Decontamination Systems Information and Research Program

**Quarterly Report
October - December 1995**

December 1995

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

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
West Virginia University
Morgantown, West Virginia

MASTER

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DECONTAMINATION SYSTEMS INFORMATION
AND RESEARCH PROGRAM

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**U.S. Department of Energy
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1000 Independence Avenue
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December 1995

EXECUTIVE SUMMARY

The projects reported for the WVU Cooperative Agreement are categorized into the following three areas: 1.0 In Situ Remediation Process Development, 2.0 Advanced Product Applications Testing, and 3.0 Information Systems, Public Policy, Community Outreach, and Economics. Summaries of the significant accomplishments for the projects reported during the period 1 October 95 through 31 December 95 are presented in the following discussions.

1.0 IN SITU REMEDIATION PROCESS DEVELOPMENT

Task 1.1: *Research on the Drain Enhanced Soil Flushing (DESF) for Organic Contaminants Removal* project reported progress with investigating the vertical discharge capacity of the Prefabricated Vertical Drains (PVDs). Conclusions of this work have shown linear relationships between PVD Headloss and fluid flowrate. The PVD transmissivity relationships showed nested data trends, where differences between data are due to PVD lengths and are not dependent on the PVD width. This is the last research task stipulated in the 1995 proposal.

Task 1.2: Work this period for the *In Situ Bioremediation of Organic Contaminants* project continued with operation of sequential and simultaneous column systems. Assessment of bioremediation of elevated concentrations of TCE was investigated with studies into using prefabricated vertical drains for field application of amendments. Increases in TCE removal efficiencies are reported and discussed. Lysimeter experimentation was operated in an aerobic mode focusing on determination of hydraulic head losses due to biological clogging of the prefabricated vertical drains.

Task 1.3: Work performed on the *Microbial Enrichment for Enhancing In Situ Biodegradation of Hazardous Organic Wastes in Soil* this period was spent on performing extended trial repeats and examining the microbial composition of selected microbial inoculants.

Task 1.4: Progress on the *Contaminant Movement Prediction in Permeable Subsurface Soils* project reported that progress was made in conducting computer simulations using data from Task 1.1 experimentation.

Task 1.5: During this quarter work on the *Development of a Standard Protocol and Barrier Design Model for In Situ Formed Barriers* project reported accomplishments on two fronts discussed separately below.

1.5a Chemical Grouting: Work on this portion focused on construction of the Grout Testing Chamber and sand rain device, and development of the draft report. All tasks have been completed including the draft final report.

1.5b Circulating Air Barriers (CAB): Work in this area has included the following: 1) Development of the draft Operating Plan and Operating Permit for METC, 2) Experiments on sand packs which produced data comparable with published data, and 3) Successful demonstration of testing on core saturation, desaturation, and air-water equilibrium.

2.0 ADVANCED PRODUCT APPLICATIONS TESTING

Task 2.1: Work this period on the *Chemical Destruction of Chlorinated Organic Compounds* project continued with improvement on the synthesis of a polymer as an electron carrier for dechlorination of PCBs. An efficient synthetic pathway to a trimer as a precursor to producing the corresponding cyclic hexamer as well as polymer was developed. Work on a model reaction for coupling the trimer to hexamer and polymer was also investigated during this reporting period.

Task 2.2: Progress on the *Continued Development of an Atmospheric Monitoring Mass Spectrometry System* project reported progress in obtaining chemical ionization spectra, however the project experienced continued technical and equipment difficulties which essentially halted their efforts to mobilize for a field demonstration. Equipment modifications and computer software modifications are currently being performed. The project is planning a restart by mid-February and has been given a time extension.

Task 2.3: During this reporting period equipment modifications were completed on the reactor and feed gas systems on the *Capture of Hazardous Wastes Materials Utilizing Fluidization Coating Technology* project. Experimentation was performed to test the reactor system using toluene as the test organic material. Estimation of toluene destruction efficiency was in excess of 98%.

Task 2.4: There has been no activity on the *Remediation of Hazardous Sites with Steam Reforming* (MTCI) project since the last quarter report.

Task 2.5: The *Carbon Products for Waste Stream Cleanup* project was completed during the last reporting period. The draft final report was submitted for METC/DOE review with the last quarterly report deliverable.

3.0 INFORMATION SYSTEMS, PUBLIC POLICY, COMMUNITY OUTREACH, AND ECONOMICS

Task 3.1: The *Winfield Lock and Dam Remediation* project reported that the excavation of the dioxin contaminated soil from the site and removal of certain buildings was completed. The Principal Investigator will continue monitoring dust during the excavation process which is expected to last into February 1996. These efforts will conclude the required tasks on this project.

Task 3.2: Progress on the *GIS-Based Infrastructure for Site Characterization and Remediation* project reports the successful completion of all 1995 contract tasks, and achievement of all objectives. This quarter saw completion of Tasks 1,2, and 3 which dealt with configuring the client/server database, preliminary analysis of the West Virginia Ordinance data acquired from the CORPS of Engineers, and configuration of the field computer for gathering on-site data.

Task 3.3: Efforts on the *Small Business Support Program* for this period included:
1) Presentation of a poster session at a DOE/METC sponsored small business conference, 2) Dedication of the West Virginia High Tech Consortium, 3) Locating the environmental technology incubator on the WVU campus, and 4) Meeting with representatives from the Institute of Gas Technology (IGT) in Chicago and at WVU.

Task 3.4: The *Approach for Assessing Potential Voluntary Environmental Protection, Kanawha Valley Area* project reported that meetings were held with the Director of the WV Division of Environmental Protection (WVDEP), and individuals from companies located in the Kanawha Valley. The WVDEP Director expressed support and willingness to participate in future negotiations for site clean-ups. The industrial contacts have expressed interest to continue meeting to develop the issue of using new DOE technologies in private site clean-ups.

Task 3.5: The *Waste-Management Education & Research Consortium National Environmental Design* project was completed during the second quarter.

Task 3.6: The *Interagency Environmental Technologies Office (IETO) Graduate Intern Program* project reported the completion of the student intern program and three of the five intern positions were extended to the end of December 1995. The students gained valuable experience for developing their professional futures and established important contacts within the agencies they worked.

Task 3.7: During this quarter, the *West Virginia High Tech Consortium Foundation Environmental Technology Support Program* completed work on the planning and start-up of the Small Business Environmental Technology Incubator. Work on the Incubator's policies and procedures have begun, and public information folders and sheets have been developed.

TABLE OF CONTENTS

Executive Summary

Project Titles with Principal Investigators

Administrative Issues

Budget and Schedule Updates

Quarterly Technical Progress Reports

1.0 IN-SITU REMEDIATION PROCESS DEVELOPMENT

- 1.1 USE OF DRAIN ENHANCED SOIL FLUSHING (DESF)
FOR ORGANIC CONTAMINANTS REMOVAL
- 1.2 IN-SITU BIOREMEDIATION OF CHLORINATED ORGANIC
SOLVENTS
- 1.3 MICROBIAL ENRICHMENT FOR ENHANCING IN-SITU
BIODEGRATION OF HAZARDOUS ORGANIC WASTES
- 1.4 CONTAMINANT MOVEMENT PREDICTION IN PERMEABLE SUBSURFACE
SOILS
- 1.5 DEVELOPMENT OF STANDARD TEST PROTOCOLS & BARRIER DESIGN
MODELS FOR IN-SITU FORMED BARRIERS
 - 1.5a Chemical Grout Barriers
 - 1.5b Circulating Air Barriers (CAB)

TABLE OF CONTENTS (cont.)

2.0 ADVANCED PRODUCT APPLICATIONS TESTING

- 2.1 CHEMICAL DESTRUCTION OF CHLORINATED ORGANIC COMPOUNDS
- 2.2 CONTINUED DEVELOPMENT OF AN ATMOSPHERIC MONITORING
MASS SPECTROMETRY SYSTEM
- 2.3 CAPTURE OF HAZARDOUS CHEMICAL WASTE MATERIALS UTILIZING
FLUIDIZATION COATING TECHNOLOGY
- 2.4 SOIL DECONTAMINATION BY STEAM REFORMING
- 2.5 CARBON PRODUCTS FOR WASTE STREAM CLEANUP

3.0 INFORMATION SYSTEMS, PUBLIC POLICY, COMMUNITY OUTREACH AND ECONOMICS

- 3.1 WINFIELD LOCK AND DAM ASSISTANCE PROGRAM
- 3.2 A GIS BASED INFRASTRUCTURE FOR SITE CHARACTERIZATION
AND REMEDIATION
- 3.3 SMALL BUSINESS SUPPORT PROGRAM
- 3.4 APPROACH FOR ASSESSING POTENTIAL VOLUNTARY
ENVIRONMENTAL PROTECTION - KANAWHA RIVER AREA
- 3.5 WASTE-MANAGEMENT EDUCATION & RESEARCH CONSORTIUM
(WERC) NATIONAL ENVIRONMENTAL DESIGN
- 3.6 IETO GRADUATE INTERN PROGRAM
- 3.7 WV HIGH TECHN CONSORTIUM (WVHTC)
ENVIRONMENTAL TECHNOLOGY INCUBATOR CENTER (ETIC)

PROJECT TITLES WITH PRINCIPAL INVESTIGATORS

1.0 IN-SITU REMEDIATION PROCESS DEVELOPMENT

1.1 USE OF DRAIN ENHANCED SOIL FLUSHING (DESF) FOR ORGANIC CONTAMINANTS REMOVAL

M. Gabr, Dept. of Civil & Environmental Eng.

1.2 IN-SITU BIOREMEDIATION OF CHLORINATED ORGANIC SOLVENTS

W. Sack and P. Carriere,
Dept. of Civil & Environmental Eng.

A. Shiemke, Dept. of Biochemistry

1.3 MICROBIAL ENRICHMENT FOR ENHANCING IN-SITU BIODEGRADATION OF HAZARDOUS ORGANIC WASTES

A. Sexstone, Dept. of Plant & Soil Science

1.4 CONTAMINANT MOVEMENT PREDICTION IN PERMEABLE SUBSURFACE SOILS

H. Bilgesu and S. Ameri, Dept. of Petroleum Eng.

1.5 DEVELOPMENT OF STANDARD TEST PROTOCOLS & BARRIER DESIGN MODELS FOR IN-SITU FORMED BARRIERS

C. Black, NRCCE

1.5a CHEMICAL GROUTING

M. Gabr, Dept. of Civil & Environmental Eng.

1.5b CIRCULATING AIR BARRIERS (CAB)

S. Ameri & K. Aminian, Dept. of Petroleum Eng.

2.0 ADVANCED PRODUCT APPLICATIONS TESTING

2.1 CHEMICAL DESTRUCTION OF CHLORINATED ORGANIC COMPOUNDS

K. Wang, Dept. of Chemistry

2.2 CONTINUED DEVELOPMENT OF AN ATMOSPHERIC MONITORING MASS SPECTROMETRY SYSTEM

F. King, Dept. of Chemistry

2.3 CAPTURE OF HAZARDOUS CHEMICAL WASTE MATERIALS UTILIZING FLUIDIZATION COATING TECHNOLOGY

R. Turton, Dept. of Chemical Eng.

2.4 SOIL DECONTAMINATION BY STEAM REFORMING

R. Lovett, NRCCE

2.5 CARBON PRODUCTS FOR WASTE STREAM CLEANUP

C. Irwin, NRCCE and J. Zondlo, Dept. of Chemical Eng.

3.0 INFORMATION SYSTEMS, PUBLIC POLICY, COMMUNITY OUTREACH AND ECONOMICS

3.1 WINFIELD LOCK AND DAM ASSISTANCE PROGRAM

R. Lovett, NRCCE

3.2 A GIS BASED INFRASTRUCTURE FOR SITE CHARACTERIZATION AND REMEDIATION

E. Cook, Dept. of Civil & Environmental Eng., and

J. Hooper, Marshall Univ.

3.3 SMALL BUSINESS SUPPORT PROGRAM

E. Cook, Dept. of Civil & Environmental Eng.

3.4 APPROACH FOR ASSESSING POTENTIAL VOLUNTARY
ENVIRONMENTAL PROTECTION - KANAWHA RIVER AREA

R. Lovett, NRCCE

3.5 WASTE-MANAGEMENT EDUCATION & RESEARCH CONSORTIUM
(WERC) NATIONAL ENVIRONMENTAL DESIGN

B. Reed, Dept. of Civil & Environmental Eng.

3.6 IETO GRADUATE INTERN PROGRAM

E. Cook, Dept. of Civil & Environmental Eng.

3.7 WV HIGH TECH CONSORTIUM (WVHTC)
ENVIRONMENTAL TECHNOLOGY INCUBATOR CENTER (ETIC)

K. Jones

ADMINISTRATIVE ISSUES

Administrative Summary

Background

West Virginia University (WVU) and the U.S. Department of Energy Morgantown Energy Technology Center (DOE/METC) entered into a Cooperative Agreement on August 29, 1992 titled "Decontamination Systems Information and Research Programs" (DOE Instrument No.:DE-FC21-92MC29467). Requirements stipulated by the Agreement require WVU to submit Technical Progress reports on a quarterly basis. This report contains the efforts of the research projects comprising the Agreement for the 4th calendar quarter of 1995, and is the final quarterly report deliverable required for the period ending 31 December 95.

Administrative Issues

During this period, the 1996 WVU Cooperative Agreement Proposal was submitted for the period January 1 - December 31, 1996. Of the nineteen 1995 funded projects, nine were selected for funding continuation into 1996, and four new projects were proposed. To date, a decision regarding the continuation of Kanawha Valley has not been made. If deemed favorable, this project will continue under a no-cost extension.

The following discussion addresses the administrative and scheduling issues regarding work performed during the 4th calendar quarter of 1995. An asterisk (*) is placed by the 1995 task number for projects which are continuing into 1996; the 1996 project task number is referenced in the right hand column.

Project Variances, Accomplishments, and Problems

This quarter saw the successful completion of all scheduled activities for the following projects listed below:

<u>1995 TASK No.</u>	<u>PROJECT</u>	<u>1996 TASK No.</u>
1.1*	Research on the Drain Enhanced Soil Flushing (DESF) for Organic Contaminants Removal	1.2
1.2	In Situ Bioremediation of Chlorinated Aliphatic Hydrocarbons	
1.3	Microbial Enrichment for Enhancing In Situ Biodegradation of Hazardous Organic Wastes in Soil	

<u>1995 TASK NO.</u>	<u>PROJECT</u>	<u>1996 TASK NO.</u>
1.4	Contaminant Movement Prediction in Permeable Subsurface Soils	
1.5*	Technical Support for In Situ Formed Barriers (BDM)	1.5
1.5a*	Formation of In Situ Polyurethane Grout Barriers for Waste Containment	1.3
1.5b*	In Situ Circulating Air Barrier (CAB)	1.4
2.3*	Capture of Hazardous Waste Materials Utilizing Fluidization Coating Technology	2.2
2.5*	Environmental Pollution Control Devices Based on Novel Forms of Carbon	2.4
3.2*	A GIS - Based Infrastructure for Site Characterization and Remediation	2.1
3.3*	Small Business Support Program	3.2
3.5	Waste Management Education & Research Consortium (WERC) National Design Contest	
3.6	The Interagency Environmental Technologies Office (IETO) Graduate Intern Program	
3.7*	West Virginia High Tech Consortium Foundation Environmental Technology Support Program	3.1

Discussion of the following projects which reported uncompleted tasks/deliverables is warranted:

Task 2.1: Chemical Destruction of Chlorinated Organic Compounds project reported two tasks uncompleted for FY 95. These are: Synthesis of Polymers ended at 85% completion and Dechlorination by Chemical Processes ended at 50% completion. Research is continuing to complete these tasks and the results are expected to be included in the final report deliverable.

- Task 2.2: Continued Development of an Atmospheric Monitoring Mass Spectrometry System project was hampered by problems which resulted in deficiencies on seven tasks. The project was given a time extension until May 96 to complete the outstanding deliverables. Continued reporting will be made in order to track the progress of the corrective actions.
- Task 2.4: The Remediation of Hazardous Sites with Steam Reforming project has not made any progress in the last six months. The MTCI project manager (V. Monsour) has been notified to submit the final report.
- Task 3.1: The Winfield Lock and Dam Remediation project reported one task that lagged the planned schedule. This task dealt with monitoring the field construction process and due to construction set backs this task was delayed. The project will be monitored by Ray Lovett of NRCCE until complete, at which time the final report will be prepared.
- Task 3.4: The Approach for Assessing Potential Voluntary Environmental Protection, Kanawha Valley Area project reported slow progress throughout the year. The project is currently being reviewed by DOE/METC and WVU for possible extension. Meetings are scheduled in February to determine the project's future.

Accounting Issues

All projects were reviewed by the Department of Civil and Environmental Engineering (CEE) at the end of October. It was requested that each Principal Investigator encumber all expenses by November 15, 1995 in an effort to have them all paid by 31 December 95 to make a better estimate of the roll-over amount for 1996 and reduce the differences between the accrued and cash balance sheets. Because there still remains outstanding encumbrances, cash adjustments were necessary, and the differences have been reconciled. The 31 December 95 estimated roll over figure is approximately \$180,000.

An accrued accounting system was adopted by (CEE) for the year 1995 to provide a real time accounting by showing the actual expenses when incurred. Due to the amount of adjustments required for reconciliation, a simplified accounting system has been developed for 1996. The new report will contain an extra column for accrued expenses and obligated amounts that have not been disbursed, and all adjustments will be made in this column. This reporting method will still provide METC/DOE with a timely update of accrued expenses, but will show the actual expense in the month it is paid as opposed to when incurred.

All extended budgets and NRCCE administrative budgets were closed out last quarter. To represent the total amount budgeted in 1995, a line was added called "other" on the summary sheet. Of the total funds authorized under the direction of the CEE department, 94% were utilized in support of research efforts.

*Budget removed.
ds*

**QUARTERLY TECHNICAL
PROGRESS REPORTS**

TASK 1.0
IN-SITU REMEDIATION
PROCESS DEVELOPMENT

Table of Contents

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 PURPOSE	1
3.0 BACKGROUND	1
4.0 WORK PERFORMED THIS PERIOD	2
5.0 CONCLUSIONS	2
6.0 WORK PLANNED FOR NEXT PERIOD	2
ATTACHMENT "A"	3

1.0 INTRODUCTION

Work on this project is conducted to investigate the use of Prefabricated Vertical Drain (PVD) systems for remediation of contaminated sites with fine grained soils. PVD systems are relatively simple in operation and installation. They require no drilling rig equipment and are expected to significantly reduce remediation and installation costs, and at the same time increase the efficiency of the remediation effort.

The use of PVDs in the current state of practice has been in the area of soil improvement. Other than the work performed in the first phase of this project, no research work has been conducted to investigate the feasibility of using PVDs for enhanced soil flushing.

2.0 PURPOSE

The main objective of this research phase is to investigate major parameters influencing the efficiency of contaminant extraction using PVD systems. Research in this phase is focused on conducting bench-scale tests with soils for simulation of in situ conditions. Specific objectives are as follows:

1. Development of the effective diameter for in situ characterization of the PVDs;
2. Investigating the effect of smear and well resistance on the hydraulic efficiency of the PVDs, and
3. Investigating the method of installation and its effect on the recovery efficiency of the PVD system.
4. Full development and Beta testing of the PVDs' contaminant transport model developed in Phase I.
5. Field demonstration program and testing, cost analysis, and performance of the recovery process using the PVDs.

3.0 BACKGROUND

The PVD system is used to shorten the drainage path of the groundwater flow and therefore promote subsurface liquid movement and expedite the soil flushing process in low permeability soils. Proved technologies exist for the in situ soil flushing for sites with granular soils (hydraulic conductivity approximately 1×10^{-2} cm/s). However in the case of sites where the soil is fine-grained with corresponding hydraulic conductivity ranging 1×10^{-3} to 1×10^{-7} cm/s, implementation of the traditional soil flushing technology is ineffective and cost prohibitive.

In the previous phase of this project progress was advanced along the following three fronts:

1. Contaminant and Soil Characterization: A study soil was developed and categorized in accordance with ASTM standards. The testing program included column and batch studies on contaminated soils with the study surfactant being anionic aqueous solution of sodium dodecylsulfate.
2. Injection/Extraction Flushing Concept: Several pilot scale Contaminant Recovery Cells (CRCs) were used to evaluate the flow characteristics of the soils sampled and the concept of using PVDs. Soil samples were prepared in the CRCs and PVDs were installed in rectangular and circular configurations.
3. A predictive model for PVD enhanced soil flushing was developed. The model was developed assuming full saturation and no diffusion or decay. Parameter studies were performed to predict soil flushing rates using a PVD system.

4.0 WORK PERFORMED THIS PERIOD

Work performed during this reporting period included the following tasks:

- Task #1. Continued experimentation on the Effective Diameter and Smear Effects.
- Task #2. Experimentation on the influence of PVD layout on chloride capture efficiency.
- Task #3. Experimentation on the influence of PVD Head Losses under vacuum extraction operation.

5.0 CONCLUSIONS:

The work on Tasks 1 & 2 was still underway during preparation of this report. The efforts on Task #3 are reported and discussed in Attachment A.

6.0 WORK PLANNED FOR NEXT PERIOD:

Tasks planned for the next reporting period include completion of all outstanding testing currently underway on Tasks #1 & #2 concurrent with commencing activities on Phase III of the project.

ATTACHMENT “A”

TOPICAL REPORT

for

PREFABRICATED VERTICAL DRAIN

WELL RESISTANCE CHARACTERIZATION

WELL RESISTANCE

DISCUSSION

In this section the internal resistance of the PVDs, termed well resistance, and its effect on the vertical discharge capacity of the prefabricated vertical drains is presented and discussed. The topic is presented beginning with the developments made from previous research on soil improvement then followed by research focusing on PVDs as applied to enhanced soil flushing.

The injection of the flushing solution in a field application can be accomplished using a constant head gravity system or a positive pressure pump system where head losses can be overcome. Therefore research into the delivery system losses was not performed at this time.

For PVD liquid extraction, the literature review of soil improvement applications (consolidation) identified a considerable amount of past research that focused on quantifying the relationships between the PVD discharge capacity and lateral effective stresses under gravity drainage conditions. Findings show a decreasing discharge capacity through the PVDs with increasing lateral soil consolidation pressure. This effect is the predominant mechanism attributed to the PVD's discharge reduction. The increased lateral loads cause the filter material to close into the core's channels. This results in the channel cross-sectional area being partially to completely closed-off to liquid flow (Hansbo, 1987).

Additional factors attributed to reducing the PVD discharge include siltation and kinking. Siltation occurs as a result of fine-grained soil particles passing through the filter fabric and settling in the PVD core channels. The siltation depends on the filter permeability and ability to retain the fine particles. The kinking or PVD buckling occurs as a result of large vertical strains imposed on the PVD from settlement of the surrounding soil (Hansbo, 1987).

The scheme of the drain-enhanced soil flushing application is to accomplish liquid extraction through the PVD via a negative air pressure head that is distributed through the drains to the surrounding soil. The extraction process is balanced with a liquid injection at adjoining rows of PVDs. This operation is designed to maintain a saturated subsurface during the remediation process through the mass balance of the injected and extracted surfactant liquid.

Factors of importance for soil improvement (lateral earth pressure effects, siltation, and kinking) are not necessarily significant in this application. The reduction in liquid discharge due to lateral stress compressing the PVD will not be significant since no soil volumetric change occurs. With the absence or minimization of soil consolidation, the PVD kinking effect is no longer significant. While PVD siltation build-up in the core may be a potential problem. Selection of appropriate geotextile wrapping based on existing filter fabric criterion should alleviate the clogging potential.

Where PVDs have been used for vacuum-assisted consolidation, Cognon, et. al (1994) reported that the foremost practical problem encountered in the field was maintaining a maximum vacuum efficiency of 75 percent. Cognon listed the following considerations governing the effectiveness and economy of vacuum-assisted consolidation: 1) integrity of the

surface cover membrane, 2) perimeter seal between the ground and membrane, 3) soil stratification having permeable seams within the consolidated soil, and 4) the in situ groundwater depth.

Existing Testing Procedures

Several testing procedures for PVDs used in consolidation applications have been published. Some of these are the ORF test (Ontario Research Foundation on Aldrain), CTH test (Chalmers University of Technology), Tokyu Construction test, Delft test, and the California test (Hansbo, 1983). ASTM has established separate procedures for determining geotextile permitivity and transmissivity, ASTM D 4491 and D 4716, respectively.

The PVD, being a composite, and made from a solid core for fluid transmission and geotextile jacket to filter fine-grained particles. does not meet the requirements for evaluation by either of the existing ASTM procedures mentioned above. In order to evaluate the PVD's fluid head loss under vacuum conditions, it was necessary to design a testing program which simulated the field remediation application. This testing program is presented and discussed in the following subsection.

MATERIALS & METHODS

MATERIALS

The PVD used for this phase of testing was the NILEX type MD-7407. The PVD core is a corrugated cross-section shape and is shown in Figure 1(a), the manufacturer specifications are listed in Table 1 (NILEX, 1995). An air pressure gage (0 to 100 kPa) and tap water were used during the testing program. The water temperature maintained was approximately 13° Celsius.

METHODS

The testing program for this part of the project was designed considering that after exposure to the fine-grained soil the transmissivity (in-plane flow) component through the jacket was considered negligible compared to the transmissivity component occurring along the PVD's core. In order to quantify the head loss within the PVD from vacuum-assisted liquid extraction the testing focused on:

- a) quantifying the head loss in the PVD along the length of the core for various lengths and widths and at different vacuum pressures. Table #2 lists the PVD specimen widths and lengths tested.
- b) quantifying the relationship between the applied air flow rate developed through the vacuum application with the extracted liquid flow rate developed through the PVD.

The experimental apparatus used for this testing is shown in Figure 1(b). The PVD specimens were sealed using multi-layers of 20 mil plastic sheeting. The PVDs were cut the desired width, then the plastic sheeting was wrapped and glued using an aerosol adhesive. This assembly technique minimized air infiltration and vacuum loss along the PVD's length.

The experimental procedure followed is outlined below. Duplicate trials were performed for each set of the tests performed.

Step 1: Establish the water flowrate supplied to the reservoir.

Step 2: Set and apply the testing vacuum pressure then collect and record the amount of extracted liquid in the graduated cylinder during set time intervals.

Step 3: Increase the applied air vacuum, and repeat step 2 until all testing of all desired vacuum pressure levels is complete.

RESULTS & DISCUSSION

The analysis procedure followed for determining the headloss through the PVD were based on the Bernoulli and the continuity equations shown below. Refer to Figure 1(b) for the subscript reference locations.

$$\frac{P_1}{\gamma_w} + Z_1 + \frac{V_1^2}{2g} = \frac{P_2}{\gamma_w} + Z_2 + \frac{V_2^2}{2g} + Hf_{PVD} \quad (1)$$

$$Q = A * V \quad (2)$$

Where:

$\frac{P_1}{\gamma_w}, \frac{P_2}{\gamma_w}$: Pressure Head (cm) at points 1 & 2, respectively,

Z_1, Z_2 : Elevation Head (cm) at points 1 & 2, respectively,

$\frac{V_1^2}{2g}, \frac{V_2^2}{2g}$: Velocity Head (cm/s) at points 1 & 2, respectively,

Hf_{PVD} : PVD Head Loss (cm) between points 1 & 2, respectively

Q : PVD Extracted Flowrate (cm³/s)

A : Cross sectional area of connection tube (cm²)

Determination of the PVD Head Loss was accomplished directly and is shown in final form in Equation 3 below. The pvc pipe length shown in Figure 1(b) was as long as the PVD tested. The pipe resistance was dropped from the headloss calculations because of the length was not deemed significant in comparison with the 3,4, and 5 meter PVD lengths tested, and the pipe was mounted vertical such that the fluid did not have significant flow in contact with the pipe surface. This type of connection was used for testing as it would emulate field installation conditions.

$$Hf_{PVD} = - \left[\frac{P_2}{\gamma_w} + Z_2 + \frac{V_2^2}{2g} \right] \quad (3)$$

Calculation of the PVD transmissivity was based on the following equation (4):

$$\theta = \frac{Q * L}{W * H} \quad (4)$$

Where: θ = Transmissivity (cm³/s-cm)
 L = PVD length (cm)
 W = PVD width (cm)
 H = Headloss (cm)

Computations were performed in a spreadsheet format and the results are shown graphed in Figures 2 through 8. These figures are discussed separately below.

Figure 2 VACUUM AIR FLOWRATE vs VACUUM PRESSURE: This graphs shows the relationship between supply the Air Flowrate and Vacuum Pressure for the vacuum compressor equipment. This graph is significant because it relates the vacuum pressure, with corresponding air flowrate, required to develop flow through the PVD. A regression of the data points was performed to obtain an equation relating the air flowrate as a function of the applied vacuum pressure. This equation was subsequently used to develop a graph of the air flowrate versus the extracted liquid flowrate from the PVD.

Figure 3 VACUUM AIR FLOWRATE vs EXTRACTED WATER FLOWRATE:

Shown in these three graphs are the relationships between the applied air flowrate and the extracted water flowrate for the three different PVD widths and lengths tested. The data show very close duplication for the two trials performed. The graphs show an approximate linear, inverse relationship between the air flowrate and the water flowrate. This is demonstrated in Figure 3(a) as the supply air flowrate decreases from 1087 to 670 cm^3/s as the extracted fluid flowrate increases from 2.8 to 8.3 cm^3/s , respectively.

The maximum flowrates were extracted from the PVDs at the lowest air flowrate, this was consistent for each of the different PVD widths and lengths tested. This is consistent with the air flowrate vs vacuum pressure relationship shown in Figure 2.

Data comparisons between Figure 3- a), b), and c) shows an increasing water flowrate consistent with increased PVD width. At an air flowrate of approximately 1050 cm^3/s , the PVD width increases from 2.5 cm to 7.6 cm (204% increase) while the corresponding water flowrate increases from 3.0 to 10.0 (233% increase).

Figure 4 PVD FLOWRATE vs TOTAL HEAD (MD-7407): The graphed data show approximately linear relationships between the applied vacuum head and the PVD water flowrate for the three different PVD widths. The 10 kPa Vacuum Head offset between the data for the 3,4, and 5 meter lengths, corresponds to the 1.0 meter difference in the PVD length.

Figure 5 PVD HEAD LOSS (cm/m) vs FLOWRATE: These graphs indicate a positively increasing linear relationship between the headloss (cm/m) and extracted water flowrate. This data show the width/length relationships are approximately constant for a specific PVD width.

