DOE/MC/29467 -- 5265
(DE96011345)

Decontamination Systems Information And Research Program

Quarterly Report
April - June 1996

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July 1996

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

For

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

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

By
West Virginia University
Morgantown, West Virginia

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1000 Independence Avenue
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Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
West Virginia University
Civil and Environmental Engineering
P.O. Box 6103
Morgantown, West Virginia 26506-6103

July 1996

EXECUTIVE SUMMARY

The projects for the 1996 WVU Cooperative Agreement are categorized into three task focus areas: Task 1.0 Contaminant Plume Containment & Remediation, Task 2.0 Cross Cutting Innovative Technologies, and Task 3.0 Small Business Support Program. Summaries of the significant accomplishments for the subtasks reporting under these categories during the period 1 April 96 through 30 June 96 are presented below.

Task 1.0 CONTAMINANT PLUME CONTAINMENT & REMEDIATION

Subtask 1.1 Analysis of the Vortec Cyclone Melting System (VMS) for Remediation of PCB Contaminated Soils Using CFD: Work this period focused on assessing proposed equipment modifications consisting of chamber geometry changes for improved performance. The results of this work have resulted in the Vortec engineers incorporating WVU's modifications into the Vortec designs. This is a note worthy accomplishment for the project.

Subtask 1.2 Drain Enhanced Soil Flushing (DESF) Using Prefabricated Vertical Drains: This reporting period saw the first phase of the field demonstration efforts. Activities accomplished included site assessment and sample collection, laboratory testing of field samples, and initiating the necessary environmental permitting activities with the West Virginia State inspectors. An Ashland Petroleum service station has been selected as the candidate field test site which is located in Weston, WV. The project is set to under-go field start-up of the site demonstration by mid August 1996.

Subtask 1.3 Performance and Characteristics Evaluation of Acrylates as Grout Barriers: Work this period included continued permeability testing on grout samples and with mobilization into the METC B-17 facility. Technical accomplishments were reported in the areas of grout chemical resistance and permeability, and with the near completion of the sand raining device.

Subtask 1.4 Development of Standard Test Protocols Barrier Design Models for Desiccation Barriers: During this quarter the project reports the move into METC's B-17 facility and submission of the final METC Operating Permit application. Technical accomplishments were noted with soil density and grain size relationships on bench scale specimens for sizing-up to large scale testing.

Subtask 1.5 Development of Standard Test Protocols & Barrier Design Models for In Situ Formed Barriers - Technical Support: During this quarter progress was reported on the movement of WVU researchers into DOE's METC B-17 facility. Modifications to the B-17 facility were completed and the newly created laboratory space and occupancy of the space will be complete by mid August 1996. Continued interaction between BDM and the WVU researchers is taking place for the upcoming METC laboratory safety permitting phase.

Subtask 1.6 In Situ Bioremediation of Chlorinated Solvents at the Portsmouth Gaseous Diffusion Plant: Work was begun this quarter on simulating and predicting the effectiveness of bioremediation at the Portsmouth Gaseous Diffusion Plant. Technical accomplishments in the lab included a 98% removal of TCE in simultaneous column studies. Work is progressing with development of surrogate contaminants to model the bioremediaton process at the Portsmouth site. This project is continuing with operation of existing simultaneous and sequential columns for studying TCE degradations using native microorganisms.

Subtask 1.7A Development and Implementation of a Decision Support System for Management of the EM50 Technology Development Program: This is the first quarter of work for this project and during which meetings were held with co-university researchers from Virginia Tech and WVU to discuss issues on the project subtasks. The project reports progress with interpretation of data base information and prioritization of problems and technological needs within the DOE/EM program.

Subtask 1.7B Development of a Prototype Database and Decision Support System for Management of the EM50 Technology Development Program: Work performed this period includes an analysis of available decision support tools, analysis of the data requirements and work to be accomplished, and the plans for the design of an on-line help system for documentation of the subsurface contaminants focus area domain.

Task 2.0 CROSS CUTTING INNOVATIVE TECHNOLOGIES

Subtask 2.1 A GIS-Based Infrastructure for Site Characterization and Remediation: This project reported progress in work with the US Corps of Engineers at the Huntington district office to map and model the WV Ordinance site using the GIS system. Work has begun on modeling the effect of an aquifer pump-and-treat operation on the plant life surrounding a wetlands area of the ordinance site. Work has also begun on building the prototype interactive tutorial system using the Director 4.0 software. A framework for the chapters and lessons has been built.

Subtask 2.2 Treatment of Mixed Wastes via Fluidized Bed Steam Reforming: During this reporting period the gas chromatograph was upgraded with a flame ionization detector and successfully calibrated for toluene and dichlorobenzene. Calibration of the equipment and temperature profiles within the equipment reactor were established and monitored. The project is working towards investigating the destruction efficiency of organics in a steam reforming atmosphere.

Subtask 2.3 Use of centrifugal Membrane Technology with Novel Membranes to Treat Hazardous/Radioactive Waste: In this second quarter the SpinTek technology was used to treat two oil grease wastes. The results of these experiments showed average removal efficiencies of 98 percent. Problems with equipment operation, specifically fouling of the membrane discs and clogging of the pores, are being investigated. Continued work will be directed at operating the equipment under tighter temperature control and with the trial of a ceramic membrane on the oil/ grease waste stream.

Subtask 2.4 Environmental Pollution Control devices Based on Novel Forms of Carbon: During this period the project reported continued progress with the experimentation using carbonaceous materials to remove metal ions from solution. Research on removal of nickel, lead, and strontium was continued. The removal of uranium from an inlet waste stream was examined and results indicate that recovery concentration of uranium was 99%. Work planned for the next period includes continued removal of metals from laboratory surrogate waste streams and investigation into removal from industrial samples.

Subtask 2.5 Development of Instrumental Methods for Characterization and Analysis of Nuclear Wastes and Environmental Contaminants: This project is on schedule and results continue to be encouraging. Test methods developed for the analysis of iodide, iodate, and perrhenate in standard solutions have been refined and further refinement is planned.

Subtask 2.6A Production and Evaluation of Biosorbents and Cleaning Solutions for Use in Decontamination and Decommissioning: During this project's first reporting period biosorbent samples and decontamination solution samples were prepared and sent to WVU for filtration tests. The literature review was begun and focused on information regarding development of standard solutions for performing the decontamination and decommissioning (D&D) testing using the biosorbents. Information continues to be compiled on different types of solution/wastewaters relevant to D&D activities.

Subtask 2.6B Use of SpinTek Centrifugal Membrane Technology and Sorbents/Cleaning Solutions for D&D Work: The SpinTek centrifugal membrane system was successful in concentrating biological waste that mimicked a biosorbent waste from a D&D effort. Results of this work to date indicate that the permeate flux increased with temperature and rotational speed of the equipment. The permeate turbidity increased with increasing temperature and decreasing rotational speed. Work for the next period will continue with testing activated sludge and with testing of a kaolin clay to mimic a zeolite sorbent.

Task 3.0 SMALL BUSINESS SUPPORT PROGRAM

Subtask 3.1 WVHTC - West Virginia High Tech Consortium Foundation - Environmental Technology Support Program: Work this second quarter dealt with completing the development of the business plan for the incubator, attending an annual association conference, and formulating a model upon which the business plan is to be based. The Environmental Technology Incubator has aggressive plans slated for the second half of 1996.

Subtask 3.2 Small Business Interaction Opportunities: Activities accomplished this period include: terminating work on the GeneSyst project, initiating efforts on a new project Subtask 1.6, "Chemically Enhanced In Situ Bioremediation of Chlorinated Solvents", performing site visits to SpinTek at Huntington Beach, CA to discuss the direction of current research and planned efforts in the 1997 program, and a site visit to Concurrent Technologies Corp. in Johnstown, PA to explore mutual areas of interest. WVU researchers attended a DOE meeting regarding EM50 initiates on the ex situ vitrification technology developed by the Vortec Corp. Ground-work was laid for WVU to support this effort.

Subtask 3.4 Approach for Assessing Potential Voluntary Environmental Protection - Kanawha River Area: This period saw continued interaction with the State of West Virginia Division of Environmental Protection and the US EPA on development of a memorandum of understanding between the respective parties.

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1.3 PERFORMANCE AND CHARACTERISTICS EVALUATION OF ACRYLATES AS GROUT BARRIERS

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2.5 DEVELOPMENT OF INSTRUMENTAL METHODS FOR CHARACTERIZATION AND ANALYSIS OF NUCLEAR WASTES AND ENVIRONMENTAL CONTAMINANTS

2.6A PRODUCTION AND EVALUATION OF BIOSORBENTS AND CLEANING SOLUTIONS FOR USE IN DECONTAMINATION AND DECOMMISSIONING

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PROJECT TITLES WITH PRINCIPAL INVESTIGATORS

1.0 CONTAMINANT PLUME CONTAINMENT & REMEDIATION

1.1 ANALYSIS OF THE VORTEC CYCLONE MELTING SYSTEM (VMS) FOR REMEDIATION OF PCB CONTAMINATED SOILS USING CFD

I. Celik, Dept. of Mechanical & Aerospace Eng.

1.2 DRAINED ENHANCED SOIL FLUSHING (DESF) USING PREFABRICATED VERTICAL DRAINS

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

1.3 PERFORMANCE AND CHARACTERISTICS EVALUATION OF ACRYLATES AS GROUT BARRIERS

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

1.4 DEVELOPMENT OF STANDARD TEST PROTOCOLS & BARRIER DESIGN MODELS FOR DESICCATION BARRIERS

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

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

B. Overby and C. Locke, BDM

1.6 IN SITU BIOREMEDIATION OF CHLORINATED SOLVENTS AT PORTS

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

1.7A DEVELOPMENT AND IMPLEMENTATION OF A DECISION SUPPORT SYSTEM FOR MANAGEMENT OF THE EM-50 TECHNOLOGY DEVELOPMENT PROGRAM

R. Malinovsky, WPI

1.7B DEVELOPMENT OF A PROTOTYPE DATABASE & DECISION SUPPORT SYSTEM FOR MANAGEMENT OF THE EM-50 TECHNOLOGY DEVELOPMENT PROGRAM

J. Denton, College of Business and Economics

2.0 CROSS CUTTING INNOVATIVE TECHNOLOGIES

2.1 A GIS BASED INFRASTRUCTURE FOR SITE CHARACTERIZATION AND REMEDIATION

J. Hooper, Marshall University

2.2 TREATMENT OF MIXED WASTES VIA FLUIDIZED BED STEAM REFORMING - CAPTURE OF HAZARDOUS CHEMICAL WASTE UTILIZING FLUIDIZATION COATING TECHNOLOGY

R. Turton, Dept. of Chemical Eng.

2.3 USE OF CENTRIFUGAL MEMBRANE TECHNOLOGY WITH NOVEL MEMBRANES TO TREAT HAZARDOUS/RADIOACTIVE WASTE

B. Reed, Dept. of Civil & Environmental Eng.
W. Green, SpinTek

2.4 ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

J. Zondlo, A. Stiller, A. Brennsteiner,
Dept. of Chemical Eng.

2.5 DEVELOPMENT OF INSTRUMENTAL METHODS FOR CHARACTERIZATION AND ANALYSIS OF NUCLEAR WASTES AND ENVIRONMENTAL CONTAMINANTS

V. Remcho, Dept. of Chemistry
N. Ballou, Battelle-Pacific Northwest Ntl. Laboratories

2.6A PRODUCTION AND EVALUATION OF BIOSORBENTS AND CLEANING SOLUTIONS FOR USE IN DECONTAMINATION AND DECOMMISSIONING

J. Kilbane and V. Srivastava, IGT

2.6B USE OF SPINTEK CENTRIFUGAL MEMBRANE TECHNOLOGY AND SORBENTS/CLEANING SOLUTIONS FOR DECONTAMINATION AND DECOMMISSIONING WORK

B. Reed, Dept. of Civil & Environmental Eng.
W. Green and R. Hays, SpinTek

3.0 SMALL BUSINESS SUPPORT PROGRAM

3.1 WVHTC - WEST VIRGINIA HIGH TECH CONSORTIUM FOUNDATION ENVIRONMENTAL TECHNOLOGY SUPPORT PROGRAM

J. Berkow, WVHTCF

CONTINUATION FROM 1995

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

R. Lovett, NRCCE

Administrative Summary

Background

West Virginia University (WVU) and the US Department of Energy, Morgantown Energy Technology Center (DOE/METC) entered into a Cooperative Agreement in August 1992 titled "Decontamination Systems Information and Research Programs" (DOE Instrument No.: DE-FC21-92MC29467). Requirements stipulated by the Agreement require WVU to submit quarterly Technical Progress reports. This report contains the efforts of the research projects comprising the Agreement for the 2nd calender quarter of 1996.

Administrative Issues

For the period 1 April through 30 June 1996 four new projects were brought on-line: Task 1.7A, *Decision Support System for Technology Management*; Task 1.7B *Prototype Database & Decision Support System;* Task 2.6A *Production and Evaluation of Biosorbents and Cleaning Solutions for use in Decontamination and Decommissioning*; and Task 2.6B *Use of SpinTek Centrifugal Membrane Technology and Sorbent/Cleaning Solutions in the decontamination and Decommissioning of DOE Facilities.* These four projects reported impressive progress during their first quarter or work.

Project Variances, Accomplishments, and Problems

Discussion of the following two subtasks is warranted:

Subtask 1.4 Development of Standard Test Protocols & Barrier Design Models for Desiccation Barriers: The actual project progress lags the planned schedule on two tasks (Adiabatic Cooling, and Liquid Storage and Migration). This delay is attributed to difficulties associated with the project move into the METC B-17 facility. The researchers

are aware of this issue and are working to recover the delay.

Subtask 2.2 Treatment of Mixed Wastes via Fluidized Bed Steam Reforming - Capture of Hazardous Chemical Waste Utilizing Fluidization Coating Technology: During the first quarter of 96 the project reported schedule delays as a result of equipment modification difficulties. The Research Principal Investigator has stepped up efforts and the result is that the project is gaining ground on the schedule lag, however the project has not reached the schedule recovery. Continued work is planned to bring the project up to the planned schedule requirements.

Accounting Issues

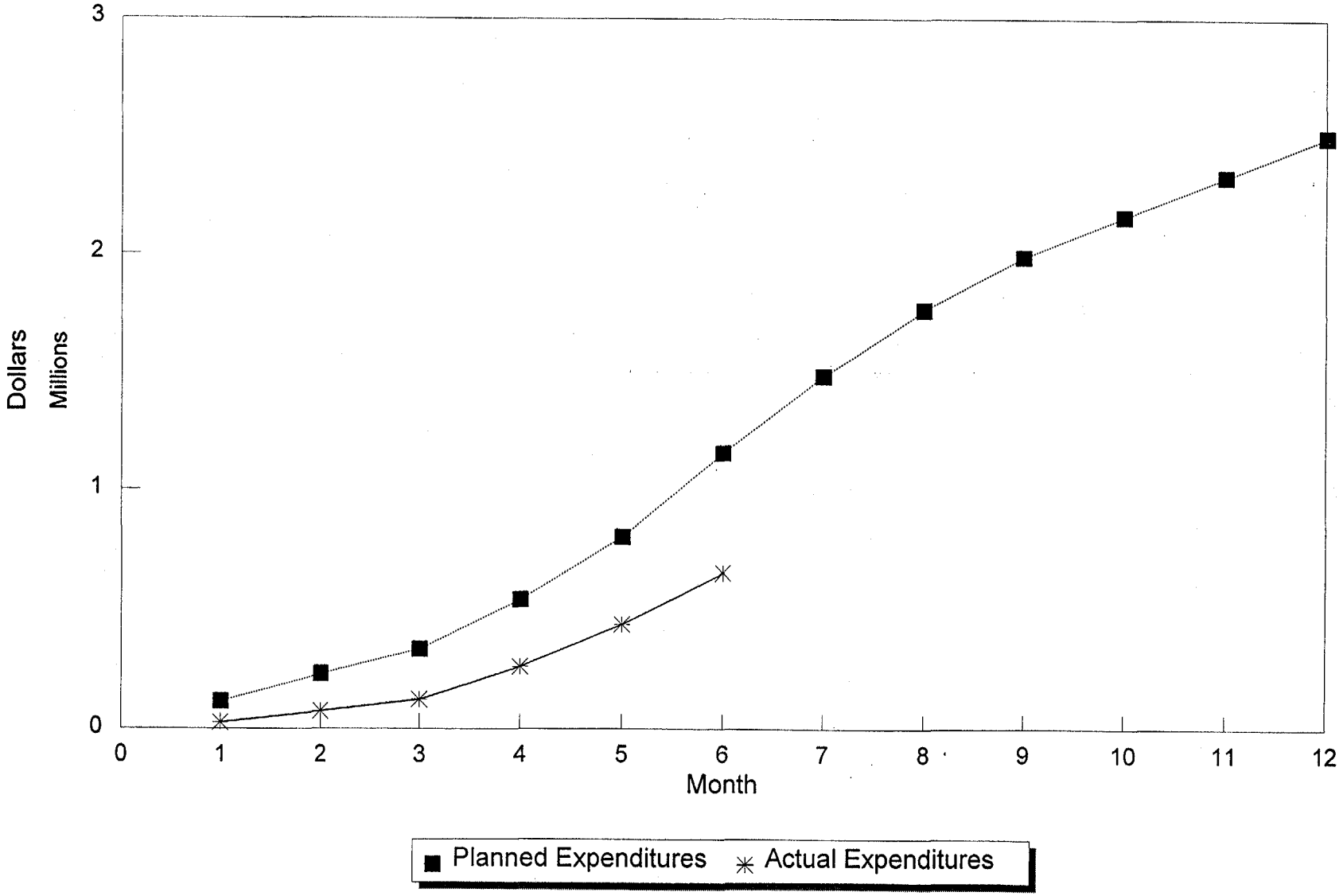
An accrued accounting system was developed by Civil and Environmental Engineering (CEE) for the 1995 to provide a real time accounting by showing the actual expenses when incurred. Due to the amount of cash adjustments required for reconciliation, a simplified accounting procedure has been adopted for 1996. The new reports contain a column for accrued expenses and obligated amounts that have not been disbursed by the WVU controller's office. All adjustments, except subcontractor expenses were made in this column. For the 2nd calendar quarter of 1996 the following accrued adjustments were made:

