next 30 years. There are a variety of technologies available for treatment of contaminated sites and groundwaters. In the past, the conventional method of remediation has been pump-and-treat (P&T) technology where groundwater is pumped from the contaminated aquifers, treated and then discharged. For example, Olsen and Kavanaugh (1993) note that in fiscal year 1990, 43 remediation decisions were finalized for Superfund sites for groundwater contaminated with chlorinated solvents. At 40 of these sites, P&T technology was chosen. In most cases, the goal of the treatment was to reduce groundwater contaminant levels to below the Safe Drinking Water Act Maximum Contaminant Levels (MCLs).

While P&T technology may effectively contain the dissolved-phase contaminant plume and reduce the amount of contamination in an aquifer, cleanup is often far from complete. An evaluation of 28 sites by the U.S. EPA and a national laboratory showed that cleanup times and cost estimates routinely exceeded original projections. An 80 % cost increase over that originally projected was typical and cleanup times are projected to be as much as three times longer than originally estimated. At the beginning of a P&T operation, contaminant concentrations drop rapidly, but then level off at a plateau above the MCL's. The concentrations decrease slowly once the plateau is reached resulting in long cleanup periods. A number of reasons are given to explain the long tailing-off phenomenon. These include: 1) preferential flow of the pumped flow in areas of high permeability with subsequent slow diffusion from the low permeability areas, 2) slow release of contaminants from the soil due to immobile water zones and low desorption rates, and 3) the existence of continuous sources of contamination due to residual chemicals in the unsaturated zone and the presence of nonaqueous phase liquids (NAPLs) present in the soil which serve as a sink of free product.

Alternative remediation technologies are under development to enhance or replace P&T methods. These include soil vapor extraction, injection of chemicals into saturated zones to destroy contaminants or enhance solubility and desorption of contaminants, and *in-situ* bioremediation. While no single technology will be applicable to all contaminants or site conditions, in-situ bioremediation is expected to play a major role in many cases. *In-situ* bioremediation has a number of advantages for destruction of organics. Many other processes such as sorption or volatilization do not destroy contaminants, but rather just concentrate them or transfer them to another medium. Abiotic treatment (chemical transformation) is not normally cost-effective in groundwaters and may even result in production of more toxic chemical species. Soil flushing methods, as noted earlier have a number of limitations and may actually increase the risk of health hazards by bringing the contaminants to the surface with potential human exposure.

This review focuses on the in-situ bioremediation of chlorinated organic solvents. While a variety of other organics are also found at DOE sites, chlorinated aliphatic compounds are one of the most widespread contaminant classes and one of the most troublesome to remediate. These compounds are found nationwide in municipal and industrial wastewaters, landfills and landfill leachates, industrial sludges, waste disposal sites, and groundwaters. They are produced in very large quantities. For example, the production of TCE, PCE, and TCA in 1989 amounted respectively to 82, 215, and 353 thousands of metric tons (Wolf and Cramm, 1987; Wolf et al., 1991). Chlorinated alkanes and alkenes, such as trichloroethane and trichloroethylene, are used as dry cleaning fluids, refrigerants, degreasing agents, solvents, and in the the production of decaffeinated coffee (Chapelle, 1993).

Heavy usage in a variety of applications has led to widespread contamination of shallow aquifers since past practice has often been to dump these chemicals into unlined trenches. While it is true that a very significant fraction of the solvents will evaporate in a few days due the high vapor pressure, some will inevitably migrate through the soil profile and reach the groundwater table. As will be shown later, the low octanol-water coefficients of the chlorinated solvents give them a relatively low affinity for sorption onto soils and allow them to migrate. Once captured in the soil-groundwater system, rates of volatilization are greatly diminished and these compounds may persist for long periods of time. The widespread occurrence of halogenated aliphatic compounds in aquifers reflects their resistance to microbial attack under aerobic conditions.

Table 1 lists the frequency of occurrence of a variety of volatile organic chemicals (VOC'S). It may be seen that the chlorinated aliphatic compounds are widely noted in groundwaters. The first column in Table 1 lists VOC'S found in groundwater that has been treated for use as drinking water. It may be seen that the four most prevalent compounds are the trihalomethanes (THM'S) which are formed due to addition of chlorine for disinfection. Hence the THM'S are not major contaminants of groundwater itself. Another group high on the list (especially at CERCLA Sites) are the chlorinated solvents tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-Trichloroethane (TCA). Other somewhat less prevalent compounds on the list such as vinyl chloride (VC), 1,1-Dichloroethane (1,1-DCA),

and 1,1-Dichloroethylene (1,1-DCE) are often produced as daughter products from chemical and biological transformation of the original chlorinated solvents.

Table 1. Frequency of Occurrence of Volatile Organic Chemicals

VOC	<u>Order of Frequency</u>	
	Treated Goundwater ^a	CERCLA Sites ^b
Chloroform	1	7
Bromodichloromethane	2	
Dibromochloromethane	3	
Bromoform	4	
Tetrachloroethylene	5	4
Trichloroethylene	6	1
1,1,1-Trichloroethane	7	6
1,1-Dichloroethane	8	9
1,2-Dichloroethylene	9	12
Carbon tetrachloride	10	15
1,1-Dichloroethylene	11	10
m-Xylene	12	5
o,p-Xylene	13	15
Toluene	14	3
p-Dichlorobenzene	15	11
1,2-Dichloropropane	16	13
Dichloriodomethane	17	
Benzene	18	2
Ethylbenzene	19	7
Bromobenzene	20	
Vinyl chloride	21	8

^a Based upon survey of treated groundwater used for drinking-water Supply (Westrick et al., 1984).

^b U.S. EPA, 1990.

Based on the above considerations, this review will focus on bioremediation of the three major chlorinated solvents (TCE, PCE and TCA) and other associated chlorinated aliphatic compounds as noted in Table 2.

Table 2. Common Halogenated Aliphatic Contaminants*

Chemical	Formula	Acronym	U.S.Drinking Water MCL (µg/l)
<u>Selected Chlorinated Methanes</u>			
Carbon tetrachloride Methene chloride	CCl ₄ CH ₂ Cl ₂	CT MC	5
<u>Chlorinated Ethenes</u>			
Tetrachloroethylene	$\begin{array}{cc} \text{Cl} & \text{Cl} \\ & \text{C} = \text{C} \\ \text{Cl} & \text{Cl} \end{array}$	PCE	5
Trichloroethylene	$\begin{array}{cc} \text{Cl} & \text{H} \\ & \text{C} = \text{C} \\ \text{Cl} & \text{Cl} \end{array}$	TCE	5
cis-1,2-Dichloroethylene	$\begin{array}{cc} \text{H} & \text{Cl} \\ & \text{C} = \text{C} \\ \text{Cl} & \text{Cl} \end{array}$	c-1,2-DCE	70
trans-1,2-Dichloroethylene	$\begin{array}{cc} \text{H} & \text{Cl} \\ & \text{C} = \text{C} \\ \text{Cl} & \text{Cl} \end{array}$	t-1,2-DCE	100
1,1-Dichloroethylene	$\begin{array}{cc} \text{Cl} & \text{H} \\ & \text{C} = \text{C} \\ \text{Cl} & \text{H} \end{array}$	1,1-DCE	7
Vinyl chloride	$\begin{array}{cc} \text{Cl} & \text{H} \\ & \text{C} = \text{C} \\ \text{H} & \text{H} \end{array}$	VC	2
<u>Chlorinated Ethanes</u>			
1,1,1-Trichloroethane	CCl ₃ CH ₃	TCA	200
1,1-Dichloroethane	CHCl ₂ CH ₃	1,1-DCA	
1,2-Dichloroethane	CH ₂ ClCH ₂ Cl	1,2-DCA	5
Chloroethane	CH ₃ CH ₂ Cl	CA	

* Adapted from Semprini et al. (1992)

Properties of selected chlorinated aliphatic compounds are shown in Table 3 to aid understanding their behavior when released to the groundwater environment. It may be seen that most of them are reasonably soluble in water and may migrate as a dissolved phase in flowing water. However, most are significantly denser than water and will tend

Table 3. Properties of Selected Chlorinated Aliphatic Compounds

Chemical	Density ^b	Water Solubility ^b (mg/l)	Log Kow ^a	Henry's Law constant ^c (m ³ katm/mole) at 17.5°C
Tetrachloroethylene (PCE)	1.625	150	2.88	0.0117
Trichloroethylene (TCE)	1.460	1100	2.29	.00632
(c) 1,2-Dichloroethylene (DCE)	1.248	800		.00265
(t) 1,2-Dichloroethylene (DCE)	1.257	600		.00660
1,1,1-Trichloroethane (TCA)	1.325	4400		
Vinyl Chloride	0.912	1100		.0193
Carbon Tetrachloride	1.595	800	2.64	.0211

Sources ^a Fetter, 1993
 ^c Gossett, 1987

^b Verschuereen, 1983

to migrate vertically downward through an aquifer as a dense non aqueous phase liquid. They have relatively low octanol water coefficients and yet will sorb to some degree on organic soils. Finally, they are quite volatile.

The purpose of the literature review is to become familiar with the most promising approaches to bioremediation of the chlorinated solvents, identify existing limitations which hinder the effectiveness of the technology and formulate a research plan which will lead to effective utilization of bioremediation at DOE sites. The scope of the review will include both laboratory-scale research and full-scale development and remediation projects.

5.1.2 Biodegradation of Chlorinated Solvents

Introduction.

As noted earlier, the chlorinated solvents are both toxic and persistent in the environment. As a result, a significant amount of effort has recently gone into understanding the biodegradation of these compounds (TCE, TCA, PCE, VC, etc.). At present, the microbial degradation of trichloroethylene (TCE) has been more thoroughly characterized than that of other chlorinated solvents. The results of laboratory studies on the biodegradation of TCE are summarized in Table 4, and will be discussed below. For the purposes of this review we assume that the biodegradation of other chlorinated solvents takes place by a similar mechanism. Where appropriate, the biodegradation of other chlorinated solvents will be compared and contrasted with the biodegradation of TCE.

Table 4. Rates of Microbial TCE Degradation

Microorganism	Growth Substrate	Original TCE Conc.	Percent Removal	Removal Rates
Methanotroph	Methane	150 ug/L	95	
Methanotroph (strain 46-1)	Methane	400 ug/L	40	
Methanotroph (strain OB3b)	Methane			>1.2 mmol/hr/g.protein
Methanotroph (species CL-M)	Methane		24	1.2 ug/g protein
Methanotroph	Methane	100 ug/L		2.0E-6 mmol/hr/g protein
<i>P. cepacia</i>	Propane	250 ug/L		350.mg/day/g cells
<i>P. putida</i>	Toluene	200 nM		<.2 uMol/day
<i>P. putida</i>	Toluene	80 uM	68	1.8 nmol/min/mg protein

Propane oxidizer	Propane	20 uM	29 - 99	
N.europea	Ammonia	1000 ug/L		2.8 umol/hr/g protein
Methanotrophs + Propane users (mixed culture)	Methane Propane		90	
Phenol/Toluene oxidizers	Phenol Toluene	100 ug/L		to nondetectable
Methanogens	Methanol Formate	5.5 - 7.0 uM		to nondetectable

Mineralization refers to the conversion of toxic compounds to innocuous products, such as CO₂, H₂O, and Cl⁻. TCE and other chlorinated solvents are extremely resistant to chemical mineralization. However, several pathways are available for biomineralization, some of which have been demonstrated in laboratory experiments. Aerobic mineralization is catalyzed by the oxygenases found in many types of bacteria. Methanotrophic bacteria are organisms that have an obligate requirement for methane as the sole carbon source (Hanson, 1980). These bacteria contain a non-specific monooxygenase (referred to as methane monooxygenase, or MMO) that functions in vivo to fix methane and oxidize it to methanol (Anthony, 1986). The further oxidation of methanol provides cell-carbon and energy for the bacteria. Methane monooxygenase also initiates the biodegradation of TCE by methanotrophs (Little et al., 1988; Tsien et al., 1989). An ammonia monooxygenase enzyme (AMO) occurs in ammonia oxidizing bacteria and has many similarities to MMO (Vannelli et al., 1990). Accordingly, ammonia oxidizing bacteria can also degrade TCE. The propane monooxygenase found in propane oxidizing bacteria appears to be a more efficient catalyst of TCE oxidation than either MMO or AMO (Wackett et al., 1989). The toluene and phenol dioxygenase enzymes found in toluene and phenol oxidizing bacteria confer TCE biodegradation activity as well (Folsom et al., 1990; Zylstra et al., 1989; Nelson et al., 1987; Wackett and Gibson, 1988). Lastly, methanogenic bacteria can catalyze the reductive dehalogenation of TCE and many other chlorinated solvents, producing compounds that can be readily mineralized by a variety of organisms, including those mentioned above (Sims et al., 1990). All of these organisms have in common the general ability to degrade TCE. However, the specifics of their behavior toward TCE differ, as discussed below.