Figure 6 PVD TRANSMISSIVITY vs TOTAL HEAD: The graphed data show very similar trend characteristics. The trends deviate only with regards to the horizontal offset along the TOTAL VACUUM HEAD axis. A offset shift of 10 kPa accounts for the difference in PVDs between the 3,4, and 5 meter lengths. All of the graphs show the data tending to level-off in Transmissivity between 5 to 10 $\text{cm}^3/\text{s-cm}$.

SUMMARY & CONCLUSIONS

The preliminary results of these tests tend to indicate the following:

- 1) There is an approximately linear relationship between the PVD Headloss and Flowrate. And that the horizontal offset shift between the flowrates, for the same PVD width, is due to the differences in PVD lengths.

Previous research into the smear effect, Quarterly report for the period July - September 1995, showed that for a study soil containing 80% sand and 20% kaolin, there was no change in the PVDs zone of influence with the doubling of the applied extraction pressure. This indicates that the PVDs are not flowrate limiting to the fluid extraction process and the only flowrate limiting component is the hydraulic conductivity of the soil. The PVDs have demonstrated that their flowrate capability is greater than that of the study soil.

- 2) The Headloss per unit length of PVD is linear, with the offsets occurring in the flowrate between graphs is due to different PVD widths and associated area.
- 3) The Transmissivity versus Total Vacuum Head graphs shows nested data trends, where the differences between the data are due changes in the PVD lengths, and are not dependent on PVD width.

PRACTICAL SIGNIFICANCE

The observations of the limited testing performed here are significant when applied to the engineering and equipment design process for the field application phase. The required vacuum compressor (air flowrate & pressure) and support injection and extraction piping may be approximated using the data trends presented here.

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List of Tables

TABLE 1	PVD Manufacturer Product Specifications
TABLE 2	PVD Specimen Dimensions

List of Figures

Figure 1	(a) NILEX MD-7407 Prefabricated Vertical Drain (b) PVD Well Resistance Apparatus
Figure 2	VACUUM AIR FLOWRATE vs VACUUM PRESSURE
Figure 3	VACUUM AIR FLOWRATE vs EXTRACTED WATER FLOWRATE
Figure 4	PVD FLOWRATE vs TOTAL HEAD (MD-7407)
Figure 5	PVD HEAD LOSS (cm/m) vs FLOWRATE
Figure 6	PVD TRANSMISSIVITY vs TOTAL HEAD

TABLE 1
PVD Manufacturer Product Specifications^(a)

Properties	Test Method	Units	MD - 7407
PHYSICAL			
Drain Body			
Material			Polypropylene
Color			White
Filter			
Material			Polypropylene
Color			Grey
Weight	ASTM-D-1777	g/m	75
Thickness	ASTM-D-5199	mm	3.4
Mass of Filter	ASTM-D-1777	g/m ²	154
MECHANICAL			
Discharge Capacity			
@ 10 kN/m ²	ASTM D-4751	m ³ /s	140 x 10 ⁻⁶
@ 300 kN/m ²	ASTM D-4751	m ³ /s	105 x 10 ⁻⁶

(a): NILEX Corporation, 1995

TABLE 2
PVD Specimen Dimensions

Test	Width(cm)	Length (m)
1	2.5 (1")	3, 4, 5
2	5.0 (2")	3, 4, 5
3	7.6 (3")	3, 4, 5
4	10.2 (4")	3, 4, 5

(a)

(b)

Figure 1
a) NILEX Inc. MD7407 PVD
b) PVD Well Resistance Apparatus

Figure 2
Vacuum Air Flowrate vs Vacuum Pressure

TRIAL #1	TRIAL #2
3 m	3 m
4 m	4 m
5 m	5 m

Figure 3 : VACUUM AIR FLOWRATE vs EXTRACTED WATER FLOWRATE (MD7407)

(a) 2.5 cm Width (b) 5.0 cm Width (c) 7.5 cm Width

TRIAL #1	TRIAL #2
3 m	3 m
4 m	4 m
5 m	5 m

Figure 4 : PVD FLOWRATE vs TOTAL HEAD (MD7407)
(a) 2.5 cm Width, (b) 5.0 cm Width, (c) 7.6 cm Width

TRIAL #1	TRIAL #2
3 m	3 m
4 m	4 m
5 m	5 m

Figure 5 :PVD HEADLOSS (cm/m) vs FLOWRATE (MD 7407)
a) 2.5 cm Width, b) 5.0 cm Width, c) 7.6 cm Width

TRIAL #1	TRIAL #2
○ 3 m	● 3 m
□ 4 m	■ 4 m
△ 5 m	▲ 5 m

Figure 6 : PVD TRANSMISSIVITY vs TOTAL HEAD (MD7407)

(a) 2.5 cm Width, (b) 5.0 cm Width, (c) 7.6 cm Width

SITE REMEDIATION TECHNOLOGIES
IN SITU BIOREMEDIATION OF ORGANIC CONTAMINANTS
METC TASK No. 1.2

Quarterly Technical Progress Report
for Period October 1 through December 30, 1995

Work Performed Under
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For
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Office of Fossil Energy
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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 pollutants to another medium, less risk of health hazards due to human exposure and cost-effectiveness in many cases. This research seeks to exploit the natural symbiotic relationship between methanogenic and methanotropic microorganisms. The methanogens are able to carry out the anaerobic reductive dehalogenation (RD) of highly chlorinated solvents producing methane. The methanotrophs, in turn, utilize the end products of the methanogens, including methane, to aerobically degrade the residual compounds to environmentally acceptable end products. Both groups of organisms work cometabolically and require a primary substrate.

The project is divided into two main tasks and a number of subtasks. Under task 1, controlled testing will be performed in columns to find optimum conditions for the complete mineralization of trichloroethylene (TCE) to innocuous end products. Columns will be set up to examine both sequential and simultaneous mineralization. In the sequential columns, RD will be accomplished first with conditions that favor methanogens followed by aerobic conditions that favor methanotrophs. In the simultaneous column, an attempt will be made to set up conditions which promote anaerobic microzones within the columns so that RD and aerobic oxidation take place almost continuously along the column. It is planned to use hydrogen peroxide as an electron acceptor for the methanotrophs.

In task 2, delivery of amendments (such as the primary substrate and electron acceptor) to low permeability soils using prefabricated wick drains (PVD's) will be evaluated using a box lysimeter. Use of wick drains for delivery of amendments and possible ground water recirculation is a unique application of this technology and offers significant improvement over existing methods which require a large number of wells in "tight" soils.

Executive Summary

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 pollutants to another medium, less risk of health hazards due to human exposure and cost-effectiveness in many cases. The objective of this research is to evaluate and optimize the ability of methanotrophic, methanogenic, and other selected bacteria for cost-effective biotransformation of a mixture of chlorinated solvents as are often found at DOE sites. A five phase workplan is utilized which involves the systematic manipulation of environmental conditions to enhance the rate and extent of biodegradation of the candidate VOC's. It is planned to take advantage of the natural symbiotic relationship between the methanogenic and methanotrophic bacteria so as to promote sequential anaerobic/aerobic mineralization of the chlorinated solvents.

Both sequential and simultaneous column systems were continued to be operated to evaluate the effects of a variety of variables on performance in order to optimize mineralization of TCE. Assessment of bioremediation of elevated concentrations of TCE was investigated. In addition, evaluation of prefabricated vertical drains for field application of amendments using box lysimeters was performed.

For the sequential column, the effects of adding methanol into Port 2 on TCE removal and hot spot addition on column performance were investigated. As noted, TCE removal was significantly increased during the addition of methanol into Port 2 of the sequential column from 50.8% to 65.6% even though the TCE concentration had risen from 5.0 mg/L to 20.0 mg/L. When the amount of methanol added to Port 2 was increased from 50 to 150 mg/L, the removal again increased and near the end of the period TCE removal was nearly total. On the twelfth day of the change to 150 mg/L TCE, the removal began to significantly increase.

The DP most easily oxidized was VC, followed by trans-DCE, cis-DCE, and 1,1-DCE. As observed, not only did an increase in TCE reduction occur in Port 3 with respect to Port 1, but also DP reduction was also occurring. By using a mole balance, 88.9% of the TCE and DCE isomers removed went to VC. This indicated that the remaining 11.1% of the DPs went to ETH production.

A major slug load of TCE was added to the sequential column system. For the first four days of the slug, the TCE concentration throughout the column was extremely high, with the largest TCE concentration occurring in Port 3 at the end of 24 hours (1521 mg/L). The slug was not seen in Port 6 until 96 hours had passed, and it had a value of (1273 mg/L). By the fifth day after the slug addition, the TCE mass flowrate dropped considerably. By day eleven after the addition of the slug, all ports showed a mass flowrate less than the influent except Port 6, which showed removal on day twelve. A mass balance on TCE over this period showed a removal of 96.9%. The percent removal in the column for the days following the twelfth was 88.9% for Port 6 with respect to the influent, and 93.1% for Port 3 with respect to the influent. All of the DPs reached a very high concentration during the first four days of the slug passage. The highest concentration of cis-DCE occurred on the 24th hour of the slug passage in Port 3 and reached a concentration of 7985.8 µg/L. 1,1-DCE reached its highest concentration on hour 48 in Port 6 and had a maximum concentration of 3135.2 µg/L. VC had a maximum concentration at hour 24 in Port 3, which was at a concentration of 7296.8 µg/L. After day five, the concentrations of DPs became steady-state values. These values were compared to the period before the addition of the TCE slug in Table 6. VC had a dramatic drop in

production after the slug passed through the system dropping by 21.5 times the previous rate, while the production of 1,1-DCE increased by 7 times. The cis-DCE also had a drop in production of 2.3 times from the previous period.

For the simultaneous column, the effects of different peroxide and ammonia concentrations were investigated. Also, the effect of elevated influent TCE concentrations and hot spots was investigated. The removal rate increased with increase in the H_2O_2 concentration at port H2. The growth of the aerobic organisms could have been enhanced by the increased peroxide concentration. As a result, more TCE and DPs were degraded. While there was about 15% increase in the over all percent removal, the percent removal at port 4 increased by 18.7% when the concentration at H2 was increased from 75 to 100 mg/L. The mass removal rates increased by 117.2% and 76.3% at ports 4 and 7 respectively. Port 4 is representative of the facultative zone while port 7 represents the final aerobic zone. The increase in the H_2O_2 concentration therefore seemed to have improved the functioning of the organisms in the facultative zone as well as the aerobic zone. It was found that the mass removal rate of TCE increased by 25% when the NH_4Cl concentration of the influent ground water was decreased from 56.6 mg/L to 28.3 mg/L. The non specific nature of the MMO enzyme probably allowed ammonia to inhibit the TCE degradation by methanotrophs.

The TCE concentration in the column was increased in the simultaneous column from 5 to 22 mg/L. As noted, the percent removal rate increased by 10.8%, 9.2%, and 12.9% at ports 2, 4, and 7, respectively. The mass removal rates on the other hand, experienced phenomenal increases of 826%, 650%, and 665% at ports 2, 4, and 6 respectively. Decrease in the influent TCE concentration from 22 to 16.5 mg/L resulted in a decrease in percent as well as mass removal rates. While the percent removal rates for case 3 were about 4% less than that for case 1, the mass removal rates were about 350% higher. This indicated that the increase in TCE concentration resulted in an increase in the mass removal rate of TCE.

For 400 and 800 mg/L TCE slugs injected in the simultaneous column, the percent TCE removal was 43 and 56%, while DPs production increased by 376 and 704%, respectively.

The lysimeter experiment was continued this quarter in an aerobic mode. Only four centimeters of head were needed on the first day of adding substrate to the system. Three days later, the head tank had to be raised to nearly double the head to keep the same flow (approximately 8 L/d). On day 36 the constant head tank was raised for the final time to a head of eleven centimeters. The major headloss occurred from the PVD to the first piezometer.

TABLE OF CONTENTS

	PAGE
1.0 INTRODUCTION.....	1
2.0 PURPOSE.....	1
3.0 BACKGROUND.....	1
4.0 METHODOLOGY.....	2
Phase 1. Literature Review.....	2
Phase 2. Batch Studies to Evaluate Optimum Concentration of Growth Enhancing Agents in Both Liquid and Soil Cultures.....	2
Phase 3. Column Studies to Evaluate the Rate and Extent of Degradation of Candidate VOCs.....	2
Phase 4. Comparison of TCE Biotransformation by Particulate and Soluble Methane Monooxygenase.....	2
Phase 5. Investigation of the Utilization of the Symbiotic Relationship Between Methanogenic and Methanotrophic Bacteria for VOC Degradation Without Addition of Exogenous Methane.....	2
5.0 WORK PERFORMED THIS PERIOD.....	3
6.0 RESULTS AND DISCUSSION.....	3
6.1 Sequential Column.....	3
6.1.1 Effect of Methanol Addition into Port 2 of Sequential Column.....	4
6.1.2 Hot Spot Addition.....	9
6.2 Simultaneous Column.....	12
6.2.1 Effect of H ₂ O ₂	12
6.2.1.1 Aerobic and Anaerobic Zone Distribution.....	12
6.2.1.2 TCE Removal.....	12
6.2.1.3 DP Production and Removal.....	13
6.2.2 Effect of NH ₃ -N Concentration.....	14
6.2.2.1 TCE Removal.....	14
6.2.2.2 DP Production and Removal.....	15
6.2.3 Effect of Elevated TCE Concentration.....	15
6.2.3.1 TCE Removal.....	16

6.2.3.2 DP Production and Removal.....	16
6.2.3.3 Effect of H2O2 Concentration for Elevated TCE Concentration.....	17
6.2.4 Effect of 400 mg/L TCE Slug.....	18
6.2.5 Effect of 800 mg/L TCE Slug.....	19
6.2.6 TOC Removal Vs. TCE Removal.....	21
6.3 Lysimeter with Prefabricated Vertical Drain.....	22
7.0 CONCLUSIONS.....	23
8.0 WORK PLANNED FOR NEXT QUARTER.....	24
9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES.....	24
10.0 REFERENCES.....	24
11.0 APPENDIX.....	28

LIST OF FIGURES

Figure 1.	Sequential Column Setup.....	29
Figure 2.	Column Conditions for Methanol Addition in Port 2 of Sequential Column.....	30
Figure 3.	Mass Flowrate TCE during Methanol Addition in Port 2.....	31
Figure 4.	Mass Flowrate cis-1,2-DCE during Methanol Addition in Port 2.....	32
Figure 5.	Mass Flowrate trans-1,2-DCE during Methanol Addition in Port 2...	33
Figure 6.	Mass Flowrate 1,1-DCE during Methanol Addition in Port 2.....	34
Figure 7.	Mass Flowrate VC during Methanol Addition in Port 2.....	35
Figure 8.	Amount Daughter Products Present in Port 6 for Varying Amounts of MeOH Added in Port 2.....	36
Figure 9.	Amount Daughter Products Present in Port 3 for Varying Amounts of MeOH Added in Port 2.....	37
Figure 10.	ORP during Methanol Addition in Port 2 of Sequential Column.....	38
Figure 11.	ORP Removed in Port 6 with respect to Port 4 Compared to Percent cis-DCE Removal in Port 6 with respect to Port 3.....	39
Figure 12.	ORP Removed in Port 6 with respect to Port 4 Compared to Percent VC Removal in Port 6 with respect to Port 3.....	40
Figure 13.	ORP Removed in Port 3 with respect to Port 1 Compared to Percent TCE Removal in Port 3 with respect to Port 1.....	41
Figure 14.	Mass Flowrate TCE for First Four Days of 200 g/L TCE Slug.....	42
Figure 15.	Mass Flowrate TCE after First Four Days of 200 g/L TCE Slug.....	43
Figure 16.	Mass Flowrate cis-1,2-DCE for First Four Days of 200 g/L TCE Slug	44
Figure 17.	Mass Flowrate 1,1-DCE for First Four Days of 200 g/L TCE Slug....	45
Figure 18.	Mass Flowrate VC for First Four Days of 200 g/L TCE Slug.....	46
Figure 19.	Mass Flowrate cis-1,2-DCE after First Four Days of 200 g/L TCE Slug.....	47
Figure 20.	Mass Flowrate 1,1-DCE after First Four Days of 200 g/L TCE Slug..	48
Figure 21.	Mass Flowrate VC after First Four Days of 200 g/L TCE Slug.....	49
Figure 22.	ORP Values for 200 g/L TCE Slug.....	50
Figure 22a.	Simultaneous Column.....	51
Figure 23.	Simultaneous Column: Effect of Hydrogen Peroxide (ORP at Different Ports).....	52

Figure 24. Simultaneous Column: Effect of Hydrogen Peroxide (ORP at Different Ports).....	53
Figure 25. Simultaneous Column: Effect of Hydrogen Peroxide (TCE Removal at Port 4).....	54
Figure 26. Simultaneous Column: Effect of Hydrogen Peroxide (TCE Removal at Port 7).....	55
Figure 26a. Simultaneous Column: Effect of Hydrogen Peroxide (TCE Removal at Different Zones).....	56
Figure 27. Simultaneous Column: Effect of Hydrogen Peroxide (Dps at Port 2).....	57
Figure 28. Simultaneous Column: Effect of Hydrogen Peroxide (Dps at Port 4).....	58
Figure 29. Simultaneous Column: Effect of Hydrogen Peroxide (Dps at Port 7).....	59
Figure 30. Simultaneous Column: Effect of Hydrogen Peroxide (% Dps at Port 2)	60
Figure 31. Simultaneous Column: Effect of Hydrogen Peroxide (% Dps at Port 4)	61
Figure 32. Simultaneous Column: Effect of Hydrogen Peroxide (% Dps at Port 7)	62
Figure 33. Simultaneous Column: Effect of Hydrogen Peroxide (Distribution of Dps).....	63
Figure 34. Simultaneous Column: Effect of Hydrogen Peroxide (Distribution of Dps).....	64
Figure 35. Simultaneous Column: Effect of Hydrogen Peroxide (Distribution of Dps).....	65
Figure 36. Simultaneous Column: Effect of Ammonia Nitrogen at 75 ppm Hydrogen Peroxide (Port 4).....	66
Figure 37. Simultaneous Column: Effect of Ammonia Nitrogen at 75 ppm Hydrogen Peroxide (Port 7).....	67
Figure 38. Simultaneous Column: Effect of NH ₃ -N Concentration (Distribution of Dps).....	68
Figure 39. Simultaneous Column: Effect of NH ₃ -N Concentration (Distribution of Dps).....	69
Figure 40. Simultaneous Column: Effect of NH ₃ -N Concentration (Distribution of Dps).....	70
Figure 41. Simultaneous Column: Effect of NH ₃ -N Concentration at 75 ppm Hydrogen Peroxide (Port 4).....	71
Figure 42. Simultaneous Column: Effect of NH ₃ -N Concentration at 75 ppm Hydrogen Peroxide (Port 4).....	72
Figure 43. Simultaneous Column: Effect of NH ₃ -N at 75 ppm Hydrogen Peroxide (Effluent Port 7).....	73

Figure 44. Simultaneous Column: Effect of NH ₃ -N at 75 ppm Hydrogen Peroxide (Effluent Port 7).....	74
Figure 45. Simultaneous Column: Effect of Elevated TCE Concentration (Port 2)	75
Figure 46. Simultaneous Column: Effect of Elevated TCE Concentration (Port 4)	76
Figure 47. Simultaneous Column: Effect of Elevated TCE Concentration (Effluent Port 2).....	77
Figure 48. Simultaneous Column: Effect of Elevated TCE Concentration on Percent TCE Removal at Various Ports.....	78
Figure 49. Simultaneous Column: Effect of Elevated TCE Concentration on Mass Removal Rate of TCE at Various Ports.....	79
Figure 50. Simultaneous Column: Effect of Elevated TCE Concentration on DP Production (Port 2).....	80
Figure 51. Simultaneous Column: Effect of Elevated TCE Concentration on DP Production (Port 4).....	81
Figure 52. Simultaneous Column: Effect of Elevated TCE Concentration on DP Production (Port 7).....	82
Figure 53. Simultaneous Column: Effect of Elevated TCE Concentration on DP Distribution(Port 2).....	83
Figure 54. Simultaneous Column: Effect of Elevated TCE Concentration on DP Distribution(Port 4).....	84
Figure 55. Simultaneous Column: Effect of Elevated TCE Concentration on DP Distribution (Port 7).....	85
Figure 56. Simultaneous Column: Effect of Elevated TCE Concentration on Effluent Dps.....	86
Figure 57. Simultaneous Column: ORP at Elevated TCE Concentration (Effect of Hydrogen Peroxide).....	87
Figure 58. Simultaneous Column: Effect of 400 ppm TCE Slug (Concentration of TCE at Port 2).....	88
Figure 59. Simultaneous Column: Effect of 400 ppm TCE Slug (Concentration of TCE at Port 4).....	89
Figure 60. Simultaneous Column: Effect of 400 ppm TCE Slug (Concentration of TCE at Port 7).....	90
Figure 61. Simultaneous Column: Effect of 400 ppm TCE Slug (TCE Removal)....	91
Figure 62. Simultaneous Column: Effect of 400 ppm TCE Slug (Production and Removal of cis-1,2 DCE).....	92
Figure 63. Simultaneous Column: Effect of 400 ppm TCE Slug (Production and Removal of 1,1 DCE).....	93

Figure 64. Simultaneous Column: Effect of 400 ppm TCE Slug (Production and Removal of VC).....	94
Figure 65. Simultaneous Column: Effect of 800 ppm TCE Slug (Concentration of TCE at Port 2).....	95
Figure 66. Simultaneous Column: Effect of 800 ppm TCE Slug (Concentration of TCE at Port 4).....	96
Figure 67. Simultaneous Column: Effect of 800 ppm TCE Slug (Concentration of TCE at Port 7).....	97
Figure 68. Simultaneous Column: Effect of 800 ppm TCE Slug (TCE Removal)....	98
Figure 69. Simultaneous Column: Effect of 800 ppm TCE Slug (Production and Removal of cis-1,2 DCE).....	99
Figure 70. Simultaneous Column: Effect of 800 ppm TCE Slug (Production and Removal of 1,1 DCE).....	100
Figure 71. Simultaneous Column: Effect of 800 ppm TCE Slug (Production and Removal of VC).....	101
Figure 72. Simultaneous Column: TCE Removal Vs. TOC Removal.....	102
Figure 73. Lysimeter Setup.....	103
Figure 74. Changes in Head over Time in the Lysimeter.....	104
Figure 75. Differences in Head along the Length of the Lysimeter for Day 18	105
Figure 76. Average Difference in Head along the Length of the Lysimeter on Day 18.....	106
Figure 77. Differences in Head along the Length of the Lysimeter for Day 27	107
Figure 78. Average Difference in Head along the Length of the Lysimeter on Day 27.....	108
Figure 79. Differences in Head along the Length of the Lysimeter for Day 38	109
Figure 80. Average Difference in Head along the Length of the Lysimeter on Day 38.....	110
Figure 81. Differences in Head along the Length of the Lysimeter for Day 51	111
Figure 82. Average Difference in Head along the Length of the Lysimeter on Day 51.....	112
Figure 83. Differences in Head along the Length of the Lysimeter for Day 62	113
Figure 84. Average Difference in Head along the Length of the Lysimeter on Day 62.....	114

Figure 85. Comparison of Height of Constant Head Tank to Headloss through the PVD.....	115
Figure 86. Average Difference in Head at Each Length of the Lysimeter.....	116

LIST OF TABLES

Table 1. Simulated Groundwater Make-up.....	4
Table 2. Concentration and Mass Flowrate Throughout the Sequential Column for the Addition of Methanol into Port 2.....	5
Table 3. TCE Removal Rates and Percentages throughout the Sequential Column for Addition of Methanol into Port 2.....	6
Table 4. Removal of Daughter Products in Port 6 with Respect to Port 3 for Methanol Addition into Port 2.....	8
Table 5. Average ORP Values (mV) throughout the Sequential Column for Addition of Methanol into Port 2.....	9
Table 6. Comparison of Average Daughter Product Creation Before and After 200 g/L TCE Slug in Sequential Column.....	11
Table 7. Removal of Daughter Products in Port 6 with Respect to Port 3 after 200 g/L TCE Slug Passed through the Sequential Column.....	11
Table 8. Effect of H ₂ O ₂ Concentration on TCE Removal Rates.....	13
Table 9. DP Removal from Port 4 to Port 7.....	14
Table 10. Effect of NH ₃ -N Concentration on TCE Removal.....	15
Table 11. Effect of NH ₃ -N Concentration on DP Production and Removal.....	15
Table 12. Effect of Elevated TCE Concentration on TCE Removal.....	16
Table 13. Effect of Elevated TCE Concentration on Production and Removal of Dps.....	17
Table 14. Effect of H ₂ O ₂ Concentration on TCE Removal Rate for Elevated TCE Concentration.....	18
Table 15. Effect of H ₂ O ₂ Concentration on Effluent DP Levels for Elevated TCE Concentration.....	19
Table 16. Effect of 400 mg/L Slug on the Mass of TCE in the Effluent.....	19
Table 17. Effect of 400 mg/L Slug on DP Production.....	19
Table 18. Effect of 800 mg/L Slug on the Mass of TCE in the Effluent.....	20
Table 19. Effect of 800 mg/L Slug on DP Production.....	21
Table 20. Simultaneous Column: TOC/TCE Ratio.....	22

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, methanogenic, and other selected bacteria for cost-effective 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 and methanogenic bacteria and introduction of non-native organisms should not be necessary. Also, only relatively benign enhancing compounds will be added in non-toxic concentrations. It is envisioned to take advantage of the natural symbiotic relationship between the methanogenic and methanotrophic bacteria so as to promote sequential anaerobic/aerobic mineralization of the chlorinated solvent contaminants.

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. Our original proposal was organized into five phases, as follows:

Phase 1: Literature Review.

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

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

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

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

A comprehensive literature review of biodegradation of chlorinated solvents was completed and submitted as part of the second quarterly report. As a result of this review we realized the potential for developing the relationship between the methanotrophs (aerobic) and the methanogens (anaerobic) for mineralization of both highly chlorinated and less chlorinated compounds. Emphasis was given to this approach in subsequent phases of the workplan.

The methanotrophs have an obligate requirement for methane, which is complemented by the methane production of methanogenic organisms. Furthermore, the methanogens ability to dehalogenate more oxidized (more halogenated) pollutants, generating vinyl chloride, is complemented 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 might be advantageous to induce methanotrophic growth at the point where all (or most) of the more chlorinated compounds have been dehalogenated to vinyl chloride. 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.

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). It is interesting to note in this regard that Kastner (1991) reported that an aerobic enrichment culture's ability to dechlorinate cis-1,2-dichloroethylene was shown to be dependent on a cyclic transition from aerobic to anaerobic conditions and limited oxygen supply. 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.

5.0 WORK PERFORMED THIS PERIOD

This quarter, the columns were combined to operate in a sequential mode. Parameters such as TCE hot spot addition and methanol addition into Port 2 were evaluated for the sequential column. The simultaneous column is operating. Parameters such as TCE hot spot addition, hydrogen peroxide, and $\text{NH}_3\text{-N}$ concentration were evaluated this quarter. The lysimeter was run to evaluate the performance of PVD drains for amendments delivery.

A brief summary of progress on the tasks is presented below.

1.1 Optimization of Sequential Mineralization--90 % Complete

This task was continued this quarter in the combined columns by investigating the influence of a variety of variables on performance.

1.2 Design and Construction of Simultaneous Mineralization Column--100% Complete

This task was completed when the funds became available (in March).

1.3 Development and Testing of Protocol to Locate Zones--100 % Complete

A microsystem was located that allows measurement of the oxidation reduction potential (ORP) externally and measurements were carried out on both the anaerobic and aerobic columns. The system allows the use of ORP measurements to locate the anaerobic and aerobic zones.

1.4 Optimization of Simultaneous Mineralization--40 % Complete

The system is now constructed and running.

1.5 Assessment of Potential Bioremediation of High Concentrations of CAH Compounds --35 % Complete

Hot spots were added to both columns.

2.1 Design and Construction of Lysimeters Equipped with PVD's--100 % Complete

The lysimeters were designed this quarter and are operating to evaluate the performance of PVD for amendment delivery.

2.2 Amendments Delivery and Potential Clogging--10 % Complete

3.0 Preparation and Submission of Quarterly and Final Reports--75 % Complete

Assuming equal weight for each of the 8 project tasks noted above, it is estimated that the overall project is 68.75% complete.

6.0 RESULTS AND DISCUSSION

6.1 Sequential Column

The anaerobic and aerobic columns have been operating together for the past two quarters in a continuous upflow mode under a variety of conditions. A schematic diagram of the sequential setup is given in Figure 1. This quarter, the effects of adding methanol into Port 2 on TCE removal and hot spot addition on column

performance were investigated. In Table 1 the chemical compounds entering the sequential column are presented.

Table 1. Simulated Groundwater Make-Up

Chemical	Concentration	Chemical	Concentration
NH ₄ Cl	29.81	HBO ₃	0.580
K ₂ HPO ₄	2.92	NiCl ₂ ·6H ₂ O	1.92
KH ₂ PO ₄	2.11	Na ₂ MoO ₄ ·2H ₂ O	0.768
MgCl ₂ ·6H ₂ O ¹	5.76	L-cysteine C ₂ H ₂ NO ₂ S·HCl·H ₂ O	25.0
MnCl ₂ ·4H ₂ O	1.92	NaHCO ₃	76.8
CoCl ₂ ·6H ₂ O	3.84	Yeast Extract ²	5.0
ZnCl ₂	1.92	FeCl ₂ ·4H ₂ O	1.15
CaCl ₂ ·2H ₂ O	6.34	Na ₂ S·9H ₂ O	25.0

6.1.1 Effect of Methanol Addition into Port 2 of Sequential Column

Based on TOC measurements throughout the anaerobic column, it was noted that most of the TOC was consumed in the first four inches of the column. As a result, TCE removal occurred only in the bottom section of the anaerobic column. To utilize more effectively the entire column, methanol was added in Port 2 of the anaerobic column. Methanol was the only form of available TOC to the methanogens as acetic acid use had previously been discontinued. Initially, only 50 mg/L of methanol was added in Port 2 with the influent methanol concentration being dropped from 750 to 700 mg/L. It was observed an increase in TCE removal. Then after approximately two weeks, the methanol in Port 2 was increases from 50 to 150 mg/L, while the influent methanol concentration was lowered to 600 mg/L. No methanol was added to Port 2 for a week due to syringe pump problem. Finally, 150 mg/l of pulse feed methanol was introduced to Port 2 twice daily. Figure 2 contains the column conditions for the addition of methanol into Port 2 of the sequential column.

The mass flowrate of TCE during the addition of methanol into Port 2 of the sequential column is presented in Figure 3 and Table 2. In Table 3, the TCE removal at various locations within the column is presented.