Outlays:	$241,606
Obligated Encumbrances:	$672,873
TOTAL ADJUSTMENT:	$914,479

Budgets Removed at from various pages

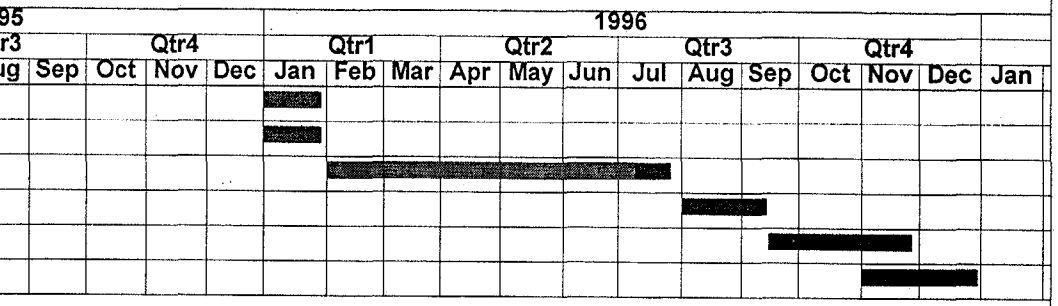
Summary of Planned Versus Actual Expenses

1996 WVU Cooperative Agreement



METC Task 1-1 Refinement of Combustion & Melting System

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Information Search: Conceptual Design Criteria	1M	100.00%
3	Recuperator Base Analysis	6M	90.00%
4	Recuperator Analysis	1.5M	0.00%
5	Analysis of Separator/Reservoir	2.5M	0.00%
6	Analysis of Results	2M	0.00%

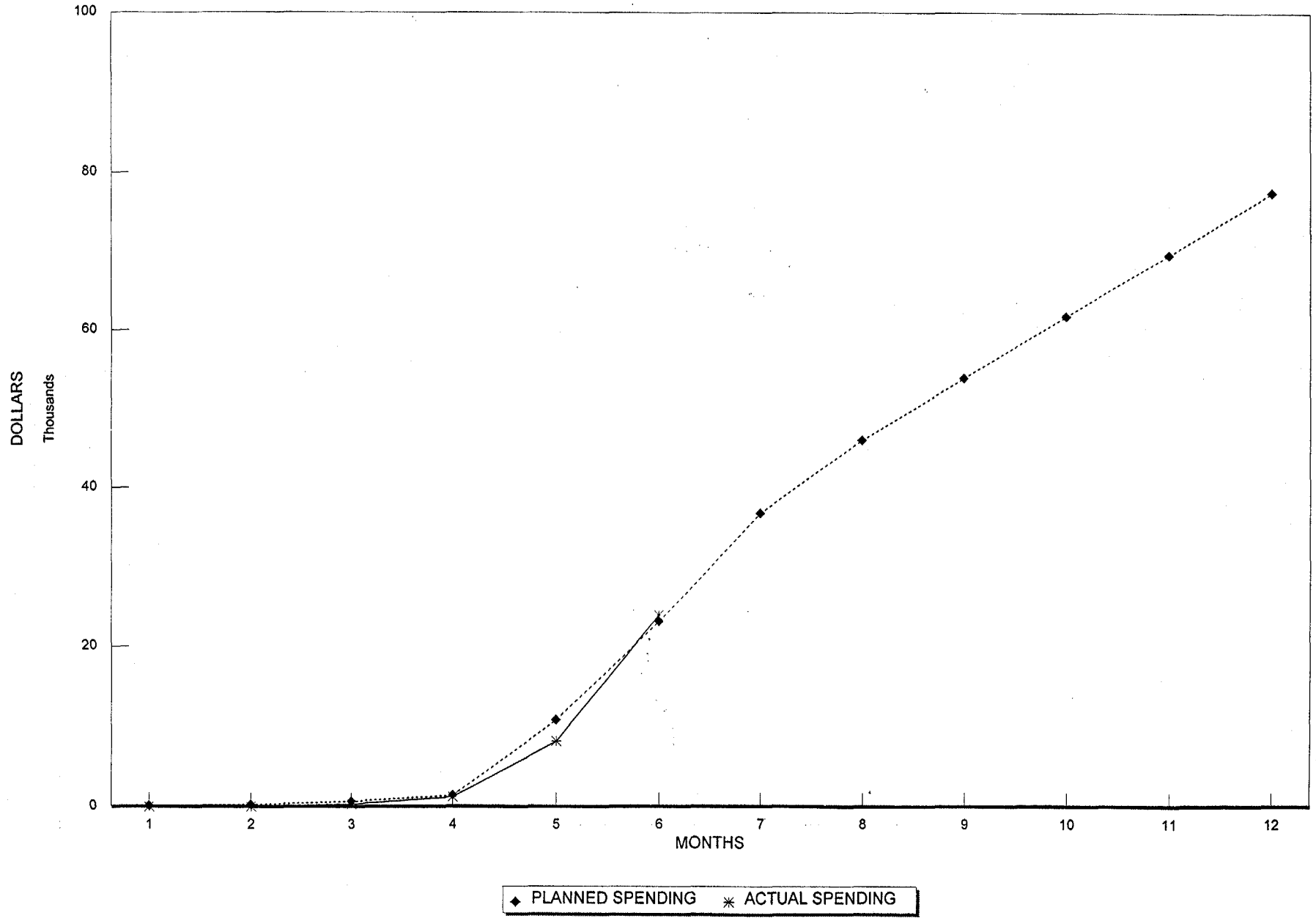


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SubTask 1.1 - Analysis of Vortec Cyclone Melting System for Remediation

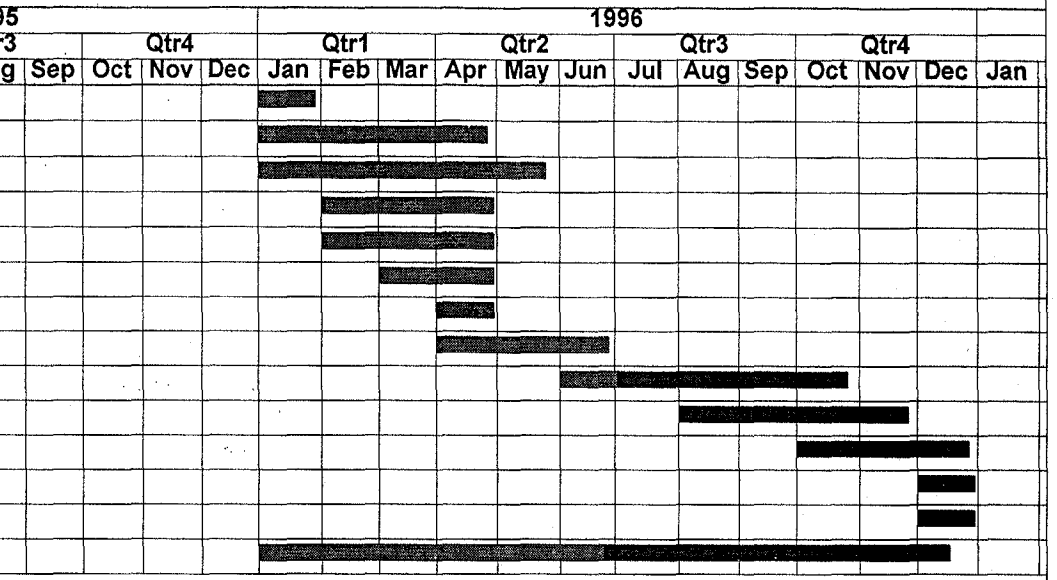
PRINCIPAL INVESTIGATOR: I. Celik



METC Task 1-2

Drain-Enhanced Soil Flushing

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Pilot-Scale Experiment Design	4M	100.00%
3	Field Site Selection	5M	100.00%
4	Engineering Design & Drafting	3M	100.00%
5	Permit Application Process	3M	100.00%
6	Procure Equipment & Supplies	2M	100.00%
7	Field Mobilization & Layout	1M	100.00%
8	Construction & Setup	3M	100.00%
9	Testing Phase	5M	20.00%
10	Chemical Lab Analysis	4M	0.00%
11	Testing Completion & Equipment Breakdown	3M	0.00%
12	Site Closure & Restoration	1M	0.00%
13	Equipment Final Disposition	1M	0.00%
14	Data Reduction & Report Preparation	12M	50.00%

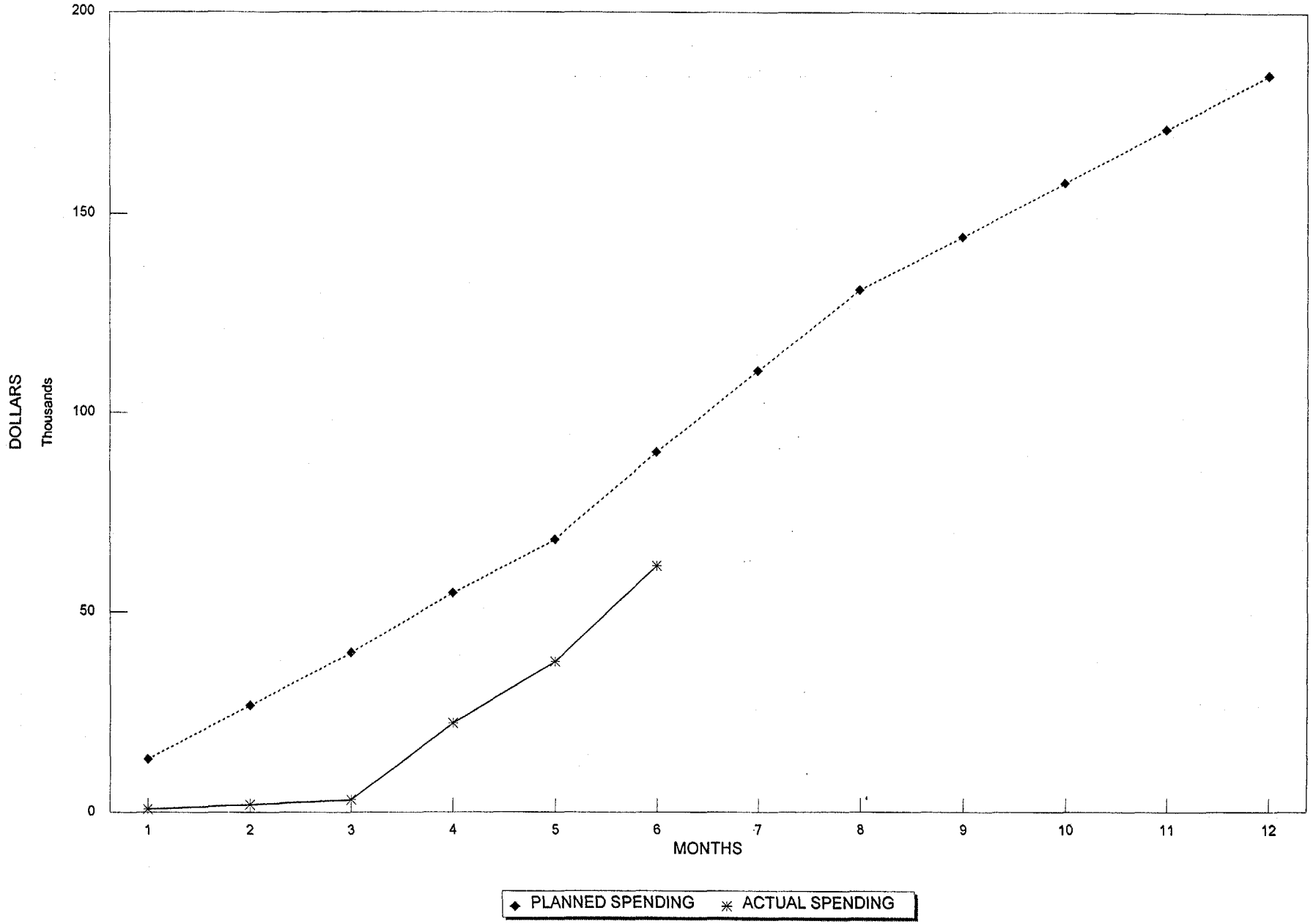


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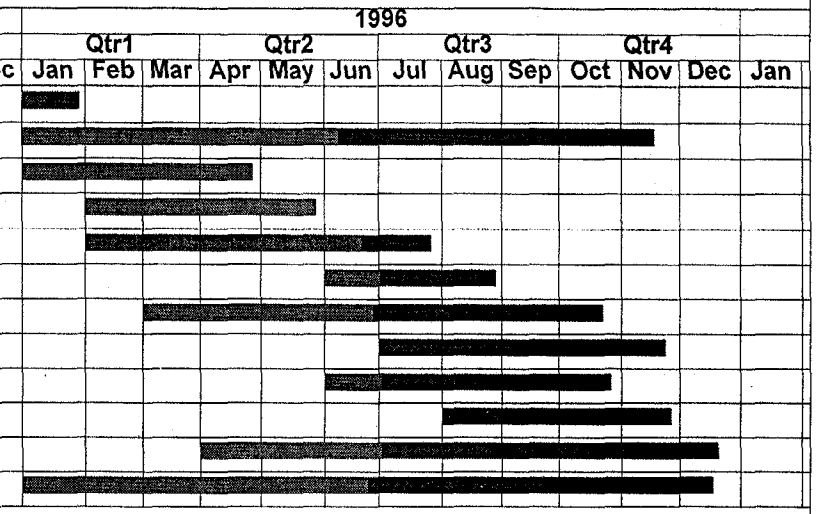
Sub-Task 1.2 - Drained Enhanced Soil Flushing Using Prefabricated Vertical Drains

PRINCIPAL INVESTIGATOR: M.A. Gabr



METC TASK 1-3 Evaluation of Acrylates as Grout Barriers

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Grout Development & Characteristics Testing	11M	50.00%
3	Viscosity Tests	4M	100.00%
4	Setting Time Tests	4M	100.00%
5	Immersion Tests	6M	80.00%
6	Durability	3M	33.00%
7	Permeability	8M	50.00%
8	Shear Strength	5M	0.00%
9	Compressibility Characteristics	5M	20.00%
10	Toxicity	4M	0.00%
11	Grout Performance Testing	9M	35.00%
12	Data Reduction & Report Preparation	12M	50.00%

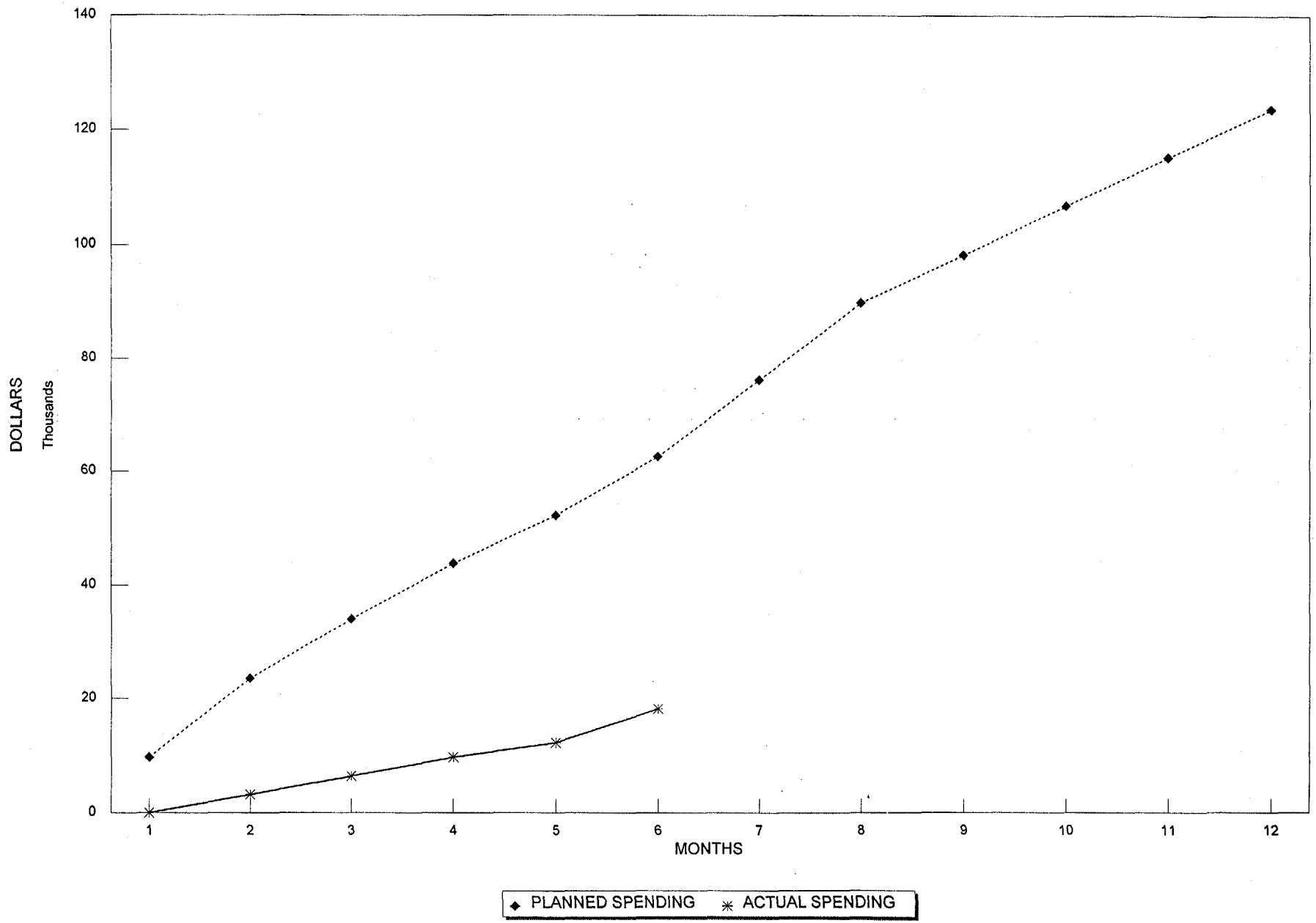


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Quarterly Report for April - June 1996

Sub-Task 1.3 - Evaluation of Acrylates as Grout Barriers for In-Situ Containment

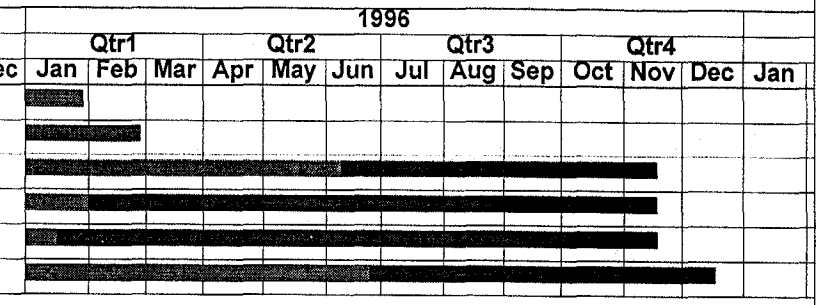
PRINCIPAL INVESTIGATOR: M.A. Gabr



METC TASK 1-4

Desication Barriers

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Testing Protocol Development	2M	100.00%
3	Sand Pack Characterization	11M	50.00%
4	Adiabatic Cooling	11M	10.00%
5	Liquid Storage & Migration	11M	5.00%
6	Data Reduction & Report Preparation	12M	50.00%