Methanotrophs

Figure 1

Aerobic Oxidation

Methanogens

Figure 2

Anaerobic Reductive Dehalogenation

organisms, including the methanotrophic bacteria mentioned above (Fogel et al., 1986). Thus, it appears that a consortium of methanogenic and methanotrophic bacteria would be quite effective for mineralization of TCE and other chlorinated solvents. The optimal system would be engineered such that degradation occurred in a sequential manner, with the anaerobes performing the dehalogenation and the aerobes oxidizing the dehalogenated products. The number of chlorines dramatically effects the rate of anaerobic degradation: the more chlorines the faster the rate of degradation (Sims et al., 1990). A higher number of halogen substituents results in a more oxidized compound making it more susceptible to biological reduction. The relative reduction and oxidation rates of chlorinated organic contaminants are depicted in Figure 3. This behavior is a result of the chlorine atoms increasing the redox potential of the pollutant, and thereby increasing the driving force of the reductive dehalogenation reaction. This anaerobic degradation of chlorinated solvents does exhibit a lag phase; evidently the bacteria require acclimation to the xenobiotic (Fogel et al., 1986). Although methanogenic bacteria will not grow in the presence of oxygen, the reductive dehalogenation reaction is somewhat oxygen tolerant. The rate of TCE degradation is reduced under micro-aerophilic conditions, but not completely blocked (Freedman and Gossett, 1989). Under these conditions a suitable source of reducing equivalents must be provided (eg. methanol, hydrogen, acetate, and formate).

Metabolic Factors Affecting Degradation. Reducing equivalents must also be supplied for aerobic TCE degradation. The oxygenase enzymes that initiate TCE degradation require reducing equivalents to activate O_2 for substrate oxidation. MMO from methanotrophic bacteria is quite non-specific, relative to most other monooxygenases (Anthony, 1986). It will oxidize most small (<8 carbons) straight-chain hydrocarbons, and many aromatic and heterocyclic compounds. Furthermore, the rate of substrate oxidation by MMO is inversely proportional to the size of the substrate. Reducing equivalents can be supplied to methanotrophs in the form of methane, or any of the intermediates in their methane oxidation pathway (methanol, formaldehyde, or formate) (Henry and Grbic-Galic, 1990). For TCE degradation methanol is observed to work best (Little et al., 1988; Tsien et al., 1989). The MMO preferentially binds methane, causing inhibition of TCE degradation at moderate methane concentrations of greater than 15% in air (Russell et al., 1992). In contrast, methanol is a weak inhibitor, and only affects TCE degradation rates at very high concentrations (Henry and Grbic-Galic, 1990). The bacteria are unable to use the products of TCE degradation as a source of energy; in most cases an exogenous reductant is present, and TCE degradation stops when the reductant is depleted (Palumbo et al., 1991). However, some strains of methanotroph are able to synthesize polymers of β -hydroxybutyrate when methane is present in excess. These organisms can then use this storage polymer as an energy source, and consequently will continue TCE degradation in the absence of exogenous reductants (Henry and Grbic-Galic, 1990).

Two forms of MMO are known to be expressed in certain strains of methanotrophic bacteria (DiSpirito et al., 1992). One is found in the cytosol and is referred to as soluble MMO (sMMO), whereas a completely unrelated form is found in the plasma membrane and is referred to as the particulate MMO (pMMO). Most species of methanotroph that have been characterized appear to express only pMMO, which has been less well characterized. Of the two forms of MMO, the soluble enzyme appears to be more effective for TCE

Figure 3. Relative Redox Rates of Chlorinated Organic Contaminants

Figure 4. Sequential Degradation of TCE by Methanogenic and Methanotrophic Bacteria

degradation (Tsien et al., 1989). Expression of the soluble enzyme is repressed by copper, and the presence of $\sim 0.25 \mu\text{M}$ copper sulfate has been shown to significantly inhibit TCE degradation by those methanotrophs that are able to express both forms of MMO (Tsien et al., 1989). TCE degradation by propane oxidizing bacteria probably proceeds by a mechanism similar to that of the methanotrophs. The propane monooxygenase probably initiates the degradation, and appears to operate at a faster rate than MMO (Wackett et al., 1989). As with the methanotrophs, the propane oxidizers can also degrade vinyl chloride, the major product of anaerobic reductive dehalogenation.

Many compounds have been shown to inhibit TCE degradation in laboratory studies. In all cases, TCE is toxic at concentrations above a threshold level, which varies among the different organisms. For most organisms this threshold appears to be in the range of 300-400 μM for pure cultures, but is dependent on the cell density (Henry and Grbic-Galic, 1990). Other compounds that can serve as substrates for the oxygenase enzymes will cause competitive inhibition of TCE degradation. For the methanotrophs such compounds include (but are not limited to) carbon monoxide, methane, ammonia, methanol, ethanol, and other small hydrocarbons (Henry and Grbic-Galic, 1990; Russell et al., 1992; Palumbo et al., 1991). The presence of metal chelators will also affect TCE degradation by methanotrophs but the precise mechanism is not known (Tsien et al., 1989; DiSpirito et al., 1992). Both forms of MMO are metallo-enzymes (Cu for pMMO, and Fe for the sMMO). Of the two forms, pMMO appears to be more sensitive to inhibition by metal chelation (DiSpirito et al., 1992). The membrane-bound MMO is the more prevalent form, but appears to be less efficient for TCE degradation (Tsien et al., 1989; DiSpirito et al., 1992). However, it has not yet been demonstrated that addition of chelators will induce expression of the soluble enzyme in the field. The effect of metals and metal-chelators on the rate of TCE degradation remains an area for future research. Bromoethanesulfonic acid (BES) is a very potent inhibitor of anaerobic TCE degradation by methanogenic bacteria (Sims et al., 1990). This compound is well known to inhibit the methyl reductase enzyme of these bacteria, but it is not known if inhibition of TCE degradation operates by the same mechanism, or if BES simply causes cell death. A mechanism of inhibition that all bacteria are susceptible to is the grazing of yeast and fungi, which has been amply demonstrated in many reactor systems (Phelps et al., 1990).

Conclusions for 5.1.2 (Biodegradation of Chlorinated Organic Solvents)

Our current understanding of the metabolic pathways utilized by methanotrophic and methanogenic bacteria for degradation of volatile chlorinated solvents suggests that the efficiency of bioremediation could be greatly improved if the symbiotic relationship between the two were encouraged. The methanotrophs have an obligate requirement for methane, which is complimented by the methane production of methanogenic organisms. Furthermore, the methanogens ability to dehalogenate more oxidized (more halogenated) pollutants, generating vinyl chloride, is complimented by the ability of the methanotrophs to mineralize vinyl chloride and other small mono-chlorinated hydrocarbons. The rate limiting step of mineralization under anaerobic conditions is the dehalogenation of vinyl chloride. Thus, it would be advantageous to induce methanotrophic growth at the point where all (or most) of the more chlorinated compounds have been dehalogenated to vinyl chloride. Initial

stimulation of methanogenic growth could be subsequently inhibited by the addition of oxygen, at a determined optimum time. The methane remaining from methanogenic metabolism, together with the exogenous oxygen should suffice to stimulate growth of methanotrophic and heterotrophic bacteria, thus completing the mineralization process. A schematic depicting the sequential degradation process is shown in Figure 4. It may also be possible to increase biodegradation rates by alternating methanogenic and methanotrophic growth conditions, thus limiting the accumulation of potentially toxic byproducts, as well as optimizing the alternating production of methane rich and oxygen rich conditions.

The cometabolic degradation of halogenated VOCs involving non-specific enzymes may also be used to enhance remediation. Methods to increase the preference of methane monooxygenase for chlorinated solvents and their byproducts would prove beneficial. Furthermore, optimizing conditions for the expression of sMMO by controlling metal concentrations, or using chelating agents would be of great significance to this effort. The determination of optimal conditions for growth of microbes containing the hydroxybutyrate polymers as possible energy storage would also be beneficial.

Exploration of sequential anaerobic and aerobic metabolism and the cometabolic pathway used by methane monooxygenase for halogenated VOC degradation under aerobic and anaerobic conditions appears to be a promising direction for enhancing the efficiency and attractiveness of in situ bioremediation. It seems highly possible that the methanotrophic and methanogenic bacteria can be encouraged to degrade the target contaminant, and such encouragement would make bioremediation a preferred and viable option.

5.1.3. Field Applications

The true test of the efficacy of in-situ bioremediation is its application in the field under a variety of different site conditions. This section will review important site considerations affecting field application of bioremediation technology for cleanup of soils contaminated with chlorinated solvents. The focus of the review will be to briefly discuss the major factors affecting the fate and transport of contaminants and identify current limitations in field applications which should aid in design of the current research program. This section will begin with a review of site considerations, soil-contaminant interactions, and contaminant transport. Next, application methods and techniques for implementation are presented, and finally a number of past and current field studies are reviewed with respect to methodology and degree of success or failure.

Site Considerations, Soil-Contaminant Interactions, and Contaminant Transport

Knox et al, 1993, divides the processes affecting the subsurface fate and transport of contaminants into three categories: 1) hydrodynamic, 2) abiotic and 3) biotic. These processes are summarized in Table 5 with respect to the influence of various subsurface and contaminant properties. It should be recognized that the three groups of processes are interrelated.

A thorough site investigation in which biological, contaminant, and aquifer characterization data are integrated, is essential for the successful implementation of a bioremediation system. An understanding of the soil system and its relation with organic contaminants is necessary in order for an accurate site characterization to be performed. Characteristics of both the vadose (unsaturated) zone and the saturated zone must be evaluated.

As noted by Sims, 1990, soil (vadose zone) may be described as a complex system, consisting of four phases:

- 1) soil gases;
- 2) soil water;
- 3) inorganic solids; and
- 4) organic solids.

Gases and water, which are found in the pore spaces of the soil, together comprise about 50% (by volume) of a typical soil as shown in Figure 5. An organic contaminant, depending upon its solubility and its tendency to volatilize may be found in varying proportions in these two phases. Pore sizes and continuity and relative proportions of water and air in the pores are examples of factors that affect the mobility of the contaminants (both upward out of the soil and downward to the saturated zone) in a specific soil. Depending upon site-specific soil characteristics and constituent-specific chemical and physical properties, constituents in these two phases may be relatively mobile or immobile. Immobile water zones may exist within the soil grains in micropores or in fractures (Olsen and Kavanaugh, 1993). In this case, slow diffusion from the immobile to the mobile water zone will control contaminant release.

Abiotic solute transport (Table 5) is dependent on both soil properties and contaminant properties in the formation. Processes affecting abiotic transport include adsorption, volatilization, ion exchange, hydrolysis, precipitation/dissolution, cosolvation, redox, and colloid transport. Soil solids are comprised of organic and inorganic components. The inorganic components or minerals are primarily sand, silt, and clay particles in most soils. The solids may contain highly reactive charged surfaces that play an important role in

Table 5. Subsurface Processes and Corresponding Subsurface and Contaminant Properties and Interactions Affecting the Fate and Transport of Contaminants

Process	Subsurface Property	Contaminant Property	Interactions
Hydrodynamic Solute Transport Advection Dispersion Preferential flow	Ground water gradient, hydraulic conductivity, porosity Dispersivity, pore water velocity Pore size distribution, fractures, macropores	Independent of contaminant Diffusion coefficient	Dispersion coefficient
Abiotic Solute Transport Adsorption Volatilization Ion Exchange Hydrolysis Precipitation/Dissolution Cosolvation Redox Colloid Transport	Organic content, clay content, specific surface area Degree of saturation Cation exchange capacity, ionic strength, background ions pH, competing reactions pH, other metals Types and fraction of cosolvents present pE, pH pH, ionic strength, flow rate, mobile particle size, aquifer and particle surface chemistry	Solubility, octanol-water partition coefficient Vapor pressure, Henry's constant Valency, dipole moment Hydrolysis half life Solubility versus pH, speciation reactions Solubility, octanol-water partition coefficient pK _a Sorption, reactivity, speciation, solubility	Colloid stability
Biotic Metabolism/Cometabolism	Microorganisms, nutrients, pH, pE (electron acceptors), trace elements	BOC, COD, degree of halogenation, etc.	
Multiphase Flow	Intrinsic permeability, saturation, porosity	Solubility, volatility, density, viscosity	Relative permeability, residual saturation, wettability, interfacial tension (surface tension), capillary pressure

Source: Sabatini and Knox, 1992

immobilizing organic constituents in a specific soil. Certain types of clays are especially high in negative charges, thus exhibiting a high cation exchange capacity. Clays may also contain positively charged surfaces and act as anion exchange media for negatively charged constituents.

Soil organic matter also has many highly reactive charged surfaces and may aid in retaining organic constituents in a soil system. Hydrophobic organic contaminants may partition from the soil water into soil organic matter and thus become less mobile in the soil system. Immobilization of the constituents may result in additional time for biodegradation to occur. However, immobilization also could result in less bioavailability to microorganisms. Dragun, 1988, notes that a general review of the published literature revealed that adsorbed organic chemicals generally tend to be less subject to degradation by soil microorganisms. However, further research is needed to better understand the overall effects of adsorption and to discover whether immobilization constitutes adequate treatment if the constituent is so tightly and irreversibly bound that it poses no harm to human health and the environment.

Soil solid/organic chemical interactions may be quite complex. Contaminant properties which affect the solute immobilization and/or transport have been summarized by a number of authors (Dragun, 1988, Knox, et al. 1993). These include the structure of an organic constituent, as it effects such properties as molecular volume, water solubility, octanol-water partition coefficient, and vapor pressure, determines the magnitude of sorption onto the surfaces of a specific soil. Specific aspects of chemical structure that affect sorption onto the soil surface include: molecular size, hydrophobicity of the contaminant, charge of the functional groups, and presence of hydrogen bonding, and coordination.