Table 2. Concentration and Mass Flowrate throughout the Sequential Column for the Addition of Methanol into Port 2

	H ₂ O ₂ = 75 mg/L	H ₂ O ₂ = 85 mg/L	H ₂ O ₂ = 150 mg/L
Concentration Port 6 (µg/L)	3286.9	3029.0	2300.1
Concentration Port 4 (µg/L)	3248.8	2926.8	2312.4
Concentration Port 3 (µg/L)	3502.0	2935.7	2449.7
Concentration Port 1 (µg/L)	3809.6	3422.6	2548.5
Concentration Influent (µg/L)	6997.6	5901.3	4613.8
Mass Flowrate Port 6 (µg/h)	27.25	21.20	22.50
Mass Flowrate Port 4 (µg/h)	26.62	20.60	22.46
Mass Flowrate Port 3 (µg/h)	27.56	19.85	22.79
Mass Flowrate Port 1 (µg/h)	29.63	22.87	25.35
Mass Flowrate Influent (µg/h)	53.60	39.22	45.76

Table 3. TCE Removal Rates and Percentages throughout the Sequential Column for Addition of Methanol into Port 2

Port - Ref. Port	Methanol = 50 mg/L	Methanol = 150 mg/L	None	Pulse Feeding
Removal Rate (µg/L·h)				
Port 6 - Influent	244.2	287.6	623.6	409.9
Port 3 - Influent	337.2	594.2	1263	841.2
Port 6 - Port 3	151.2	-19.1	-15.8	-21.4
Port 3 - Port 1	NA	NA	153.2	59.8
Percent Removal				
Port 6 - Influent	65.59	74.10	98.0	94.6
Port 3 - Influent	43.56	70.67	99.4	95.3
Port 6 - Port 3	39.03	-13.28	-257.0	-15.4
Port 3 - Port 1	NA	NA	96.2	54.4

As noted, TCE removal was significantly increased during the addition of methanol into Port 2 of the sequential column from 50.8% to 65.6% even though the TCE concentration had risen from 5.0 mg/L to 20.0 mg/L. When the amount of methanol added to Port 2 was increased from 50 to 150 mg/L, the removal again increased and near the end of the period TCE removal was nearly total. On the twelfth day of the change to 150 mg/L TCE, the removal began to significantly increase. This period was needed to induce a viable population of methanogens around Port 2. The removal stayed to nearly 100% for the period when no methanol was added to Port 2. This is may be due to the production of methanogenic biomass during the methanol addition. So, when the substrate began to decline at the end of the period, the TCE removal started to decrease. During this time, Port 1 became accessible for daily sampling. It was then noted that the TCE removal in Port 3 with respect to Port 1 had increased so that 96.2% of the contaminant available in Port 1 was destroyed by the time it had reached Port 3. Therefore, this is evidence that TCE removal was occurring throughout the anaerobic column. When pulse feeding was used, the removal rate and percent removal decreased. This could have been caused either by the rise in influent TCE concentration or due to the previous period when no methanol was added into Port 2 destroying the methanogenic population. The significant rise in Port 1 on day 147 can be attributed to an unintentional TCE slug of 80 mg/L entering the anaerobic column due to fluctuating groundwater feed rates. As can be seen, the column came back to normal four days later.

The massflowrate of the individual DPs are presented in Figures 4 to 7, while the cumulative totals of DPs in Ports 6 and 3 are presented in Figures 8 and 9, respectively. In Table 4, the removal of each DP in Port 6 with respect to Port 3 is presented.

The DP that was easily oxidized was VC, followed by trans-DCE, cis-DCE, and 1,1-DCE. Near the end of the second period, the only isomer of DCE that was formed was cis-DCE. The non-production of trans-DCE continued until the end of the methanol addition to Port 2 study. 1,1-DCE was noted in Port 1 when it began to be sampled, but was removed before the top of the anaerobic column (Port 3). This showed that not only did an increase in TCE reduction occurred in Port 3 with respect to Port 1, but also DP reduction was also occurring. For the period when no methanol was added to Port 2, the removal from Port 3 with respect to Port 1 of TCE, cis-DCE, and 1,1-DCE was 28.39 $\mu\text{g/h}$, 6.11 $\mu\text{g/h}$, and 0.70 $\mu\text{g/h}$, respectively. During the time Port 1 was sampled, the amount of VC generated from Port 1 to Port 3 increased by 15.90 $\mu\text{g/h}$. By using a mole balance, 88.9% of the TCE and DCE isomers removed went to VC. This indicated that the remaining 11.1% of the DPs went to ETH production. Though ETH was believed to be created during earlier runs, this was the first case when ETH production was clearly noted.

Table 4. Removal of Daughter Products in Port 6 with Respect to Port 3 for Varying H₂O₂ Concentrations

Contaminant	CH ₃ OH = 50 mg/L	CH ₃ OH = 150 mg/L	None	Pulse Feeding
Removal Rate (µg/L·h)				
cis-DCE	5.67	2.48	-1.19	0.085
trans-DCE	0.980	0.945	---	---
1,1-DCE	0.561	0.027	---	0.309
VC	8.09	15.6	33.9	16.9
Percentage Removed				
cis-DCE	31.85	4.39	1.04	7.35
trans-DCE	38.54	25.60	---	---
1,1-DCE	14.36	0.08	---	14.90
VC	78.13	41.48	36.88	17.22

The percent removal of cis-DCE and VC dropped as the concentration measured in the column increased. This is believed to be caused by a toxic effect due increased amount of CAHs entering the column. Previous research has suggested that as the influent contaminant concentration was increased, the amount of methane produced declined. This was thought to be due to more of the reducing equivalents going to TCE reduction than methane production. Therefore, as CAH reduction increases within a system, the amount of methane produced drops. This could have been the reason for less oxidation occurring in the aerobic column. The initial increase in DP removal could have been from the methanotrophs having a reduction in methane concentration, which would allow more CAH oxidation to occur in the aerobic column. After time, the removal decreased due to only small amounts of methane entering the aerobic column for growth of new cells and cell maintenance. Therefore, in order to determine if this is the case, either methane samples from the effluent of the anaerobic column should be run, or methane-sparged water should be fed into the influent of the aerobic column to determine if the methanotrophs are methane limited.

The ORP values of the sequential column are presented in Figure 10 and Table 5.

Table 5. Average ORP Values (mV) throughout the Sequential Column for Addition of Methanol into Port 2

Reference Port	CH ₃ OH = 50 mg/L	CH ₃ OH = 150 mg/L	None	Pulse Feeding
Port 6	-36.0	38.0	34.2	63.9
Port 4	-9.9	45.9	41.3	76.3
Port 3	-113.0	-107.2	-96.5	-114.6
Port 1	-100.3	-102.1	-91.9	-113.5

As noted earlier, the ORP did not return to a positive value (oxidative conditions) until the methanol added to Port 2 was increased to 150 mg/L. The difference in ORP values between Ports 4 and 6 showed the extent of use of oxygen by the aerobic microorganisms. As this difference became smaller, the percent removal of cis-DCE decreases for each period while VC decreases except for the pulse feeding period. This is shown in 11 and 12, respectively. This shows that the microorganism population in the aerobic column was dropping, possibly due to a decrease in methane available to the bacteria. The difference in ORP values between Ports 1 and 3 shows the amount of TOC consumed by the anaerobic bacteria. As this number becomes lower, the amount of TCE removed in Port 3 with respect to Port 1 decreases. This is shown in Figure 13. This could be caused by the healthy culture created due to the feeding of methanol into Port 2 followed by the decrease in biomass caused by the lack of feeding of methanol into Port 2 for a week.

6.1.2 Hot Spot Addition

To better understand how microorganisms react to high concentrations of TCE, a major slug load of TCE was added to the system. The volume of the slug was 5 mL and it contained a concentration of 200 g/L TCE. Therefore, the total TCE added to the system was 1 g. This concentration of TCE was greater than the solubility of TCE in water (1100 mg/L), so part of the TCE should be present as a dense, non-aqueous phase liquid (D-NAPL). This amount of TCE was 10,000 times greater than the normal concentration added to the system (20 mg/L) and during normal

operating conditions, it would take 417 days to see the same amount of TCE entering the system.

The mass flowrate of TCE for the first four days of the experiment is presented in Figure 14, while the mass flowrate of TCE after the initial four days in Figure 15. For the first four days of the slug, the TCE concentration throughout the column was extremely high, with the largest TCE concentration occurring in Port 3 at the end of 24 hours (1521 mg/L). The slug was not seen in Port 6 until 96 hours had passed, and it had a value of (1273 mg/L). The reason that the concentration was able to go above the solubility of TCE in water was because the TCE was first solubilized in methanol, which may have increased the solubility. This showed that most of the TCE was absorbed into the methanotrophic biomass compared to the methanogenic. Also, the mass flowrate did not drop immediately down to below the influent TCE mass flowrate, it was assumed that the TCE was acting as a D-NAPL at the bottom of the anaerobic column. By the fifth day after the slug addition, the TCE mass flowrate dropped considerably. By day eleven after the addition of the slug, all ports showed a mass flowrate less than the influent except Port 6, which showed removal on day twelve. A mass balance on TCE over this period showed a removal of 96.9%. Therefore, the column could still operate at concentrations near the the water solubility limit. The percent removal in the column for the days following the twelfth was 88.9% for Port 6 with respect to the influent, and 93.1% for Port 3 with respect to the influent.

The DP production for the first four days of the slug passage is presented in Figures 16 to 18, while for days 5 to 15, the results are presented in Figures 19 to 22. All of the DPs reached a very high concentration during the first four days of the slug passage. The highest concentration of cis-DCE occurred on the 24th hour of the slug passage in Port 3 and reached a concentration of 7985.8 µg/L. 1,1-DCE reached its highest concentration on hour 48 in Port 6 and had a maximum concentration of 3135.2 µg/L. VC had a maximum concentration at hour 24 in Port 3, which was at a concentration of 7296.8 µg/L. After day five, the concentrations of DPs became steady-state values. These values werre compared to the period before the addition of the TCE slug in Table 6.

As observed, VC had a dramatic drop in production after the slug passed through the system dropping by 21.5 times the previous rate, while the production of 1,1-DCE increased by 7 times. The cis-DCE also had a drop in productin of 2.3 times from the previous period. The reason for this could be due to a drop in biomass in the anaerobic column due to the toxicity of the slug in the anaerobic column killing many of the bacteria. When the bacteria began to remultiply, the organisms incorporated the CAH compounds into the cell and therefore showed less of the CAH compounds exiting the column. This could be the reason for such low amounts of cis-DCE and VC appearing in the column effluent.

The removal of daughter products for the steady-state values following the slug passage is presented in Table 7.

Table 6. Comparison of Average Daughter Product Production Before and After 200 g/L TCE Slug in Sequential Column

Contaminant Port	Before Slug Additon	After Slug Addtion
Concentration ($\mu\text{g/L}$)		
cis-DCE Port 6	515.63	379.7
cis-DCE Port 3	517.68	333.7
1,1-DCE Port 6	9.85	78.7
1,1-DCE Port 3	17.26	182.8
VC Port 6	2175.93	106.8
VC Port 3	2581.63	119.7
Mass Flowrate ($\mu\text{g/h}$)		
cis-DCE Port 6	6.362	2.78
cis-DCE Port 3	6.867	2.47
1,1-DCE Port 6	0.142	0.825
1,1-DCE Port 3	0.246	1.731
VC Port 6	26.686	1.24
VC Port 3	32.230	1.09

Table 7. Removal of Daughter Products in Port 6 with Respect to Port 3 after a 200 g/L TCE Slug Passed through the Sequential Column

Contaminant	After Steady-State
Removal Rate ($\mu\text{g/L}\cdot\text{h}$)	
cis-DCE	-0.168
1,1-DCE	4.335
VC	-0.539
Percentage Removed	
cis-DCE	-12.6
1,1-DCE	52.6
VC	-13.8

As noted from the above tables, there was an increase in VC and cis-DCE from the anaerobic column to the aerobic column due to the influent high concentration of CAH compounds. But, 1,1-DCE showed a decrease.

The ORP throughout the anaerobic column for the slug addition is given in Figure 21. The ORP in Port 3 with respect to Port 1 became only slightly more negative during this time. This showed that most of the methanol was removed in the bottom portion of the column. It also showed that the methanogens located in the bottom of the column acclimated better than the biomass located around Port 2. The general trend did show values becoming less reductive with time, which might show that there was a decrease in biomass within the anaerobic column. The ORP values in Port 6 with respect to Port 4 show that change in ORP continued to occur which signified that the organisms continued to survive within the column.

6.2 Simultaneous Column

A 24 inch simultaneous column was set up towards the end of the second quarter. The schematic is shown in Figure 22. An integrity test was performed last quarter and the column was inoculated with anaerobic and aerobic microorganisms. The column was run with an influent TCE concentration of 5 mg/L throughout last quarter. The hydrogen peroxide concentrations at ports H1 and H2 were gradually increased from 25 to 75 mg/L. This quarter, the effect of different peroxide concentration was investigated. Also, the influent TCE concentration was increased to 16.5 and 22 mg/L. Also, 400 and 800 mg/L TCE slugs were injected in the column to evaluate the effect of hot spots in the column.

6.2.1 Effect of H_2O_2

6.2.1.1 Aerobic and Anaerobic Zone Distribution

The column was fed with aerobic microorganisms after increasing the H_2O_2 concentration at H1 and H2 from 25 to 50 mg/L. ORP measurements were taken at all the sampling ports to determine the distribution of aerobic and anaerobic zones in the column. The goal was to obtain an initial anaerobic zone followed by a facultative zone where both aerobic and anaerobic bacteria coexist. The effluent or final zone was desired to be predominantly aerobic to obtain maximum removal of the daughter products. The average ORP values for different H_2O_2 concentrations are plotted in Figure 23. The ORP values for 75 and 100 mg/L H_2O_2 at H1 and H2 respectively, indicated the development of the desired zones in the column. The influent port and port 2 had negative ORP values indicating anaerobic region and the increase in ORP value from port 1 to 2 indicated reductive dehalogenation. Injection of H_2O_2 before port 3, increased the ORP to positive at port 3 and 4. Injection of peroxide before port 5 further increased the ORP, while the decrease in ORP from port 6 to 7 indicated aerobic degradation. Both Figures 23 and 24 indicated a gradual development of ideal conditions with the increase in H_2O_2 concentrations.

6.2.1.2 TCE Removal

The effect of H_2O_2 concentration on TCE removal is illustrated in Figures 25, 26 and 26a. The percent and mass removal rates at port 4 and 7 are listed in Table 8.

Table 8. Effect of H₂O₂ concentration on TCE Removal Rates

Phase #	H ₂ O ₂ Conc.		Avg. Influent TCE (µg/L) ¹	Port 4		Port 7 (Effluent)	
	H1	H2		% Rem	Amt Rem	% Rem	Amt Rem
1	50	50	5820	39.86	20.56	53.72	27.6
2	75	75	3244	27.23	6.47	42.3	10
3	75	100	3462	45.93	14.05	57.17	17.63

¹measured at port 1

The influent TCE concentration for 50 mg/L H₂O₂ concentration was 5820 µg/L. As noted, the corresponding removal rates were approximately 40 and 54% at port 4 and 7, respectively. The influent TCE for the second and third case are however comparable. The removal rate increased with increase in the H₂O₂ concentration at port H2. The growth of the aerobic organisms could have been enhanced by the increased peroxide concentration. As a result, more TCE and Dps were degraded. While there was about 15% increase in the over all percent removal, the percent removal at port 4 increased by 18.7% when the concentration at H2 was increased from 75 to 100 mg/L. The mass removal rates increased by 117.2% and 76.3% at ports 4 and 7 respectively. Port 4 is representative of the facultative zone while port 7 represents the final aerobic zone. The increase in the H₂O₂ concentration therefore seemed to have improved the functioning of the organisms in the facultative zone as well as the aerobic zone.

6.2.1.3 DP Production and Removal

The effect of H₂O₂ concentration on the DP production is illustrated in Figures 27 to 29. The concentration, mass flowrate, and percent distribution of each of the DPs are plotted in Figures 33 to 35, for the different concentrations of H₂O₂.

When the H₂O₂ concentration was 50 mg/L, the major DP was 1,1 DCE constituting 70.3% of the total DPs in the effluent. The cis- DCE concentration increased gradually at all the ports, with increase in the H₂O₂ concentration (Figures 30, 31, and 32) and emerged as the major DP by the end of the experimental period. It constituted 17.14%, 50.1% and 69.4% of the total DPs at the effluent, when the H₂O₂ concentration at H2 were 50, 75, and 100 mg/L respectively. Also, during the 100 mg/L feed period, a new DP, 1,2 dichloroethane (1,2 DCA) was detected at very low concentrations, constituting 1.24% of the total DPs in the effluent. The use of a new custom standard for the GC from day 55 facilitated the measurement of this DP. This indicates a deviation in the reductive dehalogenation pathway: TCE→DCE→VC. 1,2 DCA may be formed either by hydrogenation of 1,2 DCE or by dechlorination of TCA (trichloroethane) which in turn are formed by the dechlorination (1,2 DCE) or hydrogenation (TCA) of TCE (Figure 30).

The production and removal of DPs is plotted in Figures 27 to 29. The maximum amount of DPs was measured at port 2 which is situated at the end of the initial anaerobic region corresponding to the maximum percent TCE removal occurring in the anaerobic zone. Port 4 is located midway between the facultative zone. Both DP formation as well as degradation occur in the facultative zone and hence no comparison can be made between DP concentrations measured at ports 2 and 4. A decrease in the DP concentrations and mass flowrates from port 4 to port 7 indicated degradation of DPs in the portion of the facultative zone following

port 4 as well as the final aerobic zone. The percent decrease in the DP concentrations from port 4 to port 7 is listed in the following Table 9.

Table 9. DP Removal from Port 4 to Port 7

Phase #	H ₂ O ₂ conc. (mg/L)		cis 1,2 DCE		1,1 DCE		VC		1,2 DCA	
	H1	H2	port 4 conc (µg/L)	% decrease	port 4 conc (µg/L)	% decrease	port 4 conc (µg/L)	% decrease	port 4 conc (µg/L)	% decrease
1	50	50	4.94	31.2	13.19	-5.8	4.44	34.7	-	-
2	75	75	15.29	22.83	13.43	21.52	3.94	18.8	-	-
3	75	100	151.3	23.23	39.87	42.94	15.88	32.43	4.08	20.8

It can be seen from Table 10 that all the DP concentrations significantly increased during the last phase of the experimental period. This corresponds to an increase in TCE removal during the same phase. The TCE removal however, did not increase as significantly as the DP formation. This indicates that abiotic removal of TCE might have contributed to the percent TCE removal in phases 1 and 2 resulting in low DP production. Considerable decrease or complete cessation of abiotic removal following the achievement of steady state growth conditions might have led to in high DP concentrations in the last phase.

The NH₄Cl concentration in the feed was decreased from 56.65 to 28.3 mg/L during the second phase of the experiment. The percent removal of DPs also increased from phase 2 to phase 3. The increase in TCE and DP removal may therefore be due to the increase in aerobic growth (due to increase in peroxide concentration) as well as prevention of competitive inhibition by ammonia (due to decrease in NH₄Cl concentration). Also the percent increase in the DP removal was more pronounced for 1,1 DCE and VC when compared to cis 1,2 DCE. This may be due to the ability of the methanotrophs to degrade the less chlorinated compounds better than compounds with higher levels of chlorination.

6.2.2 Effect of NH₃-N Concentration

Due to its low substrate specificity the MMO enzyme has the ability to oxidize ammonia. The nutrient feed for the column contained NH₄Cl as the nitrogen source for the anaerobic microorganisms. Since this hinders the TCE degradation by competitive inhibition, the NH₄Cl concentration was decreased from 56.65 to 28.3 mg/L on day 52. The extent of decrease in the NH₄Cl concentration was determined based on ammonia analysis of samples taken from the anaerobic portion of the sequential column.

6.2.2.1 TCE Removal

TCE concentrations at ports 1 (influent), 4 and 7 (effluent) from days 48 to 68 are plotted in Figures 36 and 37. All other parameters were constant during this time. The H₂O₂ concentration at H1 and H2 was 75 mg/L. The removal rates of TCE at ports 4 and 7 are listed in Table 10. Port 2 was not sampled during the first phase of the experimental period. There was a 22.5% increase in the percent

removal at port 4, while the overall percent TCE removal in the column increased by 22% on decreasing the $\text{NH}_3\text{-N}$ concentration in the column. The amount of TCE removed increased by 80% and 81% at ports 4 and 7 respectively. Thus the decrease in the NH_4Cl concentration had almost the same effect at both the ports with respect to TCE removal.

Table 10. Effect of $\text{NH}_3\text{-N}$ Concentration on TCE Removal

Phase #	NH_4Cl Conc (mg/L)	TCE Removal			
		port 4		port 7	
		%	Amt ($\mu\text{g/h}$)	%	Amt ($\mu\text{g/h}$)
1	56.65	24	4.44	37.36	6.83
2	28.3	29.4	8	45.53	12.37

6.2.2.2 DP Production and Removal

The trend in DP production during the entire experimental period is illustrated in Figures 38 to 40. The DP concentration and percent distribution are plotted in Figures 41 to 44, on a daily basis. Figures 38 to 40, and Table 11, indicate the trend in DP production and removal for the two phases of the experiment. The port 4 average concentration and mass flowrate values are the maximum for phase two, indicating that most of the TCE removal and DP production occurred in the anaerobic region. Cis-1,2 DCE was the major DP formed in both the phases of the experiment. Only cis-DCE experienced a 6.5% increase in concentration at port 4 from phase 1 to 2, while the other two DPs' concentrations remained the same.

From Table 11, it can be seen that the percent decrease in the 1,1 DCE and VC concentrations from port 4 to 7, increased with reduction in the NH_4Cl concentration. While the removal of cis-DCE decreased by about 5%, there was 34.8% and 21.36% increase in the removal of 1,1 DCE and VC respectively. This indicates that ammonia inhibits aerobic degradation of the DPs.

Table 11. Effect of $\text{NH}_3\text{-N}$ Concentration on DP Production and Removal

Phase #	NH_4 Conc (mg/L)	cis DCE		1,1 DCE		VC	
		port 4 Conc ($\mu\text{g/L}$)	% Decrease	port 4 Conc ($\mu\text{g/L}$)	% Decrease	port 4 Conc ($\mu\text{g/L}$)	% Decrease
1	56.65	14.53	26.6	13.14	-8.1	3.84	1.04
2	28.3	15.47	21.9	13.13	26.7	3.84	22.4

6.2.3 Effect of Elevated TCE Concentration

The TCE concentration in the column was increased from a target value of 5 mg/L to 22 mg/L on day 90 in order to evaluate the ability of the microorganisms in

degrading higher concentration levels of TCE, representative of contaminated site conditions. While the average TCE concentration was maintained at approximately 22 mg/L for the first 9 days, it was reduced to about 16.5 mg/L for the remaining 23 days. The H₂O₂ concentration was maintained at 75 (H1) and 100 (H2) mg/L for the first nine days and changed to 50 (H1) and 150 (H2) mg/L for the remaining 23 days.

6.2.3.1 TCE Removal

The daily trend in TCE removal at ports 2, 4, and 7 are shown in Figures 45 and 47. The percent and mass removal rates of TCE for influent concentrations of 5, 22, and 16.5 mg/L are listed in Table 12. The influent peroxide concentrations were maintained at 75 (H1) and 100 (H2) mg/L for all the three cases. The comparison of percent and mass removal rates for the three cases is also illustrated in Figures 48 and 49.

Table 12. Effect of Elevated TCE Concentration on TCE Removal

Case #	Influent TCE (mg/L)	Percent Removal Rate (%)			Mass Removal Rate (µg/h)		
		Port 2 ¹	Port 4	Port 7	Port 2 ¹	Port 4	Port 7
1	5	41.62	45.9	57.17	10.81	14.05	17.63
2	22	52.4	55.1	70.04	100.1	105.4	134.82
3	16.5	36.2	37.6	54.3	53.4	55.5	80.5

The percent removal rate increased by 10.8%, 9.2%, and 12.9% at ports 2, 4, and 7 respectively, on increasing the influent TCE concentration from 5 to 22 mg/L (Figure 48). The mass removal rates on the other hand, experienced phenomenal increases of 826%, 650%, and 665% at ports 2, 4, and 6 respectively (Figure 49). Decrease in the influent TCE concentration from 22 to 16.5 mg/L resulted in a decrease in percent as well as mass removal rates. While the percent removal rates for case 3 were about 4% less than that for case 1, the mass removal rates were about 350% higher. This indicates that the increase in TCE concentration resulted in an increase in the mass removal rate of TCE.

6.2.3.2 DP Production and Removal

The daily trend on the production of DPs at ports 2, 4, and 7 for 22 and 16.5 mg/L influent TCE is shown in Figures 50 to 52. The percent distribution of the DPs at the three ports is illustrated in Figures 53 to 55. The effluent concentrations of the DPs for the different cases are compared in Figure 56. The concentration of DPs at port 4 and the removal rate between port 4 and 7 are listed in Table 13.

Table 13. Effect of Elevated TCE Concentration on Production and Removal of DPs

Case #	cis-1,1 DCE			1,1 DCE			VC			1,2 DCA		
	Port 4 (mg/L)	% Rem	Amt Rem (µg/h)	Port 4 (mg/L)	% Rem	Amt Rem (µg/h)	Port 4 (mg/L)	% Rem	Amt Rem (µg/h)	Port 4 (mg/L)	% Rem	Amt Rem (µg/h)
1	151.3	23.23	0.325	39.87	42.94	0.1	15.88	32.43	0.05	4.08	20.8	0.01
2	193.1	20.3	0.363	41.53	20.5	0.1	15.2	-154	- .145	17.9	25.5	0.07
3	117.7	- 7.2	- 0.12	40.39	-9.4	- .03	15.83	-105	- 0.14	18.08	- 27.4	- .04

It can be seen from Table 13 that the concentration of cis DCE, 1,1 DCE, and 1,2 DCA at port 4 increased with the increase in the influent TCE concentration from 5 to 22 mg/L. The concentration of VC however remained almost the same. On decreasing the concentration of the influent TCE to 16.5 mg/L the concentration of cis- and 1,1- DCE increased, while VC and DCA concentrations underwent a slight increase. From Figure 61, it can be seen that the total DPs increased with the increase in the influent TCE concentration from 5 to 22 mg/L, and decreased when the TCE concentration was dropped to 16.5 mg/L. The increase in TCE concentration from 5 to 22 mg/L resulted in an increase in the mass removal (from port 4 to 7) rate of cis DCE and 1,2 DCA by 11.7% and 600% respectively, while the mass removal rate of 1,1 DCE and VC decreased. The decrease in the influent TCE concentration from 22 to 16.5 mg/L resulted in a reduction in the concentrations negative removal rates for all the DPs. This may be due to increase in the production of DPs due to the degradation of higher levels of TCE in the facultative region between port 4 and port 7. In order to improve the removal of DPs between ports 4 and 7, the peroxide concentration was increased at port H2.

6.2.3.3 Effect of H₂O₂ Concentration for Elevated TCE Concentration

In order to improve the removal rate of TCE, the length of the initial anaerobic region was increased by decreasing the peroxide concentration at port H1 from 75 to 50 mg/L. Also, in a bid to improve the efficiency of the final aerobic zone in removing the DPs, the peroxide concentration at port H2 was increased from 100 to 150 mg/L. The ORP values (Figure 57) indicate that the required changes were obtained as expected. The increase in the length of the anaerobic region is indicated by the shift in ORP at port 3 from positive to negative. Also the increase in the ORP at ports 4,5,6 and 7, indicates an improvement in the final aerobic environment in the column.

Table 14. Effect of H₂O₂ Concentration on TCE Removal Rate for Elevated TCE Concentration

Influent TCE (mg/L)	H ₂ O ₂ (mg/L)		% TCE Rem			Amt TCE Rem (µg/h)		
	H1	H2	Port 2	Port 4	Port 7	Port 2	Port 4	Port 7
16.5	75	100	36.2	37.6	54.3	53.4	55.5	80.5
16.5	50	150	39.3	44.7	59.9	56.6	65.1	87.1

Table 15. Effect of H₂O₂ Concentration on effluent DP levels for Elevated TCE Concentration

Influent TCE (mg/L)	H ₂ O ₂ (mg/L)		Effluent DP Conc (µg/L)			
	H1	H2	cis DCE	1,1 DCE	VC	1,2 DCA
16.5	75	100	206.9	45.4	31.2	22.8
16.5	50	150	117.7	37.4	18.6	14.9

It can be seen from Figures 48 and 49, and Table 14, that the TCE removal rates increased throughout the column. While the overall percent removal rate increased by 5.6%, the mass removal rate increased by 8.2%. The trend in the effluent concentrations of DPs is shown in Figure 56 and Table 15. The increase in the peroxide concentration at port H2 resulted in decrease all the effluent DP concentrations indicating an improvement in the DP removal efficiency of the aerobic organisms in the column. The effluent concentration of cis DCE, 1,1 DCE, VC, and 1,2 DCA decreased by 43 %, 18 %, 40.3 %, and 34.6 % respectively.

6.2.4 Effect of 400 mg/L TCE Slug

The mass loading rate of TCE for 16.5 mg/L concentration at a flow rate of 8.7 ml/h is 3.44 mg/day. The TCE loading corresponding to the 5 mL of 400 mg/L slug is 2.05 mg. The slug therefore is only about 60% of the daily loading in the column or 30% of the loading per HRT (48 h). Hence, the column was expected to successfully handle the slug with out any adverse effects. The TCE concentration at ports 2, 4, and 7 are shown in Figures 58 to 60. The concentrations of TCE at port 2 and 4 shot up to about 55 mg/L and 34 mg/L after the first 12 and 36 hours respectively. They however decreased to values below the average TCE concentration level before the slug passage, in the next 12 hours (Figure 58). The TCE concentration at port 7 however did not increase phenomenally, indicating TCE removal in the column. After 120 hrs the effluent TCE concentration dropped below the average effluent concentration before the slug passage. Therefore, it was assumed that the effect of the slug in the column, ceased after 120 hours. The percent TCE removal in the column was determined based on the following calculations:

Mass loading rate of TCE due to continuous influent of 16.5 mg/L = 154.02 µg/h = 3.7 mg/day

Since the effluent showed signs of recovering from the effect of the slug after 120 hours, the corresponding influent is for 120-48 = 72 h (HRT = 48 h)

Total loading due to continuous influent TCE after 72 hours = 72/24×3.7 = 11.1 mg

Loading due to slug = 2.05 mg

Total loading for 72 hours = $11.1 + 2.05 = 13.15$ mg

The total effluent TCE obtained in the first 120 hours = 7.5 mg (Table 16)

Therefore percent removal = $(13.15 - 7.5) / 13.5 \times 100 = 43\%$

Table 16. Effect of the 400 Mg/l Slug on the Mass of TCE in the Effluent

Hours	TCE Mass flow rate (mg/h)	Mass of TCE (mg) ¹
48	0.199	1.438
60	0.116	1.394
72	0.085	1.013
84	0.073	0.876
96	0.072	0.868
120	0.078	1.869
Total Mass		7.458

¹Mass = Mass Flow Rate $\times$ Time Elapsed

The DP production increased in the column after the slug injection. Table 17 Lists the percent increase in each of the DPs. The concentration of DPs measured at each of the ports is illustrated in Figures 61 to 64. The comparison was based on the maximum DP concentrations measured for influent TCE concentrations of 16.5 mg/L and 400 mg/L (slug). All the DPs except 1,2 DCA increased in concentration. The total DP production increased by 376% in the column after injection of the slug .