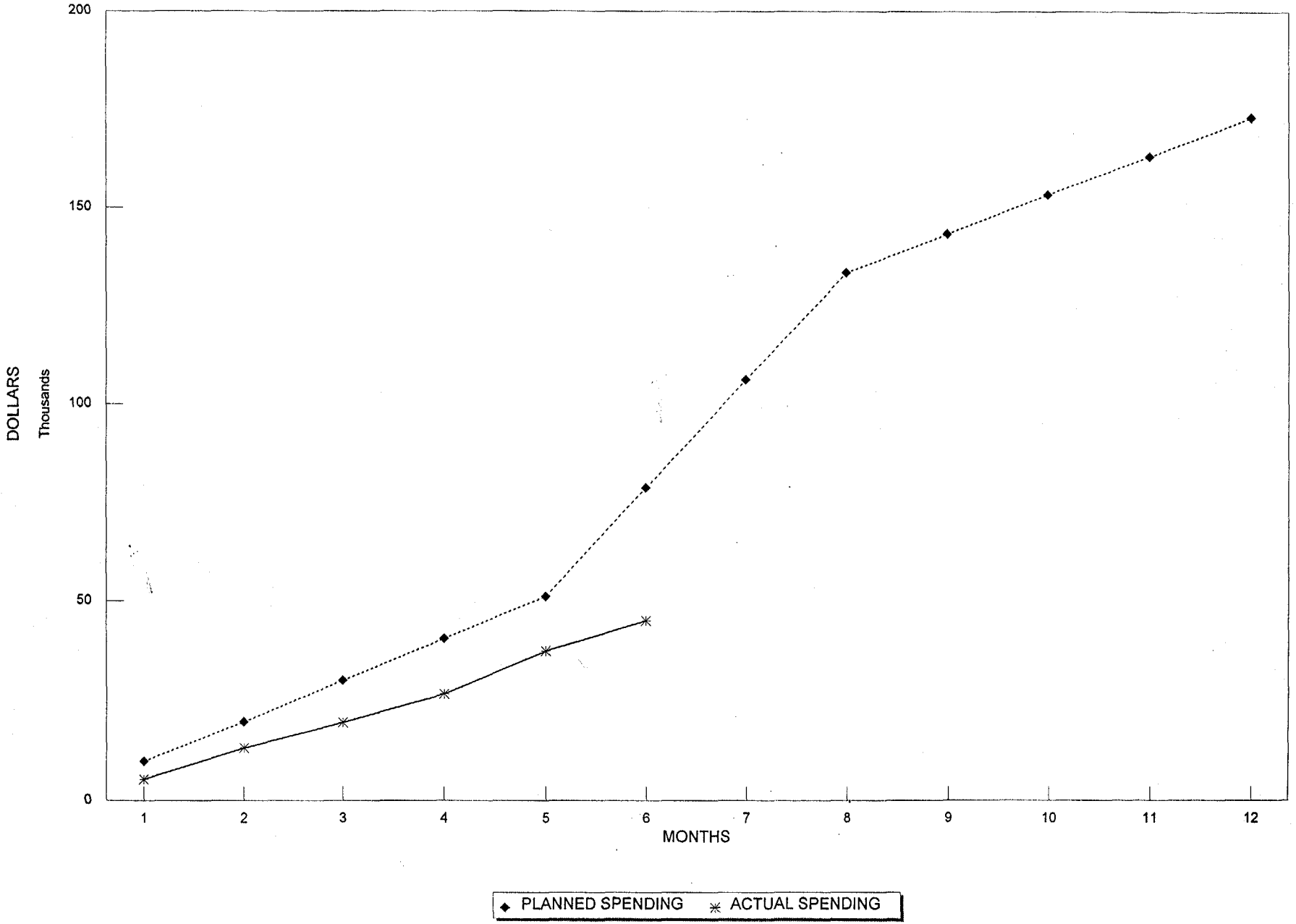


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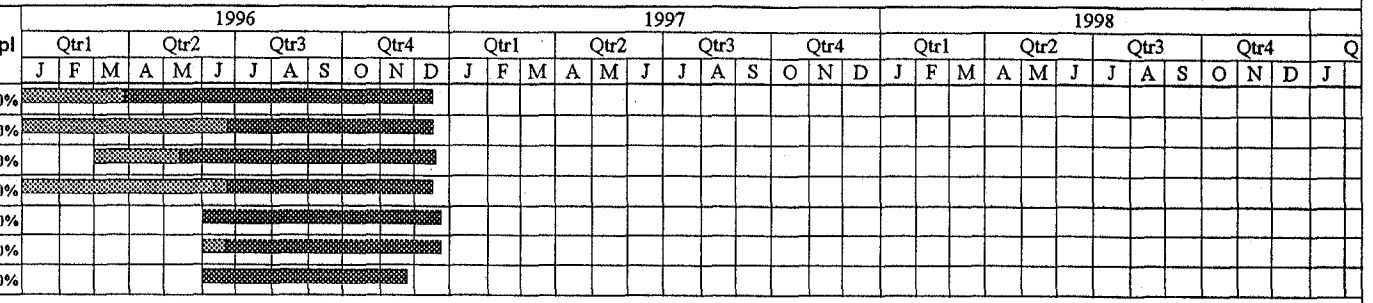
Sub-Task 1.4 - Dessication Barriers *Summary on/off campus work*

PRINCIPAL INVESTIGATOR (S): K. Aminian & S. Ameri



METC TASK 1-5 Technical Support for Barrier Test Program

#	Task Name	Dura	%Compl
1	Planning & Technology Transfer	12M	25.00%
2	Circulating Air Barrier Bench Scale	12M	50.00%
3	Circulating Air Barrier Large Scale	10M	25.00%
4	Grout Barrier Bench Scale	12M	50.00%
5	Grout Barrier Large Scale	7M	0.00%
7	Freeze Barrier Bench Scale	7M	10.00%
8	Dual Barrier System Bench Scale	6M	0.00%



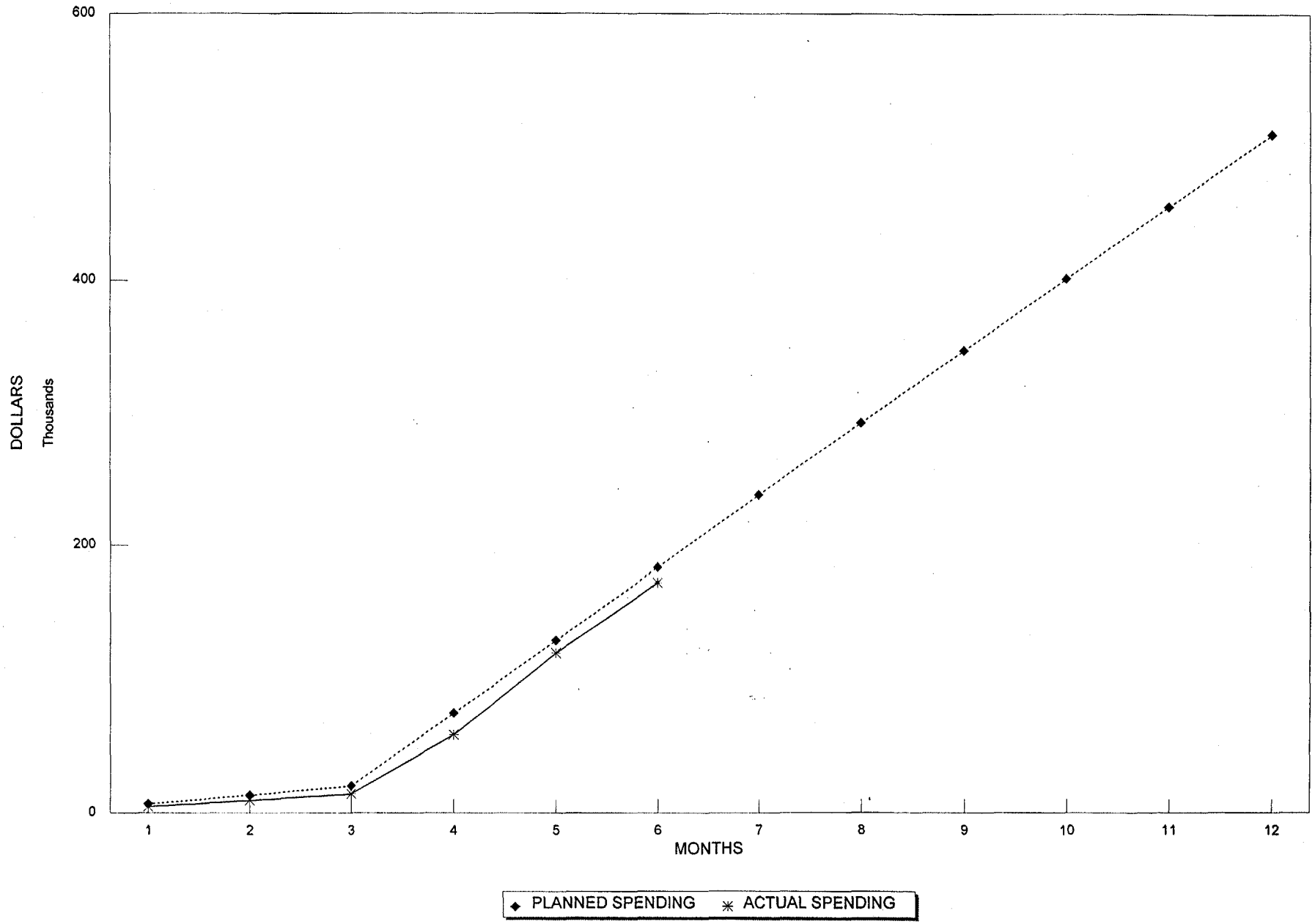
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Project Schedule

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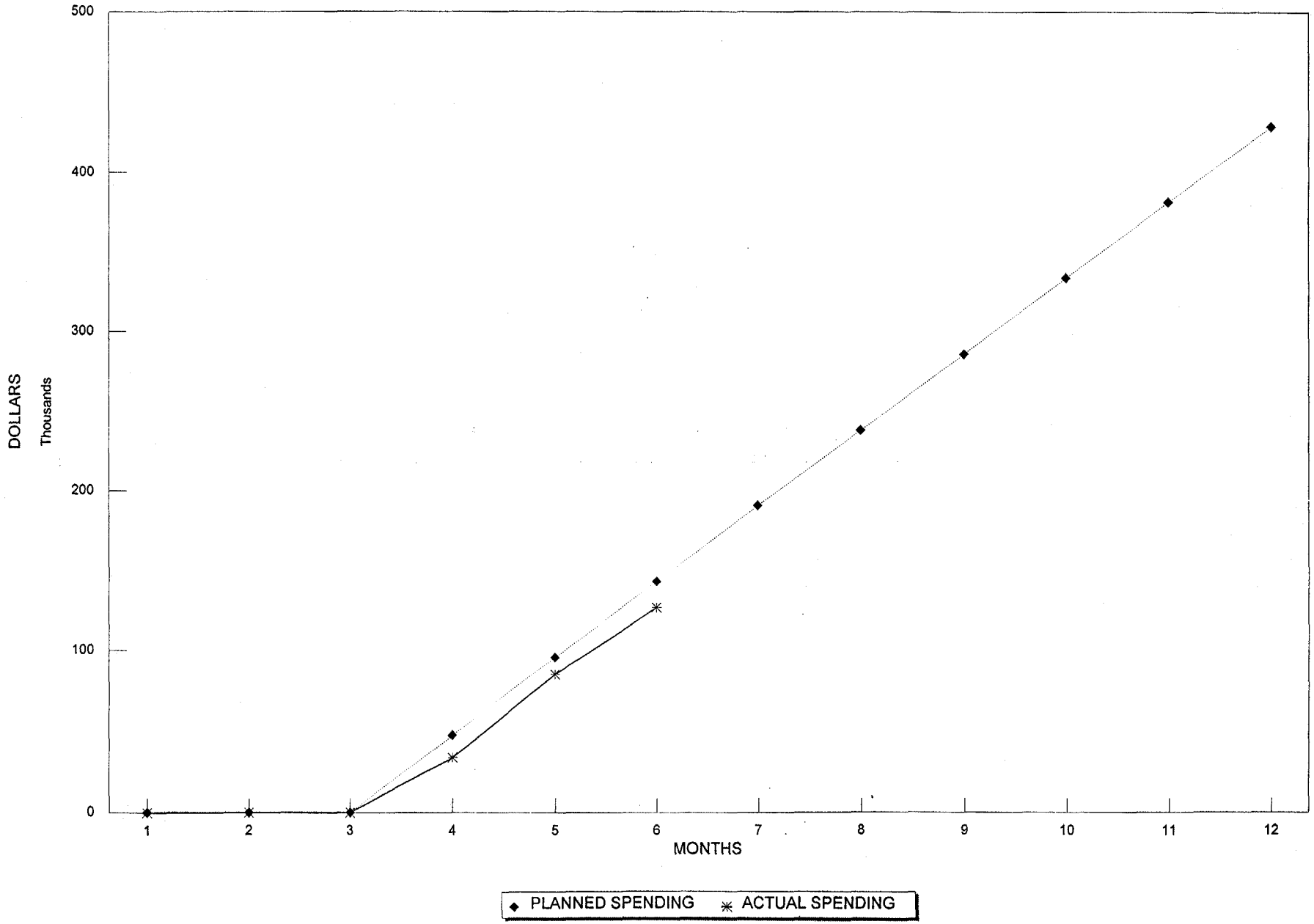
SubTask 1.5 - Standard Test Protocols & Design Models - Insitu Barriers

PRINCIPAL INVESTIGATOR (S): B. Overby and C. Locke - *** SUMMARY ***



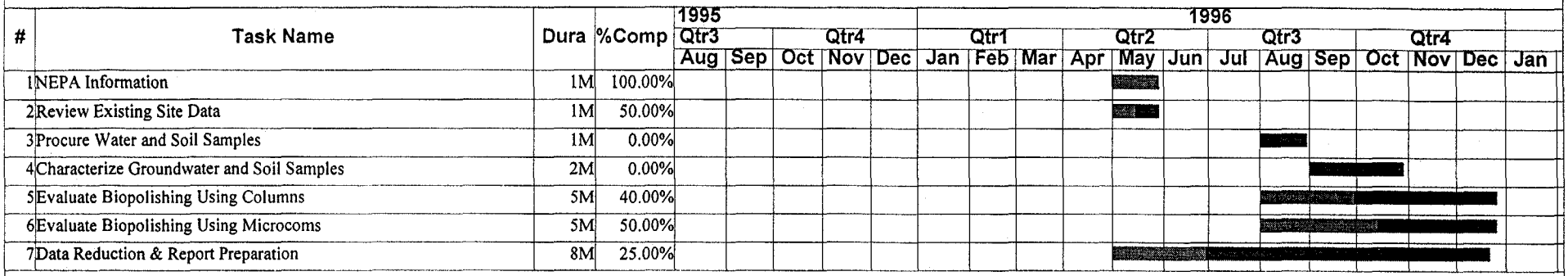
Sub-Task 1.5: BDM Federal - Technical Support for Insitu Barriers

PRINCIPAL INVESTIGATOR (S): B. Overby & C. Locke



METC Task 1-6 In Situ Bioremediation of Chlorinated Solvents

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Review Existing Site Data	1M	50.00%
3	Procure Water and Soil Samples	1M	0.00%
4	Characterize Groundwater and Soil Samples	2M	0.00%
5	Evaluate Biopolishing Using Columns	5M	40.00%
6	Evaluate Biopolishing Using Microcoms	5M	50.00%
7	Data Reduction & Report Preparation	8M	25.00%

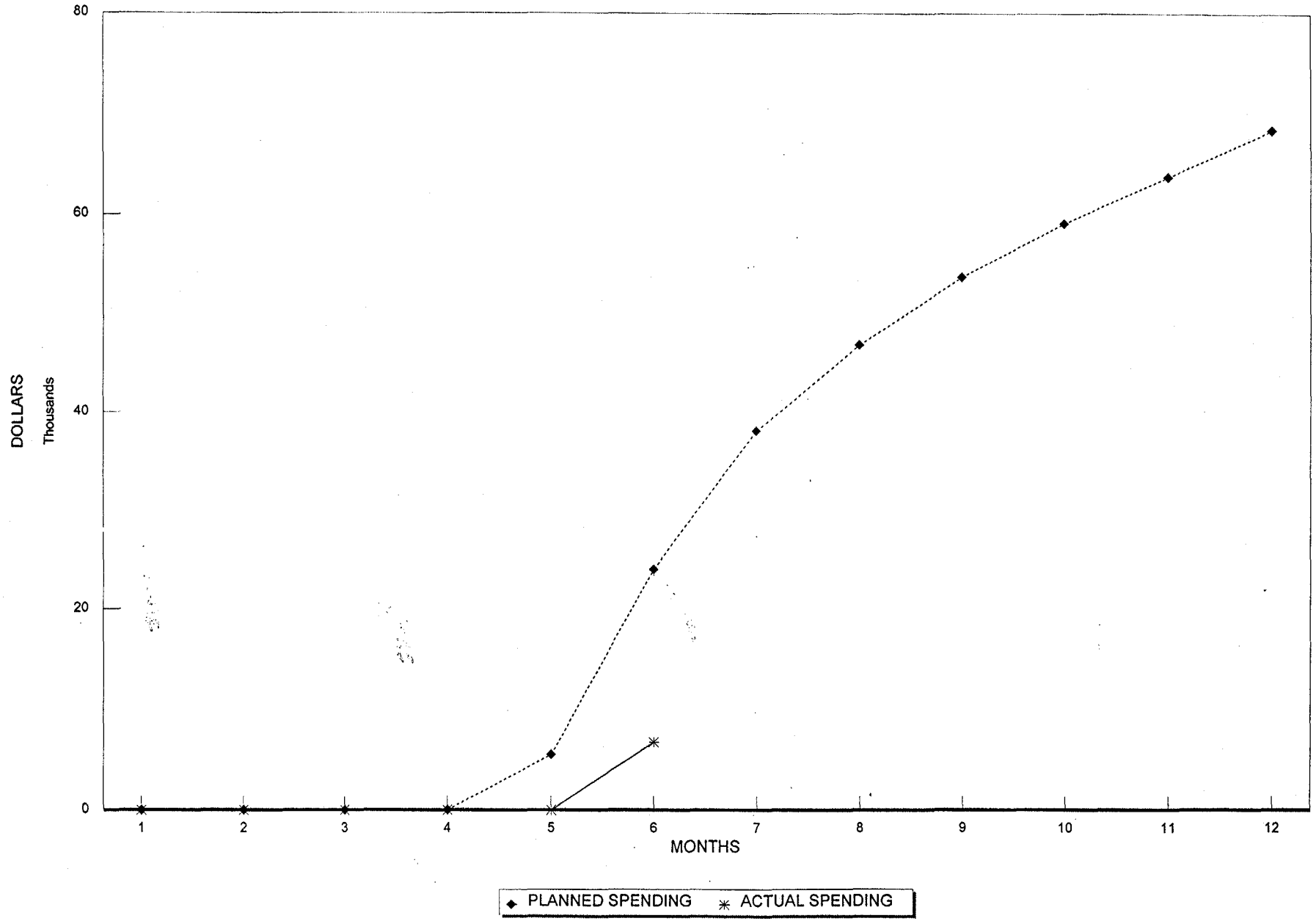


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Quarterly Report for April - June 1996