Suitable types and numbers of microorganisms must obviously be present if biotic processes are to be active in affecting the fate of subsurface contaminants. Microbiological characterization of a contaminated site should be conducted to ensure that the site has a viable community of microorganisms to accomplish biodegradation. In the past, it was often assumed that surface soils had high concentrations of biota, but that deeper strata were relatively devoid of organisms due to a low level of needed nutrients. In the last decade, procurement and handling of subsurface samples have been significantly improved. Ghiorse and Wilson (1988) summarized data from various researchers on microbial populations in a wide variety of geologic settings and at various depths for pristine and contaminated sites. They found significant counts of a wide variety of bacteria and a range of metabolic activities in essentially all cases at depths up to 1750 meters. Suflita (1989) noted that subsurface microorganisms tend to be small, mostly attached to the solid surfaces of the aquifer media, and ready to respond to increases in the limiting nutrients. It has also been noted that several metabolic processes in the subsurface may occur sequentially in series (Knox et al. 1993). As an example, where biodegradation of organic pollutants depletes the molecular oxygen, nitrate may then act as a hydrogen acceptor while undergoing denitrification to nitrogen gas.

Biotransformation studies that measure the disappearance of contaminants or mineralization studies that indicate complete destruction of contaminants to carbon dioxide and water may be used to confirm the potential for biodegradation of specific organic chemicals found in

the subsurface. Specific techniques include batch culture and respirometer studies. Controls to detect abiotic transformation of the contaminants and tests to detect toxic effects of contaminants on microbial activity should be included in the studies (Sims et al., 1990). Microbial ecologists have identified ranges of critical environmental conditions that effect the activity of soil microorganisms as summarized in Table 6.

The environmental factors presented in Table 6 as well as soil and waste characteristics, interact to affect microbial activity at a specific contaminated site. All of the above considerations are important and should be evaluated carefully when considering in-situ bioremediation.

Successful bioremediation depends on a thorough characterization and evaluation of the pathways of movement and potential removal mechanisms of the organic contaminants at a specific site. Figure 6 illustrates the fate of hazardous contaminants in a soil system.

Hydrodynamic processes affect the rate of contaminant transport by impacting the flow of groundwater (quantity and flow paths followed) in the subsurface. Table 5 (Knox et al. 1993) lists a variety of subsurface properties affecting transport including ground water gradient, hydraulic conductivity, porosity, dispersivity, fractures and macropores. It should be recognized that many of the processes are interrelated and that a number of them are involved in almost all cases.

Semprini et al.(1992) highlights the processes noted below with respect to contaminant transport in the subsurface.

1) Advection: the miscible transport in aqueous solutions under the influence of the hydraulic potential gradient. As noted in Table 5, advection is also influenced by hydraulic conductivity and porosity. Considering the combined effects of hydraulic conductivity, hydraulic gradient, and porosity, it can be expected that linear velocities of groundwater transport in uniform sand and gravel aquifers in areas of gentle topography are on the order of 1 to 1000 m/yr (Mackay et al., 1985). Hazardous waste sites frequently have groundwater velocities on the order of 10 to 100 m/yr (Semprini et al., 1990).

2) Dispersion: the mixing and spreading of concentration fronts, that arises largely from different rates of movement along the myriad individual flow paths through the porous medium. Because a wide range of hydraulic conductivities results in a large spatial variation of velocities along different flow paths, the extent of dispersion is highly dependent on the heterogeneity of the porous medium.

3) Sorption: the partitioning of a compound between the moving solution and the stationary solid phase. The halogenated aliphatic compounds do not sorb to soils and aquifer materials as readily as do many pesticides, but nevertheless, sorption in aquifer systems is sufficient to retard the rate at which they move in groundwater in relation to the movement of groundwater itself (Semprini et al., 1990). The transport rate of the constituents may be compared to the degradation rate to determine if it is significant. A means of predicting rate of transport of a constituent through a soil system is to describe its mobility by

Figure 5. Soil Constituents by Percentage (Sims, 1990)

Figure 6. Fate of Hazardous Contaminants In Soil (Sims, 1990)

predicting its retardation. Retardation is a factor that describes the relative velocity of the constituent compared to the rate of movement of water through the soil, i.e.:

$$R = V_w/V_c$$

where R = retardation factor; V_w = average water velocity; and V_c = average constituent velocity. A retardation factor greater than one indicates that a constituent is moving more slowly than water through a soil.

Table 6. Critical Environmental Factors for Microbial Activity (Paul and Clark, 1989; Sims et al., 1984; Huddleston et al., 1986)

Environmental Factor	Optimum Levels
Available Soil Water	25-85% of water holding capacity; - 0.01MPa
Oxygen	Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimal air-filled pore space of 10% by volume; Anaerobic metabolism: Oxygen concentration less than 1% by volume
Redox Potential	Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts, pH 5.5 - 8.5
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth (suggested C:N:P ratio of 120:10:1)
Temperature	15 - 45° C (Mesophiles)

A factor developed from a transport model combined with a description of sorption processes, as defined by a linear Freundlich isotherm, can be calculated from the following equation:

$$R = 1 + (pK_d/\theta)$$

where p = soil bulk density; K_d = soil water partition coefficient, which describes the partitioning between the soil solid phase and soil water; and θ = volumetric moisture content (Sims et al, 1990). This information can be used to manage a contaminated soil system (i.e., through control of soil moisture, changes in bulk density, or addition of amendments to the soil that affect the soil water partition coefficient) so that constituents can be contained within the soil system, thus allowing time for implementation and performance of bioremediation treatment techniques.

4) Immiscible transport: the migration of slightly soluble chemicals as a separate liquid phase, often downward by density differences in the case of most halogenated aliphatics. Transport of immiscible liquid phases, referred to as non-aqueous phase liquids or NAPLs, has come to be recognized as a major route of contaminant spreading at hazardous waste sites and as a significant factor affecting contaminant distribution (Huling and Weaver, 1991). The halogenated aliphatic compounds emphasized in this review are susceptible to pronounced vertical transport as immiscible phases. According to the information in Table 3, the compounds are specifically dense, slightly miscible liquids under conditions typical of the subsurface, with solubilities on the order of 0.1 to 10 g/l and specific gravities on the order of 1.1 to 2. Such compounds that are more dense than water are commonly referred to as dense non-aqueous phase liquids or DNAPLs. It should be noted from the solubility data above that the DNAPLs are not totally immiscible and that some of the product will go into solution in the saturated zone.

Physical model experiments have shown that compounds of this kind tend to migrate downward through the vadose and groundwater zone. The driving force is gravity which dominates the hydrostatic forces that cause groundwater movement and solute transport. Figure 7 depicts movement of DNAPL's.

Dense non-aqueous phase liquid, DNAPL, movement is primarily vertical which is in contrast to groundwater transport. If a spill is comprised of DNAPLs, which may sink to the bottom of the aquifer, physical recovery may be considerably more difficult to achieve (Sims et al., 1992). An exception to vertical movement is when the DNAPL encounters a barrier posed by a stratum of low permeability. In most instances the DNAPL transport does not follow the usual mode of advective solute transport. The processes governing immiscible liquid behavior in heterogeneous media needs further research before the overall effects on bioremediation can be assessed realistically.

In the vadose zone, transport of DNAPL's could involve three phases: vapors in the air phase, soluble contaminant in the aqueous phase, and contaminant in the immiscible phase (Knox et al, 1993). In the saturated zone below the water table, an immiscible contaminant is usually considered to move in two phases; the aqueous phase and an immiscible phase.

5) Diffusional transport: the slow steady migration of solute molecules into the matrix rock or dead-end pores under the influence of a driving force. Under ideal conditions the mass transport between the moving groundwater and the stationary solids is sufficiently rapid to assure equilibrium distribution of contaminants between the pore water and solids. In the field however, the evidence suggests that the fate of organic contaminants in natural

Figure 7. DNAPL Infiltration Schematic (Mercer & Cohen, 1990)

hydrogeologic settings may depend critically on rates of transport between the pore water and stationary solid phase. For example, a field-scale study suggested that organic contaminant sorption equilibrated very slowly, over a period of several years (Roberts et al., 1986; Goltz and Roberts, 1986).

Aquifer remediation may be adversely affected due to the fact that these complications are likely to hinder injection and extraction efforts during in-situ treatment by substantially reducing the rate of contaminant removal by either purging or reaction, thus extending the time duration of remediation efforts. Significant impact is likely to be exerted if contaminants are strongly sorbed and/or the porous medium is significantly heterogeneous (Semprini et al., 1990).

At the present time no firm conclusions can be made as to whether diffusional rate limitation will affect remediation significantly. Field observations will be further discussed later, but behavior at the Moffett Field and Borden sites has suggested that retardation factors greater than three can lead to significant rate limitations if a substantial portion of the sorption capacity is associated with zones having permeability significantly below average (Roberts et al., 1986; Semprini and McCarty, 1992).

Application Methods and Techniques For Implementation

In-situ bioremediation follows the same principles as other biological treatment methods except that the contaminated subsurface, rather than an engineered vessel or lagoon, functions as the bioreactor (LaGrega et al., 1992). Just as it is necessary to provide suitable environmental conditions for biological activity in a surface reactor, it is often necessary to enhance treatment in the subsurface by creation of a more favorable growth environment.

Typical Methods Used to Enhance Bioremediation. The typical methods used to achieve enhancement of biochemical mechanisms for detoxifying or degrading contaminants in-situ include:

- 1) control of factors such as moisture, pH, and nutrients, to optimize microbial activity;
- 2) addition of organic amendments (such as methane) to stimulate cooxidation or cometabolism;
- 3) control of subsurface oxygen to accomplish aerobic or anaerobic biodegradation;
- 4) addition of electron acceptors such as nitrate, gaseous oxygen or hydrogen peroxide to increase the concentration of terminal electron acceptor in the soil and enhance aerobic degradation;
- 5) augmentation with exogenous acclimated or specialized microorganisms or cell-free enzymes.

Factors that may Limit In-situ Bioremediation. Many factors may impact the feasibility of biodegradation of chlorinated aliphatic compounds. Even though a specific organic constituent has been shown to biodegrade under laboratory conditions, it may be mineralized slowly or not at all under field conditions in a specific soil/site system.

The supply of oxygen is almost always the rate limiting factor for in-situ bioremediation when aerobic conditions are required (LeGrega et al., 1992). The presence of even nominal amounts of organic contaminants will deplete the subsurface of oxygen, thereby creating anaerobic conditions which do not favor the degradation of lower halogenated compounds as rapidly as sustained aerobic conditions. Thus, in-situ bioremediation typically requires that the subsurface be artificially oxygenated.

The concentration of contaminants and pH are also examples of parameters that influence the feasibility of using biological treatment processes. However, treatment systems can be designed and engineered to accommodate waste with high contaminant concentrations and extreme pH values. Neutralization may be used to adjust the pH to within a range conducive to biological treatment. Likewise, if concentrations of contaminants are high enough to inhibit microbiological activity, a dilution step can be introduced to reduce the concentrations to within ranges conducive to biological treatment.

The presence of metals in the subsurface may be limiting to biological treatment. As previously discussed, copper present at certain concentrations (≈ 0.25 μM as copper sulfate) can affect the expression of soluble MMO (sMMO) and therefore hinder biological treatment (Tsien et al., 1989). However, in some cases, metals may be leached or complexed to reduce microbial toxicity and improve the potential for contaminant treatment (EPA, 1991). Addition of amendments such as methane may also result in localized growth inhibition if it reaches too high a concentration. At some DOE sites, relatively high levels of radionuclides exist along with the organics and may make biological treatment unsuitable.

Another general limitation for in-situ bioremediation involves low soil permeability, which can hinder supplementation of air, moisture, organic amendments, microorganisms and nutrients. Again, it is possible in some soils to control or modify the existing conditions in order to overcome these limitations. Dense non-aqueous phase liquids, such as the chlorinated solvents, have a specific gravity greater than water and may accumulate in isolated pools in low spots of an aquifer. This may make bioremediation more difficult. However, other methods of remediation may also be impacted.

Common Techniques Utilized for Bioremediation. Application methods for in-situ bioremediation are designed to consider the above limitations. While the precise methods or combination of methods employed will be tailored for site specific conditions, the following portion of this section will identify and discuss common techniques utilized during implementation of in-situ bioremediation.

Prior to implementation of in-situ biological treatment, the source of contamination and the free product in both the soil and groundwater should be removed (Thomas and Ward, 1989). The addition of oxygen and nutrients to a site containing a physically removable phase of

contamination would waste time and capital (Hurlburt, 1987). There are several well systems and vacuuming techniques available for the removal of the free phase (Thomas et al., 1987). One common method involves the contaminant being intercepted, pumped to the surface and treated. This is referred to as "pump and treat". However, the time scale for natural desorption and "pump and treat" operations to reduce contaminants to low levels can be enormously long because of the slow release from the sorbed phase (LeGrega et al., 1992).

Methods of containment and hydraulic controls are commonly used to minimize migration of the plume during the in-situ treatment process (Thomas et al., 1987). In general, hydraulic control systems are generally less time consuming and costly to install than physical containment structures such as bentonite slurry walls. Well systems also provide better flexibility with regard to replacement, location changes and variable pumping rates (Sims et al., 1992).

Well systems can serve as injection points for the addition of materials used to stimulate or establish microbial activity, as well as, for control of circulation through the contaminated zone. A typical system usually includes injection and production wells and equipment for the addition and mixing of the nutrients (Lee et al., 1988). A typical system in which nutrients are mixed with the groundwater and circulated through the contaminated aquifer by injection and extraction wells is illustrated in Figure 8.