Table 17. Effect of 400 mg/L slug on DP Production

DP	Percent Increase
cis DCE	521
1,1 DCE	94
VC	236
1,2 DCA	-60
Total DPs	376

6.2.5 Effect of 800 mg/L TCE Slug

The mass loading rate of TCE for 16.5 mg/L concentration at a flow rate of 8.7 mL/h is 3.44 mg/day. The TCE loading corresponding to the 5 mL of 800 mg/L slug is 4.1mg. The slug therefore is about 120% of the daily loading in the column or 60% of the loading per HRT (48 h). The TCE concentration at ports 2, 4, and 7 are shown in Figures 65 to 67. The concentrations of TCE at port 2 and 4 shot up to about 26 mg/L and 28 mg/L after the first 24 hours . They however

gradually decreased to values below the average TCE concentration level before the slug passage, in the next 48 hours (Figures 65 and 66). The TCE concentration at port 7 increased to about 19 mg/L after 48 hours and gradually decreased to levels comparable to the concentration before slug introduction in the next 48 hours (Figure 68). The increase in concentration for the 800 mg/L slug is not as phenomenal as that of the 400 mg/L slug, indicating higher TCE removal in the column. The gradual increase and decrease in concentrations at the three ports in accordance with their respective HRTs, also indicates that the column was handling the slug better. The effluent TCE concentration dropped below the average effluent concentration before the slug passage, after 60, 72, and 96 hours at ports 2, 4, and 7 respectively. Therefore, it was assumed that the effect of the slug in the column, ceased after 96 hours. The percent TCE removal in the column was determined based on the following calculations:

Mass loading rate of TCE due to continuous influent of 16.5 mg/L = $154.02 \mu\text{g/h}$
 = 3.7 mg/day

Since the effluent showed signs of recovering from the effect of the slug after 96 hours, the corresponding influent is for $96-48 = 48 \text{ h}$ (HRT = 48 h)

Total loading due to continuous influent TCE after 48 hours = $48/24 \times 3.7 = 7.4 \text{ mg}$

Loading due to slug = 4.1 mg

Total loading for 48 hours = $7.4 + 4.1 = 11.5 \text{ mg}$

The total effluent TCE obtained in the first 96 hours = 5.023 mg (Table 18)

Therefore percent removal = $(11.5-5.023)/11.5 \times 100 = 56.32\%$

Table 18. Effect of the 800 mg/L Slug on the Mass of TCE in the Effluent

Hours	TCE Mass flow rate (mg/h)	Mass of TCE (mg) ¹
48	0.183	2.2
60	0.1	1.2
72	0.076	0.91
96	0.03	0.713
Total Mass		5.023

¹Mass = Mass Flow Rate $\times$ Time Elapsed

The DP production increased in the column after the slug injection (Figures 68 to 71). Table 19 lists the percent increase in each of the DPs. The comparison was based on the maximum DP concentrations measured for influent TCE concentrations of 16.5 mg/L and 400 mg/L and 800 mg/L. For all the DPs the maximum concentration occurred at port 4 except for VC which recorded a maximum at port 6. All the DPs except 1,2 DCA increased in concentration. The total DP production increased by 69.1% and 704.6% in the column with respect to influent TCE concentrations of 400 mg/L and 16.5 mg/L respectively. There was a phenomenal increase in the VC production, the concentration measured at port 6 being 46.1% of the cis DCE concentration, indicating increase in reductive dehalogenation of the DPs in the facultative region between port 4 and port 6. The decrease in the concentration of 1,2 DCA for both the 400 mg/L as well the 800 mg/L slug indicates the domination of reductive dehalogenation over hydrogenation of cis DCE. The DP concentration at the three ports did not show any signs of decrease, unlike the case of the 400 mg/L slug injection because

sampling for the 800 mg/L slug injection was not continued after the drop in TCE concentration.

Table 19 Effect of 800 mg/L slug on DP Production

DP	Percent Increase	
	wrt 16.5 mg/L Inf TCE	wrt 400 mg/L slug
cis DCE	558.5	6.03
1,1 DCE	3.6	-46.7
VC	3068	843.3
1,2 DCA	-61.4	-1.3
Total DPs	704.6	69.1

6.2.6 TOC Removal Vs. TCE Removal

The influent TOC in the simultaneous column is contributed by methanol, acetic acid, and TCE. Methanol was added at the influent end (750 mg/L) as well as at ports H1 and H2 (32 mg/L each). TOC was measured at all the 7 ports and removal at each port with respect to the previous port was determined taking into account the extra 12 mg/L added before ports 3 and 5. TOC removed at ports 2, 4, and 7 was calculated for each of the experiments and plotted against the corresponding TCE removal in Figure 72. The major portion of TOC removal occurred in the anaerobic zone of the column. This is in accordance with the fact that both methanol and acetic acid are substrates for the methanogens, while methane acts the primary substrate for methanotrophs. Also a major portion of the TCE removal occurs in the anaerobic zone, while the aerobic organisms degrade the DPs. The TOC removal in the facultative and aerobic zones decreased with time. This is because of the gradual formation of the three zones. As the peroxide concentration in the column was increased in the column, the contribution of the anaerobic organisms in the facultative and aerobic zones decreased, resulting in a corresponding increase in TOC removal in the anaerobic zone. This phenomenon can be observed in the first three cases of Figure 72, where the influent TCE concentration is 5 mg/L. The corresponding TCE removal at port 2 (anaerobic zone) also increased, with improved anaerobic activity in the column. The decrease in peroxide concentration from 75 to 50 mg/L at H1 resulted in an increase in TOC removal in the anaerobic zone indicating improved anaerobic activity in the column. This therefore resulted in better TCE removal rates, as indicated in Figure 72. The decrease in TOC removal in the aerobic region, caused by increasing the peroxide concentration at H2 from 100 to 150 mg/L, indicates enhanced aerobic activity leading to better DP removal as can be seen in Figure 56. The trend in TOC removal therefore, signifies the extent to which the symbiotic relationship between aerobic and anaerobic organisms assists the TCE and DP removal in the simultaneous column.

The following Table lists the mg of TCE removed per mg of TOC consumed for different parameters in the simultaneous column. It can be seen that the ratio increased with increase in peroxide and influent TCE concentration, and decrease in $\text{NH}_3\text{-N}$ concentration.

Table 20. Simultaneous Column: TOC/TCE Ratio

Inf TCE (mg/L)	NH ₄ Cl (mg/L)	H ₂ O ₂ (mg/L)		TCE Rem (mg/L)	TOC Rem (mg/L)	TCE/TOC
		H1	H2			
3.2	56.65	75	75	1.196	292.95	0.0041
3.3	28.3	75	75	1.503	324.64	0.005
3.5	28.3	75	100	1.98	324.47	0.006
22	28.3	75	100	15.6	293.15	0.053
16.5	28.3	50	150	10	290.8	0.034

6.3.1 Lysimeter with Prefabricated Vertical Drain

Delivery of amendments (such as the primary substrate and electron acceptor) to low permeability soils using prefabricated wick drains (PVD's) was evaluated using a box lysimeter. Use of wick drains for delivery of amendments and possible ground water recirculation is a unique application of this technology and offers significant improvement over existing methods which require a large number of wells in "tight" soils. The major concern is the possibility that, over time, biological fouling could occur within the pores of the outer fabric covering.

A lysimeter was set up with a PVD acting as the sole source of influent delivery. Piezometers were used to measure the pressure at different areas within the lysimeter. A constant head tank was used to provide the simulated groundwater that passed through the PVD. The change in head was measured to determine the amount of clogging that occurred throughout the entire system with time. The results are plotted in Figure 73. As noted, only four centimeters of head were needed on the first day of adding substrate to the system. Three days later, the head tank had to be raised to nearly double the head to keep the same flow (approximately 8 L/d). On day 36 the constant head tank was raised for the final time to a head of eleven centimeters. This could be caused by an equilibrium being reached between the organisms and the TOC supplied. This carbon limitation would allow no further biological growth to occur in the column, which would prevent further biological clogging.

The headloss in each of the piezometers with respect to the influent is shown in Figures 74-83. The center row of piezometers near the PVD had a headloss that was almost constantly less than the two outside rows. This could be caused by the flow exiting the PVD traveling more longitudinal than lateral for the first 5 cm of the lysimeter. The major headloss occurred from the PVD to the first piezometer. This headloss could be considered to occur only from the PVD as the piezometer was 0.6 cm from the PVD. The headloss in the PVD started to increase on day 38 and continued until the end of the period, while the height of the constant head tank stayed constant after day 36. This phenomenon is shown in Figure 86. The average headloss at each length of the lysimeter excluding the PVD headloss for the entire study is shown in Figure 85. This showed that after the PVD, only a slight difference in head is shown throughout the length of the column.

7.0 CONCLUSIONS

Both sequential and simultaneous column systems were continued to be operated to evaluate the effects of a variety of variables on performance in order to optimize mineralization of TCE. Assessment of bioremediation of elevated concentrations of TCE was investigated. In addition, evaluation of prefabricated vertical drains for field application of amendments using box lysimeters was performed.

For the sequential column, the effects of adding methanol into Port 2 on TCE removal and hot spot addition on column performance were investigated. As noted, TCE removal was significantly increased during the addition of methanol into Port 2 of the sequential column from 50.8% to 65.6% even though the TCE concentration had risen from 5.0 mg/L to 20.0 mg/L. When the amount of methanol added to Port 2 was increased from 50 to 150 mg/L, the removal again increased and near the end of the period TCE removal was nearly total. On the twelfth day of the change to 150 mg/L TCE, the removal began to significantly increase.

The DP that was easily oxidized was VC, followed by trans-DCE, cis-DCE, and 1,1-DCE. As observed, not only did an increase in TCE reduction occur in Port 3 with respect to Port 1, but also DP reduction was also occurring. By using a mole balance, 88.9% of the TCE and DCE isomers removed went to VC. This indicated that the remaining 11.1% of the DPs went to ETH production.

A major slug load of TCE was added to the sequential column system. For the first four days of the slug, the TCE concentration throughout the column was extremely high, with the largest TCE concentration occurring in Port 3 at the end of 24 hours (1521 mg/L). The slug was not seen in Port 6 until 96 hours had passed, and it had a value of (1273 mg/L). By the fifth day after the slug addition, the TCE mass flowrate dropped considerably. By day eleven after the addition of the slug, all ports showed a mass flowrate less than the influent except Port 6, which showed removal on day twelve. A mass balance on TCE over this period showed a removal of 96.9%. The percent removal in the column for the days following the twelfth was 88.9% for Port 6 with respect to the influent, and 93.1% for Port 3 with respect to the influent. All of the DPs reached a very high concentration during the first four days of the slug passage. The highest concentration of cis-DCE occurred on the 24th hour of the slug passage in Port 3 and reached a concentration of 7985.8 µg/L. 1,1-DCE reached its highest concentration on hour 48 in Port 6 and had a maximum concentration of 3135.2 µg/L. VC had a maximum concentration at hour 24 in Port 3, which was at a concentration of 7296.8 µg/L. After day five, the concentrations of DPs became steady-state values. These values were compared to the period before the addition of the TCE slug in Table 6. As observed, VC had a dramatic drop in production after the slug passed through the system dropping by 21.5 times the previous rate, while the production of 1,1-DCE increased by 7 times. The cis-DCE also had a drop in production of 2.3 times from the previous period.

For the simultaneous column, the effect of different peroxide concentration was investigated. Also, the effect of elevated influent TCE concentrations and hot spots was investigated. The removal rate increased with increase in the H₂O₂ concentration at port H2. The growth of the aerobic organisms could have been enhanced by the increased peroxide concentration. As a result, more TCE and DPs were degraded. While there was about 15% increase in the over all percent removal, the percent removal at port 4 increased by 18.7% when the concentration at H2 was increased from 75 to 100 mg/L. The mass removal rates increased by 117.2% and 76.3% at ports 4 and 7 respectively. Port 4 is representative of the facultative zone while port 7 represents the final aerobic zone. The increase

in the H₂O₂ concentration therefore seemed to have improved the functioning of the organisms in the facultative zone as well as the aerobic zone.

The TCE concentration in the the column was increased in the simultaneous column from 5 to 22 mg/L. As noted, the percent removal rate increased by 10.8%, 9.2%, and 12.9% at ports 2, 4, and 7, respectively. The mass removal rates on the other hand, experienced phenomenal increases of 826%, 650%, and 665% at ports 2, 4, and 6 respectively. Decrease in the influent TCE concentration from 22 to 16.5 mg/L resulted in a decrease in percent as well as mass removal rates. While the percent removal rates for case 3 were about 4% less than that for case 1, the mass removal rates were about 350% higher. This indicated that the increase in TCE concentration resulted in an increase in the mass removal rate of TCE.

For 400 and 800 mg/L TCE slugs injected in the simultaneous column, the percent TCE removal was 43 and 56%, while DP's production increased by 376 and 704%, respectively.

The lysimeter experiment was continued this quarter in an aerobic mode. As noted, only four centimeters of head were needed on the first day of adding substrate to the system. Three days later, the head tank had to be raised to nearly double the head to keep the same flow (approximately 8 L/d). On day 36 the constant head tank was raised for the final time to a head of eleven centimeters. The major headloss occurred from the PVD to the first piezometer.

8.0 WORK PLANNED FOR NEXT QUARTER

A final report will be written

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

Technical difficulties were experienced this quarter when the gas chromatometer (GC) malfunctioned. GC measurements are vital in determining the amount of TCE that occurs in the influent and throughout the column.

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APPENDIX

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Figure 1. Sequential Column Setup

Figure 2. Column Conditions for Methanol Addition in Port 2 of Sequential Column

Figure 3. Mass Flowrate TCE during Methanol Addition in Port 2

Figure 4. Mass Flowrate cis-1,2-DCE during Methanol Addition in Port 2

Figure 5. Mass Flowrate trans-1,2-DCE during Methanol Addition in Port 2
of Sequential Column

Figure 6. Mass Flowrate 1,1-DCE during Methanol Addition in Port 2 of Sequential Column

Figure 7. Mass Flowrate VC during Methanol Addition in Port 2 of Sequential Column

Figure 8. Amount Daughter Products Present in Port 6 for Varying Amounts of MeOH added in Port 2

Figure 9. Amount Daughter Products Present in Port 3 for Varying Amounts of MeOH Added in Port 2

Figure 10. ORP during Methanol Addition in Port 2 of Sequential Column

Figure 11. ORP Removed in Port 6 with respect to Port 4 Compared to
Percent cis-DCE Removal in Port 6 with respect to Port 3

Figure 12. ORP Removed in Port 6 with respect to Port 4 Compared with VC Percent Removal in Port 6 with respect to Port 3

Figure 13. ORP Removed in Port 3 with respect to Port 1 Compared to TCE Removal in Port 3 with Respect to Port 1

Figure 14. Mass Flowrate TCE for First Four Days of 200 g/L TCE Slug

Figure 15. Mass Flowrate TCE after the First Four Days of the 200 g/L TCE
slug

Figure 16. Mass Flowrate cis-DCE for First Four Days of 200 g/L TCE slug

Figure 17. Mass Flowrate 1,1-DCE for First Four Days of 200 g/L TCE Slug

Figure 18. Mass Flowrate VC for First Four Days of 200 g/L TCE Slug

Figure 19. Mass Flowrate cis-DCE after the First Four Days of the 200 g/L TCE Slug

Figure 20. Mass Flowrate 1,1-DCE after the First Four Days of 200 g/L TCE
slug

Figure 21. Mass Flowrate VC after the First Four Days of 200 g/L TCE Slug

Figure 22. ORP Values for 200 g/L TCE Slug

Figure 22a. Simultaneous Column

Figure 23. Simultaneous Column: Effect of Hydrogen peroxide
Different Ports (ORP at

Figure 24. Simultaneous Column: Effect of Hydrogen Peroxide (ORP at Different Ports)

Figure 25. Simultaneous Column: Effect of Hydrogen Peroxide (TCE Removal at Port 4)

**Figure 26. Simultaneous Column: Effect of Hydrogen Peroxide
at Effluent Port 7)**

(TCE Removal

**Figure 26a. Simultaneous Column: Effect of Hydrogen Peroxide
(TCE Removal at Different Zones)**

Figure 27. Simultaneous Column: Effect of Hydrogen Peroxide
2)

(DPs at port

Figure 28. Simultaneous Column: Effect of Hydrogen Peroxide (DPs at Port 4)

Figure 29. Simultaneous Column: Effect of Hydrogen Peroxide
at Port 7)

(DPs

Figure 30. Simultaneous Column: Effect of Hydrogen Peroxide
at Port 2) (% DPs

Figure 31. Simultaneous Column: Effect of Hydrogen Peroxide
Port 4)

Figure 32. Simultaneous Column: Effect of Hydrogen Peroxide

Port 7)

(% DPs at

Figure 33. Simultaneous Column: Effect of Hydrogen Peroxide (Distribution of DPs)

Figure 34. Simultaneous Column: Effect of Hydrogen Peroxide (Distribution of DPs)

Figure 35. Simultaneous Column: Effect of Hydrogen Peroxide (Distribution of DPs)

Figure 36. Simultaneous Column: Effect of Ammonia Nitrogen at 75 ppm Hydrogen Peroxide (Port 4)

at 75

Figure 37. Simultaneous Column: Effect of NH₃ - N Concentration
ppm Hydrogen Peroxide (Influent Port 7)

Figure 39. Simultaneous Column: Effect of NH₃-N Concentration (Distribution of DPs)

Figure 40. Simultaneous Column: effect of NH₃-N Concentration (Distribution of DPs)

Figure 41. Simultaneous Column: Effect of NH₃-N Concentration at 75 ppm Hydrogen Peroxide (Port 4)

Figure 42. Simultaneous Column: Effect of NH₃-N Concentration at 75 ppm Hydrogen Peroxide (Port 4)

Figure 43. Simultaneous Column: Effect of NH₃-N at 75 ppm Hydrogen Peroxide (Effluent Port 7)

**Figure 44. Simultaneous Column: Effect of NH₃-N at 75 ppm Hydrogen Peroxide
(Effluent Port 7)**

Figure 45. Simultaneous Column: Effect of Elevated TCE Concentration (Port 2)

Figure 46. Simultaneous Column: Effect of Elevated TCE Concentration (Port 4)

Figure 47. Simultaneous Column: Effect of Elevated TCE Concentration (Effluent Port 7)

Figure 48. Simultaneous Column: Effect of Elevated TCE Concentration on Percent TCE Removal at Various Ports

Figure 49. Simultaneous Column: Effect of Elevated TCE Concentration on Mass Removal Rate of TCE at Various Ports

Figure 50. Simultaneous Column: Effect of Elevated TCE Concentration on DP Production (Port 2)

Figure 51. Simultaneous Column: Effect of Elevated TCE Concentration on DP Production (Port 4)

Figure 52. Simultaneous Column: Effect of Elevated TCE Concentration on DP Production (Port 7)

Figure 53. Simultaneous Column: Effect of Elevated TCE Concentration on DP Distribution (Port 2)

Figure 54. Simultaneous Column: Effect of Elevated TCE Concentration on DP Distribution (Port 4)

Figure 55. Simultaneous Column: Effect of Elevated TCE Concentration on DP Distribution (Port 7)

Figure 56. Simultaneous Column: Effect of Elevated TCE Concentration on Effluent DPs

Figure 57. Simultaneous Column: ORP at Elevated TCE Concentration (Effect of Hydrogen Peroxide)

Figure 58. Simultaneous column: Effect of 400 ppm TCE Slug (Concentration of TCE at Port 2)

Figure 59. Simultaneous Column: effect of 400 ppm TCE Slug (Concentration of TCE at port 4)

Figure 60. Simultaneous Column: Effect of 400 ppm TCE Slug (Concentration of TCE at Effluent Port 7)

Figure 61. Simultaneous Column: Effect of TCE 400 ppm Slug (TCE Removal)

Figure 62. Simultaneous Column: Effect of 400 ppm TCE Slug (Production and Removal of cis-1,2 DCE)

Figure 63. Simultaneous Column: Effect of 400 ppm TCE Slug (Production and Removal of 1,1 DCE)

Figure 64. Simultaneous Column: Effect of 400 ppm TCE Slug (Production and Removal of VC)

Figure 65. Simultaneous column: Effect of 800 ppm TCE Slug (Concentration of TCE at Port 2)

Figure 66. Simultaneous Column: effect of 800 ppm TCE Slug (Concentration of TCE at port 4)

Figure 67. Simultaneous Column: Effect of 800 ppm TCE Slug (Concentration of TCE at Effluent Port 7)

Figure 68. Simultaneous Column: Effect of TCE 800 ppm Slug (TCE Removal)

Figure 69. Simultaneous Column: Effect of 800 ppm TCE Slug (Production and Removal of cis-1,2 DCE)

Figure 70. Simultaneous Column: Effect of 800 ppmTCE Slug (Production and Removal of 1,1 DCE)

Figure 71. Simultaneous Column: Effect of 800 ppm TCE Slug (Production and Removal of VC)

Figure 72. Simultaneous Column: TCE Removal Vs TOC Removal

Figure 73. Lysimeter Setup

Plan

Figure 74. Changes in Head over Time in the Lysimeter

Figure 75. Differences in Head along the Length of the Lysimeter for Day 18

Figure 76. Average Difference in Head along the Length of the Lysimeter on Day 18

Figure 77. Differences in Head along the Length of the Lysimeter for Day
27

**Figure 78. Average Difference in Head along the Length of the Lysimeter
for Day 27**

Figure 79. Differences in Head along the Length of the Lysimeter for Day 38

Figure 80. Average Difference in Head along the Length of the Lysimeter for Day 38

Figure 81. Differences in Head along the Length of the Lysimeter for Day
51

Figure 82. Average Difference in Head along Length of Lysimeter for Day
51

Figure 83. Differences in Head along Length of Lysimeter for Day 62

Figure 84. Average Difference in Head along Length of Lysimeter for Day
62

Figure 85. Average Difference in Head at Each Length of the Lysimeter

Figure 86. Headloss through the PVD at a Constant Influent Head

**Microbial Enrichment for Enhancing *In-Situ* Biodegradation of Hazardous
Organic Wastes in Soil**

**WVU / METC / DOE COOPERATIVE AGREEMENT
Contract No: DE-FC21-92NC29467**

METC TASK No. 1.3

QUARTERLY REPORT: October-December, 1995

For:

**U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

By:

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(1.0-2.0)

INTRODUCTION AND PURPOSE

Superfund and RCRA regulations have mandated the restoration of millions of cubic yards of contaminated soils nationwide. The cost of excavation and hauling large volumes of soil, combined with the tighter environmental regulation of landfills has severely restricted this cleanup option. Both industry and government are actively seeking additional innovative organic waste cleanup technologies to remedy this problem. Bioremediation is often proposed as a cost-effective treatment option for on-site hazardous waste clean-up, particularly where large soil volumes are involved and incineration is not considered feasible. However, biodegradation results are influenced by local site conditions making effective remediation difficult to predict and insure. We have been investigating the effectiveness of commercially available microbial inocula for use in bioaugmented remediation of hazardous mixed organic wastes in soil. At present, we are examining *ex-situ* remediation and surface composting, a process ideally suited to incorporation of a microbial inoculant. Bioaugmentation holds great promise for degradation of compounds which are now recalcitrant in soil, however efficacy of available microbial inocula must first be critically evaluated. We are developing a generalized testing procedure and expertise, which we can employ to examine bioaugmentation / biodegradation of a variety of wastes and / or waste sites (Figure 1).

During the 1994 we concentrated on identification of superior commercially available microbial inocula for bioremediation of organic wastes. Inocula were screened for biodegradation kinetics in surface and subsurface soil samples artificially contaminated with a chemically defined model mixed organic waste. During the coming year we propose that superior products selected by our screening procedure must next be tested for effectiveness in the variety of mixed organic wastes and soils expected in real world conditions. Therefore, we will obtain soil samples from waste contaminated sites, return them to the laboratory, and quantify the effectiveness of selected inocula for bioaugmented soil remediation. We will assess effectiveness of biodegradation by monitoring substrate disappearance of parent organic compounds following their extraction from soil. To facilitate screening of a large number of soils we will also develop and apply a rapid radiorespirometric technique based on the ability of microorganisms to biodegrade ^{14}C labeled recalcitrant compounds directly injected into the mixed waste milieu of the contaminated sample. Identification of suitable inocula and development of rapid screening methods for waste biodegradation represent the next necessary step prior to large-scale deployment of bioaugmentation technology in the field.

Objectives

The overall research objective is delineation of conditions under which bioremediation can effectively be employed to enhance remediation of hazardous organic wastes. Specific objectives for the 1995 work are: 1) Verify the effectiveness of bioaugmentation in soils collected from sites previously contaminated with hazardous mixed organic wastes. Superior commercially available microbial inocula selected during our year one laboratory trials will be utilized. 2) Develop and apply a radiorespirometric technique for the rapid screening of bioaugmentation effectiveness in soil samples

previously contaminated with hazardous mixed organic wastes. A diagrammatic representation of our research approach is presented in Figure 1.

(3.0-4.0)

BACKGROUND AND METHODOLOGY

The 1995 study will be performed by researchers in WVU's Division of Plant & Soil Sciences. Contaminated soils for the study will be obtained from industrial and government sites as well as from existing production sites identified by regional oil and gas cooperatives with whom we cooperate (IOGA / WVONGA). We will concentrate on soils contaminated with hydrocarbons and solvents and will study three sites.

Waste contaminated bulk soil will be returned to the laboratory and stored at 4°C prior to use. Soils will be amended with NH_4NO_3 and K_2HPO_4 to fall within C:N:P:K ratios determined as optimum for waste degradation. Soil samples (10 g wet weight) will be distributed to replicate 250-ml Erlenmeyer flasks and adjusted to 25 % gravimetric moisture content (approximately 60 % water filled porosity, a level optimum for aerobic microbial activity in soil). Sterile control soils will be prepared by autoclaving flasks at 121°C and 103 kPa for 20 minutes on 2 consecutive days. The waste contaminated soil will be then mixed 1:1 with glass beads to improve porosity and aeration, a typical procedure for soil composting. Soils will also be amended with a water soluble dispersant chosen from the EPA/ NCPSS to enhance release of the waste from soil particles and maximize contact with the soil microflora. Half of the treated soils will be amended with the commercial microbial inocula at rates recommended by the manufacturer. Inocula selected are produced by Sybron, Interbio, and Hydrobac.

Radiorespirometry will be employed to follow mineralization of individual compounds within the mixed waste. Individual ^{14}C labeled compounds will be added to the contaminated soil at 0.9 μCi per 10 gram soil. The working assumption is that the added radiolabeled compound does not significantly increase the pool size of the component within the mixed waste, thus does not affect the mineralization rate of the compound. ^{14}C - CO_2 will be trapped into sodium hydroxide and aliquots counted in a Scintiverse cocktail using a Wallac 1409 Scintillation counter. Direct injection of a known radiolabeled hydrocarbon or solvent into the mixed waste milieu of the soil should allow rapid assessment of relative biodegradation potential. If successfully developed, this technique will allow us to rapidly screen a larger number of soil samples for effectiveness of bioaugmentation.

(5.0-7.0)

PROGRESS THIS PERIOD (October-December, 1995) RESULTS, DISCUSSION, CONCLUSIONS

During the first quarter of 1995 (Jan. to March) we monitored cumulative AMOW mineralization in the presence and absence of inocula. Inoculum addition significantly increased soil respiration compared with uninoculated soil and soil amended with sterile inocula. Addition of waste to inoculated soil inhibited soil respiration compared to non-waste amended soil. These data emphasized that use of ^{14}C labeled substrates in a radiorespirometric assay was necessary to monitor specific organic

pollutants. The second quarter (March to June) was spent in methods development. We examined a variety of assay configurations for optimum soil incubation and subsequent CO₂ trapping. We decided to use a passive base trap as illustrated in Figure 1, rather than an active gas train setup. Our rationale for this decision was ease of use and increased experimental replication. This configuration allowed us to measure mineralization of the labeled substrate by LSC as well as total mineralization by titration of the base trap. The third quarter (July-September) was spent perfecting the assay as well as performing bioremediation trials. At our meeting at METC on April 27, we agreed to concentrate on model contaminants in a variety of soils including contaminated soils from industrial production sites. Initial rates of ¹²C and ¹⁴C hexadecane, naphthalene, and anthracene mineralization over 14 days were presented.

The fourth quarter was spent performing extended trial repeats and examining the microbial composition of selected microbial inoculants. Mineralization of hexadecane, naphthalene, and anthracene was examined in 60 day trials. In all trials, maintenance of sterile controls over a 60 day period was problematic. However, it is unlikely that the mineralization observed was abiotic, therefore these data represent waste mineralization by soil re-colonizing microbial contaminants. Greatest degradation of labeled hydrocarbon was observed in hexadecane-treated soil. Although inoculation stimulated gross ¹²C mineralization, there was no apparent significant effect on ¹⁴C hexadecane mineralization. Similar results were observed with ¹²C mineralization in naphthalene and anthracene amended soils. Low rates of ¹⁴C naphthalene mineralization were observed after 40 days only in inoculated soil. No ¹⁴C anthracene mineralization has been observed in any of our trials.

As indicated previously, soil samples were obtained from an active industrial site for characterization. Three oil contaminated soils were obtained from landfarm / *ex situ* composting remediation sites located in Doddridge county, WV. The sites, owned by EQUITRANS, will be monitored by us during 1996 in a separate research project. Gravimetric recovery of waste oil from these soils is reported in Table 1. We attempted to characterize the waste contaminants in these soils during our last quarters work, however our attempts were frustrated by analytical difficulty due to total failure of our gas chromatograph. The problem is still not yet satisfactorily rectified. We intend to apply our radiorespirometric assay to follow hydrocarbon biodegradation in these soils, once we are able to characterize the waste milieu present. These data will not be available for the final report of our 1995 work.