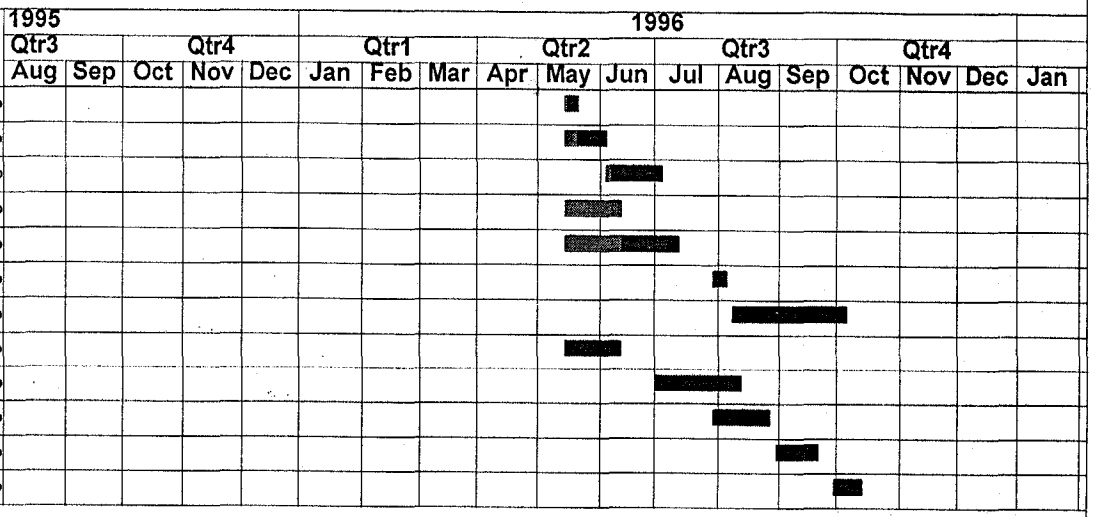
Sub-Task 1.6: In Situ Bioremediation of Chlorinated Solvents

PRINCIPAL INVESTIGATOR (S): P. Carriere & W. Sack



METC TASK 1.7A Decision Support System for Technology Management

#	Task Name	Dura	%Comp
1	Subsurface Contaminant Data Validation	0.25M	20.00%
2	Data Assembly	0.75M	30.00%
3	Data Entry	1M	10.00%
4	Exisiting Database Application	1M	100.00%
5	Database Development	2M	50.00%
6	Database Demonstration	0.25M	10.00%
7	Final Prototype Development	2M	0.00%
8	Decision Support System (DSS) Development	1M	0.00%
9	DSS Prototype Development & Demonstration	1.5M	0.00%
10	DSS Prototype Modifications	1M	0.00%
11	DSS Full Database Extension	0.75M	0.00%
12	DSS/Database Test & Demonstration	0.5M	0.00%

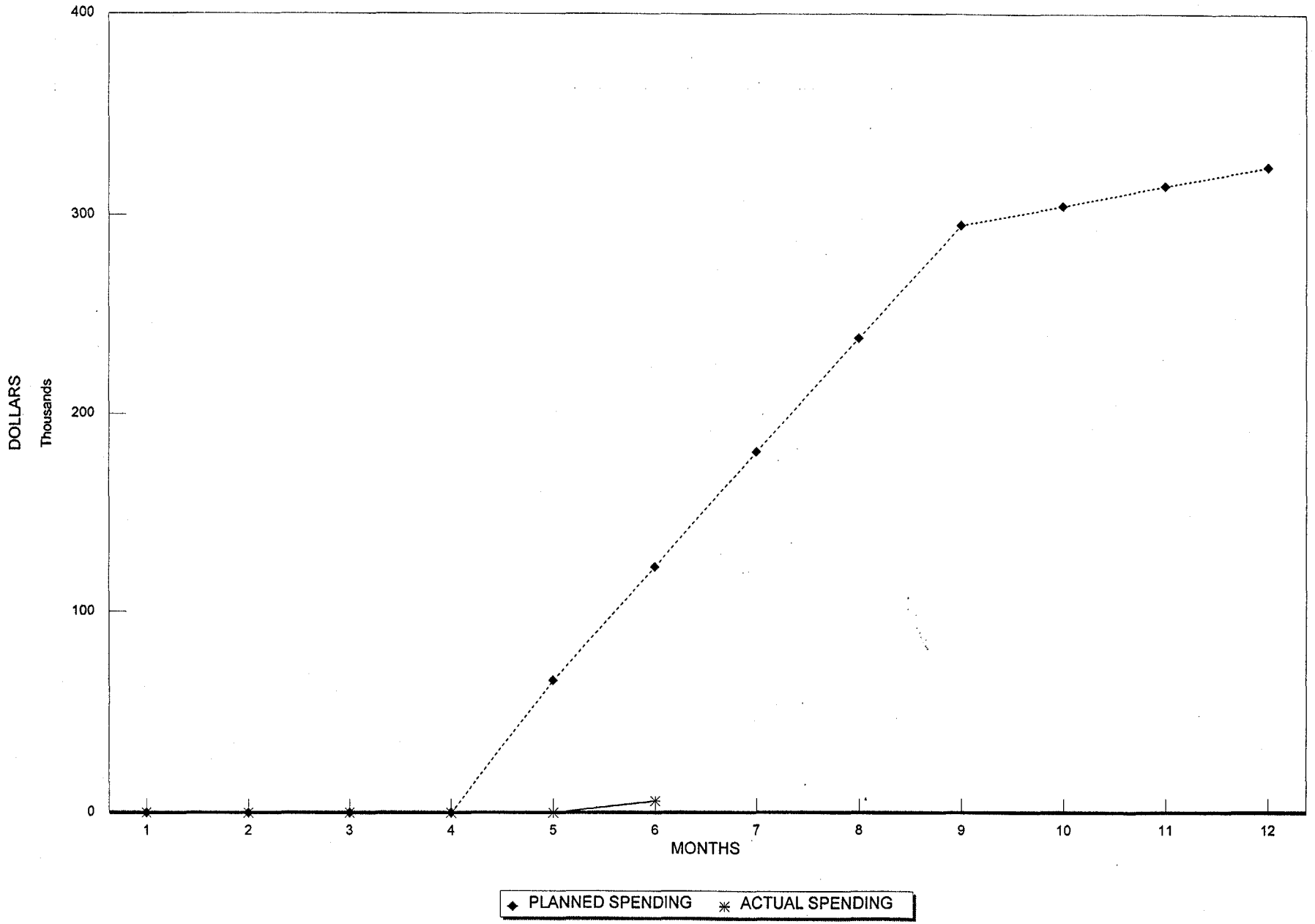


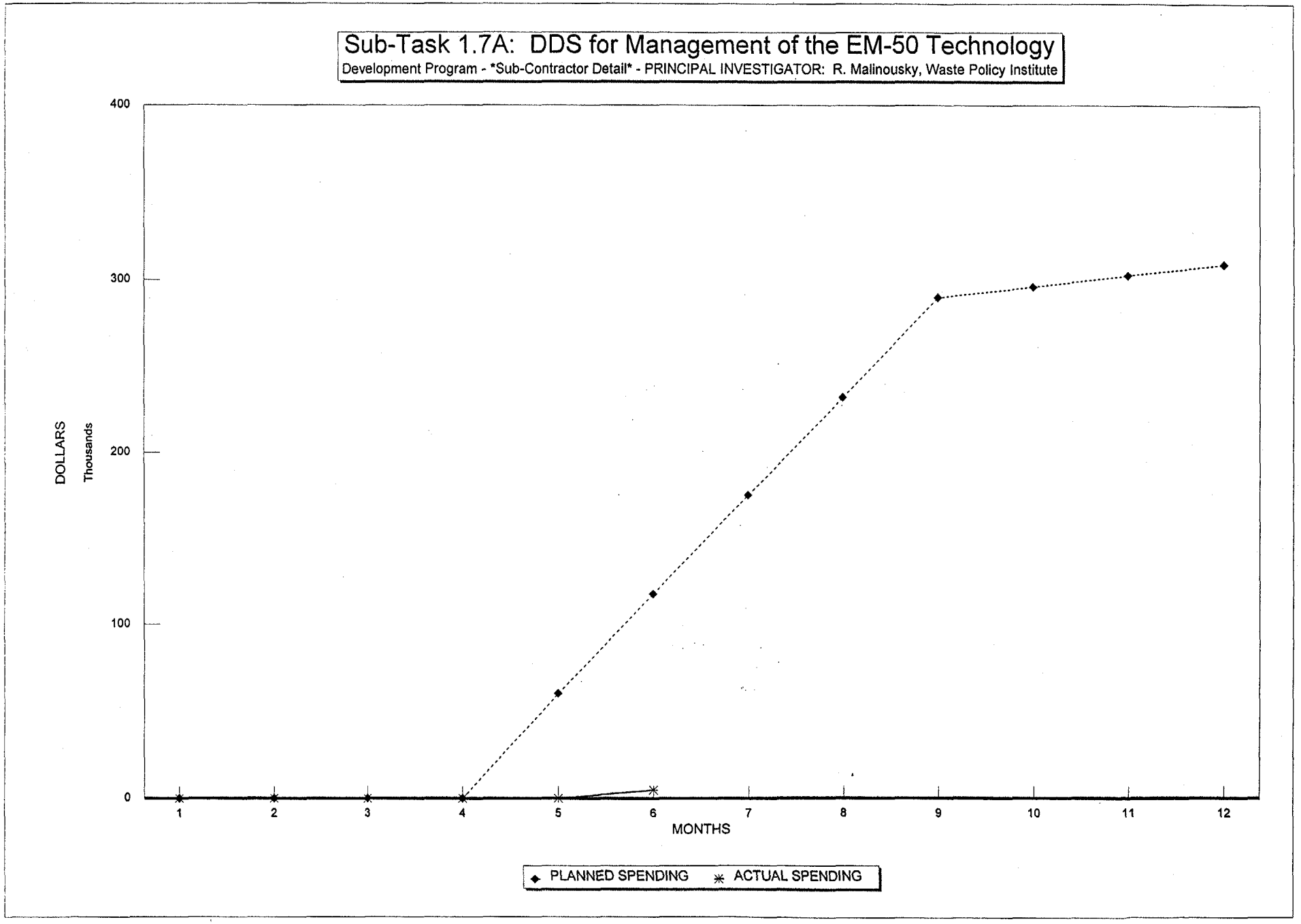
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Quarterly Report for April - June 1996

Sub-Task 1.7A: DDS for Management of the EM-50 Technology

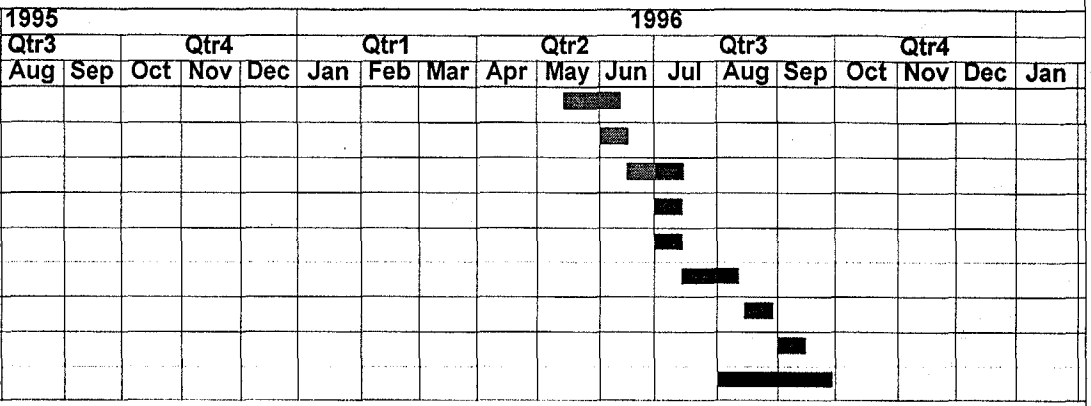
Development Program - Budget Summary




Sub-Task 1.7A: DDS for Management of the EM-50 Technology
Development Program - *Sub-Contractor Detail* - PRINCIPAL INVESTIGATOR: R. Malinousky, Waste Policy Institute
DOLLARS
Thousands
400
300
200
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3
4
5
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7
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9
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11
12
MONTHS
PLANNED SPENDING
ACTUAL SPENDING

METC TASK 1.7B Prototype Database & Decision Support System

#	Task Name	Dura	%Comp
1	Review Decision Support System (DSS) Methodologies	1M	100.00%
2	Determination of Work Plan	0.5M	100.00%
3	Review EM Nomenclature	1M	50.00%
4	Build Glossary of Terms	0.5M	0.00%
5	Help System Overall Design	0.5M	0.00%
6	Enter Topic Data	1M	0.00%
7	Add Special Features	0.5M	0.00%
8	Review and Debug	0.5M	0.00%
9	AHP Documentation	2M	0.00%

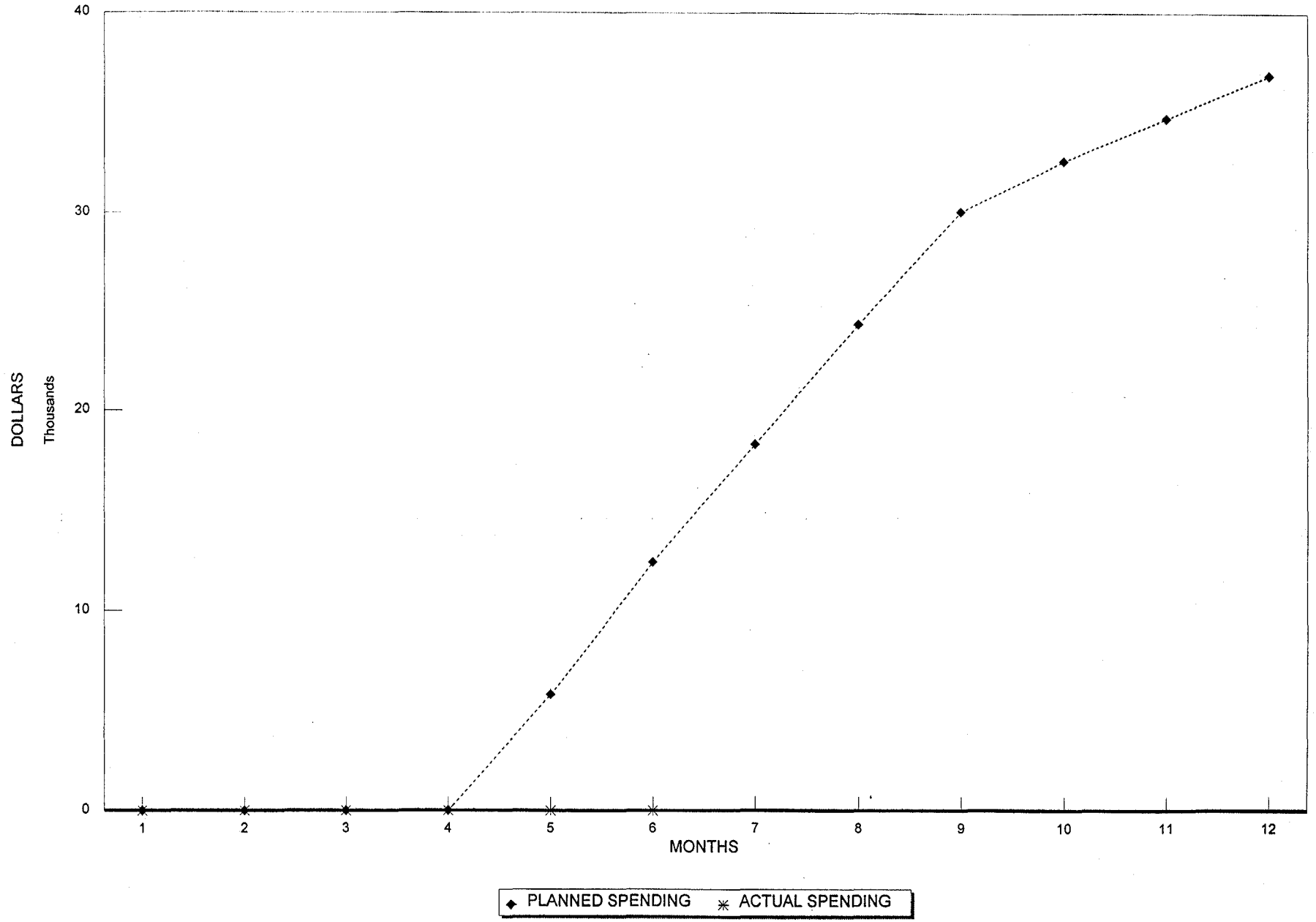


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Quarterly Report for April - June 1996

Sub-Task 1.7B: Prototype Database & Decision Support System

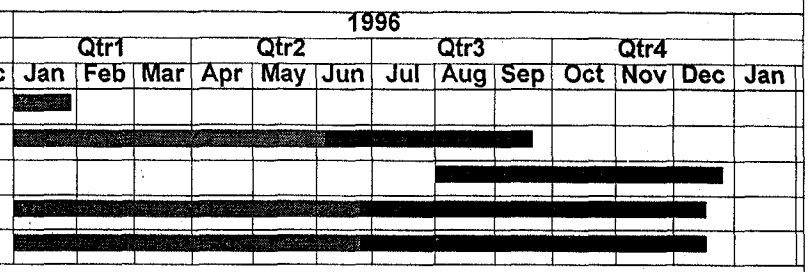
for Management of the EM-50 Technology Development Program - PRINCIPAL INVESTIGATOR: James Denton



METC TASK 2-1

GIS-Based Infrastructure

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	GIS Application	9M	60.00%
3	Assessment for D&D Use	5M	0.00%
4	Tutorial Development	12M	50.00%
5	Data Reduction & Report Preparation	12M	50.00%