A second method of introducing materials to the subsurface is through the use of infiltration galleries (Figure 9). Infiltration galleries allow for a more uniform distribution of the injection solution by releasing the materials from the surface in a trench or lagoon-type basin. The solution travels through the unsaturated zone as well as the saturated zone, resulting in potential treatment of source materials that may be trapped in the pore spaces of the vadose zone (Sims et al., 1992). This method is not nearly as effective as remediation below the groundwater table due to existence of preferential pathways. Because of preferential pathways for flow in the vadose zone, not all voids are saturated with enriched groundwater, which would fail to contact a significant portion of the mass of pollutants (LeGrega, 1992).

Another method used for in-situ bioremediation of contamination in the vadose zone is known as a "dry" method. Rather than reinjecting groundwater, air can be injected in the capillary fringe above the groundwater table and exhausted at the ground surface through an air stripping unit. With proper controls, this upflow system can stimulate biodegradation, thereby reducing the treatment requirements of the exhaust air (Ostendorf and Kampbell, 1990). Horizontal wells can be used to develop the "dry" method approach. The horizontal system is expected to provide significant advantages over conventional bioremediation nutrient delivery techniques. The increased surface area will allow better delivery of nutrients and easier recovery of gas and water, as well as minimizing formation clogging and plugging phenomena (Hazen, 1992).

Typically, the amendments are added to the contaminated aquifer in alternating pulses which reduces the tendency to clog as compared to continuous addition. Inorganic nutrients are

Figure 8. Typical schematic for aerobic subsurface bioremediation (Thomas and Ward, 1989).

Figure 9. Use of Infiltration gallery for recirculation of water and nutrients in in-situ bioremediation. (Thomas and Ward, 1989).

usually added first through the injection system, followed by the oxygen source, or in the case of halogenated organics, methane and/or oxygen, if aerobic degradation is to occur. Simultaneous addition of any two may result in excessive microbial growth close to the point of injection and consequent plugging of the aquifer. If an alternating injection approach is not used, high concentrations of hydrogen peroxide (greater than 10%) can be used to remove biofouling and restore the efficiency of the system.

Case Studies

Moffett Naval Air Station. A field-scale evaluation of in-situ bioremediation of halogenated organic contaminants, which tested the feasibility of methane monooxygenase induction to degrade alkyl halides, was performed at the Moffett Naval Air Station in Mountain View, California. The methanotrophic bacteria were stimulated in a field situation by providing supplies of methane and oxygen. Several halogenated organic contaminants, including trichloroethene (TCE), cis- and trans-dichloroethene (cis- and trans-DCE), and vinyl chloride (VC), were evaluated with regard to transformation under biostimulation conditions. The study was assessed by means of controlled addition of chemicals, frequent sampling, quantitative analysis, and mass balance comparisons. The following discussion will only attempt to summarize the highlights of the study. A more detailed discussion can be found in the results presented by Roberts et al. (1990) and Semprini et al. (1990, 1991).

Site conditions at Moffett Naval Air Station were near-ideal and led to its selection for a pilot-scale field study. Representative of a typical situation in the San Francisco Bay area, the shallow aquifer was contaminated with chlorinated aliphatics which had been used as solvents (Semprini et al., 1992). The hydrologic system was a shallow (4-6 meter), highly permeable ($K \approx 200$ ft/d) sand-gravel aquifer that was confined by overlying and underlying silts and clays (Chapelle, 1993). The soil solids exhibited a wide size range, with approximately 70 wt% > 2 mm and 10 wt% < 0.1 mm. The organic carbon content of the aquifer solids was 0.11% and the specific surface area was 5 m^2 (Semprini et al., 1992). The groundwater was also determined to be favorable for the bioremediation study. The water was moderately saline (TDS of 1500 mg/l) and had no appreciable amounts of toxic metals (Roberts et al., 1989). Nitrate and phosphate were present at 10 mg/l and 0.1 mg/l, respectively. A substantial amount of 1,1,1-trichloroethane was present in the site groundwater, but the targeted and tested for chlorinated alkenes (TCE, 1,2-DCE isomers, and VC) were not detected in the native groundwater (Roberts et al., 1990).

Transmissivity of the groundwater was shown to be sufficiently high ($\approx 100 \text{ m}^2/\text{day}$), which permitted water to be extracted at a design rate ($\approx 10 \text{ l/min}$) that did not cause excessive drawdown at the extraction well (Semprini et al., 1992). Bromide tracer tests were used to establish transport velocities and residence times in the test zone. Results confirmed that the aquifer was virtually completely permeated by the injected fluid and an overall mass balance demonstrated that tracer recovery in the extracted water was essentially complete. The ability to recover essentially all the bromide tracer reduced the error in mass balances used to estimate the degree of biotransformation of the chlorinated organics in later experiments (Roberts, et al., 1990).

- 4) An intermediate transformation product, trans-DCE oxide, was produced as a result of trans-DCE oxidation, which is consistent with the proposed transformation pathway.
- 5) Methane completely inhibited the rates of transformation of the chlorinated aliphatics.
- 6) The substitution of formate and methanol for methane temporally enhanced the rates of transformation of the chlorinated aliphatics.
- 7) Active utilization of an energy source (methane, formate, or methanol) in the biostimulated zone was required for chlorinated aliphatic biotransformation to occur.

In addition to the above results, another study was performed by Hopkins et al. (1992) that evaluated enhancement of in-situ aerobic biodegradation of cis- and trans-1-trichloroethylene and cis- and trans-1,2-dichloroethylene by phenol-utilizing bacteria at the Moffett site. Research has demonstrated that aerobic microorganisms grown in phenol or toluene can initiate the cometabolic oxidation of chlorinated aliphatic compounds to stable nontoxic end products (Wackett and Gibson, 1988). Such microorganisms possessing toluene oxygenase (TO) have good potential for bioremediating aquifers contaminated with halogenated organics and their anaerobic and abiotic transformation products. The objective of this study performed at the Moffett site was to evaluate the TO system for in-situ biodegradation of TCE, c-DCE, and t-DCE by phenol and oxygen addition (Hopkins et al., 1992).

This set of tests was performed along side of the previous zone of study to allow for a comparison of results. The same stimulus-response experimental methodology was used as in the previous study. Bromide tracer tests indicated the aquifer had good hydraulic characteristics. Next, the test zone was contaminated with TCE, c-DCE, and t-DCE at concentrations of 30 µg/l, 40 µg/l, and 40 µg/l, respectively. The transport of the compounds was retarded due to sorption onto the aquifer solids. TCE was more highly retarded than c-DCE, which agreed with previous findings (Hopkins et al., 1992). No transformation was evident with just the contaminants being present with oxygen alone.

Biostimulation was achieved by injecting phenol after steady-state contaminant concentrations were achieved. Phenol was pulse injected for 1 hour in 8 hour pulse cycles at concentrations of 50 mg/l. The phenol injection concentration was doubled after 520 hours, and then was reduced to the original concentration after 840 hours. Significant degradation of c-DCE and TCE was observed during the low level of phenol addition. The c-DCE concentration decreased by approximately 60 to 70% and TCE by 20 to 30%. Doubling the phenol concentration resulted in even greater transformations of both TCE and c-DCE. During this period TCE was transformed by 85 to 90 percent and c-DCE by over 90 percent. t-DCE was not transformed as significantly, which agrees with the observations from the laboratory (Hopkins et al., 1992).

Evidence of competitive inhibition of cometabolic transformation by phenol was seen in the field results. When phenol concentrations were high during times of pulsing, the

concentration of c-DCE and t-DCE increased, even though they were not pulsed. These results are consistent with those observed for the methanotrophs and indicate that competitive inhibition affects the cometabolic transformation rates (Hopkins et al., 1992).

In summary, for the tests performed at the Moffett site, it is evident that a phenol-utilizing and methane-utilizing population that effectively degraded TCE and c-DCE could be stimulated in-situ. The phenol-utilizing population degraded up to 90% of the TCE in a 2 meter biostimulated zone, as compared to the 20 to 30% observed by the methane-utilizing bacteria. However, there is some question to how common the phenol enzyme system (TO) is to the environment and whether a more environmentally acceptable compound can be used to induce an indigenous TO population.

Savannah River. A series of environmental technology field tests, including in-situ bioremediation, are being conducted at the Savannah River Integrated Demonstration site near Aiken, South Carolina. The Savannah River Site (SRS) is owned by the Department of Energy and has been involved in nuclear weapons manufacture since it was built in the 1940's (Chapelle, 1993). Degreasing operations were performed at the site and due to these activities TCE, TCA and PCE were discharged to a seepage basin via a process sewer pipeline. In the early 1980's, inspections revealed that the process sewer line had extensive cracks, allowing solvents to leak into the subsurface environment (Travis et al., 1993).

A technical task plan has been developed for the SRS and includes selection, demonstration, and evaluation of innovative remediation technologies, with an emphasis on in-situ methods. The first phase of the SRS Integrated Demonstration involved demonstration of in-situ air stripping to remediate both soils and groundwater contaminated with volatile organics. This was accomplished by first installing two horizontal wells below the abandoned process sewer line. A deep horizontal well, installed below the water table, has been used as an air injection well. A shallow horizontal well, installed in the vadose zone, has been used to vacuum extract volatiles from the vadose zone and upper saturated zone in the area. During the first phase, these wells were used to demonstrate a simple mass transfer process to remove VOC's from both the groundwater and vadose zone. During a 20 week test, 16,000 lbs of VOC's were extracted from the subsurface (Hazen, 1992). Currently (started up in the spring of 1992) the second phase of the demonstration is underway which involves a full-scale demonstration of in-situ bioremediation using methane injection at the same site where in-situ air stripping was employed.

The overall objective of the current project is to demonstrate the utility of stimulating indigenous microorganisms that will degrade trichloroethylene, tetrachloroethylene, and their daughter products as a treatment process for contaminated groundwater and sediment. Laboratory studies using TCE/PCE contaminated sediment and groundwater from the SRS have demonstrated that a variety of simple carbon sources, e.g. methane, will stimulate a microbial community that will degrade the contaminants to carbon dioxide and chloride (Hazen, 1992).

An additional objective is to demonstrate that the horizontal wells can be used as an effective delivery and recovery mechanism for bioremediation. The scale of the hydrologic

system at the SRS is much larger than at the Moffett site and the contaminated area is located approximately 140 feet below the land surface which created several technical problems. The most serious was to design a system of wells that could efficiently deliver oxygen and methane to the zone of contamination. The horizontal wells that form the basis for the SRS Integrated Demonstration should provide significant advantages over conventional bioremediation techniques. The increased surface area will allow better delivery of nutrients and easier recovery of gas and water, as well as minimizing formation clogging and plugging phenomena (Hazen, 1992).

The in-situ bioremediation system began by injecting air into the saturated zone, where the deep well was located, and withdrawing air from the shallower well in the unsaturated zone. After two months, methane was added to the stream of injected air at low concentrations (1 to 3% by volume). It was soon realized that a major challenge was to assess the relative effectiveness of biologic and nonbiologic processes in remediating the contamination. Simply injecting and retrieving air will effectively remove contamination because of the volatility of TCE. Thus, simply documenting decreasing concentrations of TCE in the aquifer will not sufficiently demonstrate that effective bioremediation is occurring at the site. Data from the previous demonstration of in-situ air stripping, where air alone was injected at different rates will be used to provide baseline geological, hydrological, chemical, and biological characteristics. The data from phase I will establish the effect of air injection without nutrients on the site, in effect providing a unique and dramatic control experiment for the bioremediation demonstration (phase II) (Hazen, 1992).

This difficulty of assessing the relative importance of biologic from nonbiologic effects in contamination removal is common to all in-situ bioremediation systems. While a detailed discussion of results from the SRS was not available for this review, the sampling program results show that concentrations of TCE and the population of methanotrophic bacteria were fairly constant during the injection period. However, with the addition of methane, numbers of methanotrophs increased and the concentrations of TCE declined noticeably. The data suggest that methane addition contributed to a buildup of methanotrophic bacteria with a consequent increase in TCE biodegradation rates. However, as of now the data is still indirect and inconclusive (Chapelle, 1993). The study at the Savannah River Site will be a benefit in establishing the effectiveness of biologic relative to nonbiologic processes in all bioremediation systems.

Hanford, Washington. Presently underway is a development and demonstration program that will test in-situ bioremediation technology for treating nitrates and carbon tetrachloride at the Department of Energy's Hanford Site located in southeastern Washington State. The VOC contamination at the Hanford Site is typical of the VOC problem across the DOE complex. The operations at the Hanford Site have been dedicated to nuclear materials production, generation of electricity, diverse types of research, and waste management over the last 40+ years. These operations have produced aqueous and organic waste that were subsequently discharged to the soil column. A minimum of 637 tons of carbon tetrachloride was disposed to the subsurface, primarily between 1955 and 1973 (Brouns, 1993).