Ms Payal Malhotra, M.Sc., a visiting scientist during 1995, enumerated and characterized organisms in various of the commercial inoculants. Enumeration data are presented in Table 2. She characterized four dominant strains using the Biolog identification system. Two were *Bacillus* sp and two were *Pseudomonas* sp. A mixture of these pure strains degraded petroleum in liquid culture over a 35 day period.

During the fourth quarter of 1995, we have prepared a draft of a manuscript entitled " Bioremediation of petroleum and mixed organic waste applied to soil " authored by P. Saini, J. Winger and A. J. Sexstone to be submitted in February, 1996 to Communications in Soil Science and Plant Analysis. This work presents the results of our 1994 project.

(8.0) WORK PLANNED FOR NEXT PERIOD: None. Final Report to be submitted in February, 1996

Percentage of Project Completion, MC-18, METC Task 1.3, Year 2 (1995)

1.0	Preliminary Research	8w	100
2.0	Analytical Techniques		
2.1	Evaluate Radiorespirometry	8w	100
2.2	Develop Radiorespirometric Assay	8w	100
3.0	Preparation of Trials		
3.1	Site Identification	12w	100
3.2	Site Characterization	12w	100
3.3	Waste Characterization	12w	100
3.4	Finalize QA/QC	8w	
4.0	Bioremediation Trials		
4.1	Trial 1	6w	100
4.2	Trial 2	6w	100
4.3	Trial 3	6w	100
4.4	Trial 4	6w	100
4.5	Trial 5	6w	100
5.0	Trial Repeats (concurrent)		100
6.0	Analysis and Reporting		100
6.1	Analysis and Data Reduction	8w	100
6.2	Reports and Manuscripts*	40w	90
7.0	Overall Work Complete	50w	95

* Final report to be submitted in February, 1996.

Fig. 1. *In vitro* hexadecane biodegradation in the presence or absence of microbial inoculum. S = Soil; I = Inoculum; W = Waste; SS = sterile soil; SI = Sterile inoculum. Error bars indicate standard error of means.

Fig. 2. *In vitro* naphthalene biodegradation in the presence or absence of microbial inoculum.
S = Soil; I = Inoculum; W = Waste; SS = sterile soil; SI = Sterile inoculum.
Error bars indicate standard error of means.

Fig. 3. *In vitro* anthracene biodegradation in the presence or absence of microbial inoculum. S = Soil; I = Inoculum; W = Waste; SS = sterile soil; SI = Sterile inoculum. Error bars indicate standard error of means.

Table 1. Gravimetric recovery of waste oil from EQUITRANS landfarm sites located in Doddridge County, WV.

Well Number	Average Oil Extracted (g/10 g soil)	% Oil
4703	0.780	7.80
6210	0.175	1.75
6214	0.510	5.10

Table 2. Enumeration of microorganisms in commercial inoculants.

Inoculant	Heterotrophs (X10⁷) (TSA Agar)	Oil Degradars (X10⁷) (Oil Agar)
DBC Plus R5	37.0	35.0
Interbio SSC	6.10	3.40
Hydrobac	18.3	1.30
ABR HC	2.23	1.28

CONTAMINANT MOVEMENT PREDICTION IN PERMEABLE SUBSURFACE SOILS

METC Task No. 1.4

Quarterly Technical Progress Report
Reporting Period: October 1, 1995 - December 30, 1995

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

For:
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By:
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December 1995

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ABSTRACT

Contaminations of the subsurface soils are problems encountered in many areas and especially locations with various underground and surface tanks used for storage of hazardous materials. The subsurface conditions vary at a site and the prediction of contaminant movement is a difficult task. This work focuses on the flow behavior of fluids in the porous media where drainage with prefabricated vertical drains (PVD) are used to flush the soils.

TABLE OF CONTENTS

Disclaimer.....	ii
Abstract.....	iii
Executive Summary.....	v
Introduction.....	1
Purpose.....	1
Background.....	1
Methodology.....	1
Work Performed This Period.....	2
Work Planned for Next Period.....	2
References.....	3

EXECUTIVE SUMMARY

This subtask ended as of December 31, 1995. During the funding period, the experimental data from the smear test cell and the contaminant recovery test tank are used to conduct modeling studies. A numerical model is used to perform runs under different soil properties together with varying operational parameters.

Preliminary results indicate a limited success in matching the drawdown measurements in the smear cell tests, and also in the prediction of observed drawdowns at different PVDs in the contaminant recovery cell experiments. Additionally, the permeability of the soil was determined to be the most important property among the assigned soil properties used in the model study.

WORK PERFORMED THIS PERIOD

In this quarterly period, the data from contaminant recovery test experiments were used to setup the model. Several runs were conducted using the operational parameters from recovery tests. Four experiments were available to conduct the model study. In each case eight PVDs were used. The two PVDs were used for injection and the remaining six were used for production. Based on the experimental data, uniform injection rates were used in all runs. The flow rates for the producing PVDs were varied. Additional runs were conducted with different permeability and porosity values. The permeability and porosity values were increased and decreased by one order of magnitude to study the effect of each property on the drawdown predictions. The drawdown values obtained by the model were used to prepare the contour plots.

Runs were conducted with the data from smear cell experiments. A centrally located PVD was used to produce under a vacuum. Drawdown measurements were observed at twelve different locations. The experiments cover vacuum pressures from 10 in. to 120 in. of water. The production rates vary between 2.74 ml/min and 18.13 ml/min. For injection tests the pressure values were between 5 in. and 30 in. of water. Except one experiment, all runs were conducted with a porosity value of 0.34 and a conductivity value of 0.0001 cm/sec. Runs were also conducted with different conductivity values to improve the drawdown predictions. The results from simulator runs were plotted for the end of test periods with measured data.

The model study was completed by conducting runs with all available data. A limited number of runs were conducted to determine the effect of porosity, permeability, and boundary conditions. The figures will be presented in the final report. Presently, work is continued with the preparation of the final report.

WORK PLANNED FOR NEXT PERIOD

This task ended as of December 31, 1995 and no work is planned for the next quarterly period. A final report is due by January 30, 1996.

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DEVELOPMENT of STANDARD TEST PROTOCOLS and BARRIER DESIGN MODELS
for
IN SITU BARRIERS
METC Task No. 1.5a
(Chemical Grout Barriers)

Quarterly Technical Progress Report
Reporting Period: 10/1/95 - 12/31/95

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

For:
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, WV

By:
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Evaluation of Chemical Grouts for Subsurface Containment of Wastes

Abstract: A significant effort in the U.S. and the world is undertaken to develop remediation technologies for contaminated soils and waters. However, in some cases a permanent technology in response to some urgent environmental problems is yet to be developed. For this situation, a temporary barrier may be needed to retard the advancement of the plumes until a permanent remediation technology is implemented. As a result, extensive research is being conducted to evaluate the feasibility of using permeation grouts to develop subsurface containment/confinement systems to retard, or even prevent, the advancement of subsurface contaminant plumes.

A research program was conducted to assess the effectiveness of a urethane (Scotch-Seal (TM) Chemical Grout 5610 Gel manufactured by 3M Company) and a vinyl monomer (DurasealTM manufactured by Beton-Bau-Zubehor (BBZ) of Germany) grout in controlling the subsurface migration of waste. The study was carried out on the laboratory scale, and was intended to evaluate the chemical grouts ability to create a low-permeability barrier when injected into the soil and develop standard grout evaluation and testing protocols.

The experimental program was implemented in four phases: a) Grout Development, b) Performance Testing, c) Grout Testing Chamber, and d) Computer Modeling. The first phase included the evaluation of the grouts' properties and development of viable mix ratios. The second phase of the experimental program aimed at examining the feasibility of injecting the urethane grout into a uniformly graded Ottawa sand (i.e., groutability) in large diameter (29.2 cm), acrylic columns. Samples were collected from the grout bulb and subjected to additional testing which yielded results on the grouted-sands hydraulic conductivity, compressive strength, and durability under permeation and immersion with various classes of chemicals. Phase 3 involved the design and construction of the Grout Testing Chamber (GTC) (essentially a 91.4 cm flexible-wall permeameter)

and manufacture of a device to prepare uniform specimens for the GTC. The final phase evaluated the ability of the computer model BGROUT to accurately simulate the grout injections performed in Phase 2.

The first phase of the study resulted in four urethane mixes and one vinyl monomer mix being developed for the next phase. All the urethane mixes were 10:1 (activator:gel) ratios; however, the mix additives varied. The vinyl monomer mix was comprised on 50% water and 50% gel concentrate.

Results from the second phase indicated that two of the urethane grout mixes could be easily injected into the Ottawa sand at its porosity extremes. Additionally, the larger the perforation size and perforation length on the injection probe, the larger the resulting grout bulb and bulb radius. Samples collected from the injected bulbs yielded hydraulic conductivities (k) of 2.4×10^{-7} cm/s with water and significantly increased when using chemical permeants. Grouted-sand samples from both of the grout mixes swelled excessively and decreased in strength when immersed in water, bases, and ethylene glycol solutions. Cupric sulfate, methanol, acetone, and acids appeared to have few observable affects on the samples.

The GTC was designed and is currently under construction. Additionally, a sand rain device was designed and manufactured to produce uniform density specimens for the GTC.

The results from the Phase Four indicate that BGROUT can be used to formulate more efficient grout injection strategies. This model was relatively simple and easy to use. When comparing the results obtained from the Phase Two Injectability experiments and those predicted by the model, the margin of error was 5 - 19%. However, it was discovered that mass balance inconsistencies were encountered in nearly all the simulations.

Within this paper, testing methodologies, data, and results from each phase of the experimental program are presented.

TABLE OF CONTENTS

Abstract	ii
1.0 Introduction	1
2.0 Purpose	3
3.0 Background	4
4.0 Work Performed This Period	5

Volume I - Final Report (Draft)

Volume II - Project Data

1.0 INTRODUCTION

There is a significant effort in the U.S. and the world to develop remediation technologies for contaminated soils and waters. For some contaminated medias, no technologies are feasible or fully developed to meet today's environmental problems. For example, radioactive contaminated soils are impossible to treat with current technologies. Only waste minimization/segregation techniques are applicable which results in a highly concentrated (i.e., radioactive) residual material. Because of the lack of treatment methods, confinement and containment technologies are needed to retard, or even prevent, the advancement of subsurface contaminant plumes into the environment until the development of appropriate remediation technologies are identified and implemented.

There are numerous confinement/containment (C/C) methods available in today's market. Both industry and government have Records of Decisions (RODs) implementing the installation of sheet piles, slurry walls (typically with bentonite), french drain systems, etc. These techniques are fully capable of preventing lateral migration of contaminants in soil and water; however, longitudinal migration of contaminants is not suppressed or retarded. One method that appears suitable for developing both vertical cut-off walls and/or horizontal bottom barriers is permeation (injection) grouting utilizing chemical grouts.

Permeation grouting is defined as the process of filling small interstitial voids and fissures in rock or soil (Karol 1990). Current applications include: seepage control in granular soil and shattered rock, air and fire control in underground mining, increasing the bearing capacity of soils and failing foundations, slope stability improvements, sewer/water line rehabilitation, and strengthening brick and masonry structures. Typically, permeation grouting utilizes cement, fly ash, and other pozzolanic materials. Cementitious materials are appropriate for injection into media's

with large voids and high permeabilities (e.g., fissured rocks and mines), but are incompatible for use in soils. Due to their limited applicability to soils, low viscosity (and more costly) chemical grouts are commonly employed. The chemical grout utilized for C/C must be non-toxic; chemically and biologically inert; and economically feasible.

In order to attain a viable and comprehensive C/C system, permeation grouting must be performed using a combination of drilling methods. Vertical, directional, and horizontal drilling techniques will all play pivotal roles in successful implementation of any C/C method. Once total containment is achieved (and verified), other plume retardation/treatment methods may be put in place (e.g., pump and treat of the migrating/contained waste).

If permeation grouting is proven to be preventative measure (i.e., secondary containment), as well as a post-release alternative, it would could potentially be utilized at numerous sites (Superfund and RCRA) throughout the country. This technology would be adaptable for containment of waste resulting from leaking underground storage tanks (USTs). For example, both the Hanford Reservation and the Savannah River Site have underground tanks in tank farms which have exceeded their design life. Those tanks not currently leaking will be releasing contaminants into the surrounding soils and water in the near future. Another application of this technology would be at landfills with failed liner systems or which were sited and constructed before more stringent design requirements were promulgated.

Because of the potential benefits of this technology and the large number of sites where it could be implemented, research was conducted at West Virginia University to evaluate two chemical grout's effectiveness and applicability as a subsurface barrier.

2.0 Purpose

The research conducted at West Virginia University aimed at investigating containment/confinement technologies using chemical grouts for in-situ formation of plume barriers. Unlike prior and other current studies, instead of immediately advancing from the lab-scale grout investigation to field scale injection testing, a meso-scale testing program was developed to investigate the material injectability. Two types of chemical grouts were evaluated for barrier use: Duraseal™ (a vinyl monomer compound from Germany) and Scotch-Seal (TM) Chemical Grout 5610 (a urethane gel product manufactured by 3M). Both grout materials were evaluated on their ability to form in-situ barriers (i.e., injectability/viscosity), toxicity, resistance to chemical degradation, strength properties, and permeability. The research work was divided into the following tasks:

- I. Grout Development
- II. Performance Testing
- III. Grout Testing Chamber (GTC)
- IV. Computer Modeling

Grout Development involved the identification of the grout mix ratio which exhibited optimum properties for use as a subsurface barrier. The hydraulic properties of the developed grout were then tested using rigid wall columns. In addition, physical, chemical, and engineering properties of each grout was determined.

Performance Testing utilized large diameter acrylic columns to investigate the injectability of the grout into Ottawa sand using different grout mixes and varying injection strategies. The structural and hydraulic performance of the formed barrier was also evaluated by performing

immersion/strength testing (triaxial and unconfined compression) and permeability testing on samples collected from the grouted-sand bulb.

Task III involved the design and construction of the Grout Testing Chamber (GTC), essentially a large-scale flexible wall permeameter with 3 feet diameter specimens. The selected design mixes will then to be injected and evaluated in the GTC. The GTC will be capable of simulating in-situ stress conditions and eliminates the influence of boundary effects on the performance of the boundary. It was designed to evaluate the effectiveness of the barrier system to control contaminant transport. A sub-task was the development of a device and method for preparing uniform specimens for the GTC. This was to be accomplished through the use of a sand rain device.

The final task was the development or modification of an existing computer model to predict subsurface characteristics (e.g., bulb size, barrier thickness and continuity, etc.) of the grouted barrier utilizing different injection strategies. The modeling output was then compared and verified with the results obtained from Performance Testing.

3.0 Background

Although the principles of permeation grouting were developed in the 1940's and numerous companies are in existence which specialize in this practice, none have utilized permeation grouting for waste containment. Numerous field studies (May et al. 1986, Dwyer 1994, Moridis 1995) have been conducted to evaluate chemical grouts ability to develop subsurface barriers. These studies were completed with only limited success and identified the need for a barrier verification technique. A limited number of research programs (Bodocsi et al. 1988, Bodocsi et. al. 1991, Carson 1988,

Heiser et al. 1992, Sherer 1986) have investigated the properties of various types of chemical grouts which make them amenable as a subsurface barrier. At present, there is a considerable amount of research being conducted on this topic at government facilities. Brookhaven National Laboratory, Sandia National Laboratory, and Lawrence Berkeley Laboratory have programs in place evaluating a wide array of grout materials.

4.0 Work Performed This Period

During this period, efforts were focused on data reduction and generation of the Draft version of the Final Report for this project. Attached to this report are both volumes of the Final Report. Volume I includes the report body, while Volume II includes the actual data generated during the entire project duration.

DEVELOPMENT of STANDARD TEST PROTOCOLS and BARRIER DESIGN MODELS
for
IN SITU BARRIERS
METC Task No. 1.5
(Circulating Air Barrier)

Quarterly Technical Progress Report
Reporting Period: 10/01/95 - 12/31/95

Work Performed Under Contract
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For:
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

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ABSTRACT

Significant research effort is currently being conducted in the United States and the world for remediation of contaminated soils and groundwater. In parallel to remediation efforts, confinement technologies are needed to retard, or even prevent, the advancement of contamination plumes into the environment until the implementation of remediation efforts is completed. Research proposed herein aims at developing and investigating containment/confinement technology using desiccation for in situ formation of barriers.

The desiccant barrier proposed to be investigated will be the recently developed circulating air barrier (CAB). The CAB utilizes the injection of dry gas (air, nitrogen, CO₂, etc.) to create an ultra dry zone in situ; beneath or adjacent to the zone of contamination. The CAB relies on the removal (drying) of in situ liquids (water) so that any contaminating liquids entering the zone of desiccation must replace the previously removed liquids before the contaminants can migrate further. In field application, the CAB may be established by means of specific patterns of vertical or horizontal (or a combination of vertical and horizontal) injection and withdrawal wells which enable the injected dry gas to travel through and dry the formation prior to exiting via a withdrawal well.

This research will be conducted using laboratory and meso-scale setups. In addition to conventional laboratory equipment proposed research will utilize a large scale reactor for simulating in situ conditions. Conducting the research based on a meso-scale setup will minimize problems associated with scale effects. Such problems are usually encountered when a method is developed in the laboratory with no considerations given to correlation of laboratory scale results to field implementation. The B-17 facility in METC with its infrastructure will be utilized to conduct the proposed work. The proposed experimental methodologies will simulate field conditions and should provide laboratory data to test and enhance predictions of CAB performance made by existing models and computer simulations.

TABLE OF CONTENTS

	Page No
Abstract	ii
Table of Contents	iii
List of Figures	iv
Executive Summary	v
1.0 Introduction	1
2.0 Purpose	1
3.0 Background	2
4.0 Methodology	3
5.0 Work Performed this Period	4
5.1 Task 1: SARS Activity	4
5.2 Task 2.1: Literature Review	5
5.3 Task 3: Laboratory Equipment and Preliminary Testing	6
5.3.1 Sand-Pack Tests	6
5.3.2 Core Tests	7
6.0 Results and Discussion	7
6.1 SARS Activity	7
6.2 Sand-Pack Tests	7
6.3 Core Tests	8
7.0 Conclusions	8
7.1 SARS Activity	8
7.2 Sand-Pack Tests	8
7.3 Core Tests	9
8.0 Work Planned for Next Period	9
8.1 SARS Activity	9
8.2 Sand-Pack Tests	9
9.0 Technical/Administrative Difficulties	10
10.0 References	11

LIST OF FIGURES

	Page No
Figure 1: The experimental setup for sand pack air-water equilibrium measurements	13
Figure 2: Optimum compaction water saturation for 20/30 mesh sand	14
Figure 3: Optimum compaction water saturation for 30/35 mesh sand	15
Figure 4: Sand-pack air-water equilibrium Experimental results	16
Figure 5: Berea sandstone air-water equilibrium Experimental results	17
Figure 6: Optimum compaction water saturation for 20/30 mesh sand - comparison	18

EXECUTIVE SUMMARY

This study aims at developing and investigating containment/confinement technology using a "Circulating Air Barrier (CAB)". The CAB utilizes the injection of dry air to create an ultra dry zone in situ; beneath or adjacent to the zone of contamination. The CAB system can provide many advantages, however, there are no laboratory data or CAB field performance data available in the literature. There are however are a number of issues that must be settled before it can be decided if CAB technology is applicable. Key among these issues are the influence of the soil characteristics (such as porosity, permeability, water saturation, grain size distribution, and clay content) on the drying profile. This research will be conducted using laboratory and meso-scale setups to evaluate the soil characteristics influence on CAB performance and will determine the effects of flow and sweep efficiency for fixed and mixed grain size soils. These experiments will validate and/or improve model predictions of system behavior and drying profiles of different soil types.

Sand-packs are being utilized for bench-scale testing to determine the relationship between soil characteristics and in situ barrier quality. Sand-packs are being calibrated to determine porosity, permeability, and saturation characteristics. The soil characteristics will be varied by changing grain size and sorting of the pack materials. A detailed CAB vessel assembly has been designed and been approved for experimental studies at B-17 facilities. The procurement of materials and fabrication of the assembly is in progress by EG&G at METC. Additional laboratory tests on core samples have been undertaken to evaluate the influence of porous media on air-water equilibrium and mass transfer.

1.0 INTRODUCTION

Many contaminated subsurface sites can not be economically decontaminated because of the limitations in technologies for decontamination. In such cases, containment becomes the primary technology for environmental protection. For non-excavatable sites, in situ containment is the most viable approach for preventing further spread of contamination. Different approaches for achieving in situ containment have been proposed, however, the study herein is focused on the evaluation of in situ barriers created by soil desiccation.

The desiccant barrier proposed to be investigated is the recently developed (1,2) Circulating Air Barrier (CAB). The CAB utilizes the injection of dry gas into a porous media to create an ultra dry zone in situ by removing water and reducing the water saturation below the level required for liquids to flow in order to prevent migration of underground contaminants. The CAB, once established, will also provide a means of monitoring and removing contaminants entering the zone. The proposed experimental methodology should provide laboratory data to test and enhance predictions of CAB performance made by existing models and computer simulations.

2.0 PURPOSE

The concept of the Circulating Air Barrier was conceived (1,2) to solve the subsurface contamination problems at the Hanford site used by the former Atomic Energy Commission. The references to CAB (1,2,3) are mainly related to CAB as a concept, and no field or laboratory data is available in the literature. The previous studies (1,2) concluded that a CAB system provided many advantages, however, the concept needs to be demonstrated to develop data necessary for scale-up and regulatory acceptance.

Among issues that must be settled before it can be decided if CAB technology is applicable to all DOE sites are the influence of the soil characteristics (such as, porosity,

permeability, water saturation, grain size distribution, and clay content) on the drying profile and CAB performance. The laboratory study to be undertaken will evaluate the soil characteristics influence on CAB performance and will determine the effects of flow and sweep efficiency for fixed and mixed grain size soils. These experiments will validate and/or improve model predictions of system behavior and drying profiles of different soil types.

3.0 BACKGROUND

The Circulating Air Barrier (CAB) system is a desiccant-type barrier designed to prevent the movement of liquid contaminants toward groundwater, using air circulation and a processing system to lower water saturation in a targeted subsurface zone. The concept of Circulating Air Barrier was introduced in a study (1) that evaluated the barrier systems that could be installed beneath and around the tank farms with a minimum of excavation at DOE's Hanford Site. The CAB can be installed using either vertical or horizontal wells, establishing a pattern of air injection and extraction wells. The moving air vaporizes water in the zone and carries the water vapor to an extraction well. In time, circulation of the air reduces the water saturation in the swept interval, and continues to remove, by evaporation, liquids that move into the zone such as a leaked plume. No liquids can flow through this interval until a critical saturation is achieved, a saturation level that is well above the initial saturation. In the event that a leak occurs, the CAB system serves as a tool for early leak detection and provides a means to withdraw volatile contaminants for surface treatment. The study concluded that CAB system provided many advantages including non-physical confinement, active monitoring and leak detection, commercially available oil and gas technologies and equipment, emergency response and rapid deployment capability, and high potential for integration with other remediation technologies. However, the concept needs to be demonstrated to develop data needed for scale-up and regulatory acceptance.

A follow up study by K&M/BDM (2) which addressed modeling, cold test design, and surface processing and control

design for the CAB demonstration at Hanford concluded that several issues must be settled before it can be decided if CAB technology is applicable to all DOE sites. Key among these issues is the influence of the soil characteristics such as porosity, permeability, water saturation, grain size-distribution, and clay content on the drying profile and CAB performance. This report further recommended a laboratory study to be undertaken to evaluate the soil characteristics influence on CAB performance and to find out the effects of flow and sweep efficiency for fixed grain-size and mixed grain-size soils. This would also serve to validate and/or improve model predictions of system behavior and drying profiles of different soil types. In addition, a range of geologic and climatic environments within which the CAB could successfully operate, baseline equilibrium moisture curve for a specific grain-size, and relative humidity for a specific temperature could be determined.

4.0 METHODOLOGY

Experimental procedures will be developed to address the problem of evaluating a desiccant barrier, i.e., a barrier based on creation of a dry zone of earth beneath a contaminated zone to store contaminating liquids, thus preventing their further migration. Two phases of experimental research are proposed in this study. The B-17 facility in METC with its infrastructure will be utilized to conduct the proposed work. The first phase deals with bench-scale experiments using laboratory setups. The second phase will deal with a meso-scale setup that will utilize large tanks for simulations of in situ conditions in order to minimize problems associated with scale effects.

Bench-scale testing of the CAB process parameters will utilize sand packs to determine the relationship between soil characteristics and in situ barrier quality. Sand packs will be calibrated to determine porosity, permeability, and saturation characteristics. The soil characteristics will be varied by changing grain size and sorting of the pack materials. Residual water saturation of the pack will be established by first saturating the pack with water and then

desaturating the pack by injection of water-saturated air. The pack will then be dried at various rates of air injection to determine drying characteristics as a function of rate, remaining water saturation, and soil characteristics. The final phase of sand pack testing will be to resaturate the packs with simulated contaminant fluids injected at low pressure (near atmospheric) at the top while monitoring any effluent at the bottom. This will allow determination of contaminants migration rate as well as total storage capacity of the packs.

Meso-scale performance testing will be used to investigate the effectiveness of the CAB system in containment/confinement of the study waste under simulated field conditions. The meso-scale tests of the CAB system will utilize large rectangular tanks in DOE/METC's B-17 building to create a three-dimensional test bed to verify, refine, and extrapolate the results of sand pack experiments to field like conditions. The tanks will be filled to a desired depth by slurring sand of predetermined grain size range into the tanks with water. All or part of bed will then be desaturated, dried, and "contaminated" with a safe liquid to simulate the CAB process on the meso-scale. Instrumentation and sampling ports and tubes will be placed in strategic locations in or at the tanks to monitor the status of the CAB.

5.0 WORK PERFORMED THIS PERIOD

5.1 Task 1: SARS Activity

Detailed CAB vessel assembly drawings were submitted to EG&G personnel (as approved by METC) for CAB fabrication and the machine work for the CAB vessel assembly component parts has been completed. A substantial amount of interaction with EG&G personnel transpired in an attempt to produce a CAB vessel assembly which will not only produce quality data but will also be extremely safe, durable, and easy to assemble, operate, and maintain.

During the fabrication of the CAB vessel assembly,

several minor design modifications were constituted in order to enhance the fundamental functions of the sand pack chambers, that is, enabling the repeatability of measuring sand pack properties. As a result of these modifications, the CAB vessel assembly component parts are being re-drawn to scale and are near completion.

A draft of the 'Operating Plan' (prior to preparation of the draft of the 'Operating Permit') has been completed, however, its editing and consummation which was dependent upon final CAB vessel assembly construction is near completion. This revised 'Operating Plan' will encompass the modifications made to the CAB vessel assembly during fabrication.

Additionally, two end plates have been ordered and two modified end plates have been designed and ordered from EG&G. The modified end plates should enable more accurate porosity and permeability measurements on sand packs.

5.2 Task 2.1: Literature Review

A comprehensive literature review relative to CAB was conducted and completed during previous quarters and reported earlier. A presentation relative to the results of the literature review was given on 03/30/95.

Additional literature searches relative to procedures and instrumentation for measuring and monitoring air humidity, soil moisture, and permeability have been continued during this quarter. The key issues in the selection of the instruments are those relative to the accuracy necessary for acceptable measurement and data acquisition while minimizing intrusion in the sand-pack or CAB bed.

Based on an in depth investigation of instrumentation manufacturers products and cost effectiveness; sensors, electronic packages, and data acquisition systems have been selected and ordered which should adequately provide accurate data and should also have application in the larger scaled experiments to be performed in the METC building B-17.

5.3 Task 3: Laboratory Equipment and Preliminary Testing

The air-water equilibrium plays a critical role in the CAB design and development. While there are published data for air-water equilibrium, they are not obtained in the porous media. Consequently, it is important to investigate the influence of porous media on both gas-water equilibrium and mass transfer in porous media. Two sets of preliminary experiments have been designed. These experiments are described below.

5.3.1 Sand-pack Tests

The effect of dry air on an unconsolidated porous medium at irreducible water saturation was investigated during these sets of experiments. The main portions of these experiments will be conducted at the B-17 Building at METC utilizing the CAB vessel assembly. However, this series of preliminary experiments have been designed to evaluate the protocols for determining sand pack properties.

The procedure and experimental setups for determining sand-pack porosity and permeability have been developed and previously reported. The measured porosity values based on the developed protocols have been found reasonable and repeatable. The permeability measurement instrumentation and protocols have been evaluated for accuracy and repeatability.

A series of experiments to determine the effect of an unconsolidated porous media on air-water equilibrium have been completed using a similar, yet experientially re-modified (see Figure 1) sand-pack test chamber. The methodology of experimental procedures and instrumentation has been utilized in a similar fashion such as those in the previously reported air-water equilibrium tests.

In addition to the sand compaction tests for a 20/30 mesh sand (Figure 2), sand compaction tests have been performed on a 30/35 mesh sand (Figure 3).

5.3.2 Core Tests

The effect of porous media on air-water equilibrium has been investigated utilizing Berea sandstone core samples. It should be noted that a consolidated porous media, such as a Berea sandstone core sample, does not represent the typical soils at DOE Sites. However, these series of experiments provided a foundation for evaluating the influence of porous media on air-water equilibrium when the media is at irreducible water saturation.

The experiments have been completed in terms of a static state, the results of which have been previously reported.

6.0 RESULTS AND DISCUSSION

6.1 SARS Activity

The draft form of the 'Operating Plan' and 'Operating Permit' have been completed and should be finalized and submitted for METC approval during the next quarter. This process had been contingent upon completion of the CAB vessel assembly fabrication due to minor design modifications.

Upon receipt of the completed CAB vessel assembly, the drawings of the assembly and the operating procedures for the 'Operating Plan' are in the process of being revised which will enable submission of a draft of the 'Operating Permit' for METC perusal and modification prior approval.

6.2 Sand-Pack Tests

A series of air-water equilibrium experiments have been performed on the sand packs at optimum compaction water saturation. The results (Figure 4) are deemed conclusive in comparison with the published data and the problems associated with the measurement of data and subsequent calculations has

been rectified. Experimental data collection will begin with one chamber of the completed CAB vessel assembly.