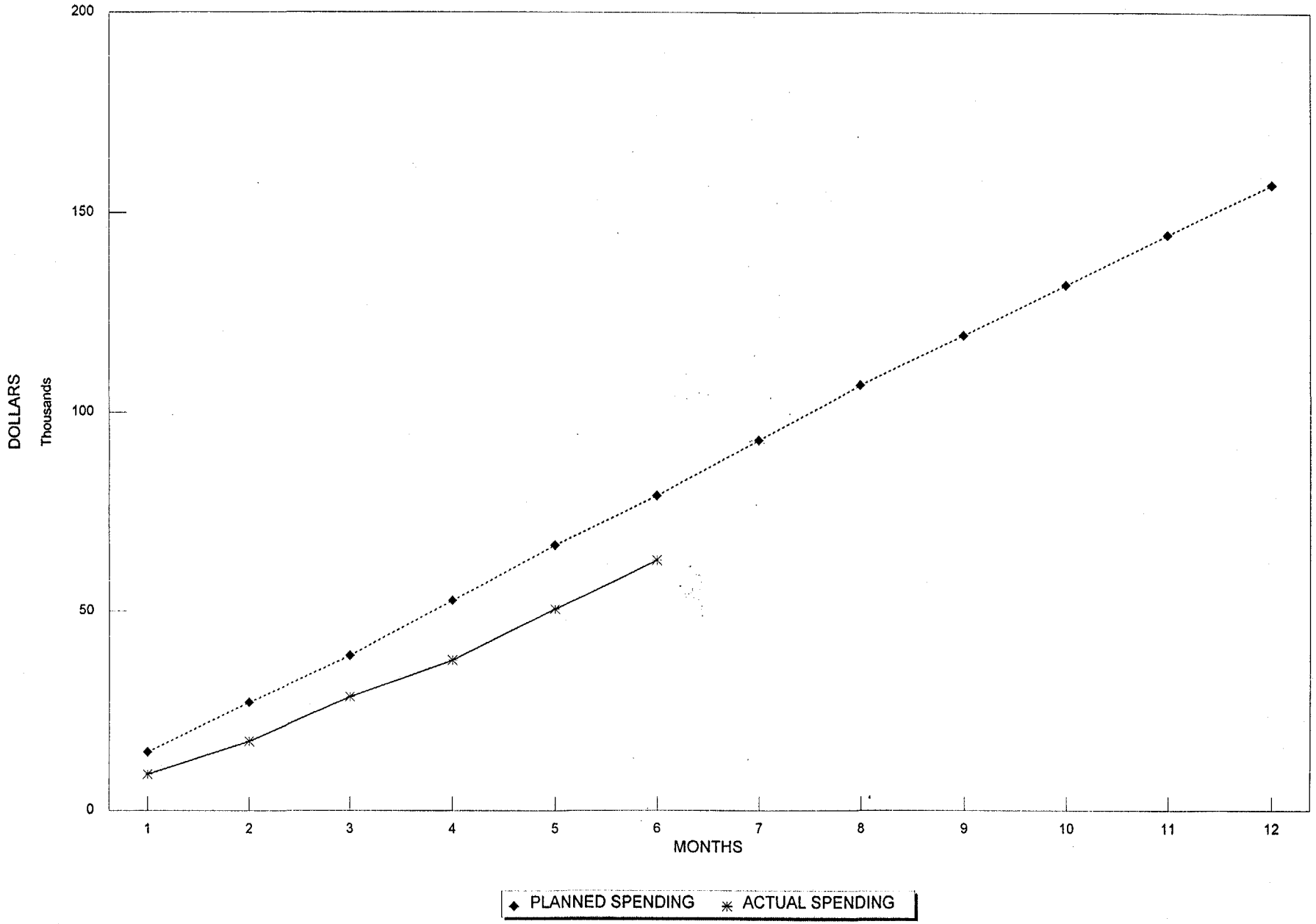


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Quarterly Report for April - June 1996

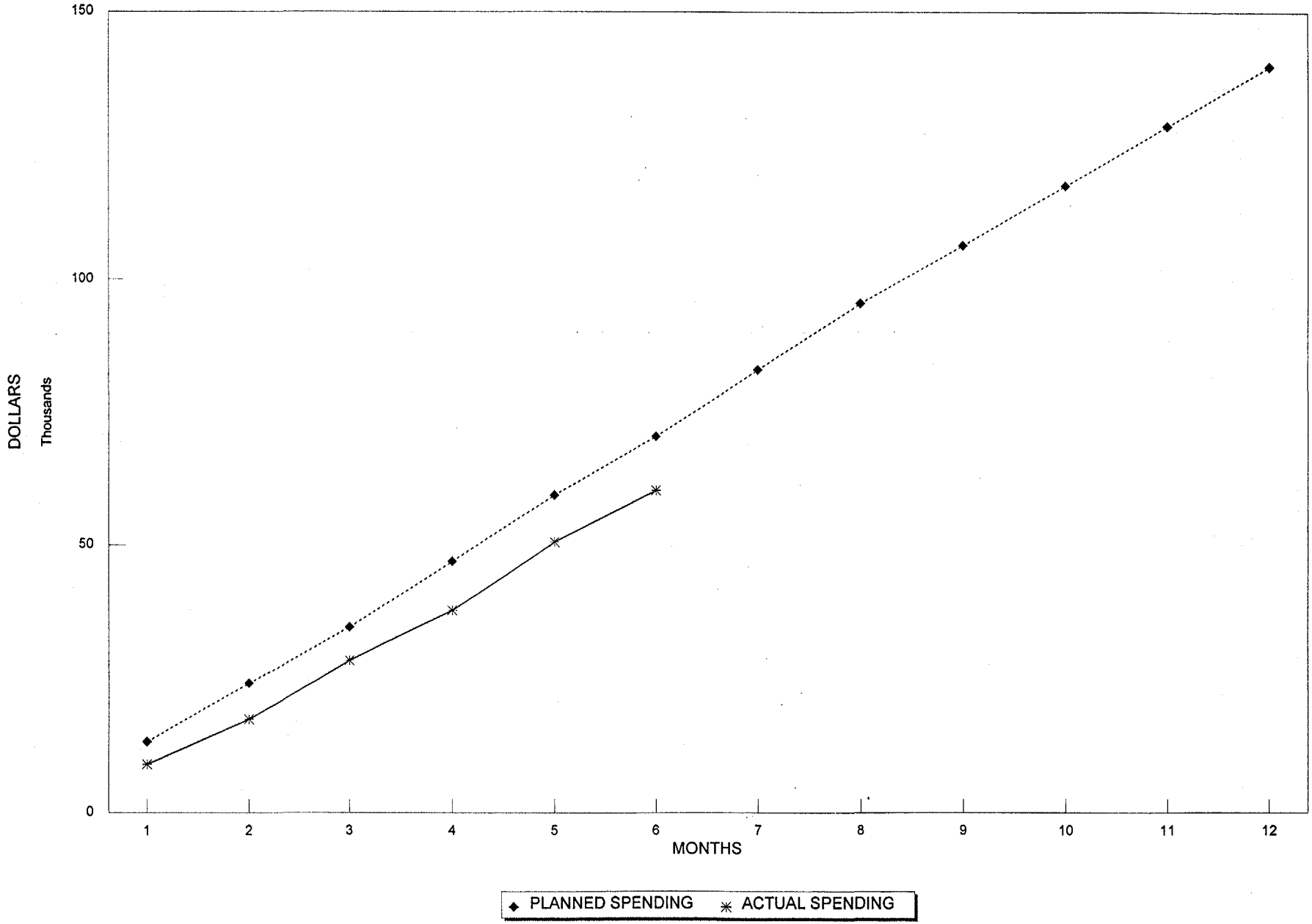
SubTask 2.1 - A GIS Based Infrastructure for Characterization & Remediation

Overall Summary



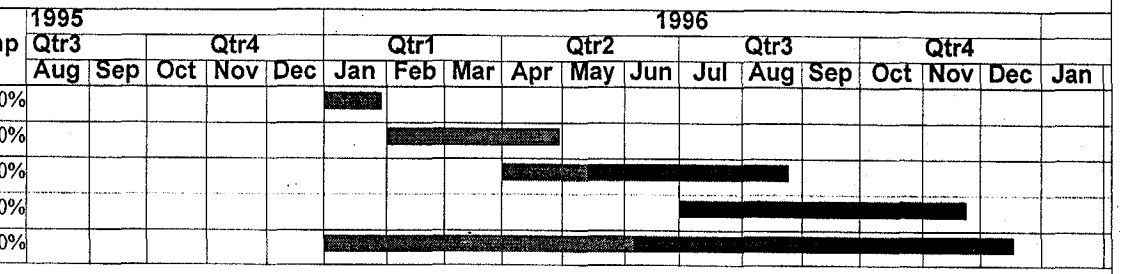
Sub-Task 2.1: GIS Infrastructure for Characterization & Remediation

PRINCIPAL INVESTIGATOR (S): J. Hooper & A. Lodgher - <<< Marshall University Detail >>>



METC TASK 2-2 Treatment of Mixed Wastes via Steam Reforming

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Calibrate GC	3M	100.00%
3	Destruction Efficiency Evaluation	5M	30.00%
4	Catalyst Evaluation	5M	0.00%
5	Data Reduction and Report Preparation	12M	45.00%

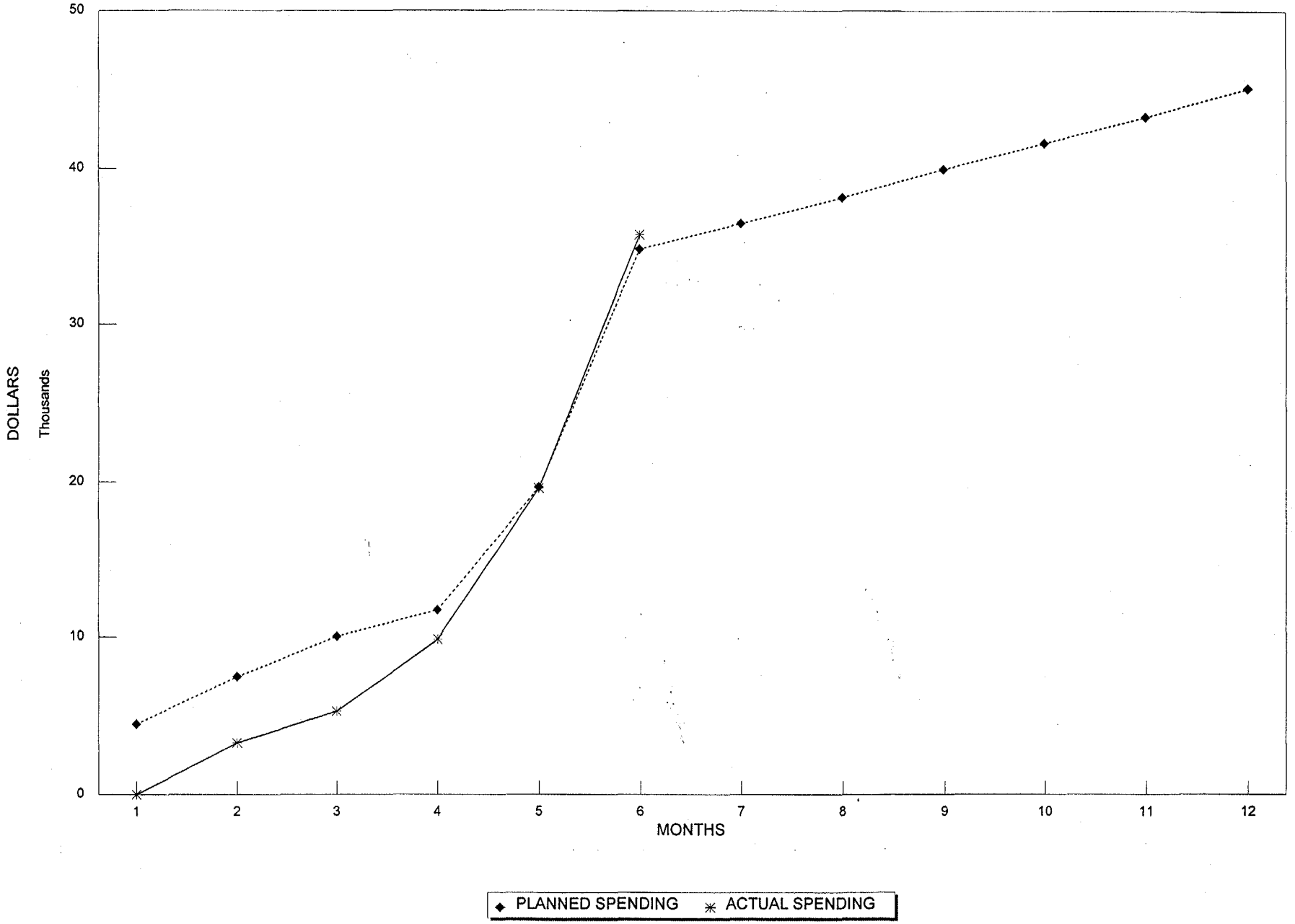


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Quarterly Report for April - June 1996

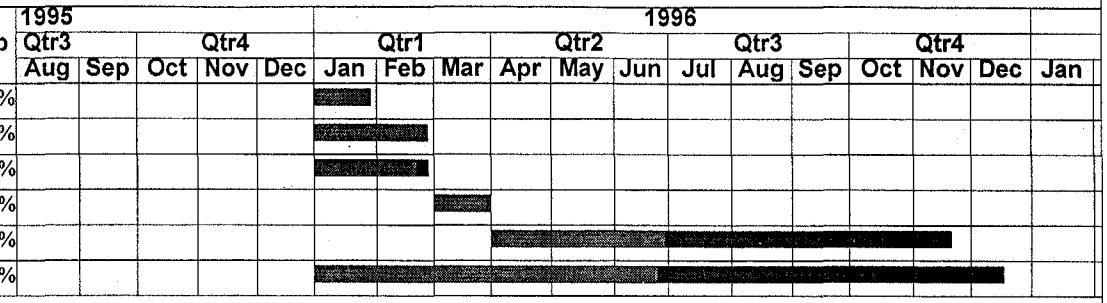
SubTask 2.2 - Trmt of Mixed Waste via Fluidized Bed Steam Reforming

PRINCIPAL INVESTIGATOR: R. Turton



METC TASK 2-3 Centrifugal Membrane Technology

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Literature Review	2M	100.00%
3	Waste & Membrane ID & Acquisition	2M	90.00%
4	Technology Modification Acquisition & Training	1M	100.00%
5	Testing & Evaluation	8M	38.00%
6	Data Reduction & Report Preparation	12M	50.00%

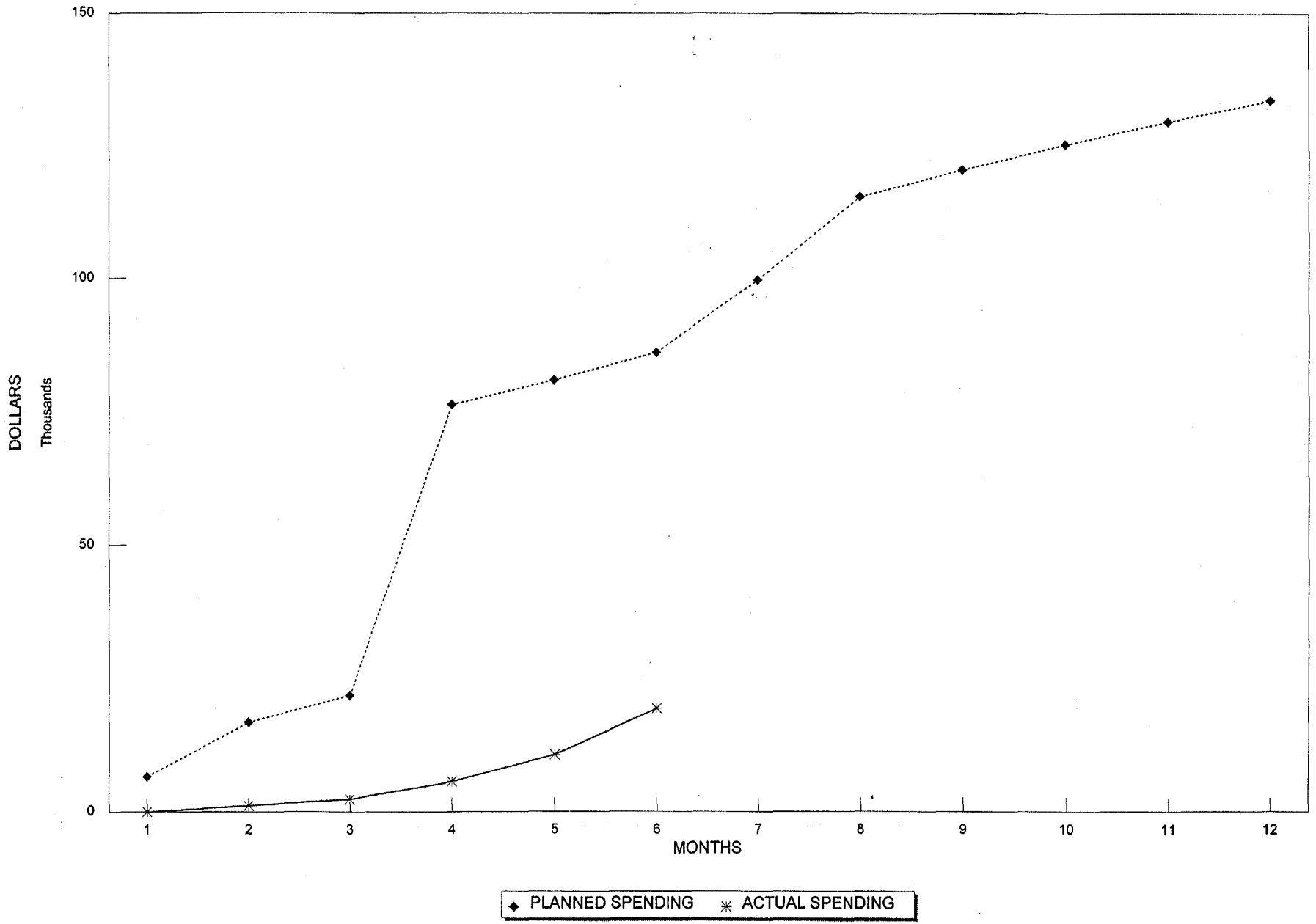


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Quarterly Report for April - June 1996