The subsurface at the area of contamination consists of approximately 58 to 65 meters of unsaturated sediments and approximately 70 meters of saturated soil overlying low permeability silts and clays and basalt rock. Carbon tetrachloride vapors have been encountered during well drilling operations. The highest concentrations of CCl_4 were measured 450 meters downgradient of the disposal facilities at levels exceeding 1000 times the U.S. EPA drinking water standards of 5 ppb (Brouns, 1993). This site has been selected by the DOE's Office of Technology and Development for a host site for the Integrated Demonstration for Cleanup of Volatile Organic Compounds at Arid Sites. The objective of the integrated demonstration is to develop, demonstrate, evaluate, and transfer for development new technologies for all phases of cleanup of VOCs and associated contaminants in the subsurface. The goal is to bring new technology forward to provide more effective, less expensive, and safer methods for cleanup. Bioremediation is one technology being evaluated to meet these goals.

The conditions that favor biodegradation of carbon tetrachloride are predominantly anaerobic and it has been demonstrated in pure cultures and consortium of denitrifying *Pseudomonas* sp. that carbon tetrachloride can be biodegraded to carbon dioxide and other metabolites (Brouns, 1993). Biodegradation of carbon tetrachloride under denitrifying conditions is of particular interest because of the occurrence of both nitrates and CCl_4 in the unconfined aquifer at the Hanford Site.

The potential for bioremediation of the Hanford Site was initiated in 1987 and number of laboratory studies have been performed. The studies have focused on the effects of important environmental conditions such as pH, temperature, redox potential, and the concentrations of substrate, electron acceptor, and contaminants as well as kinetics of degradation and growth of microorganisms. Through these types of studies and intermediate-scale flow-cell experiments, and three-dimensional computer simulations, a field test site is under development, and will be completed in early FY 1994.

Field testing at the Hanford site will focus on demonstrating: 1) destruction CCl_4 and nitrate, 2) effective nutrient addition strategies that minimize biofouling, 3) novel well designs and mixing strategies to enhance subsurface mixing, and 4) a design methodology for deploying bioremediation that includes laboratory and column studies, and 1-,2-,3-D design simulations (Brouns, 1993).

St. Joseph, Michigan. The last site to be discussed is the St. Joseph Superfund site in Michigan. This industrial facility site was selected to illustrate the use of methodologies for determining the potential for methanotrophic in-situ bioremediation which had been previously established at the Moffett site. The aquifer at the St. Joseph site is relatively homogeneous and heavily contaminated (0.8 to 8.0 mg/l) with trichloroethylene, 1,2-cis-dichloroethylene, 1,2-trans-dichloroethylene, and vinyl chloride. While no actual field studies have been performed, the objectives of this evaluation were to:

- Determine whether a native population of methanotrophs were present, and if so, evaluate their ability to degrade the contaminants.

- Determine if sorption of the contaminants to the aquifer materials would create problems.
- Use a non-steady-state model to evaluate likely designs for in-situ treatment.

To establish whether a native population of methanotrophs were present samples were retrieved from the contaminated site. To avoid sample contamination, collection of aquifer samples were performed in accordance with protocol designed by Wilson and Leach (1989). Next, column microcosm studies were performed. The glass column microcosms had a volume of 133 ml, contained about 200 g of aquifer material and were constructed and operated as described by Roberts et al. (1989). In addition to determining if the indigenous methanotrophic bacteria were present, these studies also allowed an estimate of the time required to increase the population of the bacteria to an adequate level for bioremediation and assess the capability of such a stimulated population to degrade TCE, t-DCE, and c-DCE.

The results from the microcosm studies presented by Semprini et al. (1992) revealed that the methanotrophic population may not have been evenly distributed throughout the columns and that the populations were much lower than in the Moffett study as evidenced from the low activity and methane uptake. The time required to achieve removals of 95% for VC, 80% for t-DCE, and 30% for TCE was approximately 110 days with varying removals at intervals up to this time.

The simulations studies were successful in reproducing the findings from the Moffett site and were used to analyze possibilities for application of in-situ bioremediation at the St. Joseph site. The simulations served primarily to indicate the factors in an in-situ treatment scheme and the time scales that must be considered. Semprini et al. (1992) uses the simulations to conclude that for this case a total of 480,000 m³ of aquifer would be treated in 400 days, using a total extraction rate of 400 gpm. A total of 1375 kg of the original 1617 kg of contaminants present in the treated volume would be biodegraded to nontoxic endproducts. This treatment would require 5,200 kg of methane and 19,200 kg of oxygen. Since developing in-situ bioremediation by simulations studies have not been attempted before, there are many possibilities for improvement of design. The simulations help bracket the probable range of outcomes, and thus should help enormously in the design and interpretation of demonstrations, such as the one planned for the St. Joseph site.

Conclusions for 5.1.3 (Field Applications)

A number of field-determined factors may limit the application of in-situ bioremediation of chlorinated solvents. These include the ability to deliver nutrients, electron acceptors and gases, especially where soil permeability is limited. Toxicity problems may also occur either due to substances in the formation such as heavy metals or due to high concentrations of amendments added. However, a variety of solutions are being evaluated to mitigate unfavorable site conditions. These include modification of site conditions and improved methods of delivery of needed amendments.

A review of some actual field studies underway showed that it is possible to successfully stimulate the growth of desired organisms for degradation of chlorinated aliphatic compounds achieving significant levels of removal.

5.2 Research Planned for Next Quarter

The discussion of research planned for next quarter is divided into two main sections. First a number of issues (Section 5.2.1) are discussed that must be considered when carrying out laboratory research using chlorinated aliphatic compounds so as to follow good quality control procedures. This section is based on a review of the literature in this area. The second section (5.2.2) discusses the actual work planned for the quarter.

5.2.1 Important Laboratory Control Considerations When Evaluating Biodegradation of Chlorinated Solvents

A review of the literature revealed a number of issues that must be considered when studying bioremediation of halogenated volatile organic contaminants such as TCE and PCE. The issues are divided into four groups below: biotic versus abiotic removal, the use of mass balances to quantify removal, the use of control cultures, and a discussion of culture types and culture media.

Biotic Versus Abiotic Removal. In addition to biodegradation, chlorinated volatile organic contaminants in an aquifer can undergo abiotic photodegradation or can be transferred into the vapor phase via air stripping. Photodegradation in the lab can be easily minimized or eliminated completely by the use of opaque container vessels and care during transfer. The minimization of the effects of air stripping under aerobic conditions is more difficult. While air stripping of volatile organics may go hand in hand with biodegradation as a remediation alternative, it is important in the laboratory to determine to what extent volatile removal is the result of abiotic or biotic activity. This might be accomplished by monitoring VOC concentration in the off gas during testing. Another method that has been used to quantify actual biological activity is to determine changes in the number of microorganisms or microbial growth as it occurs during contaminant degradation (Chapelle, 1993). Here it is assumed that if there is microbial growth, there will be biological degradation of the secondary substrate.

Use of Mass Balances to Quantify Contaminant Removal. In order to thoroughly understand how VOC degradation can be controlled or enhanced, proper assessment of its phase composition in a given system must be made. The amount of contaminant that is available to the microbial cells depends on its dissolved concentration in the aqueous film surrounding the matrix. This concentration depends on a number of factors, namely, the contaminant's concentration in the vapor phase, and contaminant sorption to cell components or vessel surfaces. Henry's Law may be applied to determine to what extent the contaminant will remain in solution at a given temperature, pressure and vapor:water, (volume:volume) phase ratio. It should be understood that oxidation of the contaminant in the liquid phase would result in re-equilibration between gas and liquid phases so that most of the contaminant would eventually become available to the cells (Wackett et al., 1989), but the reverse may

also be the case in a system where the vapor is recycled. As mentioned earlier, the amount of contaminant that might be removed in a recycled vapor phase (i.e. air stripping) might be determined by monitoring the off gas. In addition, careful application of Henry's Law at each volume, temperature, or pressure change would assist in this determination.

The extent to which the contaminant might be sorbed to cell components or vessel surfaces is not so easily determined. However, one method (Fogel et al., 1986) is to introduce radioactively labelled contaminants into the system such as C_{14} . The radiocarbon is then traced with time as it appears in the cell mass, or as CO_2 or as non-volatile byproducts.

Use of Control Cultures. The use of control cultures assists in determining the amount of microbial activity occurring in a system. Abiotic systems containing no microbial culture may be used to determine the extent of abiotic degradation occurring given that all other conditions remain constant throughout the sample group. Analysis of these controls may also be used to approximate Henry's Law constant under such conditions (Folsom, et al., 1990).

Killed culture samples run in parallel with live culture samples also serve to differentiate between abiotic and biotic degradation, and their use was reported in all literature reviewed. Killed cultures can determine to what extent the contaminant is sorbed to the cell components. For instance, if radioactively labelled carbon is found in the biomass of a live culture and not in the biomass of a killed control culture, it may be assumed none of the contaminant was sorbed to the cell components and was instead incorporated into the cell mass (Fogel et al, 1986).

Culture Types and Culture Media. The microbial species most often used in the literature reviewed are those originally aquired and isolated from soil samples of actual groundwater aquifers contaminated with chlorinated volatile organics. These sites include the Savannah River Site, S.Ca, Oakridge, Tennessee, Traverse City, Michigan and Moffett Field Naval Air Station, California. Other sources of these bacteria that have been used are local landfills, lagoons, river beds and sewage treatment plant digesters in close proximity to the research base. Both methanotrophs and methanogens are indigenous to these sites and are acclimated to the contaminated environments. In cases when complete mineralization is of concern, the heterotrophs indigenous to the site are cultured and used as well. The microbes can be selectively isolated by the use of commercial selective medias depending on the substrate sources required. Methanogenic and methanotrophic organisms may also be obtained in pure cultrues from sources such as the American Type Culture Collection.

All microorganisms require a source of carbon for reproduction and increasing biomass. They also require sources of energy, electron acceptors (oxidation), and donors (reduction), nutrients (N, K, P) and trace metals (Ca, Fe, Cu), for carrying out metabolic activity. As mentioned previously, for the methanotrophs, these include methane, oxygen, nitrate, and iron respectively. For methanogens, these include acetate or methanol, carbon dioxide, ammonia and iron. Normally in an aquifer, these sources are in adequate supply. In the laboratory, they must be provided, and there are numerous commercial products available

that are specific for methanotrophs and methanogens, or nonspecific for mixed populations which may or may not include heterotrophs. The same medias may be used to test for culture purity. If a suspected pure methanotrophic culture is streaked onto a media containing growth substrates that are not useable by methanotrophs and there is growth, the culture is contaminated. The microbes in the literature reviewed were isolated and maintained most often on commercial modified mineral or basal salts mediums and subcultured continuously to ensure viability. In one study, methanotrophic species were tested for heterotrophic contamination by streaking on tryptone-glucose plates (Henry et al, 1991).

Temperatures used during incubation range from 20 to 35 °C depending on the optimum growth temperature of the particular bacterial species used. Methanogens generally prefer the higher temperatures (35 °C) often found in anaerobic digesters, while the methanotrophs can withstand temperatures of a much broader range depending on the particular species. Methanotrophic cultures are fed mixures of air and methane throughout growth and maintenance either by injection into sealed storage containers or during plate incubation in dessicators. These cultures are usually incubated on rotary shakers or in continuously stirred reactors. Shaking is often minimalized or done before the introduction of volatile contaminant substrates for initiating degradation rate analysis so as to avoid abiotic oxidation that may occur. Methanogenic cultures are kept relatively quiescent to discourage the introduction of oxygen into the system. Reducing conditions can be controlled by the addition of sodium sulfide and the headspace kept as a mixture of $N_2 : CO_2$ (Kuhn and Sufliata, 1989).

5.2.2 Specific Tasks

Now that the Phase 1 task of reviewing the literature has been essentially accomplished, the Phase 2 batch studies to evaluate optimum concentration of growth enhancing agents in both liquid and soil cultures will be initiated (see task description under Section 4.0). Methanotrophic bacterial cultures, available in the WVU Department of Biochemistry, will be used initially for the Phase 2 work. It is planned that organisms obtained from sites contaminated with organic solvents will be used later in the research. Methanotrophic bacterial cultures will be grown in erlenmeyer flasks by nitrate mineral salts (NMS) media ammended with vitamins, and sodium-potassium buffer solutions. The flasks will be stoppered and attached to a vacuum methane manifold through which methane and air mixtures can be added. Cultures will be harvested by centrifugation and stored in Pipes buffer solution at pH 7. The extent of aerobic bacterial growth will be monitored using membrane filtration plate count techniques or turbidity measurement.

Methanogenic organisms will be obtained from the American Type Culture Collection. Initially, the organisms will be grown using carbon sources such as methanol, acetate and formate. Experiments will then be carried out with TCE to observe its reductive dehalogenation to compounds such as 1,2 DCE and VC. Methanogenic acitivity will be monitored, in part, using an anaerobic respirometer. In this way, the viability of a culture in relation to introduced compounds as well as the ability of the culture to use or degrade those compounds can be assessed. The respirometer will allow evaluation of liquid based and soil based bioremediation activities.

If good progress is made on Phase 2 tasks and time permits, Phase 3 (columns studies) and Phase 5 will be initiated in this quarter. Based on the literature review, the Phase 5 combination of methanogenic and methanotrophic sequential activity appears quite promising.

The literature review established that analysis of halogenated volatile organic contaminants is most often accomplished using gas chromatography with either electron capture or flame ionization detectors. In one study, a photoionization detector was used to quantify vinyl chloride, a thermal conductivity detector for quantifying methane and carbon dioxide, and a flame ionization detector used for quantifying propane (Phelps et al. ,1990). Analysis of halogenated volatile organics and their degradative byproducts, for this research project will be performed according to U.S. EPA protocol, using EPA Method 8010 for determination of volatile organic compounds via gas chromatography. Quality control procedures will follow protocols outlined in Method 8000 and will include the use of sample blanks and spikes. Samples will be analyzed using direct injection or purge and trap (Method 5030) . Solvents and standards used will be reagent grade, and samples will be contained in glass septum vials with no headspace. In those cases where headspace is produced in a vial due to removal of a sample for analysis, the partitioning of the analyte in the aqueous and vapor (headspace) phases will be taken into consideration.