6.3 Core Tests

The core saturation, desaturation, and air-water equilibrium experiments have been successfully performed and a comparison of the published and experimental air-water equilibrium data has been previously reported (see Figure 5).

7.0 CONCLUSIONS

7.1 SARS Activity

The next phase of SARS activity is completion of the preliminary form of the 'Operating Permit' and presentation to METC for approval. The completion of this document was contingent upon design and fabrication modifications of the CAB vessel assembly in order to complete the drawings and operating procedures relative to the requirements of the 'Operating Plan'. This SARS activity should be completed in the very near future.

7.2 Sand-Pack Tests

The sand-pack tests have been useful in establishing experimental protocols and identifying the necessary instrumentation for the CAB vessel assembly experimentation. The earliest experimental results indicated that accurate air-water equilibrium measurements could not be generated until an actual CAB vessel chamber is used for experimentation. However, the experimental test chambers were modified in an attempt to procure fundamental data prior to calibration and use of the CAB vessel assembly and these modifications have produced acceptable results (Figure 4).

The sand compaction tests for the 30/35 mesh sand indicated a higher water content than the 20/30 mesh sand. To determine whether these results were due to technique or sand properties, a second series of compaction tests were performed on the 20/30 mesh sand. The results (Figure 6) indicate a similar water content, however, a higher dry density than those determined earlier. This discrepancy might be due to data analysis procedures. A series of compaction tests will be performed on both sand particle sizes to further evaluate this discrepancy.

7.3 Core Tests

The core tests have provided a foundation for evaluating the influence of porous media on air-water equilibrium. As is illustrated in Figure 5, it would appear that the effect of a porous media on air-water equilibrium is one of enhancement. This enhancement can be attributed to the increased surface area (contact area) in the pore space of the porous media which seems to dominate the effects of surface tension between the two phases.

8.0 WORK PLANNED FOR NEXT PERIOD

8.1 SARS Activity

Finalize drawings and 'Operating Plan' for 'Operating Permit'. Submit 'Operating Permit' for METC approval.

8.2 Sand-Pack Tests

Calibrate CAB vessel assembly component parts (chambers) and initiate experimentation based on previously determined protocols.

Continue packing sand as per modified 'Standard Ordinary

Compaction Test', measuring porosity and permeability, and continue static air-water equilibrium experiments.

Perform similar experimentation using a sand of a different grain size.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

Delays in receiving necessary funds have created some difficulties. The monitoring equipment and sensors could not be ordered in a timely fashion. As a result, the experiments with the CAB assembly have been delayed.

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Sand Pack Air-Water Equilibrium Measurement

FIGURE 1: THE EXPERIMENTAL SET UP FOR SAND PACK AIR-WATER EQUILIBRIUM MEASUREMENTS.

Sand Compaction Test Results - 20/30 Mesh Sand

FIGURE 2: OPTIMUM COMPACTION WATER
SATURATION FOR 20/30 MESH SAND

Sand Compaction Test Results - 30/35 Mesh Sand

FIGURE 3: OPTIMUM COMPACTION WATER SATURATION FOR 30/35 MESH SAND

SAND PACK / AIR-WATER EQUILIBRIUM DATA

FIGURE 4: SAND PACK AIR-WATER EQUILIBRIUM EXPERIMENTAL RESULTS

BEREA SANDSTONE / AIR-WATER EQUILIBRIUM DATA

FIGURE 5: BEREA SANDSTONE CORE AIR-WATER EQUILIBRIUM EXPERIMENTAL RESULTS

Sand Compaction Test Results - 20/30 Mesh Sand

FIGURE 6: OPTIMUM COMPACTION WATER SATURATION FOR 20/30 MESH SAND-COMPARISON

TASK 2.0
ADVANCED PRODUCT
APPLICATIONS TESTING

Chemical Destruction of Chlorinated Organic Compounds

METC TASK NUMBER: 2.1

Quarterly Report for Period
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ABSTRACT

Chlorinated organic compounds, such as carbon tetrachloride, trichloroethylene, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and polychlorinated biphenyls (PCBs), have been widely used as organic solvents, pesticides and herbicides, dielectric fluids for transformers and capacitors, and for a variety of other purposes. The environmental problems and health risks associated with these chlorinated organic compounds have been well recognized. The chemical structures of some representative compounds are shown below.

It is the objective of this research program to develop chemical treatment procedures to transform chlorinated organic compounds to less or non toxic materials. We discovered that sterically hindered triarylboranes are excellent electron carriers for sodium metal and can be used to effectively dechlorinate PCBs from greater than 500 PPM to less than 8 PPM, far less than the 50 ppm standard set by EPA. Because PCBs are among the most inert chlorinated organic compounds, it is likely that this treatment procedure developed for PCBs could also be easily adopted for other chlorinated molecules, including particularly 2,3,7,8-TCDD because of similarity of chemical structures. We will develop a practical procedure to extend this treatment procedure further by synthesizing and fabricating new materials of triarylborane for use in dechlorination of a variety of chlorinated organic compounds. Other chemical treatment procedures for dechlorination of PCBs by using the very reactive hydroxyl radical and by nitration of PCBs to activate the aromatic ring for subsequent dechlorination will also be investigated.

TABLE OF CONTENTS

Section No.		Page No.
1.0	INTRODUCTION	1
2.0	PURPOSE	2
3.0	BACKGROUND	2
4.0	METHODOLOGY	2
5.0	WORK PERFORMED THIS PERIOD	3
6.0	RESULTS AND DISCUSSION	3
7.0	CONCLUSIONS	5
8.0	WORK PLANNED FOR NEXT PERIOD	5
	REFERENCES	5

LIST OF FIGURES

Figure		Page No.
Figure 1.	Chemical Structures of Three Representative Polychlorinated Biphenyls	1
Figure 2	An Efficient Synthesis of Trimer 3	3
Figure 3	An Efficient Synthesis of Diiodide 4	3
Figure 4	Synthesis of Biphenyl by Coupling of Phenylmagnesium Bromide	4
Figure 5	A Possible Synthetic Route to the Cyclic Hexamer 9	4

EXECUTIVE SUMMARY

We have improved two key synthetic steps toward the synthesis of a polymer as an electron carrier for dechlorination of PCBs. An efficient synthetic pathway to a trimer as a precursor to producing the corresponding cyclic hexamer as well as polymer was developed. An efficient conversion of this trimer to a reactive form for subsequent transformation to the hexamer and polymer was also established. A model reaction for coupling the trimer to hexamer and polymer was also investigated.

1.0 INTRODUCTION

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.

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 recently began 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 an 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.

2.0 Purpose

It is the purpose of this research project to first evaluate the existing technologies for in situ dechlorination of PCBs-contaminated soil. Development of a new chemical treatment procedure for dechlorination of PCBs will also be a major goal.

3.0 Background

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. We recently discovered that sterically hindered triarylboranes are excellent electron carriers for sodium metal and can be used to effectively dechlorinate PCBs from greater than 500 PPM to less than 8 PPM, far less than the 50 ppm standard set by EPA. Because PCBs are among the most inert chlorinated organic compounds, it is likely that this treatment procedure developed for PCBs could also be easily adopted for other chlorinated molecules, including particularly 2,3,7,8-TCDD because of similarity of chemical structures. The use of the very reactive hydroxyl radical for dechlorination of PCBs was also found to be a promising process.

4.0 Methodology

We will develop a practical synthetic procedure to prepare and fabricate new materials containing triarylboranes as electron carriers for dechlorination of PCBs. Synthetic methods involving organic reactions will be employed to produce these new materials. The use of the very reactive hydroxyl radical, to be generated by the Fenton reaction ($\text{FeSO}_4/\text{H}_2\text{O}_2$) and other methods, for dechlorination of PCBs will also be investigated. Furthermore, an alternative strategy involving an initial activation of the benzene rings of PCBs by nitration ($\text{HNO}_3/\text{H}_2\text{SO}_4$) followed by attacking of the activated benzene rings with NaOH could also provide a solution for degradation of PCBs.

5.0 Work Performed This Period

We have made good progress in improving two key synthetic steps toward the synthesis of a polymer containing sterically hindered triarylboryl functionalities as an electron carrier for dechlorination. The reaction efficiency in synthesizing a trimer as a precursor for the preparation of such a polymer was greatly improved. Conversion of the trimer to a reactive form for the construction of the cyclic hexamer as a model of the polymer was also successfully accomplished. A model reaction for coupling two trimers together to form the cyclic hexamer was also established. The chemical structures of the new compounds were fully characterized by the ^1H and ^{13}C NMR spectra as well as by mass spectra.

6.0 Results and Discussion

We have improved the reaction efficiency to trimer 3 to 88 % yield in a single step by using a palladium-catalyzed cross-coupling reaction between dibromide 1 with boronic acid 2 (Figure 2). The much higher efficiency of the reaction was due mainly to the use of a more reactive palladium catalyst. Because of the simplicity of the ^1H and ^{13}C NMR spectra of 3, its chemical structure was readily elucidated.

Figure 2. An Efficient Synthesis of Trimer 3

We have also worked out a reaction condition for converting trimer 3 to the corresponding diiodide 4 in high yield (Figure 3). Treatment of 3 with ICl in dichloromethane at room temperature furnished the desired diiodide 4 in 96 % yield. The reaction appeared to be very clean, and no further purification was necessary. The reaction efficiency was greatly improved because a carefully measured stoichiometric amount of ICl was introduced into the reaction mixture.

Figure 3. An Efficient Synthesis of Diiodide 4

With the diiodide **4** now readily available, we have proceeded to the next step of constructing the corresponding cyclic hexamer. In a model study, it was established that biphenyl (**7**) could be obtained in essentially quantitative yield by using CuBr to promote coupling of phenylmagnesium bromide (**6**), derived from bromobenzene (**5**) (Figure 4).

Figure 4. Synthesis of Biphenyl by Coupling of Phenylmagnesium Bromide

The synthetic method outlined in Figure 4 will be adopted for the construction of hexamer **9** from diiodide **4**. The diiodide **4** will be first converted to the bis-Grignard reagent **8** followed by treatment with CuBr for coupling (Figure 5).

Figure 5. A Possible Synthetic Route to the Cyclic Hexamer **9**

7.0 Conclusions

We now have an efficient synthetic pathway to diiodide **4** as the precursor of the cyclic hexamer **9**. It appears likely that coupling of two molecules of the diiodide **4** could lead to the formation of the cyclic hexamer **9**.

8.0 Work Planned for Next Period

While this is the last period of this research project, we will continue to develop synthetic pathways to the cyclic hexamer as well as the corresponding polymer.

References

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- (2) See reference 1 pp 172-174.
- (3) Hanson, D.J., *Chemical and Engineering News* 1993, 71, 7.

CONTINUED DEVELOPMENT OF AN ATMOSPHERIC
MONITORING MASS SPECTROMETRY SYSTEM

METC TASK # 2.2

Quarterly Technical Progress Report
10-1-95 - 12-31-95

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

For:
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

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ABSTRACT

The objective of this project is the development of a mass spectrometric methodology applicable to the field determination of Volatile Organic Compounds (VOC's), such as BTEX components (Benzene, Toluene, Ethylbenzene, and Xylenes). A combination of chemical ionization, selective ion storage, and tandem mass spectrometry will be employed with an ion trap mass spectrometry system. The Gas Chromatography Mass Spectrometry (GC-MS) interface on the ion trap system will be modified to permit direct atmospheric monitoring. Through the use of tandem mass spectrometry methods the need for chromatographic separation will be eliminated reducing the overall size and complexity of the system. Existing literature methods and newly developed methods will be compared for sensitivity, accuracy, and precision.

TABLE OF CONTENTS

Cover	i
Disclaimer	ii
Abstract	iii
Table of Contents	iv
Executive Summary	v
Introduction	1
Purpose	1
Background	1
Methodology	2
Work Performed this Quarter	2
Conclusions	2
Mass Spectrum from Water CI of Benzene	3
Mass Spectrum from Water CI of Toluene	4
Mass Spectrum from Water CI of Xylenes	5

EXECUTIVE SUMMARY

During this quarter work shifted back to restoring the ion trap system to reproduce chemical ionization of benzene, toluene, and xylenes with water. For this last quarter of the project the personnel working on the project consisted of one part-time technician. Originally the technician was supposed to work full time through the end of November, but he decided to continue his education and returned to full time student status. Because there was no time to hire replacement personnel and because of technical problems with the trap, it was decided to complete the project with this person working half-time. The technician ceased working on the trap at the contracted close date of November 30, 1995. At the end of the project approximately \$12,200 remained in the account and reverted to the funding agency. Effectively only the months of October and November were available for work during this quarter.

1.0 Introduction

In the general area of Characterization, Sensors, and Monitoring, analytical systems are needed that can provide near real-time measurements of hazardous materials and their degradation products at sites where contamination is suspected. Of particular interest are the volatile organic compounds (VOC'S) associated with petrochemicals. Presently, we are investigating the utility of atmospheric sampling mass spectrometry for the determination of benzene, toluene, ethylbenzene, and xylenes in ambient air. Preliminary methods relying on chemical ionization (CI) and/or tandem mass spectrometry (MS/MS) have been identified in a survey of the literature. It is proposed to continue this work by developing methods that employ a combination of CI and MS/MS techniques with the ion trap mass spectrometer for the identification of components in mixtures. This expands upon the previous work by examining the influence of potential interferences on the accuracy of the methods and by developing appropriate protocols to eliminate these interferences or correct for them.

2.0 Purpose

The overall objective of this project is the development of an atmospheric monitoring ion trap mass spectrometry system and associated methods for determination of volatile organic compounds. One of our ultimate goals is to develop methods that can be employed by technician level operators. We believe that this is an essential first step toward the development of truly field portable mass spectrometry systems. Toward the end of the project we anticipate using the system at field sites to demonstrate the methods' capabilities.

3.0 Background

During 1994, the NRCCE acquired an ion trap mass spectrometry system for use in atmospheric monitoring. Through funding of a project entitled "Evaluation of IR and Mass Spectrometric Techniques for On-Site Monitoring of Volatile Organic Compounds" mass spectrometric methods for separation and determination of the principal components in BTEX, (Benzene, Toluene, Ethylbenzene, and Xylenes) were identified in the literature. The literature methods indicate some interference problems that must be considered to obtain accurate data, ie. the separation of xylenes and ethylbenzene. In the 1995 project year it is proposed to develop complete methods for the speciation of 10 components in an environmental petroleum standard and the speciation of 9 components in an environmental halogenated hydrocarbon standard. Our interest in the petroleum standard is to test the ability of the system to

identify components in the atmosphere near a leaking petroleum tank; whereas, the interest in the halocarbons stems from a desire to develop monitoring for off gas from hazardous waste incinerators. During the course of the work potential interferences arising from both the sample and the monitoring environment will be identified. The original methods will then be modified by employing selective reagent chemical ionization and/or tandem mass spectrometry to selectively identify the species of interest and to eliminate the influence of the interfering species.

4.0 Methodology

It was attempted to employ selective ion storage software to enable the monitoring of the BTEX components. This was done so that parent ions corresponding to the individual sample components could be monitored and quantitation afforded. This was attempted with the GC inlet so as to avoid problems that might arise from the atmospheric interface. The nature of the software precluded independent control of ionization, mass scanning, and detection. An additional problem was that the software for selected ion storage precluded the use of tandem mass spectrometry. After the software was installed by the Varian technician, we could no longer investigate MS/MS. Work with MS/MS will resume in the final quarter.

A molecular beam interface was employed to permit direct sampling of atmospheric species. The interface did not adequately reduce the pressure admitted to the ion trap. The result was spectra with peaks too broad to be interpreted. A new pumping system has been partially installed on the ion trap system. Successful installation of this system should allow reexamination of the molecular beam interface because of its increased pumping

5.0 Work Performed This Quarter

During October progress was made and the attached water chemical ionization spectra were obtained. It is clear from the spectra, Figures 1-3, that the water CI approach successfully produces molecular ions of the analytes of interest with no fragmentation. These spectra were the result of a series of investigations into the influence of ion reaction time on sensitivity and spectral purity. At the end of these investigations the next step was going to be resumed examination of the MS/MS speciation of the various xylene isomers. At the end of October the turbomolecular pump on the ion trap failed.

November was spent attempting to replace the failed pump with a larger version available at the NRCCE. The installation of the larger pump would not only allow

continued investigation of the MS/MS method but would have also allowed reexamination of the molecular beam interface because the replacement pump would effectively quadrupled the pumping capacity. An adaptor for the pump was designed and after several modifications the November the replacement pump was mechanically in place by the end of November. At that point a problem was encountered with the system software. The system monitors the pump performance to provide a gauge of ion trap operating pressure. Unfortunately the replacement pump does not interface directly with the ion trap system- as a result the software does not get a pressure reading and the system protection software does not permit ion trap operation. Our initial contact with Varian yielded no solution to this problem. As of the present moment, we are attempting identify the protection circuit and its signal read by the software. The hope is to defeat the circuit and allow trap operation with the new pump. Once this problem is corrected, hopefully by mid-February, continued investigations with the molecular beam interface will continue.

6.0 Conclusions

Water chemical ionization was demonstrated to effectively generate molecular ions for the analytes benzene, toluene, and xylene. Continued software difficulties are hampering modification of the ion trap system to permit reexamination of the molecular beam interface. Development of MS/MS methodology will proceed during the no-cost extension period. Work on this project will continue in the absence of funding, periodic updates will be provided to the project manager.

Average of: 605 to 609 Minus: 577 to 581
100% 78

100% = 6644

SECI

Ion 1000 usec

TIC 62

IPM: ISOTOLU

Tune: 72495

100% = 2

MULT 1600
ION TIME 1000
ARC
MS/MS

Mult
Fil
RF
CI
Cal

SELECT CI GAS
ADJUST CI GAS
SCAN RANGE

Lo mass 80
Hi mass 100

185

186

Schedule Update

Task #	% Complete
1	100
2	100
3	75
4	100
5	10
6	0
7	50
8	70
9	50
10	0
11	90

ADVANCED PRODUCT APPLICATIONS TESTING

CAPTURE OF HAZARDOUS WASTE MATERIALS UTILIZING
FLUIDIZATION COATING TECHNOLOGY

TASK 2.3

Quarterly Report for Period
October 1 through December 31, 1995

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

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By:

Dr. Richard Turton
Department of Chemical Engineering
West Virginia University
Morgantown, WV 26506-6057

**Capture of Hazardous Waste Materials Utilizing
Fluidization Coating Technology**

95HZDWSTFLD

**Quarterly Technical Progress Report
Reporting Period: October 1 - December 31, 1995**

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

**For:
U.S.Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

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(i)

Abstract

The purpose of this research is to investigate how fluidization coating technology can be utilized to capture and stabilize hazardous waste materials. In particular, the fate of aqueous solutions of heavy metal compounds will be addressed. These solutions will be sprayed into a high temperature fluidized bed containing different types of solids. Due to evaporation of the solution, the non-volatile inorganic materials will either concentrate on the fluidized particles or will form an aerosol of fine particles (<1 micron) due to spray drying. The capture efficiency of the fluidized bed will be determined by evaluating the fraction of the heavy metals which is captured by the fluidized solids. The chemical form of the metals on the solids will also be determined and the leachability of the metals from the solids will be found. Techniques to further stabilize the metals on the fluidized particles will be addressed and may include a secondary spraying of stabilizing chemicals with an additional thermal treatment and over-spraying the fluidized particles with a low melting point glass.

During the 3rd quarter of 1995 the focus of this project was changed (letter to E.E.Cook dated 9//95) from the original plan outlined above. The new focus reflects a closer working relationship with ThermoChem Inc., Columbia, MD. The remainder of the first year of this project will be used to modify and test the experimental equipment to simulate the destruction of organic waste materials in a high temperature steam reforming atmosphere. This work will complement on-going research at ThermoChem, Inc. concerning the evaluation of destruction efficiencies of RCRA organics in their two-stage fluidized bed process for treating mixed wastes.

Table of Contents

1.0	Introduction	1
2.0	Purpose	1
3.0	Background	1
4.0	Methodology	2
5.0	Worked Performed in this Period	3
6.0	Results and Discussion	4
7.0	Conclusions	6
8.0	Work Planned for Next Period	6
	References	6
	Acronyms and Abbreviations	6
	Appendix	7

Figures

Figure A.1:	Location of Thermocouples within Reactor	8
Figure A.2:	Design of Cold Trap	9
Figure A.3:	Location of Feeds to Reactor	10
Figure A.4:	Calibration Curve for Peristaltic Pump for Water Feed	11
Figure A.5:	Calibration Curve for Organic Liquid Rotameter	12

Executive Summary (Current Work)

Due to a change in focus of the current research, several changes in the tasks to be performed in year 1 were made. The current emphasis for the project is to investigate the destruction efficiencies of RCRA organics and surrogates in a steam reforming atmosphere. This work ties in more closely with on-going research, being performed by ThermoChem Inc. of Columbia MD, on a two stage fluidized bed system for the destruction of mixed wastes. The purpose of the work covered under this proposal is to simulate the second stage of the ThermoChem process, in which organic materials are to be destroyed in a high temperature steam reforming atmosphere.

During the fourth reporting period of this project the modifications to the design of the reactor and feed gas systems were completed. The redesign included installing a modified cold trap to condense the reactor effluent gases which contain a large amount of steam. Currently, the steam flow is monitored by pumping water via a variable flow peristaltic pump and then vaporizing the water in the plenum of the reactor. The organic feed liquid to be tested flows under pressure through a rotameter into the water feed line. It was found to be necessary to combine the organic liquid and water prior to vaporizing, this helped reduce the formation of coke which occurs as the organic materials decompose and thermally crack at the high temperatures used in the experiments.

In order to test the reactor system two preliminary tests were performed. Toluene was taken as a test organic material and fed into the reactor with steam. The amount of toluene was approximately 1% by mole in the feed. The amount of toluene in the exit gas stream from the reactor was compared at two different reactor temperatures, 350 and 1050°C. Assuming that no toluene reacted at the lower temperature it was possible to estimate the destruction efficiency at the higher temperature, the destruction efficiency was estimated to exceed 98%.

1.0 Introduction

The capture and disposal of hazardous inorganic chemicals from liquid solutions and liquid-solid slurries currently is of great concern. Such hazardous chemicals typically contain heavy metal compounds, for example mercury, lead, cadmium, and sometimes radioactive species. The sources of these chemicals are diverse, and include: aqueous streams produced from washing contaminated soils; organic streams such as lead bearing paint; and dilute aqueous solutions of radioactive elements used in hospitals. The source and characteristics of the waste stream will often dictate the method of treatment. Methods such as adsorption on to activated carbon, incineration and gasification are all currently used to dispose of hazardous wastes containing heavy metals and radioactive species. The fate of the heavy metals and the their final chemical form is unclear, Barton et al. (1), for many treatment processes and this forms the *raison d'être* for this research.

The focus of the research was changed during the third reporting period of 1995 (Letter to E.Cook dated 11 September 1995). The current aim of the work is to evaluate destruction efficiencies of RCRA organics and surrogates in a steam reforming atmosphere. This work ties in closely with the development of a new two stage process by ThermoChem Inc. for the destruction of mixed wastes.

2.0 Purpose

The purpose of this research is to investigate the use of fluidized bed coating technology in the collection, concentration and stabilization of hazardous inorganic chemical compounds. Fluidization technology has been utilized in the destruction of waste streams in such applications as Municipal Solid Waste (MSW), Medical Waste and Hazardous Waste Incinerators. However, the emphasis has been on maximizing the destruction efficiency for organic compounds. Recently, with the increasing concern regarding the formation of dioxins and dibenzofurans in such devices, it has been suggested that gasification, rather than combustion, should be considered for the destruction of waste streams, Gallaway and Sprung (2). However, regardless of the method of destruction, if a waste liquid stream containing heavy/radioactive metals is to be fed to an incinerator/gasifier then the mechanism by which the inorganic material leaves the system needs to be investigated. Therefore, it is the purpose of this work to address what happens to such metal species when solutions of them are fed to fluidized bed waste incinerators/gasifiers.

Due to the change in focus of the research, as outlined in Section 1.0 above, the purpose of the work was changed during the third reporting period of 1995. Currently, the purpose of this work is to assess the destruction efficiencies of RCRA organic compounds and surrogates in a high temperature, steam reforming atmosphere.

3.0 Background

When considering the fate of liquid solutions of heavy metals fed to equipment containing fluidized solids, several removal mechanisms must be considered. It is assumed that the liquid stream will be sprayed into the bed via an atomizing or hydraulic spray nozzle. Clearly, it is important to disperse the liquid into the bed as a fine spray, in order to prevent excessive agglomeration and "wet quenching" of the bed. For waste incineration/gasification equipment typical bed temperatures will be high compared to the boiling point of the liquid and undesirable spray drying of the liquid waste may occur. The object when spraying the liquid feed into the fluid bed is to coat the fluidized particles with feed solution and to avoid spray drying. The efficiency of capture of the liquid is very important since liquid not deposited on particles will evaporate quickly in the vapor phase and effectively spray dry. When spray drying occurs the inorganic material, including any heavy metals, will tend to form a fine solid/aerosol mist that will be very difficult to clean from the gas stream. In fact, the formation of aerosols may so severely affect the efficiency of capture in such devices as scrubbers, bag houses and electrostatic precipitators that the majority of the metals end up in the stack gas. Therefore, the efficiency of spray capture by the fluidized particles is a very important factor in fluidized bed coating operations. For typical coating operations, the

capture efficiency ranges from 95 - 99%. However, typical coating operations do not use the level of superheat expected in combustion and gasification equipment.

The second consideration is the fate of the metals once they have been deposited on the solids surface and the liquid evaporated. Obviously, this will depend on the temperature and pressure (usually 1 atm) in the bed, the chemical composition of the bed material and the gas phase composition. The gas phase composition will be mainly, nitrogen, water, carbon dioxide and oxygen with smaller amounts of hydrogen chloride, hydrogen sulfide (gasification) and sulfur dioxide (combustion). Evidence suggests that binding of the metals with the bed material is a strong function of the bed material, Ho et al. (3,4) and that the leachability of metals from bed material is generally low.

Thus two key elements to be investigated are capture efficiency and stabilization of metals once they are on the bed material.

As mentioned above, the focus of the research has changed and currently the destruction of organic materials at elevated temperatures and in a steam reforming atmosphere is of concern. The use of a steam reforming atmosphere for the reaction and elimination of RCRA organics has been shown to significantly reduce the production of dioxin and furans during the destruction process when compared to oxidation/incineration processes. However, the efficiency of the destruction and the effect of temperature, gas residence time and composition has not yet been fully quantified. Therefore, the goal of the on-going research is to quantify the effect of these parameters on the destruction efficiency of RCRA organics and surrogates.

4.0 Methodology

The overall objectives of this work are to assess the potential of fluidized bed coating techniques to capture, concentrate and stabilize hazardous inorganic chemicals present in solution. The specific objectives are:

Identify model compounds to represent hazardous waste chemicals containing heavy metals.

Demonstrate that aqueous solutions of these model compounds may be sprayed onto a bed of fluidized particles resulting in the capture and concentration of these compounds on the particles.

Evaluate the capture efficiency of the fluidized bed coating process.

Investigate different routes to stabilize the model compounds so that the resulting bed particles have very low levels of leachable heavy metals and are hence non-hazardous.

Due to a change in focus of this project, tasks 4 and 5 for the first year have been changed. These changes are geared towards the modification of the reaction system to enable it to handle a mixture of feed gases and a feed stream of organic material.

Year 1

1. Design of a fluidized bed capable of operating at high temperatures (up to 900°C) to be used in the coating experiments.
2. Construction of fluidized bed system.
3. Choice of a model chemical system for the hazardous waste and the size and materials to be used for the fluidized particles.

4. Redesign the fluidized bed system to accommodate:

- (i) a new feed gas system to include the use of hydrogen and hydrogen/carbon dioxide mixtures as well as steam.
- (ii) new distributor plate to allow even distribution of feed gases into the bed.
- (iii) redesign the gas sampling equipment and traps to accommodate the new feed materials and operating conditions.

5. Complete a safety review for the new process conditions with emphasis on the safe use of hydrogen in the experimental program.

5.0 Worked Performed in this Period

The start of the experimental portion of this project was delayed until March 8, 1995 due to funds not being available until this time. During the period 10/1/95-12/31/95, for which this report is written, the following work was accomplished:

Item 1: Three type K thermocouples were installed in the reactor. The thermocouples are 12", 24" and 36" in length and are located 9", 19" and 33" above the distributor plate respectively, see Figure A.1 in the Appendix. The thermocouples were checked at room temperature and in boiling water and found to be within 1°C of each other and a mercury thermometer. In addition, with no flow through the bed the thermocouples read within a few (10°C) of the furnace thermocouples at the same axial locations.

Item 2: The cold trap for quenching the reactor effluent gas was redesigned and installed. The main body of the cold trap is a 12" length of 6" diameter stainless steel pipe with a cap on the bottom end and a welded plate on the top. A 9" coil made of 1/4" stainless steel tubing is installed inside the cold trap with cooling water connections. At the base of the trap there is a connection to a length of 1/4" polypropylene tubing and a valve which discharges to either the drain or a collection flask. A sketch of this equipment is given in Figure A.2 in the Appendix.

Item 3: The gas sampling port and activated carbon trap were designed, fabricated and installed. The gas sampling port consists of a 1/2" stainless steel T connection installed in the gas line leaving the cold trap. The third leg of the tee is fitted with a rubber septum through which the stream can be sampled with a syringe. The activated carbon filter consists of a 12" section of 1" diameter stainless steel tube fitted with metal screens at either end and containing a bed of 60 mesh activated carbon. The filter is flanged at both ends and is mounted in-line with the exhaust gas piping.

Item 4: The feed gas control and monitoring system were designed and installed. Originally, the flow of steam was going to be supplied from the low pressure steam header located in the Lab. However, due to a variety of difficulties in monitoring the flow of steam, e.g. excessive condensation, it was decided to use an alternative method. The steam feed to the bed is now provided by pumping water into the bed using a variable speed peristaltic pump. The feed to the bed consists of an 18" length of 1/4" stainless steel tube which sits inside the bed. The pipe is located in the middle of the plenum section and when the bed is at the operating temperature (> 800°C) the water vaporizes as it moves upward through the tube. This modification allows for the very accurate metering and control of steam into the bed while eliminating all the instrumentation difficulties associated with steam. The monitoring and control of a second gas, e.g. hydrogen or carbon dioxide, is achieved by passing the gas through a rotameter and then a regulating valve. The latter acts as a critical flow orifice and controls accurately the flow of gas to the bed.