Sub-Task 2.3: Centrifugal Membranes to Treat Haz./Radio Active Wastes

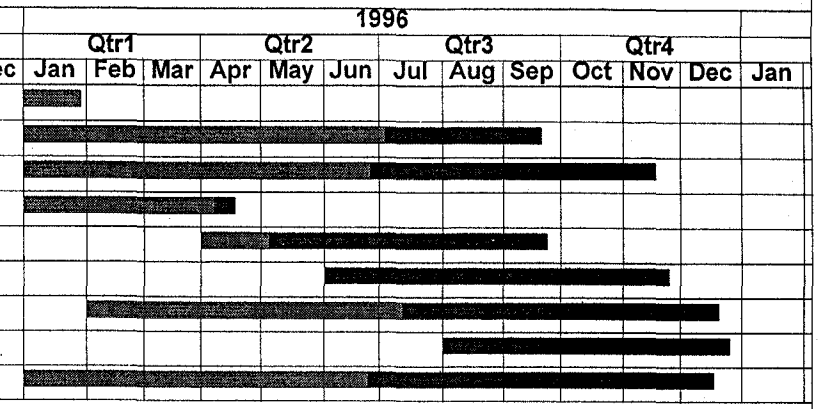
PRINCIPAL INVESTIGATOR: B. Reed



METC Task 2-4

Environmental Pollution Control Devices

#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Small Cell Carbon Tests	9M	70.00%
3	Access Metal & Radionuclide Removal	11M	55.00%
4	Construct Prototype	3.7M	90.00%
5	Parametric Studies	6M	20.00%
6	Derive Correlations	6M	0.00%
7	Test Recovery Schemes	11M	50.00%
8	Apply Prototype	5M	0.00%
9	Data Reduction & Report Preparation	12M	50.00%

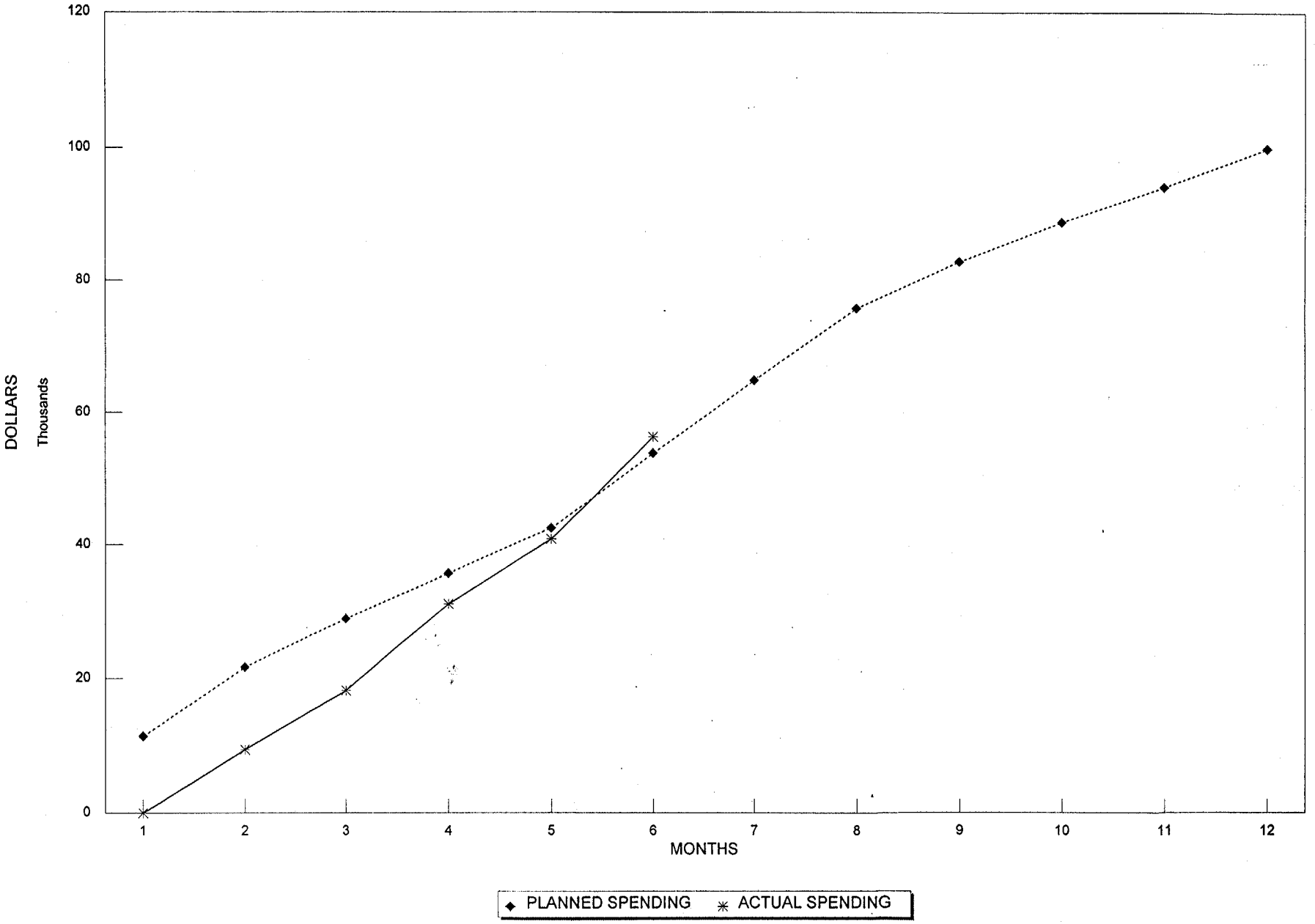


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Quarterly Report for April - June 1996

Sub-Task 2.4 - Pollution Control Devices Based on Novel Forms of Carbon

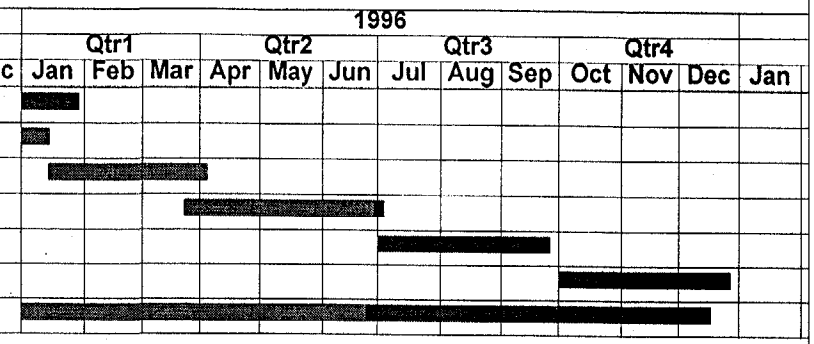
PRINCIPAL INVESTIGATOR (S): A. Stiller, J. Zondolo & A. Brennsteiner



METC Task 2-5

Development of Instrumental Methods

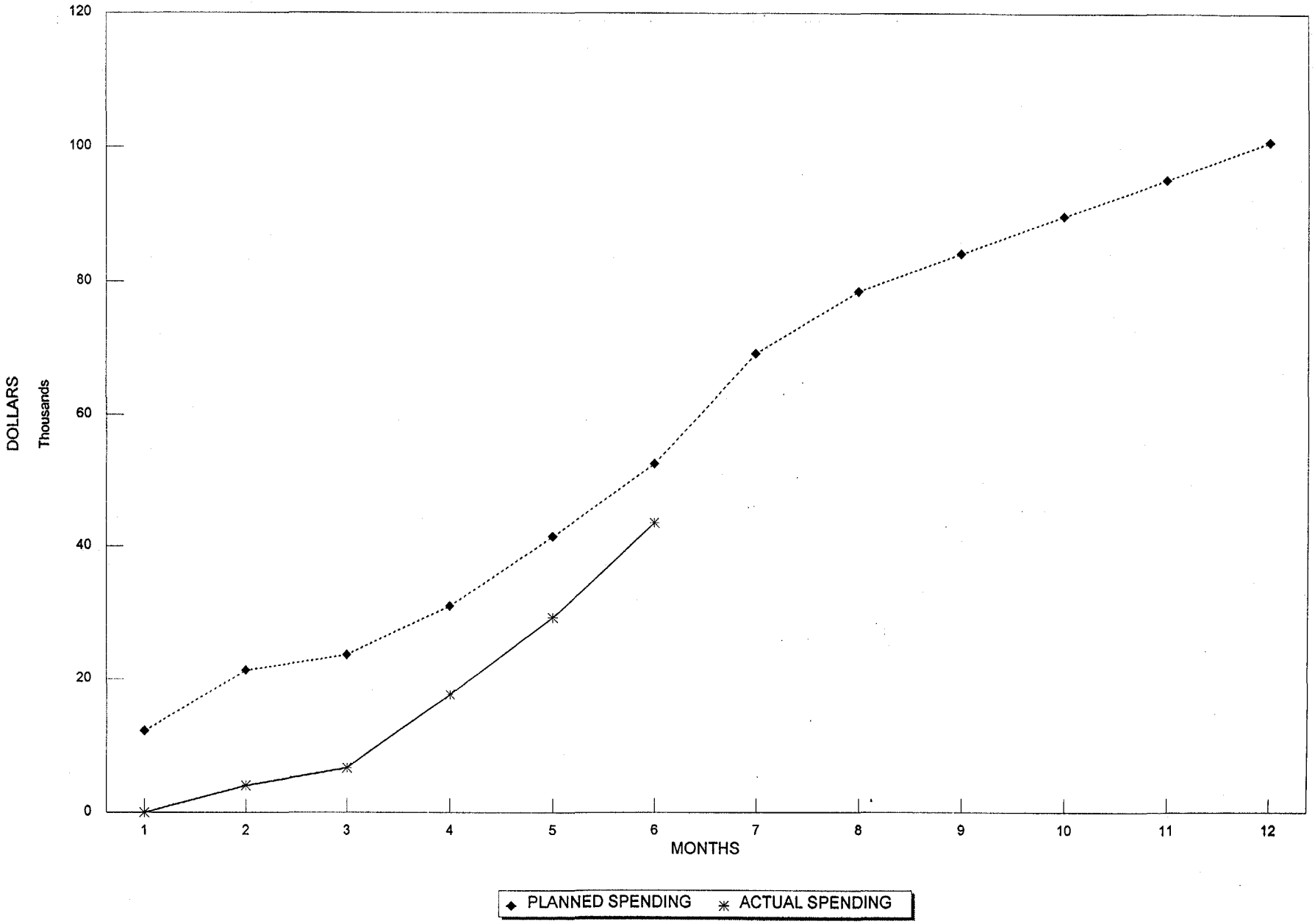
#	Task Name	Dura	%Comp
1	NEPA Information	1M	100.00%
2	Literature Review	0.5M	100.00%
3	Analysis & Speciation of Iodine	2.75M	100.00%
4	Analysis & Speciation of Re & Tc	3.5M	95.00%
5	Analysis & Speciation of Iodine	3M	0.00%
6	Analysis & Speciation of Re & Tc	3M	0.00%
7	Data Reduction & Report Preparation	12M	50.00%



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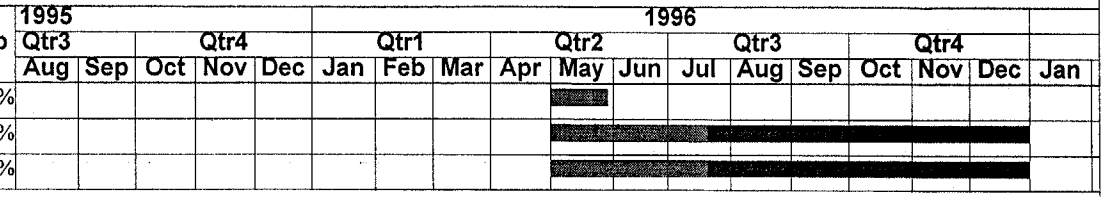
Sub-Task 2.5: Instrumental Methods for Characterization & Analysis

PRINCIPAL INVESTIGATOR (S): V. Remcho & N. Ballou



METC Task 2-6A Production & Evaluation of Biosorbents & Cleaning Solutions

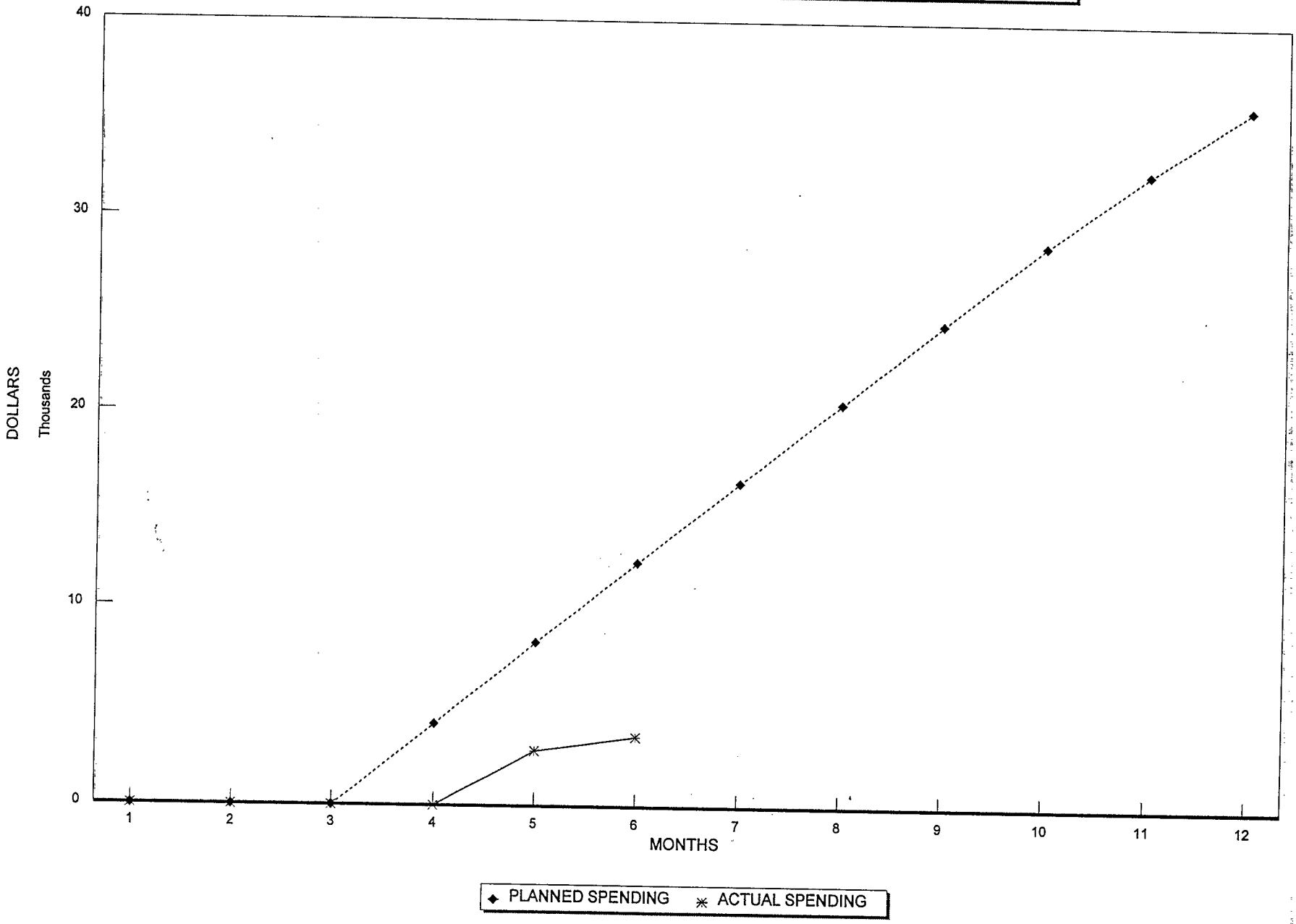
#	Task Name	Dura	%Comp
1	Development of Waste Streams	1M	100.00%
2	Selection & Evaluation of Sorbents & Cleaning Solutions	8.33M	33.00%
3	Data Reduction & Report Preparation	8.33M	33.00%



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Quarterly Report for April - June 1996

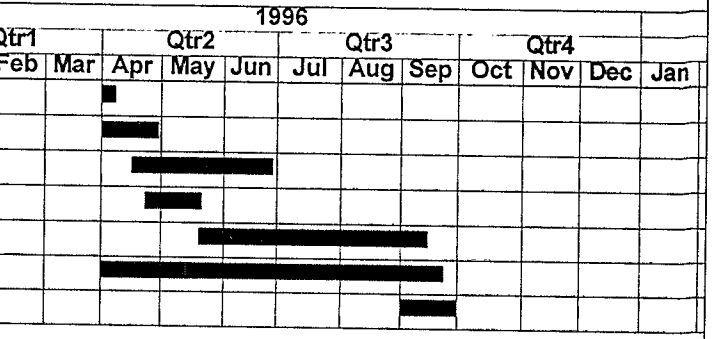
Sub-Task 2.6a: Production & Evaluation of Biosorbents and Cleaning Solutions for use in D&D - PRINCIPAL INVESTIGATOR: J. Kilbane, Institute of Gas Technology



METC Task 2-6B

Use of Spin Tek Centrifugal Membrane Technology

#	Task Name	Dura	%Comp
1	NEPA Information	0.25M	100.00%
2	Identification & Formulation of Synthetic Wastes	1M	0.00%
3	Selection & Evaluation of Sorbents & Cleaning Solutions	2.5M	0.00%
4	Membrane Selection & Procurement	1M	0.00%
5	Bench-Scale Testing of Process	4M	15.00%
6	Data Reduction & Report Preparation	6M	25.00%
7	Preparation of Joint Proposals	1M	0.00%



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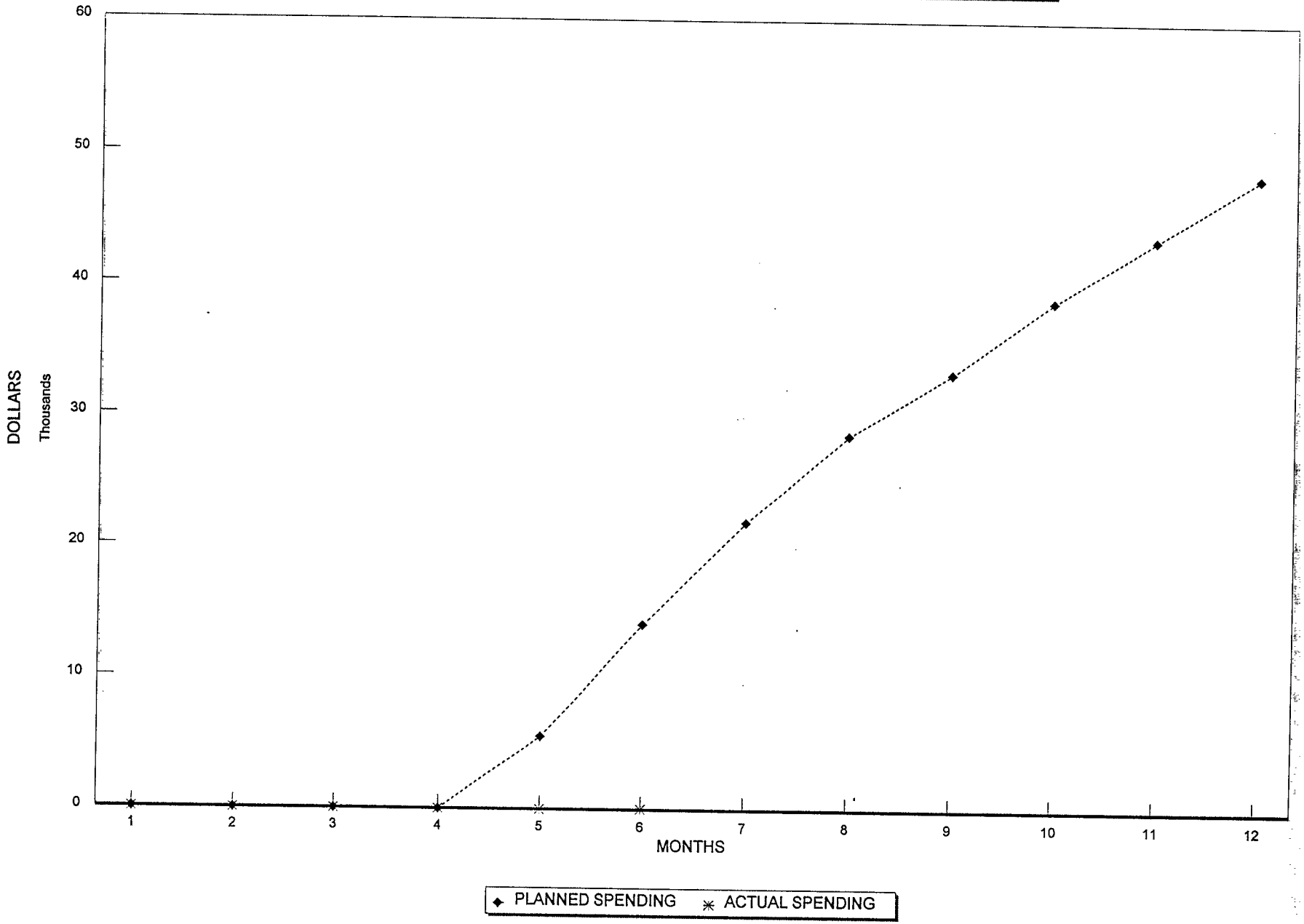
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Quarterly Report for April - June 1996