6.0 CONCLUSIONS

A major accomplishment this past quarter was completion of the literature review which is serving to guide the research program. Based on the review, it was decided to concentrate the research on bioremediation of chlorinated aliphatic solvents which are often found in the subsurface at contaminated DOE sites.

Comparison of the metabolic pathways utilized by the methanogenic and the methanotrophic groups of bacteria for degradation of chlorinated solvents suggests that the efficiency of bioremediation could be aided if the symbiotic relationship between the two were encouraged. The methanotrophs have an obligate requirement for methane, which is complimented by methane production by the methanotrophs. Furthermore, the methanogens ability to dehalogenate more oxidized (more halogenated) contaminants such as PCE, generating vinyl chloride, is complimented by the ability of the methanotrophs to mineralize vinyl chloride and other small mono-chlorinated compounds. Exploration of sequential anaerobic and aerobic biodegradation using these organisms offers to improve the attractiveness of in-situ bioremediation for mineralization of chlorinated solvents.

While a number of site-determined factors may limit the effectiveness of in-situ bioremediation, a review of some actual field studies which have been completed or are underway suggests that it is possible in many cases to overcome difficult site conditions. Actual field application of in-situ bioremediation has been shown to be able to stimulate the growth of desired organisms for degradation of chlorinated aliphatic contaminants and achieve significant levels of removal.

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Work during the next quarter is planned to evaluate the optimum concentration of growth enhancing agents in both liquid and soil cultures. Both methanogens and methanotrophs will be utilized.

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Excavation Systems for Hazardous Waste Sites: Dust Control Methods for In-situ Nuclear Waste Handling

**Quarterly Technical Progress Report
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INTRODUCTION

This project focuses on how to deal with improperly disposed of in-situ hazardous wastes for which some of the packaging or land barriers have failed and the contaminants have been mobilized. The underlying and adjacent soils become contaminated and contaminants leach from the wastes and seep into the adjacent soils. In most sites, the hazardous wastes have infiltrated the soils, and the dispersion of waste constituents over an extended period has been extensive enough to contaminate adjacent properties.

Several alternatives of remediation have been proposed by DOE or EPA for cleanup of the contaminated sites. Complete excavation or removal of hazardous wastes and contaminated soils from the sites is only recommended for some specific hazardous waste sites. The advantages of this method are:

- (1) the source of the contamination is fully removed from the site;
- (2) unrestricted future use of the site is generally possible;
- (3) no long-term monitoring, maintenance, or surveillance programs are required.

In order to safely perform the excavation/removal of in-situ hazardous wastes, equipment selection and modification of the existing dust control techniques are two major tasks to be addressed in in-situ hazardous waste material handling. A literature review was performed focusing on existing equipment and dust control techniques used in related fields. A design consideration for equipment selection emphasizing dust control is proposed.

EQUIPMENT SELECTION

Equipment selection for excavating or removing in-situ hazardous waste depends on the occurrence of the waste site, physical properties of the hazardous waste present as well as dust control methods. In other words, equipment selection is site-specific and varies with excavation/removal processes. The major factors for equipment selection are analyzed, and three excavation/removal systems are

modified according to the major factors and the surface mining methods. The equipment in the whole excavation/removal processes is divided into five types. In this report only the first type, excavation equipment will be covered.

THREE MAJOR FACTORS

The following three major factors in equipment selection were selected based on case studies with respect to waste occurrence, site contaminants and dust control methods at the different hazardous waste sites.

Waste Occurrence

So far, a total of 1,035 Superfund and other hazardous waste sites have been recorded. All of the sites are partitioned into 10 regions by EPA. Based on the case studies at 100 hazardous waste sites, the occurrence of the hazardous wastes generally appears in three types, i.e. above ground, underground and combination (above and under ground). For every type of waste occurrence, there are three scales of waste sites, i.e. small, middle and large in terms of the geometric parameters. The parameters need to be considered in the equipment selection for each type of waste occurrence are:

- a. Above Ground - covered area, height, and volume
- b. Underground - covered area, overburden depth, thickness/depth, and volume
- c. Combination (above and underground) - covered area, height, overburden depth, thickness/depth, and volume

With this classification scheme, it is very convenient to select equipment for the excavation/removal processes based on equipment suitability and capacity.

Contaminants in Waste Site

Other debris/materials are always found in an improperly disposed hazardous waste site. The estimated debris/materials occurring in a hazardous waste site range in quantity from less than 1 percent to greater than 80 percent of the total waste

founded on the site. The physical properties of the hazardous waste sites vary from site to site. Therefore, the most difficult activity of excavating or removing hazardous waste is the clean up of other contaminated materials instead of dealing with the hazardous waste itself. Twelve general categories of other contaminated materials have been found to be associated with hazardous waste materials based on the information from 100 hazardous waste sites for all 10 EPA regions, i.e. soil/sediments, metals, liquids, sludge, construction debris, wood/vegetation, asbestos, paper, plastic, glass and rubber. Although the physical properties of un-remedial waste sites have yet to be profiled, it should be noted that the percentages of the materials to be handled at the 100 hazardous waste sites are relatively constant nationwide. For example, the contaminated soil, liquid, and metals (drum, etc,) are the most common forms to be handled for most hazardous waste sites.

Dust Control Method

There have been no summary reports concerning dust control methods in the excavation/removal of in-situ hazardous waste sites because of its diversity. Based on a few individual reports on the handling of contaminated soils or soil waste, two types of dust control methods were found and are summarized as follows:

a. Free Surface Opening

The free surface opening method implies that there is no portable building, rigid-frame enclosure or other facility erected on site to control fugitive emission during waste excavation/removal processes. The excavation/removal operations can be designated as a,

- 1) Continuous operation or as a,
- 2) Discontinuous operation.

So far, the free surface opening with discontinuous operation is utilized in most cases for in-situ excavation/removal of hazardous waste sites. But, the free dust generation utilizing this method constitutes a most critical disadvantage.

b. Enclosure Surface Opening

To reduce fugitive dust release to nearby communities during the waste excavation/removal processes, the enclosure surface opening is used. The enclosure surface opening method was designed under the sponsorship of the Superfund Innovative Technology Evaluation (SITE)

program as a trial excavation. The enclosure surface opening implies that prior to excavation or the removal of any hazardous waste, the portion of the site to be excavated is enclosed with a portable building, a rigid-frame enclosure or some other facility. The excavation/removal activities takes place within the enclosed space. Under the enclosure surface opening, the operations of waste excavation/removal can have the following alternatives based on the depths of the contaminated hazardous waste materials,

- 1) Isolated single level operation or
- 2) Isolated double level operation.

One example of the enclosure surface opening with isolated double level operation was employed at McColl Superfund site.

THREE MODIFIED EXCAVATION/REMOVAL SYSTEMS

According to the three major factors discussed above and the existing surface mining methods (i.e. small surface coal mine operation, conventional surface mining and continuous surface mining), the excavation/removal systems for in-situ hazardous waste site handling are defined in this study as processes which excavate and transfer the in-situ hazardous waste materials (waste itself and contaminated materials) to offside or on-site treatment and/or disposal facilities. These excavation/removal systems are divided into three categories, i.e., small scale, conventional, and continuous systems which have been modified for the purpose of equipment selection in this project.

Small Scale Excavation/removal System

The small scale excavation/removal system is capable of exploiting small or isolated hazardous waste sites which may deposit under/or above steep slope, rolling or flat terrain with thick top-cover or small debris. The system can handle almost all types of hazardous waste sites. Both the free surface opening and the enclosure surface opening are applicable to this system.

Conventional Excavation/Removal System

This system is designed for excavating or removing medium or large hazardous waste sites with all kinds of contaminated solid materials except liquid and sludge materials. The surrounding of the sites and the occurrence of the deposited wastes can be different. Only free surface opening is recommended in consideration of the system efficiency.

Continuous Excavation/Removal System

The continuous excavation/removal system is designed to take dust control and safer operations into consideration for some specific hazardous waste sites such as high-volume, low-level nuclear wastes. The system is suitable for any dimension of soil/sediment hazardous waste sites. Both the free surface opening and the enclosure surface opening can be used for this system.

EXCAVATION EQUIPMENT FOR THREE MODIFIED EXCAVATION/REMOVAL SYSTEMS

The versatility of the three excavation/removal systems is governed by the equipment chosen based on the three major factors. According to 22 case studies of the hazardous waste sites, it is recognized that all equipment used for the excavation/removal systems can be classified into five types, i.e. excavation, packaging/loading, transportation, unloading/restoration and personal protection. Only the major excavation equipments are summarized in this report.

Excavation Equipment for Small Scale Excavation/Removal System

The excavation equipment used for a small scale excavation/removal system generally operates in a batch rather than a continuous mode. This aspect has the advantage of dealing with localized areas of contamination within a hazardous waste site. The major excavation equipment according to the statistical record for 100 case studies of the sites are:

- a. Backhoe - an excavator for subsurface work. The backhoe is the most common materials-handling equipment extensively used for solids and

sludge excavation/removal. It may be crawler-mounted (trackhoe) or wheel/tire-mounted, and is easily controlled for precise width and depth excavation. A backhoe can excavate both hard and compacted materials.

- b. **Front-end Loader** - a wheel or crawler mounted tractor with a front mounted bucket. It is utilized in excavating, loading and transporting materials. Because of its excellent flotation and traction capacities, the crawler-mounted loader is ideal for unstable uneven terrain, but the wheel-mounted loader is faster and more mobile than the crawler-mounted machine.
- c. **Bulldozer** - a crawler or wheel driven tractor with a front mounted blade for digging, ripping and pushing materials. A bulldozer is frequently used for excavating cover materials, contaminants, constructing temporary or permanent dikes, and doing compaction.
- d. **Skid-Steer Loader** - commonly referred to as a "Bobcat." It can be equipped with a variety of hydraulically controlled bucket, grapplers, and lifting attachments. Skid-steer loader has excellent application for hazardous waste site work. They can perform many of the same functions as the much larger front-end loader in a small area. Therefore, the skid-steer loaders are ideally suited for the enclosure surface opening.
- e. **Forklift Truck** - heavy-duty rubber-tired truck available for off loading of equipment from trucks, on-site hauling over short distance, and loading, staging, and transportation of drums. Although this piece of equipment requires a flat, relatively stable terrain, additional tractability can be provided with 4-wheel-drive units.
- f. **Dragline** - utilizes a long reach and the ability to dig to substantial depths below itself. The dragline can be used for the handling the in-situ hazardous waste materials. It eliminates the vertical lift for deeply located wastes. Because of its unique capacity to rotate and dump at a substantial distance, a dragline can not only remotely excavate, but can also directly load the waste materials which is often blocky or contains boulders directly onto transport vehicles.

Currently, a tele-operated remote-controlled excavator (wheel-mounted) is

being marketed. This unit can be used for excavating, bulldozing, heavy lifting, concrete breaking, or remote handling of low-level radioactive wastes. It can be operated up to a mile away via radio transmission, coaxial cable, or fiber-optic cable which provides maximum worker safety. A cab-mounted camera allows for overall or close-up viewing of the work area.

Excavation Equipment for Conventional Excavation/removal System

Basically, the equipment for the conventional excavation/removal system are arranged much the same way as those of the small scale excavation/removal system except having larger capacity. The shovel/truck operation is also recommended as major equipment for this system.

- a. Shovel - oldest type of excavation equipment. In recent years, smaller shovels are being replaced by the front-end loader. Some shovels with high capacity are still utilized in extremely rugged applications. Shovels are particularly suitable for severe digging conditions. They are available in larger sizes, but operate under flat terrain conditions.
- b. Truck - the other partner in shovel/truck operation, has expanded applications for overburden handling in continuous surface mining. The off-highway trucks are developed to match the demand of shovel/truck operation. There are two basic off-highway trucks, i.e. rear dump and bottom dump.

Excavation Equipment for Continuous Excavation/removal System

The equipment used in the continuous excavation/removal system combines several pieces of excavation equipment into one unit and consequently can dig and discharge materials simultaneously. Usually, equipment for packaging, size reduction and loading are unnecessary, since materials are discharged directly onto conveyors, trucks or other containers.

Bucket wheel tractor (BWT), which is being broadly used in continuous surface mining and in other areas such as The Portage Mountain Dam Project and Athabasca Oil Sands Project, is introduced as one type of excavation equipment for the continuous excavation/removal system. Auger is also available for this system.

There are three types of bucket wheel tractors, i.e. large stripping wheels, medium sized machines of conventional design, and small diameter fixed wheels. The smaller diameter fixed wheel with side-mounted bucket wheel tractor is recommended for handling hazardous wastes.

For major excavation equipment, a wide variation in equipment type and working capacity exists. The comparative parameters are usually size, weight and horsepower range for the representative types of equipment. Generally, equipment with smaller size, less weight or horsepower can be used in small scale and continuous excavation/removal systems, and medium size, weight or horsepower can be used in conventional excavation/removal systems. But, it is not economical to apply equipment of larger size, heavy weight or huge horsepower for handling in-situ hazardous waste materials.