Item 5: The feed liquid control and monitoring system were designed and installed. The liquid (comprising the organic material to be tested) is stored in a 1 gallon stainless steel vessel and is pressurized with nitrogen to about 30 psig. A dip tube from the bottom of the tank leads to a rotameter and a regulating needle valve prior

to entering the bed. Originally the organic material was fed to a nozzle located in the center of the distributor plate. The feed tube to the nozzle was surrounded by a water jacket to prevent vaporization prior to injection into the bed. For reasons given in the next section this method was abandoned due to excessive coking in the nozzle feed tube. The organic liquid is now mixed with the steam prior to feeding into the bed, this is illustrated in Figure A.3 in the Appendix.

Item 6: The liquid rotameter and water pump were calibrated by measuring the cumulative volume of liquid flowing through the device over a given period of time. The calibration curves are given as Figures A.4 and A.5 in the Appendix. It can be seen that at the low end of the rotameter the flow curve is non-linear and operation below 30% full-scale will be avoided.

Item 7: A new distributor plate was designed and constructed. The plate consists of a stainless steel screen sandwiched between two orifice plates. The plate will be located above the feed tube and will distribute the gases across the diameter of the bed. It should be pointed out that this plate was not used in the preliminary test runs described below. Some concerns still remain about the possibility of carbon formation in the reactor and these need to be quantified better before any potential restrictions, e.g. a new gas distributor plate, are placed in the bed.

Item 8: A safety review was completed for the reactor system. For the conditions that will be used in the present study the composition of the reactor effluent gas and operation of the reactor as a whole do not present a major safety risk. Typical flowrates to be used are on the order of 1 scfm of steam and <0.1 scfm of organic material. After condensation of the steam, occurring in the cold trap, the reactor effluent gases could contain several mole % of hydrogen and carbon monoxide and the flow could be as much as 1 scfm. In order to minimize the chance of a build up of these gases a purge gas stream, carbon dioxide or nitrogen, will be used in future experimental work. In addition, combustible gas monitors will be purchased and installed next quarter. A carbon monoxide monitor has been purchased and is used when the equipment is operating.

Item 9: A preliminary run was conducted to verify the operation of the system and to check the different sub-systems. The organic material chosen was toluene and this was reformed (gasified) using steam at two temperatures. Operation without the combustible gas monitors was deemed appropriate due to the low feed rates and absence of hydrogen feed gas. Since the product gases would contain both carbon monoxide and hydrogen, testing for CO in the lab. was deemed a reliable check for leaks.

From Items 1-9 listed above it is apparent that Tasks 1-7 on the attached schedule have been completed.

6.0 Results and Discussion (Current Period)

As mentioned in Item 9 a set of preliminary runs was designed and conducted in order to test the design of the reactor and associated feed and sampling systems. It should be noted that obtaining accurate quantitative results regarding the destruction efficiency of toluene was not the goal of these tests and that the destruction efficiencies reported here are only estimates. The conditions used for the tests are given below in Table 1.

It was found, for the high temperature condition used in the bed, that when the liquid feed was fed to the bed via the nozzle that excessive carbon formation took place within the nozzle. This was noticed during the runs as a stoppage in the flow of toluene. Upon dismantling the bed it was found that the nozzle was completely clogged with carbon/coke deposits and that the feed tube to the nozzle was also blocked. It was recognized that at the top of the jacketed tube the metal temperature could be far in excess of 100°C and that thermal cracking of the toluene was likely. In order to reduce this problem it was decided to introduce the toluene into the water/steam feed line at the base of the bed. The rationale for doing this was that by heating and vaporizing the toluene in the presence of steam the thermal cracking reaction would be greatly reduced. In addition, the wider tube diameter used in the steam feed tube would also help reduce the clogging tendency. The results for the tests using the modified feed system showed no carbon build-up as would be observed by reduced feed rates.

However, small amounts of fine carbon were observed in the liquid taken from the cold trap drain indicating that cracking and coke formation were still occurring.

Table 1: Experimental Conditions used in Preliminary Reactor Tests

	Test 1	Test 2
furnace temperature (°C)	350	1050
thermocouple temperatures (°C) at 9", 19" and 23" from distributor plate	334 318 139*	1050 1034 678*
flowrate of toluene (ml/min)	0.80	0.80
flowrate of water (ml/min)	13.3	13.3
approximate gas residence time (s)	4	2

* the third thermocouple lies outside of the furnace heating zones and hence reads a much lower temperature than the other thermocouples.

Gas samples were taken for the conditions used in Tests 1 and 2. Since it is unlikely that any reaction will occur at 350°C (662°F) the results for Test 1 are taken to be those for no reaction and by comparing these directly with those obtained for Test 2 an estimate of the destruction efficiency of the toluene at 1050°C can be made. Chromatograms for the two tests were obtained using an in-house GC fitted with an FID detector, the GC was located in Dr. E.Kugler's laboratory since the GC in Dr. Turton's lab will not be upgraded with an FID until next quarter. The results for the two tests are summarized in Table 2.

Table 2: Summary of Gas Analysis for Preliminary Reactor Tests

	Test 1	Test 2
Retention Time for Peak (min)	0.652	0.444-0.558
Peak Area Count	2,335,698	42,405
Peak Area %	98.97	91.98
Sample Volume (ml)	0.2	0.2

From Table 2 it is not entirely clear whether there is any toluene in the gas stream for Test 2 since the peaks do not coincide exactly with those of Test 1. However if we assume that these peaks do represent toluene then

we can estimate the destruction efficiency of the gasification reaction as $(2.336-0.04241)/2.336 = 0.9818$ or 98.18%. It is noted that the above analysis is only approximate since the liquid from the cold trap should also be analyzed for unreacted toluene. However, from visual observation it was noted that for Test 2 this liquid appeared odorless and no second phase was seen to appear - indicating a very low level of toluene consistent with the gas phase analysis.

7.0 Conclusions (Current Period)

From the results presented in 5.0 and 6.0 above it is apparent that all the tasks for year 1 of this project have been completed. As a result of this, the reactor system is capable of providing the conditions necessary to complete the experimental program for the second year of this project. The destruction efficiencies of different organic materials can be evaluated using different gasifying materials, e.g. steam, carbon dioxide and hydrogen, at different temperatures. In order to obtain accurate estimates of the destruction efficiencies it will be necessary to collect and analyze the liquid and gas streams leaving the unit. To facilitate this task a GC fitted with an FID will be installed in Dr. Turton's lab during the next period of this contract.

8.0 Work Planned for Next Period

The work for the next quarter will concentrate on providing information for the National Environmental Policy Act and upgrading and calibrating the GC with a flame ionization detector (FID).

References

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3. T.C. Ho, H.W.Chu and J.R.Hopper, "Metal volatilization and separation during incineration", *Waste Mgmt.*, 13,455-466 (1993)
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Acronyms and Abbreviations

FID - Flame Ionization Detector
GC - Gas Chromatograph
LEL - Lower Explosion Limit
MSDS - Material and Safety Data Sheets
MSW - Municipal Solid Waste
RCRA - Resource Conservation and Recovery Act (1976)

APPENDIX

Figure A.1: Location of Thermocouples in Reactor

Figure A.2: Design of Cold Trap fro Reactor Product Gas

Figure A.3: Location of Feeds to Reactor

Flow of Water
(ml/min)

Figure A.4: Calibration Curve for Peristaltic Pump

Flow of Toluene
(ml/min)

Figure A.5: Calibration Curve for Organic Liquid Rotameter

REMEDIATION OF HAZARDOUS SITES WITH STEAM REFORMING

**Quarterly Report for Period
September 25, 1995 through December 31, 1995
(October - December 1995)**

**Work Performed Under Contract
No.: DE-FC21-92MC29467
(MTCI No. 10070)**

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Manufacturing and Technology Conversion
International, Inc. (MTCI)
Columbia, Maryland 21044**

January 18, 1996

205

ABSTRACT

The program is on-hold pending resolution of extension of contract beyond December 1995.

TABLE OF CONTENTS

Section No.	Page No.
1. TECHNICAL BACKGROUND	1
2. EXPERIMENTAL METHODOLOGY	2
3. EXPERIMENTAL RESULTS AND DISCUSSIONS	3
4. CONCLUSIONS	4

1. TECHNICAL BACKGROUND

A complete discussion of the technical background was presented in the quarterly report for the period July 1, 1993 through September 30, 1993. For continuity of the discussion in this part, the following summary paragraph has been included herein.

The MTCI thermochemical reactor system has easily demonstrated at commercial levels its superior performance in the steam reforming of a wide variety of biomass, industrial and municipal waste feedstocks containing chlororganics as well as coal, coal liquefaction bottoms, and mild gasification char at ambient (atmospheric) conditions. The system processed a wide spectrum of feedstocks producing a hydrogen-rich product gas that is free of the diluents (primarily N₂) found in air-blown steam reforming systems and is more cost-effective than oxygen-blown systems. In addition, liquid and solid waste streams from the MTCI system show extremely low levels of toxics and leachability, permitting easier landfill or industrial toxic by-product recovery. The feasibility of developing a pressurized system based on the MTCI technology would permit even greater gains in processing yields, system modularity, and capital and operating costs for processing hazardous and other waste. This would especially be applicable to the cleanup and treatment of large volumes of soils contaminated with toxic organics, i.e., PCBs, pesticides, cyanides, RCRA metals, and dioxin/furans. Reformation of toxic organics in the oxidizing environment of incinerators are completely eliminated because of the reducing environment present in the MTCI thermochemical reactor (steam reformer).

2. EXPERIMENTAL METHODOLOGY

The test plan and methodology remain the same as previously reported.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

There has been no activity on the project since last quarter except for reporting and parts identification and handling (housekeeping).

4. CONCLUSIONS

No direct labor was expended against the contract since September 1995 except for reporting and some other system housekeeping activities. It is anticipated that start-up of the work at Baltimore will begin after resolution of the administrative and contractual items.

PLANS FOR NEXT REPORTING PERIOD

Future plans awaiting resolution of contractual items.

METC TASK NO.: 2.5

CARBON PRODUCTS FOR WASTE STREAM CLEAN-UP

Principal Investigators: J. Zondolo & A. Stiller
Department of Chemical Engineering

This project was completed during the 3rd calendar quarter of 1995.
The draft final report was submitted with the 3rd quarterly report deliverable.

TASK 3.0
INFORMATION SYSTEMS,
PUBLIC POLICY,
COMMUNITY OUTREACH,
AND ECONOMICS

**INFORMATION SYSTEMS, PUBLIC POLICY,
COMMUNITY OUTREACH AND ECONOMICS**

WINFIELD LOCK AND DAM ASSISTANCE PROGRAM

TASK 3.1

Quarterly Report for Period
October 1 through December 31, 1995

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

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By:

Raymond J. Lovett
National Research Center for Coal and Energy
Environmental Technology Division
West Virginia University
Morgantown, West Virginia 26506

October 1995

WINFIELD LOCK AND DAM REMEDIATION

Quarterly Technical Progress Report
for Period October 1 through December 31, 1995

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
Raymond J. Lovett
National Research Center for Coal and Energy
Environmental Technology Division
West Virginia University
Morgantown, West Virginia 26506

January 1996

Abstract

The United States Army Corps of Engineers (ACE) must remediate a contaminated industrial site, formerly owned by ACF Industries, Inc., in order to build a new lock on the Kanawha River at Winfield, WV. The original remediation plan, to incinerate the contaminated soil, generated much controversy in the surrounding communities, notably Eleanor, WV.

West Virginia University became involved in the project in August of 1992. Shortly after that time, a formal program to involve WVU in the solution to the remediation problem began. The WVU involvement has been two-pronged. WVU has interacted extensively with the citizens of Eleanor (and Putnam County) providing technical, logistical and financial assistance in their efforts to understand and evaluate the ACE plans for remediation. A primary objective for WVU is to inform the citizens of possible health and safety problems with proposed operations. Additionally, WVU has interacted with the U.S. Army Corps of Engineers to implement appropriate technology at the site.

These investigations are being conducted by the National Research Center for Coal and Energy (NRCCE) Environmental Technology Division (ETD) staff and WVU faculty.

Table of Contents

EXECUTIVE SUMMARY 1

1.0 INTRODUCTION

2.0 WORK PERFORMED THIS PERIOD

3.0 WORK PLANNED FOR NEXT PERIOD

4.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

EXECUTIVE SUMMARY

The contaminated material from the Winfield Lock and Dam is being excavated and shipped to Utah. As of 31 December, the excavation was not completed, but the dioxin materials had been removed and certain of the buildings disassembled. The project completion date is weather dependent, but current estimates place it in February. The digging began about August 15, 1995. WVU is conducting a dust monitoring program during the excavation which was funded to 31 December 1995. The program will continue, without DOE funding, to project completion. One monitor is currently operating full time, another is used to back up the primary unit and provide calibration.

1.0 INTRODUCTION

The site of the former ACF Industries, Inc. railroad tank car maintenance shop is contaminated by various organic and inorganic chemicals. The company abandoned the site in March 1986 and the U.S. Army Corps of Engineers (ACE) acquired the site, which was needed for the approach to expansion of the Winfield Locks and Dam. The extent of contamination, and most explicitly, the presence of dioxin at the site, had been inadequately documented before the ACE took possession of the land. The ACE, when it became aware of the extent of contamination, undertook a study which culminated in the publication of an Engineering Evaluation and Cost Analysis (EE/CA) in May 1992. The EE/CA was made public with a 30 day response period. The net conclusion of the EE/CA was that the ACE would incinerate the contaminated soil. The combination of citizen perception that they had not been appropriately informed of the problem and the proposal to incinerate the soil led to a concerted effort by the citizens to have the EE/CA reconsidered. The concerted effort, which included the involvement of the WV Congressional delegation, successfully led to reconsideration of the issue by the Army.

The subsequent reevaluation by the Army took nearly 7 months; the results, an Action Memorandum for the site, was released in December 1992. The Action Memorandum proposed that the soil be excavated, stored in temporary buildings, then remediated after further study.

As a result of the public involvement in the lock issue, Senator Robert C. Byrd of West Virginia and the Senate appropriations committee published some language which involved the Department of Energy and West Virginia University in the problem. The role of the DOE was to assist WVU financially in their efforts to safeguard the health and safety of the citizens and investigate the application of DOE technology in remediation of the site. The DOE-WVU effort is, thus, funded by this Cooperative Agreement and consists of direct assistance to the area around the site as well as certain technological investigations directed towards the choice of the eventual remediation technology (or technologies).

2.0 WORK PERFORMED THIS PERIOD

An umbrella committee meeting was held in November to discuss the disposition of the temporary storage buildings. I did not attend due to bad weather

The particulate real time air monitoring system designated by Dr. M. Gautum is the MIE Dataram. This unit can sample continuously and record up to 10,000 points designating the actual ug/m3 of respirable dust in the air. The unit are difficult to

calibrate, so they are being used as relative monitors.

The Dataram units were evaluated at the NRCCE (battery time, download method, etc.) Humid conditions provide a positive error, so a heater unit bought with the Dataram is being used. The first unit was deployed on August 30, 1995. The unit sits on the west end of the site, in the direction of Eleanor, WV. The unit was set to measure the PM10 value every minute for a week.

After the correction of the power problem in September, the unit ran flawlessly until 27 December, the last reading, when the unit was changed to measuring every 5 minutes. Some data for this quarter is appended.

3.0 WORK PLANNED FOR NEXT PERIOD

The air monitoring will continue, although the funding has ended. The final report will be written.

4.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

The development of the MS/MS system never was successful due to numerous problems. Most of the problems appear to be related to needed software changes.

METC TASK #3.1

#	Task Name	Dura	%Com	1995												1st	
				1st Quarter			2nd Quarter			3rd Quarter			4th Quarter				
				Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	
1	Evaluate Remedial Work	1M	100.00%														
2	Develop MS/MS Monitor	7M	80.00%														
3	Implement Monitor	3M	100.00%														
4	Monitor Site	7M	0.00%														
5	Reports	0M	0.00%														

221

Critical	Noncritical	Complete	Summary	External
Critical Milestone	Noncritical Milestone	Complete Milestone	Summary Milestone	External Milestone
Free Float	Total Float (+)	Total Float (-)	Baseline	Non-Resource
Delay	Effort %Complete			

225

**A GIS-BASED INFRASTRUCTURE
FOR SITE CHARACTERIZATION AND REMEDIATION**

**Task 3.2
METC/WVU Cooperative Agreement**

Quarterly Technical Progress Report
Reporting Period:
October 1, 1995 - January 2, 1996

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

For:
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By:
Marshall University
Center for Environmental, Geotechnical, and Applied Sciences
Huntington, West Virginia 25755
(304) 696-5453 (304) 696-5454 Fax

ABSTRACT

The primary goal of this work is to determine an effective GIS-based infrastructure for describing, characterizing, and remediating contaminated sites. The work is being carried out using the remediation needs of the U.S. Army Corps of Engineers Huntington, WV district office as a basis--giving the benefit of real needs of on-going remediation projects. The work includes devising and specifying an integrated system with features targeted to site remediation/restoration needs, establishing operational procedures for effective use of the integrated system, and establishing methods for effective technology transfer. The effort will also result in the establishment of a professional team at Marshall University with capability and availability to provide supporting services in the application of GIS-based tools and methods in site restoration efforts.

EXECUTIVE SUMMARY

This document constitutes the required Quarterly Report for the fourth quarter of 1995, for Task No. 3.2 under the DOE/METC/WVU Cooperative Agreement, contract no. DE-FC21-92MC29467. It documents technical accomplishments and provides cost status as of January 2, 1996.

At the end of this reporting period we have successfully completed all 1995 contract tasks, and have achieved all objectives of the contract.

We expect to make extensive use of the results from this work during the anticipated 1996 follow-on effort. The Final Report, to be provided after the 1996 follow-on effort, will provide all deliverables resulting from the multi-year work.

TABLE OF CONTENTS

ABSTRACT	ii
EXECUTIVE SUMMARY	iii
1.0 INTRODUCTION	1
2.0 PURPOSE	1
3.0 BACKGROUND	1
4.0 METHODOLOGY	2
5.0 WORK PERFORMED THIS PERIOD	4
5.1 Activities	4
5.2 Schedule and Costs	6
6.0 RESULTS AND DISCUSSION (CURRENT PERIOD)	7
7.0 CONCLUSIONS (CURRENT PERIOD)	7
8.0 WORK PLANNED FOR NEXT PERIOD	7
8.1 Activities	7
8.2 Schedule and Costs	7
9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES	8
APPENDICES	9
A. LIST OF ACRONYMS AND ABBREVIATIONS	9

1.0 INTRODUCTION

This effort focuses on determining GIS-based capabilities for site characterization and remediation. This is a pressing need, largely unsatisfied at the current time. Although there are numerous available GIS systems, and many different software components that could be useful in site characterization and remediation, there is no available system that brings together the numerous needed capabilities. The approach is to base a needs assessment for such a GIS-based system on the on-going work of the Huntington Corps district office. This will provide a realistic needs determination: the Huntington Corps office is faced with an immediate need for effective GIS-based software tools to more effectively manage site remediation in the district. Further, a working relationship has already been established between the Marshall University team and personnel within the Corps office. The U.S. Department of Energy (DOE) Morgantown Energy Technology Center (METC), and other agencies, stand to benefit from the results of this work, since it will be grounded in real needs of real, on-going remediation projects.

2.0 PURPOSE

The primary goal of this work is to determine an effective GIS-based infrastructure for describing, characterizing, and remediating contaminated sites. Objectives involved in achieving this goal include:

- (a) devising and specifying an integrated system whose features are targeted to specific needs for site remediation/restoration--including a set of GIS-based software tools and supporting computer hardware,
- (b) establishing operational procedures for effective application of the system,
- (c) establishing methods for effective transfer of technology (system, procedures) to a user organization (USACE Huntington District office, in the first instance), and
- (d) simultaneously establishing a professional team at Marshall University with the capability and availability to provide supporting services and consultation in the application of GIS-related tools in site restoration efforts.

3.0 BACKGROUND

Geographic Information Systems (GISs) are increasing rapidly in numbers and areas of application. No doubt the expansion is influenced strongly by the growing national interest in environmental protection and restoration. Numerous GIS systems are available--including commercial (e.g., ARC/INFO, Intergraph MGE, MapInfo), government-sponsored (GRASS), and university research based (IDRISI, ICASE/GRACE). The desired applicability of GISs is extremely broad (e.g., air quality monitoring, groundwater contamination, areas in a city accessible by public transport). Thus the GIS systems must be very generic in their capabilities. This genericness is attractive in providing versatility of application breadth, but of necessity limits the depth of features for a given application area.

The nation faces a massive problem relative to contaminated sites. The U.S. Department of Energy, the U.S. Army Corps of Engineers, and many other government agencies are faced with requirements to remediate contaminated sites under their purview. The Huntington District of the U.S. Army Corps of Engineers (USACE) has undertaken to assemble computer-based tools to help them in describing, characterizing, and remediating contaminated sites. They have obtained the Integrated Computer Assisted Site Evaluator / Graphical Remedial Assessment and Cost Evaluation (ICASE/GRACE) system, developed at the University of Cincinnati, for evaluation. They have also obtained and installed Intergraph's MGE system, and anticipate obtaining Intergraph's ERMA (for Environmental Resource Management Application) system, intended to support site assessment, modeling and remediation. Under a previous METC task, Marshall

University evaluated ICASE/GRACE for use by the Huntington USACE District.

4.0 METHODOLOGY

Following are descriptions of the tasks to be conducted, and associated schedules.

Task 1: Information Required for the National Environmental Policy Act

To be supplied within 60 days after contract award.

Task 2: Determine System Requirements

Interview USACE Huntington District office personnel involved with remediation projects, assess needs as they perceive them for describing, characterizing, and remediating contaminated sites. Consider approaches of other organizations with remediation requirements, including other USACE offices, and other Department of Energy-funded work. From this input, determine and specify system requirements necessary to fulfill the identified needs.

Schedule: January 1 through March 31, 1995.

Task 3: Devise and Specify an Integrated System

Undertake to determine and specify a system that satisfies the requirements identified in Task 2. Note that the outcome of this task will be a specification of a recommended system, and not an implementation as such.

Determine a GIS system to serve as the basis for the overall system--evaluating candidate GIS systems based on their inherent suitability for the role, as well as their current importance to organizations with whom data interchange may be necessary. We will emphasize commercially-available systems and government-sponsored systems to the maximum extent feasible. One GIS system we will evaluate is Intergraph's MGE system, Windows NT version, due to the fact that the USACE Nashville District office uses this MGE version, and the Huntington office must be able to interchange data with the Nashville office.

Determine a means to integrate other needed software and data sources--currently existing and anticipated--into an overall system based on an identified GIS system, with the overall system having a uniform "look and feel". Examples of other needs are a cost modeling tool in current USACE use, Modflow software, and various features of ICASE/GRACE. Means to integrate other components into a GIS system could include data translation software utilities and windows-based dialog boxes, for example. The means will be provided to augment the software complement with additional capabilities in the future.

The most desirable outcome would be that carefully-selected software can be integrated, without modification or additional software development, into a system that fully satisfies all identified requirements. In the event that is not a feasible outcome, we will determine and recommend approaches for meeting the unsatisfied requirements.

A necessary, and interwoven, aspect of this task is to ensure that the software system being devised can be accommodated by an acceptable range of computing hardware; i.e., by both lap-top PCS and high-end Pentium PCS, and even by Unix-based workstations if that is found to be a requirement.

It may be that multiple feasible approaches will be identified to accomplish some aspects of the required system. If so, we will document the options, and give trade-off considerations for making choices.

Schedule: January 1 through November 30, 1995.

Task 4: Determine Operating Procedures

Determine and describe effective procedures for using the system. This will include guidance concerning combinations--and sequences--of software tools to use for certain classes of applications, set-up assumptions for each tool, and inter-tool control and data management. Representative scenarios will be devised and documented.

If it is found to be necessary to modify some software or to develop some additional software to achieve all requirements, we will nonetheless summarize procedures involving the system features expected to be available after modification and/or development, so that a comprehensive understanding of the full resulting system can be gained, and also to offer perspective and guidance in developing and providing any additional features.

Schedule: October 1 through November 30, 1995.

Task 5: Develop Materials for Technology Transfer

Establish means for effective transfer of technology--the integrated system and operating procedures --to a user organization. The USACE Huntington District office will be the initial user organization, in concept, since we will be basing much of our requirements determination efforts on their needs. However, our efforts in technology transfer will be guided by the need for various user organizations to be accommodated.

Emphasis will be placed on development of tutorial materials, including on-line materials, and on development of seminar presentation materials to provide an overview of the tools and procedures. Full documentation of system requirements, system specification, and operating procedures will, of course, be provided as well.

Schedule: November 1 through December 31, 1995.

Deliverables:

Deliverables from this work will be:

- A written statement of requirements for software and hardware necessary to conduct site description and characterization, and assess remediation strategies--based on detailed analysis of needs of the Huntington Corps office, with participation and cooperation of their personnel
- Written descriptions of in-depth evaluations of various candidate software and hardware approaches for meeting the statement of requirements, with the relative merits of specific approaches, and rationale for each approach recommended
- A detailed description of a recommended system: hardware and software components--including use of available commercial or government software, strategies for integrating the components, and if necessary, details of a limited amount of software requiring development in order to achieve a satisfactory system
- Operating procedures for effective application of the system
- Educational/training tutorial materials to enable technology transfer for system capabilities and operating procedures
- Recommendations concerning strategies for undertaking system implementation based on the system description

5.0 WORK PERFORMED THIS PERIOD

5.1 Activities

During this period, Task 3 (Devise and Specify an Integrated System), Task 4 (Determine Operating Procedures) and Task 5 (Develop Materials for Technology Transfer) were completed.

Task 1: Information Required for the National Environmental Policy Act

This material was prepared and delivered during the first half of April.

Task 2: Determine System Requirements

Task 2 was completed successfully by the end of the second quarter.

Task 3: Devise and Specify an Integrated System

Approximately 80 percent of Task 3 was completed by the end of the third quarter. Most of the hardware and software was acquired and set up during the third quarter. During the fourth quarter, we completed the remaining work for this task by: running the database in a client/server environment, acquiring and setting up the notebook computer, setting up a mechanism for integrating external software, and conducting a preliminary analysis on the West Virginia Ordnance data acquired from the Nashville District Corps office (through the Huntington District Corps office). The sections below describe these activities in more detail.

1. Configuring the client/server database:

We have configured the database (SQL Server) to run in a client/server environment. We installed the SQL Server database on the server (TD4). The MGE suite has been installed on the TD3 (client) workstation, as well as the notebook computer (see below). The database, however, is not installed on these machines. The client computers access the server-resident database by means of the network. This mechanism allows the database to be in a central location, supporting multiple accesses.

2. The Notebook Computer:

The notebook computer acquired is the Gateway Solo S90. A brief technical description of the computer: Intel Pentium 90MHz processor, 10.4" SVGA active matrix color display, 40 MB RAM, 1.2 GB IDE removable hard drive, dual speed modular CD-ROM, 1.44MB 3.5" modular floppy drive, PCMCIA Ethernet card, speakers and internal microphone.

This notebook computer is the "field computer" which will allow us to gather data on-site, and conduct preliminary analysis. Also, this computer will allow us to make "live" presentations of real data with a GIS system. The notebook computer we have acquired is comparable to a workstation in terms of processor speed and hard disk space. The 800x600 SVGA display of the notebook computer, though not very high compared to that of a workstation, is the best that is available for notebook computers, and is adequate for its intended purpose.

We have acquired the basic MGE suite for this computer, which consists of MGE Basic Nucleus, MGE Basic Administrator, MGE Base Mapper, MGE Analyst, MGE Base Imager, MGE ASCII Loader, and MGE Map Finisher. We have installed this suite on the computer, under the Windows NT 3.51 operating system. We have

successfully thoroughly tested the software on this computer, running it independently and as a client connected to the TD4 server, using the Ethernet card and connectors. In addition, we have successfully used a PCMCIA modem (not acquired through this contract) to test data transfer to and from this machine using a telephone line. These tests establish the capability of using this computer as a field computer for data gathering and preliminary analysis, and transferring the data to (or from) a server or workstation either remotely or using high speed Ethernet.

3. Integrating External Software:

During the third quarter, we acquired MS Project as a model project management software, and the MS Office suite of software for document preparation. During this quarter we set up a mechanism of transferring project related data between MS Project and MGE. These tools are useful in and of themselves, and the data transfer mechanism developed has usefulness for integrating various non-native software components.

4. WV Ordnance Data

During the third quarter we made a trip to the Nashville Corps office, along with Huntington District Corps personnel, to understand the status of data capture for the WV Ordnance site in Mason County. In conversation with the Nashville Corps personnel, and from what we were able to view of the data, we concluded the following about the work done by the Nashville Corps personnel. (i) They have designed and created a database which consists primarily of chemical and geological data. They have not yet entered all the data from all the site locations. (ii) They were able to post certain queries based on the data. (iii) They have not yet made linkages between the data in the database and the maps of the region.

During this current quarter we finally acquired the WV Ordnance data from Nashville, through the Huntington Corps office, after resolving the legal issues. The data was packed on an 8mm tape using the Unix operating system. Since we do not have a Unix based computer, we had to rely on the Huntington Corps personnel to unpack the data. We received the data in usable form during the later half of November.

We conducted a preliminary analysis of the data, which is in Intergraph MGE format, and have determined the following profile:

1. There are six design files (.dgn files) which contain site information concerning transportation, utilities, vegetation.
2. There are 170 tables, of which 102 tables have data and 68 tables do not have any data.
3. There are 12 categories, each of which has several features associated with it. Some of these features are associated to some attribute tables.
4. There are 110 attributes.

In order to further investigate, understand, and make productive use of this data, we will have to make several contacts with the Corps personnel of the Nashville District. We anticipate doing this during the follow-on effort during early 1996.

Task 4: Determine Operating Procedures

As was mentioned in the previous section, we are using MS Project as an example of commercial-off-the shelf (COTS) project management software to integrate with MGE. We have developed an effective mechanism for data transfer from MS Project to MGE and vice-versa, and have developed some examples which illustrate this data transfer.

We are using MS Word as an example of COTS report preparation tool. We have developed mechanisms of

transferring results of queries, and other outputs of MGE, directly into reports written with MS Word. We have developed examples which illustrate this process as well.

We have installed the Environmental Resource Management Application (ERMA) suite of software. ERMA allows the integration of remediation models into MGE. We have successfully made limited use of ERMA.

Task 5: Develop Materials for Technology Transfer

We have developed an overall plan of technology transfer which consists of:

- identifying the minimum skills required of a person to learn the MGE suite,
- minimum system configuration required,
- example operating procedures for the system,
- overall plan of a tutorial system,
- sample lessons consisting of overhead transparencies and step-by-step instruction and
- a prototype of an online tutorial lesson.