Sub-Task 2.6B: Use of Spintek Centrifugal Membranes

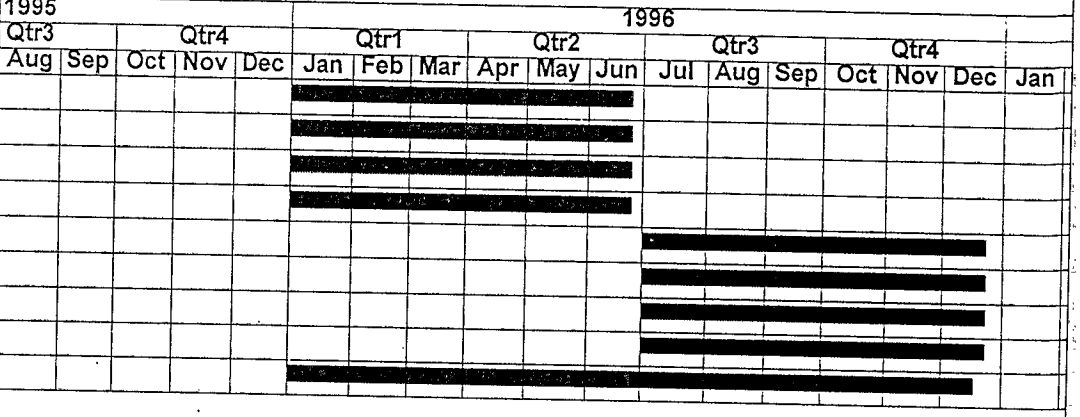
and Sorbents/cleaning solutions in D&D work - PRINCIPAL INVESTIGATOR (S): B. Reed & W. Lin



METC Task 3-1

WV High Tech Consortium

#	Task Name	Dura	%Comp
1	Phase II - Implementation	6M	100.00%
2	Start-Up Activities	6M	100.00%
3	Infrastructure Development	6M	100.00%
4	Operating Policies	6M	100.00%
5	Phase III - Continued ETI Development	6M	0.00%
6	Infrastructure Development	6M	0.00%
7	Operating Policies	6M	0.00%
8	Tenant Company Incubation	6M	0.00%
9	Report Preparation	12M	50.00%

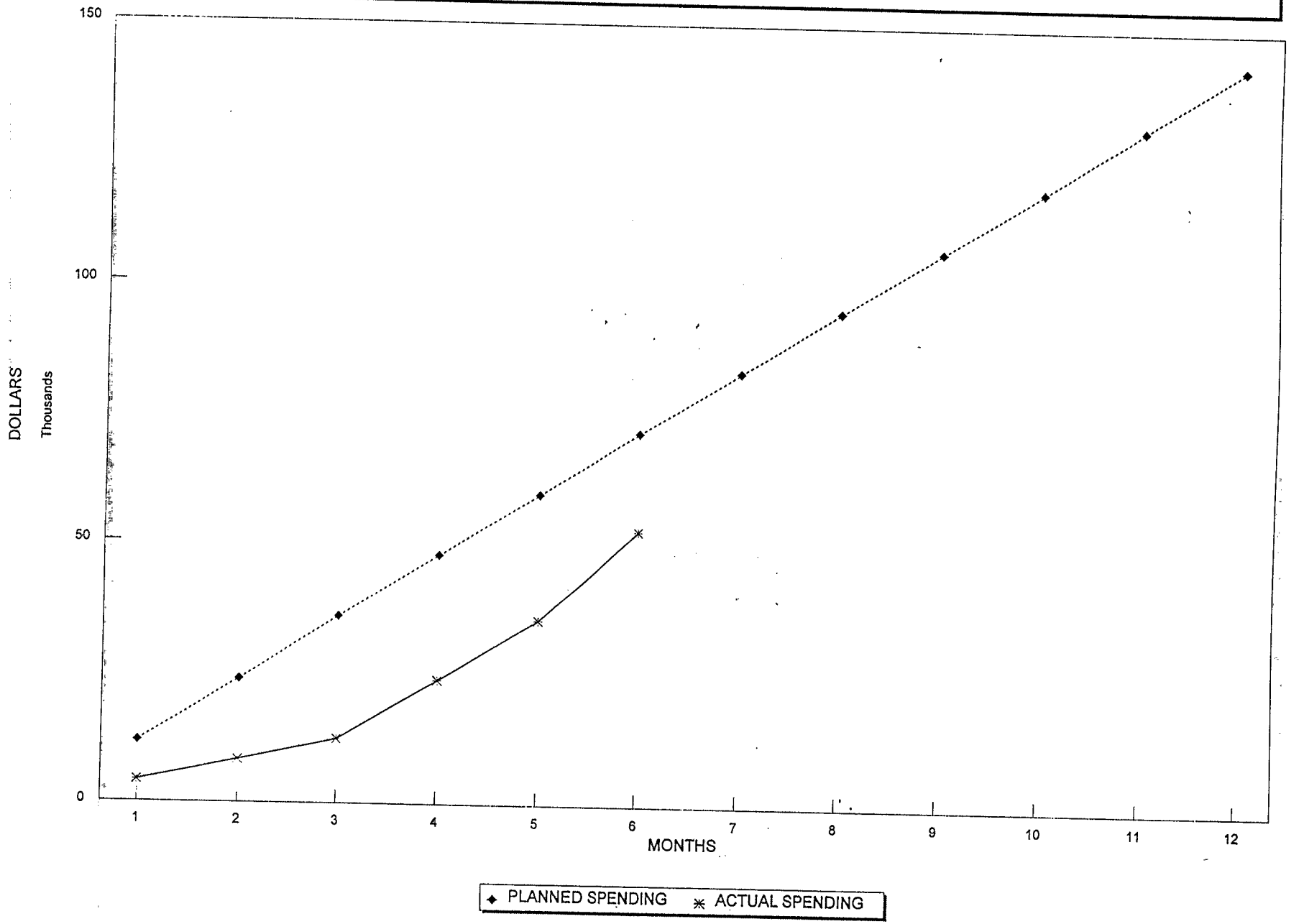


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Quarterly Report for April - June 1996

Sub-Task 3.1: WVHTC Foundation - Technology Support Program

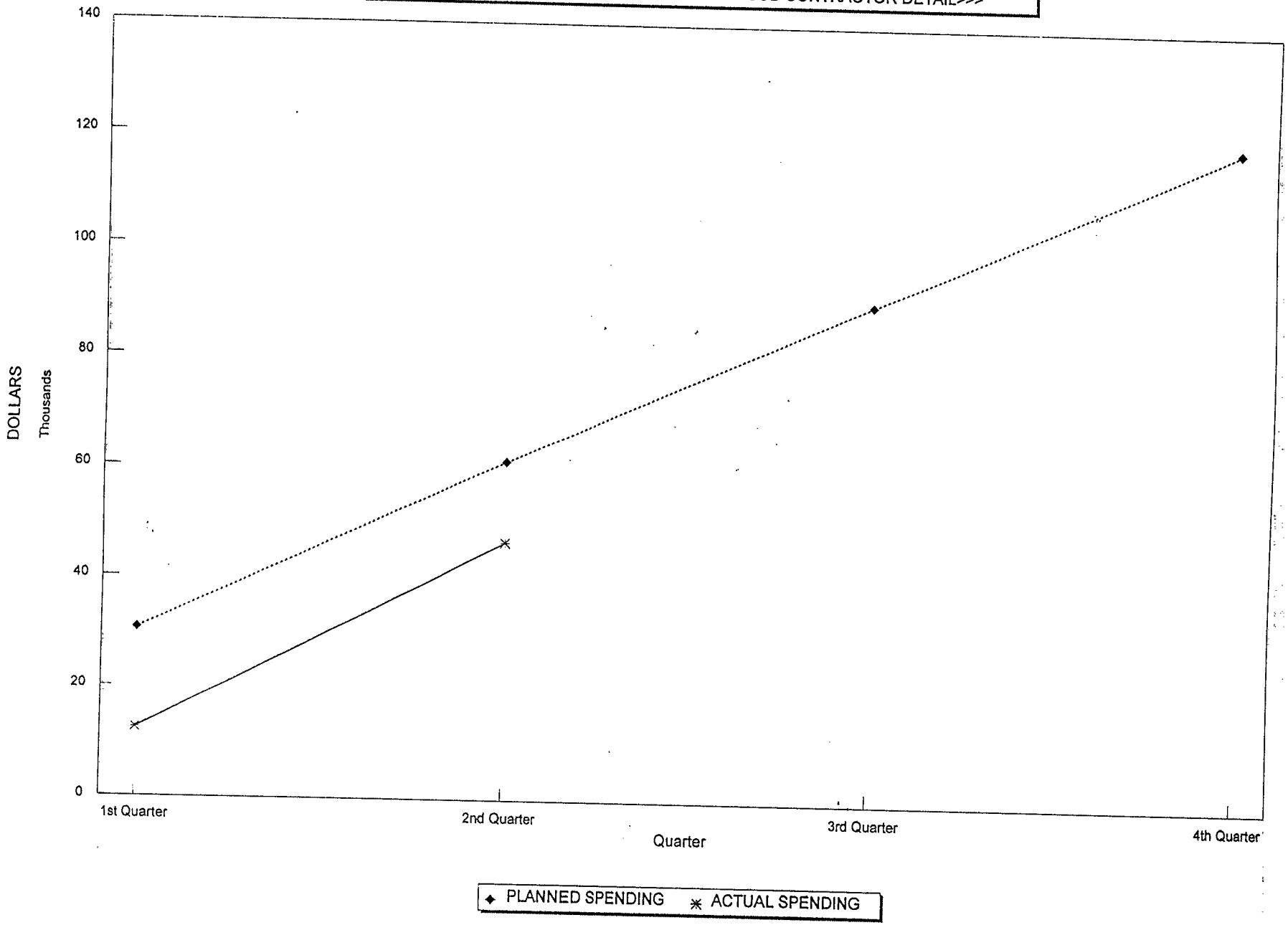
PRINCIPAL INVESTIGATOR (S): E. Cook & J. Berkow <<<SUMMARY>>>



09

Sub-Task 3.1: WVHTC Foundation, Support Program

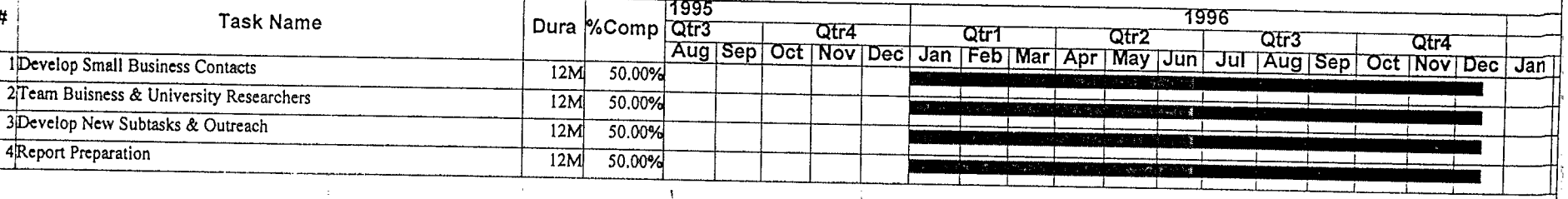
PRINCIPAL INVESTIGATOR: Jan Berkow <<<SUB-CONTRACTOR DETAIL>>>



METC TASK 3-2

Small Business Interaction Opportunities

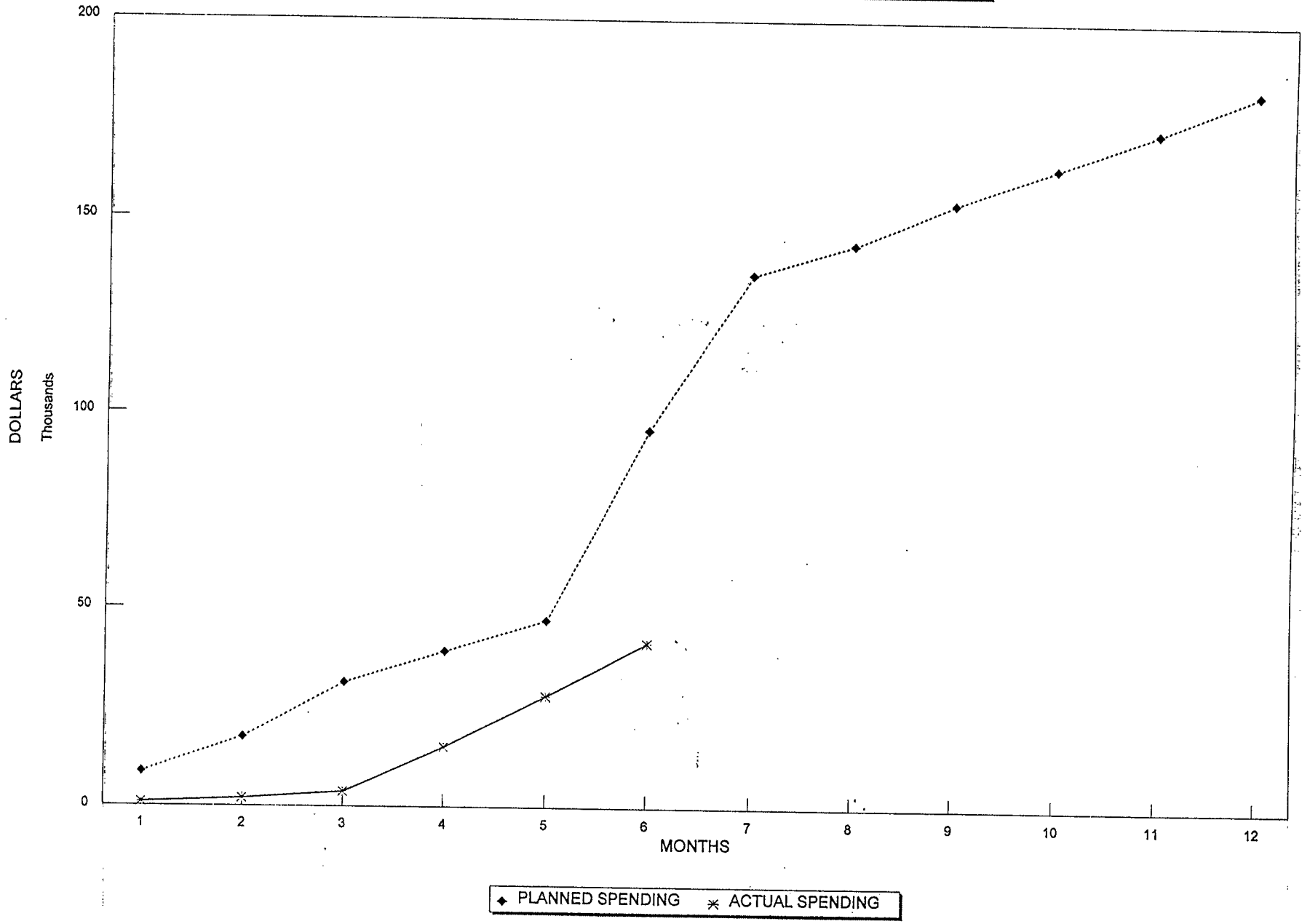
#	Task Name	Dura	%Comp
1	Develop Small Business Contacts	12M	50.00%
2	Team Buisness & University Researchers	12M	50.00%
3	Develop New Subtasks & Outreach	12M	50.00%
4	Report Preparation	12M	50.00%



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Sub-Task 3.2: Small Business Opportunities

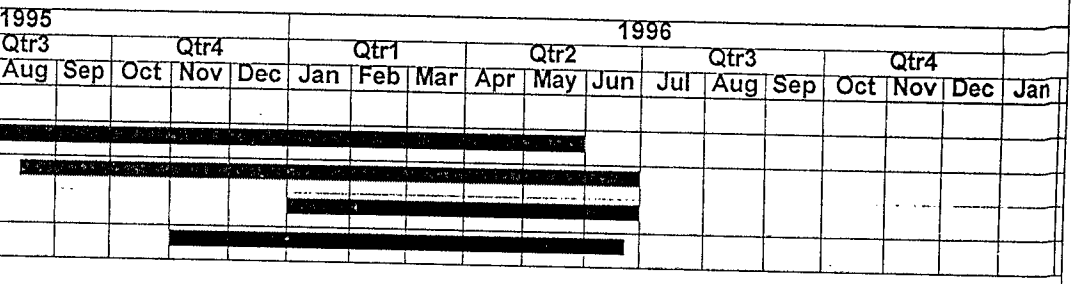
PRINCIPAL INVESTIGATOR: E. Cook



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OLD METC TASK 3-4 Voluntary Environmental Protection, Kanawha Valley

#	Task Name	Dura	%Comp
1	Initial Concact of Parties	1M	100.00%
2	Conduct Meetings with Parties	10.86M	100.00%
3	Meetings with USEPA and WVDEP	10.9M	100.00%
4	Prepare Summary of Meetings	6.19M	20.00%
5	Group Meeting	8M	0.00%