TECHNIQUES OF DUST CONTROL:

DUST/VAPOR CONTROL TECHNIQUES DURING EXCAVATION

Large quantities of fine particles are generated during excavation of hazardous wastes. Dust related problems arise when fine particles become airborne and escape into the environment. If excavated wastes are volatile organic compounds (VOCs) or contain VOCs, vapors will also appear during excavation due to VOCs' exposure to air. The presence of dust/ vapors in the work site creates a potential hazard to the health of the workers and the environment around the work site.

The control of dust/vapors has been a hot research topic in many fields such as mining, mineral processing, and waste treatment. Many studies have shown that foam is an effective and economic way to control dust/vapors. A list of the application of surfactant foam in mining and hazardous waste excavation has been compiled.

Dust-Suppressing Foam

Dust-suppressing foam has mainly been studied by investigators in the mining industry in the last 20 years. Some reported more than 90% dust suppression from laboratory tests using a boring machine for cutting a coal block. Others indicated

that when using foam, the reduction in respirable dust concentration was 52.8% at the continuous miner operator position and 47.8% at the loader position.

One study investigated the main factors affecting dust-suppressing foam in the laboratory and found:

Effect of Nozzle Type. GG3 nozzle was tested in the dust chamber with a 79% dust reduction efficiency was obtained at 483 KN/m² water pressure. A full cone type air atomizer was also tested. An average of 65% dust reduction was achieved.

Effect of Droplet Size. The overall collection efficiencies of both water and surfactant solutions increased with decrease in droplet size. With water droplet, the efficiency increased from 51% at a 200 μ m mean droplet size to 81% at a 25 μ m droplet size.

Effect of Surfactant Type and Concentration. Different types of surfactants have different dust removal efficiency. The type of surfactants selected is based on the characteristics of the dust. With an increase in surfactant concentration, the removal efficiency of dust increases.

Vapor-Suppressing Foam

Aqueous, non-draining, air foams, i.e., stabilized foams are useful for control of undesirable vapors and particulates such as those found at some industrial sites (cement factories), at waste sites accepting hazardous materials (California Class I & II sites), or at National Priority List Sites during remediation activities. The products work by forming a protective barrier over a source of vapor or particulate emissions. They are sprayed onto an area and form a tough continuous foamy layer as they "cure" in place. For time periods of at least several days, these foams provide nearly total elimination of emissions of organic chemical vapors such as benzene, trichloroethylene, cyclohexane, and complete control of particulates and dust.

IT corporation used vapor-suppressing foams to control vapors during excavation of hazardous organic wastes. The vapor-suppressing foams were made by combining a foaming agent (FX-9162) and a "stabilizer" (FX-9161) with water

and air, using an educator system, and spraying this solution through an air-aspirating nozzle. Each agent is proportioned into the water line at a concentration of 6%. The foam "sets up"(makes the transition from a fluid to a flexible solid foam) in about 2 minutes.

The effectiveness of stabilized foam as a vapor-suppressing medium is influenced by foam variables such as formulation, foam depth, expansion ratio, and age, as well as the nature of the particular hazard. Laboratory and field tests were conducted with aqueous stabilized foam to investigate the effects of foam variables and the nature of the hazard on vapor suppression performance. The following trends were noted:

- (1) For a period of days, the percentage suppression of hydrocarbons did not change significantly. In a 12-day laboratory experiment with cyclohexane and a 7-day field trial with JP-5 fuel, the suppression was greater than 97%, even after the foam had dehydrated to form a membrane.
- (2) With high-polarity VOCs such as acetone and MEK, suppression was in the 90 to 100% range for the first several hours, decreased to the 80 to 90% range after 10 hours for foam application weights of at least 0.62 g/cm². The higher polarity allows these VOCs to diffuse faster than other hydrocarbons through the aqueous matrix of the foam.
- (3) In general, vapor-suppressing properties of stabilized foams were not greatly affected by variation in concentration of the FX-9162 foamer and FX-9161 foam stabilizer components. Some improvement in suppressing acetone vapors was noted when FX-9161 stabilizer concentration was doubled from 6% to 12%, whereas a slight decrease in suppression of cyclohexane vapor was noted when the FX-9162 foamer concentration was increased.
- (4) The application weight of stabilized foam used should be determined by the nature of the hazard. Lowering the application weight of 4:1 expanded foam from 0.62 to 0.31 g/cm² did not significantly hurt performance on cyclohexane; however, doubling the application weight of stabilized foam from 0.62 to 1.24 g/cm², cut acetone emissions by more than 50%.

- (5) Both laboratory and field tests showed that vapor suppression performance was affected by the foam expansion ratio, particularly with non-polar VOCs such as cyclohexane. Foams of low expansion (4:1 to 8:1) provide the best control of many VOCs. In cases of extremely toxic emissions, low-expansion foams are recommended. In some field situations, highly irregular surfaces makes a somewhat higher foam expansion a more practical choice.

The observations during trial excavation of the McColl Superfund site showed that the foam vapor suppressants could remove vapors during excavation, but they were not as effective as expected. The foam appeared to react with the highly acidic waste and the reaction reduced the effectiveness of the foam. Because the foam contained more than 90% water, a layer of mud on the surface of wastes was formed. The mud made traction difficult for the loader and personnel footing quite uncertain.

CONCLUSIONS AND WORK PLAN

During this period, a design consideration of equipment selection in terms of dust control technique for in-situ hazardous waste site handling has been proposed based on literature reviews only. The items identified in this report, i.e. three major factors, three excavation/removal systems and five types of equipment offer a guideline to properly select excavation equipment for the contaminated waste sites.

The working plan for next quarter is:

1. Continue the literature review to integrate the design consideration and select four other types of equipment.
2. Arrange to visit two or three hazardous waste sites if NEPA approval is received. Such field studies may provide pertinent data to allow a better determination of the suitability of the design consideration.
3. Continue to investigate the application of foams in dust/vapors control.
4. Develop the criteria for selecting effective surfactants.
5. Determine the characteristics of the excavated wastes.

6. Characterize the interaction of the wastes with the selected surfactant.
7. Study main operation parameters affecting effectiveness of foams, such as surfactant concentration, expansion ratio, etc.

Chemical Destruction of Polychlorinated Biphenyls

**Quarterly Technical Progress Report
for Period January 1 through March 31, 1993**

Work Performed Under
Contract No.: DE-FC21-92MC29467

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P. O. Box 880, Collins Ferry Road
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April 1993

ABSTRACT

The general objective of this research is to first evaluate the existing technologies for destruction of polychlorinated biphenyls (PCBs) by chemical methods. Development of new chemical treatment procedures for dechlorination of PCBs will also be a major focus of this research project. The detailed reaction pathway for the dechlorination process will be carefully probed so as to gain fundamental understanding of the reaction mechanism. Such information will be invaluable in providing guidelines for designing an efficient and economical system.

In this report, the main focus will be on the assessment of the current technologies and the discussion of the basic chemical reactions behind these treatment procedures. The commercial processes as well as procedures recently published in the literature will be reviewed, including dechlorination of PCBs by sodium and other alkali metals, by the use of strong base, by catalytic dechlorination, and by photochemical degradation.

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1. EXECUTIVE SUMMARY

It is the objective of this research to evaluate the existing technologies for destruction of polychlorinated biphenyls (PCBs) by chemical methods. We will also focus on establishing chemical treatment procedures for dechlorination of PCBs. We will probe into the detailed reaction mechanisms of various dechlorination processes so as to gain fundamental understanding of the reaction pathway. Such information will provide insight in designing an efficient and economical system.

In this report, the main focus will be on the assessment of the current technologies and the discussion of the basic chemical reactions behind these treatment procedures. Three commercial vendors listed with the Environmental Protection Agency (EPA) for their involvement in chemical dechlorination of PCBs have been contacted: (1) Trinity Environmental Technologies, Inc., (2) Chemical Waste Management, Inc., and (3) Roy F. Weston, Inc.

The Trinity Environmental Technologies, Inc. utilizes sodium metal to dechlorinate PCBs to inert biphenyl and sodium chloride. A general discussion of dechlorination of PCBs by sodium and other alkali metals is included in this report.

The Chemical Waste Management, Inc. utilizes a nucleophile-based process (the KGME process) that enables the destruction of halogenated aromatic compounds through the successive replacement of one or more halogen atoms with 2-methoxyethoxy moiety. A demonstration of this process was given at the ReSolve Superfund site at North Dartmouth, Massachusetts in the summer of 1992 under the sanction of EPA. Destruction of PCBs by nucleophilic displacement of chlorine atoms with a strong base is also reviewed in this report.

The procedure employed by Roy F. Weston, Inc. involves the use of zinc and a mild organic acid to generate nascent (atomic) hydrogen, which replaces aromatic halogen atoms in toxic organics in the presence of gentle heat and an unspecified catalyst. This process has been tested only in the laboratory in gram quantity and has not been scaled up to pilot plant level. Other catalytic dechlorination processes are also discussed in this report.

The direct photodegradation of PCBs with UV or sunlight irradiation proceeds with low efficiency. However, the efficiency of photodegradation can be dramatically enhanced with appropriate photo-sensitizers and other additives. The basic reaction mechanism of the photodegradation process is discussed in this report.

2. INTRODUCTION

2.1 Background

Polychlorinated biphenyls, commonly referred to as PCBs, are one of the major organic pollutants in the environment. The chemical structures of three representative polychlorinated biphenyls are shown in Figure 1. The large scale use of PCBs for a variety of purposes, especially as a dielectric material in capacitors and transformers as well as plasticizers and solvents in plastics and printing inks, coupled with the chemical stability of PCBs against degradation have resulted in their worldwide accumulation in the environment.

Figure 1. Chemical Structures of Three Representative Polychlorinated Biphenyls

The total worldwide production of PCBs through 1980 is estimated to be approximately 2.4 billion pounds. Of the 1.25 billion pounds of PCBs estimated to have been produced in the United States, mainly by Monsanto under the registered trademark of Aroclor, about 24 million pounds are believed to have been released to the environment.

The toxic effects of PCBs have been well documented. One of the most famous cases occurred in Japan in 1968 when PCBs from a defective heat exchanger were leaked into rice oil which was then consumed by more than 1000 people.¹ For those who consumed more than 0.5 grams (average consumption was 2 grams), severe acne, darkened skin, and eye damage developed. Recovery was slow and these symptoms were still present even after three years. Numerous studies have also reported the toxic effect of PCBs to a wide range of wildlife, including mink, some species of shellfish, shrimp, and fish, and especially those birds that are at the top of the food chain, such as eagles, hawks, falcons, and pelicans.² The chronic (long-term) toxicity to humans and other species is yet to be fully realized.

2.2 Destruction of PCBs

Because of the thermodynamic stability of PCBs, destruction by incineration and other chemical degradation processes are difficult. Disposal of untreated PCBs by landfill is virtually banned by the Resource Conservation and Recovery Act (RCRA). Currently, incineration is still the most widely used method for treating many hazardous wastes, including PCBs. Incinerators are strictly regulated to assure effective destruction of PCBs. For example, the regulation requires 99.9999% (six-9's) efficiency for the degradation of nonliquid PCBs by incineration. However, despite such strict regulations it is possible that trace amounts of PCBs as well as other combustion byproducts, including the much more toxic polychlorinated benzofurans and dioxins, could still be released to the environment through stack emission. Concerns about the

health impact of PCBs, dioxins, and other organic compounds formed and emitted into the environment have on surrounding communities have created many controversies and strong opposition from various environmental groups. It is now typical to take more than ten years and prolonged legal battle before an incinerator for industrial hazardous wastes could be constructed and operated. One recent example involves the Waste Technologies Industries (WTI) facility in East Liverpool, Ohio which will soon begin its test burn only after 13 years of planning and construction, more than 20 court cases, and even the intervention of the Vice President of the United States. In a recent article of the *Chemical and Engineering News*, many issues concerning hazardous waste incineration were raised and discussed.³ It is clear that there is a need to continue research and development of alternative chemical processes for treating hazardous wastes in general and PCBs and other chlorinated aromatic compounds in particular.

2.3 Purpose and Scope of Report

It is the purpose of this report to evaluate the existing technologies for the destruction of PCBs by chemical methods. We will focus mainly on the current commercial processes as well as procedures recently published in the literature, including dechlorination of PCBs by sodium and other alkali metals, by the use of strong base, by catalytic dechlorination, and by photochemical degradation. The basic chemical reactions behind these dechlorination processes will also be discussed.

3. CHEMICAL DESTRUCTION OF PCBS

Development of chemical process for the destruction of PCBs and other chlorinated aromatic compounds continues to be a research area of intense interest. Limited success has been achieved in some specific cases. Excellent review articles of the chemical processes are available in the literature.⁴ In addition, a recent monograph by Mitchell D. Erickson covered broad issues concerning PCBs, especially the analytical procedures.⁵ In this report, four general methods for chemical destruction of PCBs will be reviewed.

3.1 Dechlorination of PCBs by Sodium and Other Alkali Metals

The Goodyear Tire and Rubber Company patented a sodium-naphthalide process for PCB destruction in 1981 and later released it for public use.⁶ This process removes chlorine atoms from the PCBs and combines them with sodium to form sodium chloride (table salt).