We will include all of these materials in the Final Report.

5.2 Schedule and Costs

We are on target for both the schedule and spending rate in the fourth quarter. At the end of this quarter, we have expended the entire project budget. We have completed all scheduled tasks for this project.

The Task status is as follows:

Task 1: Completed
Task 2: Completed
Task 3: Completed
Task 4: Completed
Task 5: Completed

Costs invoiced in the fourth quarter are summarized below. Note that some amounts were expended in the third quarter, but were invoiced in the fourth quarter, due to delayed billing by the vendors. (This is an unofficial cost summary; Marshall University Research Corporation is the agent for formal contract and financial transactions.)

Personnel (including fringe benefits)	\$25,897
Travel and Training	1,901
Telephone/Report Preparation	479
Equipment	
Hardware	6,383
Software	123
Indirect Cost (less Hardware)	10,798
Total	\$45,581

6.0 RESULTS AND DISCUSSION (CURRENT PERIOD)

We have completed all 1995 Tasks (1 through 5) successfully. We received usable data from the Corps very late during this year. But we were able to make limited use of it effectively, and are well situated to begin the anticipated 1996 follow-on effort.

7.0 CONCLUSIONS (CURRENT PERIOD)

At the end of this reporting period we have successfully completed all of the 1995 tasks, 1 through 5, included in this contract, and have achieved the objectives stated in Section 2.0 (PURPOSE). The Final Report, to be provided after the 1996 follow-on effort, will provide all deliverables resulting from the multi-year work.

8.0 WORK PLANNED FOR NEXT PERIOD

8.1 Activities

The work reported during the quarter successfully brings to a close the 1995 contract. We anticipate that work on a 1996 follow-on contract will begin immediately following the current reporting period.

8.2 Schedule and Costs

Following is a chart which summarizes final schedule and costs as of January 2, 1996. For convenience, a summary of task titles and durations are repeated here.

Task 1 Information Required for the National Environmental Policy Act: due within 60 days
after award

Task 2 Determine System Requirements: January 1 through March 31, 1995

Task 3 Devise and Specify an Integrated System: January 1 through November 30, 1995

Task 4 Determine Operating Procedures: October 1 through November 30, 1995

Task 5 Develop Materials for Technology Transfer: November 1 through December 31, 1995

Schedule and Costs: Final, January 2, 1996

1995	first qtr.			second qtr.			third qtr.			fourth qtr.		
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec

Tasks:

1												
2	=====											

3	=====											

4												
5												

Legend: == original
 *** revised
 ^ completion

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
first qtr.	second qtr.	third qtr.	fourth qtr.								

Costs by quarter:

\$15,920.79	\$46,676.40	\$94,214.45	\$45,580.66*
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* Adjustment from third quarter where \$1,704.30 in indirect was charged on items determined to be equipment.

Cumulative:

\$15,920.79	\$62,597.19	\$156,811.64	\$200,688
Actual			

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

None.

APPENDICES

A. LIST OF ACRONYMS AND ABBREVIATIONS

ASCII	American Standard Code for Information Interchange
CD-ROM	compact disk read only memory
COTS	commercial off-the-shelf
DOS	disk operating system
ERMA	Environmental Resource Management Application (an Intergraph product)
GB	gigabyte; approximately 1,000 MB
GIS	geographic information system
HP	Hewlett Packard
HTRW	hazardous, toxic & radioactive waste
ICASE/GRACE	Integrated Computer Assisted Site Evaluator/Graphical Remedial Assessment and Cost Evaluator
IP	Internet protocol
LCD	liquid crystal display
MB	megabyte; approximately one million bytes
MGE	Modular GIS Environment (an Intergraph product)
MHZ	megahertz
MS	Microsoft
NT	New Technology (as part of Windows NT)
PC	Personal Computer
PCMCIA	Personal Computer Microchannel Interface Adaptor
RAM	random access memory
RIS	relational interface system
SCSI	small computer systems interface
SQL	system query language
SVGA	super video graphics adapter
TD 3	Technical Desktop 3
TD 4	Technical Desktop 4
UPS	un-interruptible power supply
USACE	United States Army Corps of Engineers

**INFORMATION SYSTEMS, PUBLIC POLICY,
COMMUNITY OUTREACH AND ECONOMICS**

SMALL BUSINESS SUPPORT PROGRAM

TASK 3.3

**Quarterly Technical Progress Report
October 1 through December 31, 1995**

**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, 3610 Collins Ferry Road
Morgantown, West Virginia**

By:

**E.E. Cook
Department of Civil Engineering
West Virginia University
Morgantown, West Virginia 26505-6103**

December 1995

Executive Summary

A poster and paper were presented at the METC sponsored Small Business Conference "Environmental Technology Development Through Industry Partnership". The West Virginia High Tech Consortium small business incubator was dedicated and candidate small businesses will be selected soon. Outreach occurred to numerous agencies, research entities and small businesses for possible interaction and complementary research opportunities through the WVU Cooperative Agreement. Great efforts have been made to tailor and change the projects funded through the WVU Cooperative Agreement so that the 1996 Program reflects both DOE/METC's needs and the needs of the METC sponsored small businesses developing the innovative site remediation technologies.

1.0 Introduction

Task 3.3, Small Business Support Program, was initiated to address the technical problems or barriers to commercialization of the innovative site remediation technologies developed by the small businesses that are funded by METC. Once a problem or opportunity was defined, researchers from WVU, Marshall or other sources would be solicited to work with the small business in a research project to solve the problem or alleviate the barrier.

2.0 Purpose

The Small Business Support Program was initiated to explicitly address the problems and barriers to commercialization of the innovative site remediation technologies developed by the small businesses funded by METC.

3.0 Background

Over the past two years the METC/WVU Cooperative Agreement has funded numerous projects at WVU and Marshall University. This has resulted in defining at least three areas of core competencies at WVU which may be called upon to provide assistance to the small businesses that METC funds in the area of site remediation.

The core competencies are found mainly in the in-situ remediation area including:

- * Remediation Processes such as surfactant flushing of soils and chemical and biological destruction of polyaromatic chlorinated hydrocarbons
- * Confinement Barriers such as the Circulating Air Barrier and Chemical Grouting Barriers
- * Fluid Recirculating Systems such as the Drain Enhanced Surfactant Flushing

4.0 Methodology

By attending the kickoff meetings and other periodic meetings of the small businesses funded by METC an understanding of the project is obtained. During the presentations, value added opportunities for collaboration between the small businesses and university researchers are carefully watched for. Discussions with program managers also

provide opportunities for interaction. The Environmental Waste Management Technical Product Team also provides opportunities to determine needs of the small businesses and resulting research opportunities. For the long range research opportunities, the initiative at DOE HQ level bringing together elements from DOE, DOD, NASA, Commerce and others to coordinate interagency site remediation capabilities and needs will be very helpful.

Also, attendance at various meetings and conferences on site remediation provides insights to research needs.

From all of the previous sources research opportunities are ferreted out and projects are developed with university faculty to carry them out.

5.0 Work Performed This Period

This period began with the METC sponsored small business conference titled "Environmental Technology Development Through Industry Partnership". The 1995 WVU Cooperative Agreement Program was presented in a poster session and a paper was written for inclusion into the conference proceedings. Many new contacts have developed from this and numerous calls for more information from all over DOE have occurred. The next time this conference is held the WVU program should be presented. Work is being initiated by an MS student (a METC employee) to try to determine what are the needs for these METC small businesses that may be addressed through the WVU Cooperative Agreement, UNDEERC and other resources provided by METC.

Meetings began with the West Virginia High Tech Consortium on placing an environmental technology incubator on the WVU campus. It will be located at the National Research Center for Coal & Energy (NRCCE) and the Grand Central Station on the WVU campus. The incubator was dedicated on October 6, 1995 in a ceremony held at NRCCE. Selection of candidate small businesses will begin next quarter. WVU investigators on the WVU Cooperative Agreement have been greatly encouraged to get their projects very closely tied to DOE's needs and especially to technical problems experienced by the small businesses that are funded by METC developing innovative site remediation technologies. To not do so greatly lessens the probability of future funding of a given project. Continual efforts have been made to make these ties and some success has occurred.

Outreach for cooperative opportunities with other agencies, organizations and research entities has occurred. Visits have been made with the Institute of Gas Technology (IGT) in Chicago and at WVU to discuss future cooperation in

complementary research areas. There appear to be some exciting areas that may be feasible for future cooperation.

The 1996 WVU Cooperative Agreement Proposal "Decontamination Systems Information" and Research Program was submitted during this period.

6.0 Results and Discussion N/A

7.0 Conclusions N/A

Task33.out

**INFORMATION SYSTEMS, PUBLIC POLICY,
COMMUNITY OUTREACH AND ECONOMICS**

**APPROACH FOR ASSESSING POTENTIAL VOLUNTARY
ENVIRONMENTAL PROTECTION,
KANAWHA VALLEY AREA**

TASK 3.4

Quarterly Report for Period
October 1 through December 31, 1995

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

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By:
Raymond J. Lovett
National Research Center for Coal and Energy
Environmental Technology Division
West Virginia University
Morgantown, West Virginia 26506

James J. Kohanek
Clean Sites, Inc.
Alexandria, VA

Paul Hill
National Institute for Chemical Studies
Charleston, WV

APPROACH FOR ASSESSING POTENTIAL VOLUNTARY ENVIRONMENTAL PROTECTION, KANAWHA VALLEY AREA

Quarterly Technical Progress Report
for Period October 1 through December 31, 1995

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
Raymond J. Lovett
National Research Center for Coal and Energy
Environmental Technology Division
West Virginia University
Morgantown, West Virginia 26506

James J. Kohanek
Clean Sites, Inc.
Alexandria, VA

Paul Hill
National Institute for Chemical Studies
Charleston, WV

January 1996
ABSTRACT

This project concerns investigation of the feasibility of establishing voluntary remediation programs in the Kanawha Valley, WV.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

The United States contains numerous hazardous waste sites. Many sites are on private land near operating units of various companies. An effort is being made to determine the conditions under which such sites can be remediated voluntarily. Such voluntary remediation would result in an accelerated clean-up of U.S. sites and a significant cost savings. Meetings are being held with U.S. companies to evaluate the potential for actually initiating voluntary clean-ups.

1.0 INTRODUCTION

The objective of the project will be to first assess the interest and willingness of industry in the Kanawha River Valley to participate in discussions that would lead toward voluntary cleanup activities. The second will be to implement the activities agreed upon by the interested parties. The project will first involve individual discussions with the industrial, government, and other organized groups in the area. These discussions will help determine the feasibility of organizing voluntary efforts. If the discussions indicate that conditions may be favorable for developing individual or group voluntary cleanup projects, a working group will be convened to establish the environmental goals of the project as well as the technical approach for achieving those goals.

2.0 WORK PERFORMED THIS PERIOD

Discussions between the principals, Raymond Lovett of West Virginia University, Paul Hill of the National Institute of Chemical Studies, and Jim Kohanek, late of Clean Sites now with TLI (and participating here as a consultant to Clean Sites) derived a strategy to have Paul Hill discuss the concept with selected individuals in the Kanawha Valley to determine the initial interest. These initial discussions led to a presentation before the Kanawha Valley Chemical Plant Managers group detailing the project. Subsequent to that meeting, individual meetings with the companies were scheduled, two of which occurred in this quarter and two last quarter (a total of four companies have been approached).

The two meetings were conducted in the strictest confidentiality. The gist of all the meetings is a continuing willingness of the companies to develop the issue and a definite interest in using new technologies in clean-ups.

We also met with the West Virginia Manufacturer's Association regarding a Brownfields proposal to be developed in the West Virginia legislature this year. That legislation will focus on using flexible clean-up criteria to help increase industrial reutilization of contaminated property. The concept dovetails with our efforts and we will stay informed of the bill's progress.

A meeting with the Director of the West Virginia Division of Environmental Protection resulted in a commitment from him to assist us in any way and a willingness to participate in any negotiations. He especially wants sites cleaned up and supports the use of site specific standards.

3.0 WORK PLANNED FOR NEXT PERIOD

Meetings with another company is scheduled. Meetings with regulatory agencies and citizen's groups will follow.

4.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES -

METC TASK #3.4

1995

#	Task Name	Dura	%Com	1995															
				1st Quarter	2nd Quarter	3rd Quarter	4th Quarter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1	Initial Contact of Parties	1M	100.00%																
2	Conduct Meetings with Parties	1M	50.00%																
3	Scoping meetings with USEPA and WVDEQ	2M	0.00%																
4	Prepare summary of meetings	0.5M	0.00%																
5	Group Meeting	1M	0.00%																

242

Critical Milestone
 Free Float
 Delay

Noncritical Milestone
 Total Float (+)
 Effort %Complete

Complete Milestone
 Total Float (-)

Summary Milestone
 Baseline

External Milestone
 Non-Resource

METC TASK NO.: 3.5

WERC NATIONAL DESIGN CONTEST

Principal Investigators: B. Reed
Department of Civil and Environmental Engineering

This project was completed during the 3rd calendar quarter of 1995.
The draft final report will be submitted under separate cover.

**INFORMATION SYSTEMS, PUBLIC POLICY,
COMMUNITY OUTREACH AND ECONOMICS**

**INTERAGENCY ENVIRONMENTAL TECHNOLOGIES OFFICE (IETO)
GRADUATE INTERN PROGRAM**

TASK 3.6

**Quarterly Technical Progress Report for Period
October 1 through December 31, 1995**

**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, 3610 Collins Ferry Road
Morgantown, West Virginia**

By:

**E.E. Cook
Department of Civil Engineering
West Virginia University
Morgantown, West Virginia 26506-6103**

December 1995

EXECUTIVE SUMMARY

From Task 3.6, five interns were provided from WVU to the Interagency Environmental Technologies Office (IETO) to provide assistance to IETO and provide a training opportunity for the students over the three (3) month summer period. The IETO is to foster private/public collaborations that stimulate environmental technology development, reduce regulatory barriers and increase global market share. Three of the interns contracts were extended to December 31, 1995. Through the extended internship the students were able to solidify relationships with important contacts as well as gain valuable skills for their professional futures. The students were also able to experience first hand the governments effect on the city of D.C. and its people. The time period in which the internship took place gave the students a chance to witness fascinating government changes. The budget negotiations and the appropriations committee work were causing a degree of uncertainty in all of the agencies and for the individual employees as well. At the end of the internship, because of these uncertain times, the IETO office was being closed and the activities that were taking place at IETO were moved back to the White House under the direction of Dave Rejeski in the Office of Science and Technology Policy.

1.0 Introduction

Task 3.6, Interagency Environmental Technologies Office (IETO) Graduate Intern Program was initiated to provide help to IETO and provide a training opportunity for students.

2.0 Purpose

The IETO is to foster private/public collaborations that stimulate environmental technology development, reduce regulatory barriers and increase global market share. It is a one stop shopping place for information on federal environmental technical programs. Through an interagency environmental technology office, experts can share information with individuals and organizations within and outside government.

3.0 Background

The hazardous site remediation program has been fragmented throughout the federal government with each federal agency "doing its own thing". There has been much repetition, overlap and outright duplication in technologies utilized by the various agencies to remediate their hazardous waste sites. This, along with difficulties in gaining acceptance of proven site remediation technologies by the various agencies create barriers to commercialization of the technologies.

4.0 Methodology

Interns assisted the executive director of IETO by conducting research, analysis and documentation in the field of environmental technology development and commercialization. Interns were residents of the Washington metropolitan area, serving on a half-time basis during the academic year and on a full time basis during the summer. Depending on background, experience and interest, opportunities were available in four areas.

1. Development of integrated government technology data bases to establish a "one stop shop" private sector focused business and technology information exchange.
2. Facilitation of improved government technology collaboration to increase market understanding, stimulate technology development cooperation, reduce applied technology costs, and enhance decentralization of decisionmaking.
3. Stimulation of the rapid commercialization of "nearly ready" technologies through focused cooperative management initiatives that accelerate government, business

planning and investment decisions.

4. Coordination of agency actions directed toward the elimination of procurement, program, organizational and regulatory barriers to the use of innovative advanced environmental technology.

5.0 Work Performed This Period

The Interagency Environmental Technologies Office (IETO) internships were extended through December 1995 for three West Virginia University graduate students, Annie Lieving, Susan Herrmann and Jude Mahoney. To be selected as an IETO Intern, the students must have demonstrated both "excellence" in their chosen field of undergraduate study and "leadership" in contribution to community. The interagency responsibility requires all staff to have the skill to interface with 12 major federal agencies covering a wide variety of environmental technical and service topics. The director, Tom Parker, worked with the students to set up an interesting and educational project based on the individual's interests and talents. The interns used the extended period to become further involved with the activities in more long-term projects. This contrasted from the summer months where the interns were exposed to a diverse variety of subjects and projects.

Annie Lieving worked as an IETO representative at the Global Environment and Technology Foundation (GETF) and the US Environmental Protection Agency. The work on this project related to the information dissemination business line for IETO. The project centered on the International Organization for Standardization's (ISO) Environmental Management Standards. This well respected private sector standards organization is creating internationally accepted standards for Environmental Management Systems. The standards are designed for organizations of any size or industry to establish a comprehensive and documented Environmental Management System that addresses their individual needs. The draft forms of these standards are available now, but the finalized standards will not be available until sometime in the Spring of 1996.

GETF is working in conjunction with the American representative to the ISO, the American National Standards Institute (ANSI) in order to disperse information through the Internet and professional conferences. Ms. Lieving wrote informational articles about the standards and the certification process that were placed on the Internet for easy access to organizations world wide. On December 14, 1995 GETF and ANSI co-hosted a one day conference on the ISO Environmental Management Standards. The conference was geared towards state and federal government employees as a source of information as well as a locus for discussion. Twenty three states and twelve federal agencies were represented at the conference. Ms. Lieving was an integral part in the preparation and planning of the event.

The US EPA is actively involved with the ISO Environmental Management Standards

through their EPA Standards Network. Ms. Lieving worked directly with the director of the standards network who is also the vice chair of the ANSI committee on the standards. Ms. Lieving was able to help the director with correspondence within the EPA regarding the ISO Environmental Management Standards. As the vice chair of the ANSI committee the director utilized Ms. Lieving's knowledge of the standards to assist in preparation of presentations to the ISO committee.

Susan Herrmann served as public, private, and international sectors analyst and researcher, making analytical contributions to the development of the first United States, National Environmental Technology Strategy (NETS). Her role in private sector analysis provided significant insight into the building of improved non-governmental participation methodologies, enhanced international environmental technology investment understanding and the building of better public private partnerships.

Ms. Herrmann organized the fall period into three main projects. The first project included analyzing private sector, environmental technology outreach methods for IETO and NETS. With the aid of *Environmental Business Journal* editors, Mr. Walter Howes and Mr. Andrew Williams, Ms. Herrmann compiled documentation that illustrates the applicability of utilizing the information dissemination mechanisms already established by national associations to reach both the supply-side and demand-side of the environmental technology market (contact Mr. Jim Miller at GETF for a copy of the document).

The second project Ms. Herrmann worked on was based out of the Environmental Enterprises Assistance Fund (EEAF) office. EEAF is a non-profit investment fund which gives low-interest loans to small companies developing environmental technologies in developing countries which include Central America, the Phillipines and Indonesia. While working with EEAF, Ms. Herrmann wrote *Environmental Guidelines for Investment*. The draft document is an ongoing effort by EEAF's investment staff to create guidelines for preliminary assessments to small, developing countries and private sector businesses. The guidelines will serve as a supplement to local environmental standards. Sectors covered include: Demand-side Management, Energy Efficiency, Sustainable Agriculture, Sustainable Forestry, Pollution Abatement, and Nature Tourism. Ms. Herrmann also analyzed an EEAF water treatment proposal submitted by the company's Costa Rican office and identified technical and monetary incongruencies within the proposal. All identified problems were immediately modified by EEAF's President and Central American Financial Manager.

The third of Ms. Herrmann's projects was held at the U.S. Environmental Protection Agency's Office of Research and Development. As the ORD Director's Assistant, Ms. Herrmann represented the director at interagency private sector roundtable meetings, wrote a Communications Plan for the office's Environmental Technology Verification (ETV) Program, managed by Penny Hansen and Alfred Lindsey.

Jude Mahoney worked with a private sector contractor as an IETO representative at

the Environmental Export Council. The project contributed research to a communication outreach program that the Environmental Export Council was creating. Ms. Mahoney was able to use her previous work experience and her graduate studies in communications to add valuable assistance to the assigned project.

Through the extended internship the students were able to solidify relationships with important contacts as well as gain valuable skills for their professional futures. The students were also able to experience first hand the governments effect on the city of D.C. and its people. The time period in which the internship took place gave the students a chance to witness fascinating government changes. The budget negotiations and the appropriations committee work were causing a degree of uncertainty in all of the agencies and for the individual employees as well. At the end of the internship, because of these uncertain times, the IETO office was being closed and the activities that were taking place at IETO were moved back to the White House under the direction of Dave Rejeski in the Office of Science and Technology Policy.

6.0 Results & Discussion N/A

7.0 Conclusions N/A

**WVHTC Foundation's
Environmental Technology Support Program
METC Task No. 3.7**

**Quarterly Technical Progress Report
Reporting Period: October - December 1995**

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

For:

**U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

By:

**West Virginia High Technology Consortium Foundation
200 Fairmont Ave, Suite 100
Fairmont, WV 26554**

January 2, 1995

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Table of Contents

Executive Summary	1
1.0 Introduction	1
2.0 Purpose	1
3.0 Background	2
4.0 Methodology	2
5.0 Work Performed this Period	2
ETI Dedication and Conference	3
Budget Narrative	3
8.0 Work Planned for Next Period	4

ETI - Second Quarterly Report
October 1996 - December 1996

Executive Summary

The second quarter of the West Virginia High Technology Consortium Foundation's Environmental Technology Support Program kicked off with the Environmental Technology Incubator Dedication and Conference held in early October 1995. The conference was attended by many local and state business, government and community leaders. West Virginia University faculty and staff members also comprised a significant portion of the audience at the conference. The highly successful event was designed to gain community support for the incubator and to promote the new initiative. Other highlights for the quarter included the development of the Environmental Technology Incubator (ETI) Policies and Procedures, the signing of a lease agreement with Grand Central Station, the initiation of two environmental studies and the formation of the Environmental Technology Incubator Advisory Board which is comprised mainly of regional industry leaders. Additionally, negotiations with four environmental firms are in progress.

An estimated total of \$49,440.34 of the \$68,000 awarded funds was spent during the first two quarters of the project. Personnel costs were below those initially estimated due to delays during the first quarter of operation. The second phase of the project will begin on January 1, 1996, and will require \$119,000 of West Virginia University Cooperative Agreement funds. Plans for the next quarter include additional infrastructure development, recruitment of incubator companies, the formation of environmental support groups and the continuation of incubator start-up activities.

1.0 Introduction

The West Virginia High Technology Consortium (WVHTC) Foundation's Environmental Technology Support Program was funded in July 1995. The support program involves an advanced concept for the accelerated commercialization of environmental technologies. The program also will help establish an Environmental Technology Incubator in Morgantown, West Virginia. We have requested a total of \$187,000 in funds from the Department of Energy to support the management and operation of the new Environmental Technology Incubator which will be established in Morgantown, West Virginia. This funding will support the WVHTC Foundation's Environmental Technology Support Program. Funds for the program are also in place from the U.S. Small Business Administration and the Environmental Protection Agency to further the initiative. Phase 1 of the project has been completed and Phase 2 of the program will begin on January 1, 1996.

2.0 Purpose

The WVHTC Foundation's mission is to create a high technology business sector in north central West Virginia, and this mission will be supported through the efforts of the new environmental support program. The new program will enhance the development and growth of the environmental industry in our region. Further, the Foundation's

Environmental Technology Support Program will facilitate technology transfer and the commercialization of Department of Energy technology.

3.0 Background

The WVHTC Foundation is currently working with government, business and educational entities to coordinate the economic development efforts of these three groups, and the Foundation's Environmental Technology Incubator will foster this endeavor. As a catalyst organization for economic change, the Foundation will link entrepreneurs with the technology, capital and knowledge they need to develop into sustainable high technology environmental businesses.

4.0 Methodology

The methodology for the establishment of the Environmental Technology Incubator includes a three phase implementation schedule. The three phases are as follows:

Phase 1 - Planning and Start-up (July 1995-December 1995)

Phase 2 - Implementation (January 1996-June 1996)

Phase 3 - Continued ETI Development (July 1996-December 1996)

The WVHTC Foundation has initiated the formation of a small business Environmental Technology Incubator to develop expertise and competitiveness in emerging high technology areas of environmental remediation. The WVHTC Foundation has been funded for the first phase of the project and has received verbal approval for the second phase funding. Four specific tasks were assigned during Phase 1 of the assignment. These tasks included:

- Task 1: Plan the formation of the small business Environmental Technology Incubator, work out the details for operation of the incubator and find an appropriate site for its location,
- Task 2: Begin to inventory Department of Energy technologies for the incubator clients,
- Task 3: Begin to establish regional environmental technology know-how networks, and
- Task 4: Provide quarterly reports to Dr. E. E. Cook, Director of the WVU Cooperative Agreement.

* All Phase 1 tasks have been completed 100 percent and Phase 2 of the project will be underway beginning January 1, 1996.

5.0 Work Performed this Period

During the second quarter, the WVHTC Foundation completed work on the planning and start-up of the Environmental Technology Incubator. The Foundation has completed all four tasks of the assignment and has created the small business Environmental Technology Incubator. The Environmental Technology Incubator's main office is located at the National Research Center for Coal and Energy (NRCCE) in Room 104, and offices for incubator clients include two rooms, 104A and 104B, located at the NRCCE. An additional nine incubator company offices are located at the

Grand Central Station Business and Enterprise Center also located in Morgantown, West Virginia. The lease for office space at Grand Central Station was signed in late November, and offices are available for occupancy. The rate for the offices has been established at \$7.50/per square foot. The WVHTC Foundation will use their technical and facility support funds to subsidize the start-up companies' rent at the Environmental Technology Incubator.

The Environmental Technology Incubator Policies and Procedures have been established and will be presented for approval at the first ETI Advisory Board meeting to be held on January 9, 1996. Four candidate companies have been slated for review by the selection committee which will also be appointed at the upcoming ETI Advisory Board meeting. Applications and business plans have been collected and are awaiting approval by the selection committee. Pending candidate approval, subleases will be created for occupancy in the new incubator. Advisory Board members include a variety of local and state business, government and community leaders who will be instrumental in creating the incubator's know-how network.

Public information folders and information sheets have been developed for broad distribution to promote the newly established incubator and to recruit potential incubator clients in Phases 2 and 3 of operation. Continued marketing and promotion of the new incubator is being planned for throughout 1996 by the WVHTC Foundation's marketing coordinator, Barbara Frye.

ETI Dedication and Conference (See attached folder)

On October 6, 1995, the WVHTC Foundation's Environmental Technology Incubator Dedication and Conference was held at the National Research Center for Coal and Energy, home of the new Environmental Technology Incubator. The conference was designed to promote the new incubator and to bring community awareness to the project. The conference brought together community leaders with experts on the creation of environmental incubators. Karen Livesay from the Thousand Oaks Environmental Business Cluster in southern California, Phil Helgerson of the Center for Environmental Enterprise in Portland, Maine, and Stuart Claggett from the Global Environment and Technology Foundation, located in the Washington D.C. area, shared their experiences in developing and supporting environmental incubators. Information gathered at the conference is being used to help structure the organization of the new Environmental Technology Incubator.

The conference had over one hundred and twenty-five attendees and helped lay the foundation for regional environmental technology know-how networks to be developed. Many local and state leaders participated in the conference including representatives from the Morgantown Energy Technology Center, the National Research Center for Coal and Energy, West Virginia University, the Morgantown Area Economic Partnership, the West Virginia Development Office and the Waste Policy Institute. In short, the conference played a key role in beginning to establish the regional environmental technology know-how networks needed to support the new, start-up environmental firms locating in the new Environmental Technology Incubator. The conference provided the ground work for the implementation and use of this know-how network during Phase 2 of the project.

Budget Narrative

The budget for the Environmental Technology Incubator totaled \$68,000. During the first and second quarters of the project, an estimated total of \$49,440.34 has been spent on the project. During the first quarter, a total of \$8,498.70 was spent of allocated funds. However, as things began to get underway in the second quarter, a total of

\$40,941.64 was expended. During the both quarters, the personnel funds were used to hire a part-time graduate student and an Assistant Incubator Director to help with the project. The majority of the technical and facility support funds were used to support the development of two environmental studies. Incubator space was secured at the National Research Center for Coal and Energy and Grand Central Station, and office supply funds were used to make this space operational. Additionally, public information services funds were used to create literature on the new incubator and the services it would provided as well as the creation of information packets for the Environmental Technology Incubator Dedication and Conference held in early October. Travel charges were incurred by national environmental industry leaders who participated in the conference. The charges for the first two quarters break down as follows:

<u>Category</u>	<u>Amount Expended</u>
Personnel	\$11,679.76 (estimated)
Overhead	\$ 9,441.92 (estimated)
Technical/Facility Support	\$17,995.00
Office Supplies	\$ 2,768.28
Public Information Services	\$ 2,485.53
Travel	\$ 2,381.60
Subtotal	\$46,752.09 (estimated)
General & Administrative	\$ 2,688.25 (estimated)
Total	<u>\$49,440.34</u>

An estimated total of \$49,440.34 of the awarded \$68,000 of West Virginia University Cooperative Agreement funds was used during the first phase of the project. An invoice for the remaining charges will be sent by January 20, 1996, as agreed upon in earlier phone conversations.

8.0 Work Planned for Next Period

The West Virginia High Technology Consortium Foundation has planned a rigorous schedule for 1996. The second phase of the Foundation's Environmental Technology Support Program will begin on January 1, 1996. We will kick off the new year with the first Environmental Technology Incubator Advisory Board meeting on January 9, 1996. Immediately following this meeting and the approval of the new Policies and Procedures, we will begin to admit companies into the new incubator.

Phase 2, implementation, will be accomplished from January 1996 through June 1996. This phase of the project will include the development of additional infrastructure and support programs, the finalization of policies and procedures and the completion of start-up activities. Phase 3, continued ETI development, will be completed during July 1996 through December 1996. This phase of the Foundation's support program will ensure continued ETI development through the on-going review, evaluation and expansion of Environmental Technology Incubator assistance programs.

The first phase of the Environmental Technology Support Program has created a solid foundation for the development of new environmental companies in our region. The Environmental Technology Incubator's mission is to facilitate the development of start-up environmental businesses, and we will work to recruit, serve and graduate new and expanding environmental firms.