The use of sodium metal for the dechlorination of aromatic compounds is well established in the literature.⁷ The reaction mechanism is believed to involve first transferring an electron from sodium to the chlorinated aromatic compound, such as chlorobenzene (1) to form the corresponding radical anion, such as (2) (Fig. 2). The radical anion 2 then loses a chloride ion to form phenyl radical 3, which then acquires an electron from sodium to form phenyl anion 4. Subsequent quenching of 4 with water affords the dechlorinated adduct as benzene (5). In the case of PCBs, such reaction cycle is repeated several times until all the chlorine atoms are removed. The resulting anions then are quenched with water.

Figure 2. Dechlorination of Chlorobenzene by Sodium

Because sodium metal is not very soluble in organic solvents, the Goodyear process uses naphthalene as an electron carrier to improve the efficiency of electron transfer. The process normally takes 2 hours at 60°C for complete dechlorination. However, to effectively remove low levels of PCBs (ca. 100 parts per million, ppm) from contaminated oil down to ca. 3 ppm, far lower than the requirement set by the Environmental Protection Agency (EPA), a large excess of the reagent is required. Typically, the reagent to chloride molar ratio must be from 25 to 500 to obtain significant reduction of the PCB concentration. Quenching the excess sodium-naphthalide reagent with water must be conducted slowly and with extreme caution. This is because generation of hydrogen gas will occur if sodium is contacted with water, creating a potentially dangerous situation for explosion.

In 1984, Goodyear disclosed an improved process with the elimination of the water quench step.⁸ The difficulties and disadvantages associated with a water quench of the alkali metal aromatic radical anion reagent are overcome by utilizing carbon dioxide (CO₂) as the excess reagent quenching material. No hydrogen gas is involved and at no time does water enter the system. The exclusion of water from the process allows for the recovery of the reaction solvent, such as tetrahydrofuran, in pure, dry form, eliminating additional process step, does not generate a waste water stream for disposal, and improves overall process safety.

The Goodyear process uses naphthalene, which has been classified as a priority pollutant by EPA, and its use is restricted. A number of processes have since been developed, utilizing other compounds as substitute for naphthalene.⁹⁻¹¹ The Sunohio, Inc. of Canton, Ohio developed proprietary compounds to replace naphthalene in a sodium-based process for reclamation of transformer oils containing PCBs. The Sunohio procedure was reviewed previously.⁹

In a recently patented procedure, ammonium salt was used to accelerate the reductive cycle of dechlorination and to serve as a proton source to hydrogenate and quench the dehalogenated polyhaloaromatics.¹⁰ It was also reported in a separate patented procedure that liquid hydrosiloxane could facilitate the reductive dechlorination so that it will proceed to

completion at room temperature in relatively short times.¹¹ It was claimed that PCBs are dechlorinated to biphenyl and its higher molecular weight oligomers with greater than 99% efficiency.

Currently, the sodium-based process is employed by the Trinity Environmental Technologies, Inc., using a modified version of the Goodyear process. It is claimed that this process is cost competitive compared to incineration for the treatment of PCB oils. However, this process will not be able to treat PCB contaminated soil. A block diagram of the Trinity process is given in Figure 3.

3.2 Destruction of PCBs by the Use of Strong Base

The use of strong base to attack PCBs has been investigated. The KPEG process, which uses potassium metal (K) and polyethyleneglycol (PEG) to destroy PCBs, is an example of such a treatment procedure.^{4a} Potassium metal reacts with polyethyleneglycol, such as diethyleneglycol (6), to form the correspond alkoxide (7), a strong base, which then attacks PCBs by nucleophilic displacement (Fig. 4).

Figure 4. Destruction of PCBs by the KPEG Process

Figure 3. Block Diagram of the Trinity PCB Treatment Process

Although the exact reaction mechanism of the KPEG process probably has not been fully established. It can be speculated that for the highly chlorinated biphenyls, the electron deficient benzene ring could be attacked by **7** to form **8**. Subsequent loss of a chloride ion from **8** could lead to **9** with the net effect of replacing a chlorine atom with a polyethyleneglycol. After successive replacement of chlorine atoms with polyethyleneglycol, complete dechlorination to form polyhydroxylated biphenyls **10** could thus be achieved.

It is also possible that a competing reaction pathway involving the formation of a benzyne intermediate **11** may also be responsible for the dechlorination process (Fig. 5).¹²

Figure 5. The KPEG Process via the Benzyne Pathway

Initial dehydrochlorination of PCBs to form benzyne **11** followed by the attack of **11** with an alkoxide would lead to **12**. Subsequent proton transfer could also result in the displacement of a chlorine atom by a polyethyleneglycol as shown in **9**.

Currently, a modified KPEG process is being utilized by the Chemical Waste Management, Inc. for the destruction of PCBs. The reagent, KGME (**14**), is generated in situ via the addition of KOH to 2-methoxyethanol (glycol methyl ether, GME, **13**), followed by azeotropic removal of water (Fig. 6). The use of KOH instead of potassium metal as in the KPEG process is an improvement which avoids the generation of hazardous hydrogen gas during reagent preparation.

Figure 6. Preparation of the KGME Reagent

A demonstration of the KGME process was conducted at the ReSolve Superfund sit at North Dartmouth, Massachusetts in the summer of 1992 under the sanction of EPA. Although a final report on the demonstration is not available at the present time, a private communication with Dr. Richard J. Ayen, Vice President and General Manager of the Chemical Waste Management, Inc., indicates that the KGME process is more expensive to operate than thermal desorption of PCB contaminated soil followed by off-site incineration of the resulting oil.

In early 1991, reports started to appear in the press indicating that quicklime, or calcium oxide (CaO), could destroy PCBs.¹³ A success in such a process could mean a low cost remediation of PCB pollution. However, many researchers were skeptical of those reports because the basic chemical reaction between quicklime and water generates mainly Ca(OH)₂, which is a source of hydroxide ion. Hydroxide ion had not been shown to effectively destroy PCBs. Preliminary results from an independent study by the EPA's Risk Reduction Engineering Laboratory in Cincinnati suggest that the reduction of PCB content is mostly attributable to volatilization and is not due to actual PCB destruction.^{13,14}

3.3 Catalytic Dechlorination of PCBs

The catalytic dechlorination of PCBs at 180°C to biphenyl with 5% platinum or palladium on 60/80 mesh glass beads over hydrogen gas was reported by Berg *et al.* in 1972.¹⁵ The use of 69% nickel on kieselguhr in the presence of sodium hydroxide and 50 atm of hydrogen gas at 115°C for 6 hours also effectively dechlorinated Aroclor 1248.¹⁶ It was later discovered that sodium borohydride could replace hydrogen gas as the reducing agent.¹⁷ One example of the study showed that 0.3 mmol of Aroclor 1254 could be most effectively reduced to biphenyl (97%) by treating with 2.0 mmol of NiCl₂ and 60 mmol of sodium borohydride in 2-propanol at ambient temperature and pressure. The disadvantage of this process is that a rather large ratio of sodium borohydride to PCBs is required to reach complete dechlorination.

In a process patented by the Union Carbide Corporation in 1983,¹⁸ 100 mg of a commercial Aroclor in 1 mL of methanol was treated with 0.03 g of NiCl₂, 0.5 g triphenylphosphine, 0.25 g NaI and 1.0 g of zinc dust in 10 mL of wet *N,N*-dimethyl formamide (DMF) at 60°C for 4 hours. The zinc dust in the presence of sodium iodide serves as the reducing means to keep the nickel in a zero valance state for effective catalytic dechlorination.

Currently, the Roy F. Weston, Inc. uses a catalytic dehydrochlorination procedure to remediate soils, sludges, and sediments contaminated with PCBs. The process uses zinc and a mild organic acid to generate nascent (atomic) hydrogen, which replaces aromatic halogen atoms in toxic organics in the presence of gentle heat and an unspecified catalyst. However, this process has been tested only in the laboratory in gram quantity and has not been scaled up to pilot plant level.

3.4 Photochemical Dechlorination of PCBs

The use of photochemical methods for the destruction of PCBs have received considerable attention. The direct photodegradation of PCBs with UV or sunlight irradiation proceeds with low efficiency. This is because once the heavier chlorinated and more photo-sensitive biphenyls are depleted, the dechlorination process becomes very slow. Typically, only about 25% of Aroclor 1254 and 10% of Aroclor 1260 are reacted after 10 hours.^{19a} However, the efficiency of photodegradation has been shown to be dramatically enhanced with appropriate photosensitizers and other additives. For example, it was reported that amines,²⁰ borohydrides,¹⁹ alkaline alcohols,²¹ and hydroquinones²² greatly enhanced the rate of photodechlorination of PCBs in solution.

Recently, the use of acetone as a photosensitizing agent in alkaline 2-propanol has been shown to be particularly promising, allowing dechlorination of Aroclor 1254 at wavelengths compatible with those available from the sun.²³ Total disappearance of Aroclor 1254 and the formation of biphenyl occurred in less than 25 minutes.

A free radical chain reaction has been proposed to be the pathway of the photodechlorination process (Fig. 7). The acetone molecule is excited by irradiation to a high energy triplet state, T_1 (n, π^*), which then abstracts a hydrogen atom from 2-propanol to give the ketyl radical **15**. The ketyl radical then loses a proton to the alkaline medium, producing the ketyl radical anion **16**. The Aroclor in turn reacts with the ketyl radical anion through an electron-transfer process given unstable aryl radical anion **17** which releases a chloride anion, producing the aryl radical **18**. The aryl radical then abstracts a hydrogen atom from 2-propanol to furnish dechlorinated biphenyls **19** and the ketyl radical **15**, allowing the propagation cycle for dechlorination of PCBs to continue until all of the chlorine atoms are removed.

The acetone-induced photodegradation of PCBs is a very attractive method because of the low costs of the reagents. Unfortunately, under similar conditions photodechlorination of extracts of Aroclor 1254 contaminated soil proceeded with low efficiency. Clearly, continued research is needed to bring the photodegradation method to practical use.

4. CONCLUSIONS

In this report, four general methods for chemical destruction of PCBs have been reviewed. These technologies have achieved limited success in some commercial-scale

operations. The laboratory scale studies suggest that these remediation processes have good potential for effective dechlorination of PCBs. Continued research in the area of chemical remediation is still needed to adapt these chemical processes to an extremely complex problem of PCB pollution in the environment. The PCB pollutant in the environment may exist in the soil matrices, in aqueous solution and in transformer oil with varying concentrations, and may coexist with other pollutants. It is unlikely that one single chemical remedial procedure will be able to address all these problems. A variety of procedures need to be developed for effectively removal of PCBs from the environment.

Figure 7. Acetone-Induced Photochemical Degradation of PCBs

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**Development of Organic Sensors:
Monolayer and Multilayer Self-Assembled Films for Chemical Sensors**

**Quarterly Technical Progress Report
for Period January 1 through March 31, 1993**

Work Performed Under
Contract No.: DE-FC21-92MC29467

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P. O. Box 880, Collins Ferry Road
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April 1993

TABLE OF CONTENTS

1.0 EXECUTIVE SUMMARY 1

1.0 EXECUTIVE SUMMARY

Work accomplished in this quarter is subdivided into three areas.

Hiring of a technician:

The paperwork for the creation of the Research Assistant I position was completed and submitted. The position was approved and posted by WVU Human Resources. No applicants appeared for an interview.

Acquisition of equipment:

Purchase orders were submitted for the Surface Acoustic Wave Microbalance hardware, hardware for a vapor phase generator, a computer, and hardware and software that permits computer control of the vapor phase generator and data acquisition. None of the equipment arrived during the quarter.

Literature search:

The P.I. made contact with an expert in SAW devices for sensor design, Dr. Anthony J. Ricco of Sandia National Laboratories. Dr. Ricco kindly supplied reprints relevant to the research project. These reprints and other references in the literature formed the basis for improvements in the design of the vapor generator and the electronic apparatus interfaced to the SAW devices, as noted below:

The vapor generator and the SAW device must be kept at tightly regulated temperatures ($\pm 0.01^\circ\text{C}$) in order to achieve stable oscillation frequencies as baselines. If there is any difference in temperature between the SAW device and the vapor generator, there must be a thermal transfer line (i.e. a 5 - 10 meter loop of gas flow line) preceding the SAW device and inside the same thermal chamber as the SAW device in order to bring the flowing gas to the same temperature as the SAW device. The problem of temperature sensitivity will have to be addressed later in the project in order to develop any field-operable sensor.

The reference crystal oscillator of the SAW device (which helps to compensate for the temperature sensitivity noted above) should be kept in a separate chamber containing pure carrier gas (dry air). Adsorption of sample gases to the reference crystal oscillator can lead to spurious signals.

The sample crystal oscillator will change its frequency in response to changes of mass, viscoelastic properties, and conductivity of the attached film. The conductivity sensitivity arises from the interaction of the electric fields at the surface of the crystal oscillator with mobile ions in the contacting film. The conductivity effect is either a potential problem or a potential mechanism for sensor design since the proposed multilayer films are based on ionic polymers. Currently the P.I. regards this effect as a problem since it should make the polyion films very sensitive to small changes in the relative humidity of the gas stream. Fortunately the conductivity sensitivity can be eliminated by first depositing a metal film of ca. 100 nm thickness on the SAW crystal, and then depositing the polyion film on top of the metal film.

Either changes in mass or changes in viscoelastic properties of the polyion film can signal the adsorption of the analyte gas. To distinguish between these two mechanisms, it will be necessary to monitor both the frequency changes and the loss of power of the mechanical wave traveling across the crystal.

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