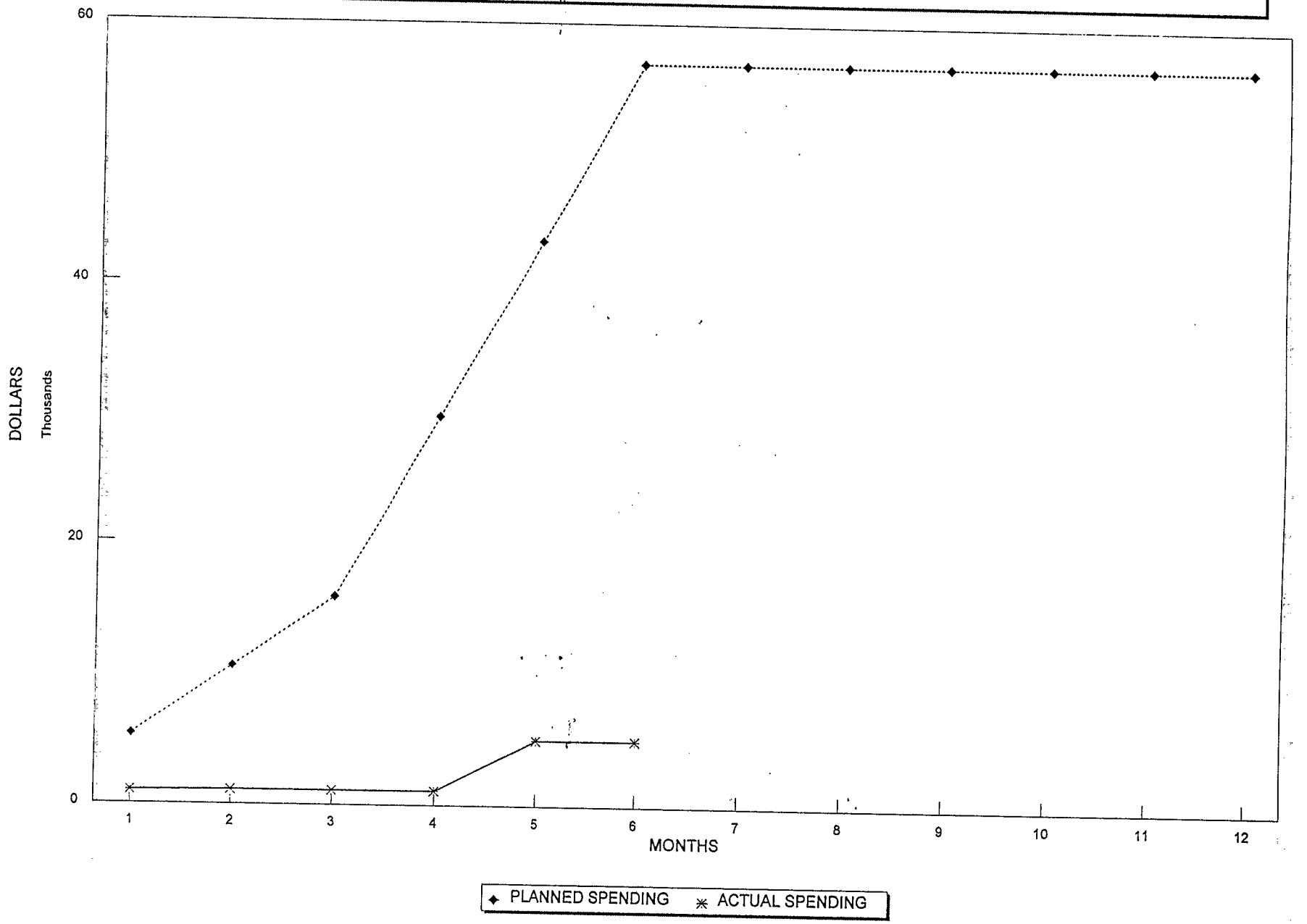


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Baseline

Quarterly Report for April - June 1996

Sub-Task *OLD 3.4* - Kanawha River Area Environmental Protection

PRINCIPAL INVESTIGATOR: Ray Lovett - Note: Continuation from 1995, only 1996 work shown



ANALYSIS OF THE VORTEC CYCLONE MELTING SYSTEM (CMS™) FOR REMEDIATION OF PCB CONTAMINATED SOILS USING CFD

METC Task No. 1.1

Quarterly Technical Progress Report
Reporting Period: April 1 - June 29, 1996

Work Performed Under Contract
No.: DE-FE21-92MC29467

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

by

Ismail Celik, Ph.D.

Department of Mechanical and Aerospace Engineering
West Virginia University
Morgantown, WV 26506-6106

ABSTRACT

In this report, the results of flow and heat transfer analysis for selected retrofits of a cyclone melting system (CMS) are presented. The analysis is based on computational fluid dynamics (CFD) simulations. The assumptions, approximations, and the implications of the results with respect to the gas residence time, flow patterns, and temperature distribution, and conversion and destruction rates for selected chemical species are discussed. Problem specific mathematical models are presented. Recommendations are made for improved flow conditions that will lead to longer residence times, and higher conversion and destruction efficiency. Specific application target is the CMS™ of Vortec Corporation. The results are summarized in the executive summary section as they become available for each quarterly reporting period.

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6.0	Results and Discussion (Current Period)	5
7.0	Conclusions (Current Period)	13
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LIST OF TABLES

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EXECUTIVE SUMMARY (current period)

Work continued in this period on the residence chamber using the ***old geometry*** and a newly suggested geometry. The Vortec's engineers has assessed using the results from our preliminary calculations, as well as their engineering calculations and decided to select a ***new geometry*** with a vortex finder tube located in the central region of the chamber. The flow field, pressure drop, and residence time with various assumptions are calculated for the new geometry and results are presented in this report. The influence of wall roughness, and heat loss are also investigated. Literature survey on PCB kinetic rates are continued and reaction rates are compiled for selected PCB reactions. Some computational problems were encountered with regards to convergence and pressure drop calculations during three-dimensional simulations. These have been resolved.

The computer simulations of the three-dimensional, turbulent, isothermal flow inside the residence chamber with the vortex finder showed that the system pressure drop in the total pressure is about 300 Pa. The gas-residence time calculated in several ways is greater or equal to 2.0 seconds. Recirculation zones are detected inside the outer tube which act as a trap for the scalar quantities and particulate matter. This increases the residence time, but may be not so desirable when particle deposition is considered. The swirl inside the vortex finder tube is relatively weak. The wall roughness does not seem to have a significant effect on the overall flow structure nor on the system pressure drop. Preliminary results with about 4% heat loss from the walls of the residence chamber indicate a temprerature drop of about 70 K from the inlet to the exit of the residence chamber. This shall be investigated closely in the next quarterly period. PCB reaction rate data compilation is near completion. Conversion rates will be calculated for some critical compounds in the next quarterly period.

1.0 INTRODUCTION

The low level radioactive waste and other hazardous waste materials such as Polychlorinated Biphenyls (PCB) has become an important risk factor in endangering human health and environment. Each year millions of tons of contaminated soil is identified and classified for clean up only in the United States. An efficient and safe way to reduce and in most cases eliminate this risk factor to health and environment is the so called vitrification and remediation process via thermochemical treatment at high temperatures. In this process the hazardous waste and the contaminated residuals are heated, where most organic contaminants are vaporized and oxidized, while the inorganic contaminants are immobilized within a glassy, vitrified matrix. One such system has been developed by Vortec Corporation (here and after referred as Vortec) which has been demonstrated to be flexible in processing a wide variety of contaminated soils, sludges, and other hazardous materials. The system consists of a counter rotating combustor (or melter), a separation unit where liquid phase is separated from the gas phase, a residence chamber to provide reaction time to complete the conversion processes, and a recuperator which provides further residence time in addition to providing hot air/gas to be used as a heating source for the combustor (see Figure 1). The design, refinement, and retrofits of such systems require calculation of optimum design parameters such as residence time, heat loss, pressure drop, mixing rates, and the flow field dependent conversion and destruction (C&D) rates.

In practice where detailed flow and temperature distributions are not available, usually a plug flow assumption is used to calculate the gas residence time from empirical relations(see e.g. Van Dell et al., 1994a, 1994b; Van Dell and Mahle, 1992; Duvall and Rubey, 1977). This is a crude assumption and it may lead to significant errors. For example Van Dell and Mahle's calculations show a two-three fold difference in residence time even in a controlled, bench-scale laminar flow reactor due to temperature differences within the same reactor. Such errors directly translate to the calculation of species concentrations, hence may lead to quite erroneous information for design of PCB destruction systems. Celik and Chattree (1988) developed a rigorous method for calculating mean gas and particle residence times in an entrained flow reactor. This method (which will also be used for the present analysis) takes into account the gas temperature and density changes locally in the reactor as well as the recirculation zones. Their results also showed significant differences between the particle and gas residence time due to inertia and gravitational effects.

Furthermore, the destruction rates of PCB's are usually modeled by a simple Arrhenius type rate expressions where the gas temperature is assumed to be constant. To obtain more accurate results the gas temperature needs to be varied locally within the reactor and the reaction rates should be generalized to account for reformation of the compounds. Thus the resulting rate expression should include both the coefficients for the rate of formation as well as for the rate of destruction. Such a model has been proposed by Van Dell et al. (1994a) and it is a good candidate to be used in the present analysis.

The computation and optimization of the above mentioned design parameters can be accomplished in a cost effective way using Computational Fluid Dynamics (CFD) analysis. With CFD codes the flow field, temperature distribution, and species concentrations can be calculated at many discrete spatial points inside the reactor as well as temporal (or transient) variations. These primitive flow variables, in turn, can be used, by appropriate post processing to calculate integral design parameters of interest. The calculated design parameters along with the detailed information and virtual visualization of flow patterns can increase our understanding of the physical processes involved, and hence reduce the risk and the cost of experimental testing and/or validation.

2.0 PURPOSE

The primary objective of the proposed research work is to provide via computer simulations, needed design information such as gas residence time, temperature distribution, species concentrations, and heat and pressure losses for refining the proposed design and/or validation of the assumptions made during the design of sub-component of a cyclone melting system (CMS) currently under development by the Vortec Corporation. The analysis is to focus on specific needs for remediation of PCB contaminated soils. A secondary objective is to develop and implement a global kinetic model for the formation and destruction of selected PCB's such as *o*-dichlorobenzenes in conjunction with a readily available computational fluid dynamics (CFD) code. This model will rely upon experimental information available in the literature (see. e.g. Van Dell et al., 1994a, 1994b; Sethuraman et al., 1992; Ritter and Bozzelli, 1990; Tsang, 1990;). If successful, the proposed analysis will allow important enhancements for processing capabilities, and it will further reduce the development risk associated with commercial implementation of the CMS^{TM} technology.

3.0 BACKGROUND

An extensive research and development (R&D) program is being implemented by the Vortec Corporation with considerable funding from the Department of Energy(DOE) to provide waste processing equipment and services for industrial and institutional waste generators, and to manufacture glass and ceramic products from these waste materials. In particular, Vortec is planning to modify their existing high temperature waste processing and recycling units and retrofit it with appropriate units so that the system can be used for efficient remediation of PCB (PolyChlorinated Biphenyls) contaminated soils. This requires determination of optimum design parameters, such as residence times, heat loss, pressure drop, and size for each subcomponent of the system. The conceptual system consists of four interconnected sub-components, namely, a cyclone melting system (CMS^{TM}), separation reservoir, recuperator base (or residence chamber), and recuperator (see Figure 1). The gas residence time in each of these components is strongly dependent on the degree of turbulent mixing and the presence of recirculation zones. The time required for complete conversion of the PCB compounds is, in turn, depends on the residence time as well as the temperature distribution. The very complex nature of the particle laden flow within the above mentioned units requires the use of sophisticated computer simulations to obtain a detailed and accurate description of the flow field, temperature distribution, species concentrations as well as calculating the total heat loss and the overall pressure drop within each unit.

Although this study specifically targets the CMS^{TM} of Vortec Corporation, the end results could also be used, with minor modifications, in assessment of other type of incinerators for waste material. More importantly, this analysis can be extended to such cases where severely toxic and radioactive materials can be tested with computer simulations which would otherwise be impossible.

4.0 METHODOLOGY

The difficulties mentioned above can be resolved effectively using a readily available and extensively tested computational fluid dynamics (CFD) code. In this way, the PCB tracking can be done dynamically during the computation of the flow field where the local variations in the gas properties are automatically taken into account. Heat transfer and flow analysis, and PCB tracking will be performed using a commercial CFD code to numerically simulate the processes in the above mentioned units with the objective of providing supplemental information to improve the conceptual designs towards the most efficient system. Once such a code is reconfigured to simulate a certain unit, the key parameters can then be easily changed, and results can be obtained within a matter of days to determine optimum operating conditions.

The present computations are performed using the commercial code FLUENT (FUG-V4.3, 1995) This is a general purpose, multidimensional CFD code suitable for simulating flows in complex geometries. However, application to turbulent reacting flows is not

trivial. To achieve properly converged solutions, and to avoid misinterpretation of large amounts of numerical data, extreme caution and expertise both in physics of fluids and in computational fluid dynamics is necessary. Moreover, the chemistry sub-model for PCB tracking is not available in any of these codes. Such a model shall be developed and attached to the main code as a subroutine. It may be necessary to use the well known chemical kinetics code, CHEMKIN (Kee et al., 1980) and/or the general purpose chemical equilibrium code, CET (Gordon et al., 1984) in an interactive manner with the hydrodynamic data that will be obtained from the CFD code.

5.0 WORK PERFORMED THIS PERIOD

Work continued in this period on the residence chamber (or the recuperator base) first using the geometry reported in the previous quarterly report (referred to as the ***old geometry***). This geometry is without the vortex finder and the tangential air inlet is located at the bottom of the chamber (see Figure 2.1 and 2.2). The Vortec's engineers has assessed using the results from our preliminary calculations, as well as their engineering calculations and decided to select a ***new geometry*** with a vortex finder tube located in the central region of the chamber (see. Figure 3.0, and 3.1). The flow field, pressure drop, and residence time with various assumptions are calculated for the new geometry and results are presented in this report. The influence of wall roughness, and heat loss are also investigated. Literature survey on PCB kinetic rates are continued and reaction rates are compiled for selected PCB reactions. Some computational problems were encountered with regards to convergence and pressure drop calculations during three-dimensional simulations. These have been resolved.

6.0 RESULTS AND DISCUSSION

6.1 3D Flow Calculations (*old geometry*)

Figure 2.1 shows the geometry of the old residence chamber along with the contours of swirl velocity. For these simulations the diverging and converging sections of the chamber is represented by a step geometry in order to avoid the use of boundary fitted coordinates which increases the convergence time significantly. The swirl velocity of about 20m/s (positive W indicates counterclockwise direction) introduced at the inlet reduces rapidly to 10 m/s over most of the chamber volume. Near the center of the chamber there is a region of clockwise swirl velocity. Some sample particle trajectories are shown in Figure 2.2 to illustrate the motion of fluid particles in this geometry. These particles are representative fluid particle with five micron size, hence the trajectories are essentially streamlines (or streak lines).

During the simulations of this geometry problems are encountered in obtaining acceptable solution in the upper sections of the residence chamber which is basically a pipe flow. When pipe flow calculations are done in strictly three-dimensional space, convergence of the solution to a fully developed pipe flow with maximum velocity being at the center requires very stringent convergence criteria, e.g. residuals for the pressure and the axial velocity component should be less than 1.0E-5 at least. This difficulty related to the CFD code was not anticipated in advance and has caused considerable delay in obtaining accurate solutions for the other cases.

6.3 Results for the New Residence Chamber with Vortex Finder

Figure 1a & b show the geometry and the numerical mesh (fine grid) used for the three-dimensional simulations of the residence chamber for further reference.

Figure 3.1(a) shows the velocity vectors and profiles on a plane normal to the side walls as well as those on planes of two circumferential angles. The notation here is such that z-is the axial direction, y- is the radial direction, and x- is the circumferential direction, with respective velocity components, u, v, and w in z-, y-, and x-direction). Close up views of total velocity vectors are shown in Figures 3.1(b-d) at three planes, top (Fig. 3.1b), middle (Fig. 3.1c), and bottom (Fig. 3.1d). These figures reveal the following observations about the flow structure, (i) the flow seems to be fairly axisymmetric except maybe in the vicinity of the bottom inlet to the vortex finder tube. The swirl is much stronger in the outer tube compared to the inner tube, as expected, because the friction force dissipates the angular momentum initially imparted to the fluid at the inlet. Figure 3.1(d) shows how the direction of swirl is preserved in the inner tube in spite of the very complex nature of the two opposing fluid jets colliding with each other at the entrance to the vortex finder tube. It can be seen that the flow has a preferred direction for swirl which is counter clockwise, in spite of the fact that the inlet geometry is symmetric. Note also the presence of two counter rotating eddies on both sides of the main entrance jets. The

collision of the two jets is more clearly illustrated in Figure 3.2(a) where only the u-v components of the velocity vector is shown. It is apparent from this figure that the two jets spread towards the wall of the inner tube after colliding with each other. This leads to larger velocity near the wall. Thus the flow inside the vortex finder tube is significantly different than a conventional pipe flow.

Figures 3.2(a)-((d) show the u-v components of the velocity vectors where the plot is restricted only to the negative values indicating only the regions where the convection is in the negative z-direction towards the bottom. From these figure it is clearly seen that the flow is not uniformly distributed over the length of the outer tube. There are distinct regions where the flow reverses direction. These regions can be identified as recirculation regions where particulate matter and trace species can get trapped for a long time. These regions should lead to an increase in gas-residence time but considering particulate matter they may be the critical in that where deposition can occur with eventual pilling up of solid residues. These observations are confirmed by particle trajectory calculations as shown in Figure 3.5(a).

The contours of the swirl velocity component are shown in Figures 3.3(a)and (b). It is seen that, in general, the swirl strength decreases from the outer wall towards the inner wall, and it also decreases towards the bottom of the outer tube with changing local minima and maxima. The presence of a high degree of swirl as the flow enters the inner tube is noteworthy. The swirl inside the vortex finder tube is about one third of the initially imparted swirl.

Pressure Drop Calculations:

Pressure drop calculations are obtained from contour plots such as those shown in Figures 3.4 (a) and (b). The pressure drop calculations from FLUENT are verified for the case of a 3D pipe flow of diameter, D=0.61m, length, L=12.2m with an inlet velocity of 16.65 m/s. The calculated pressure drop is 18.46 Pa compared to the estimated pressure drop of 13.1 Pa from Moody's diagram for a fully developed flow in the same pipe. Considering the fact that in the simulated case there would be significant entrance loss, the agreement between the calculated and estimated pressure drops is found to be adequate.

The calculated drop in the total pressure from the inlet to the outlet of the residence chamber for various cases are shown in Table 2. It is seen that the system pressure drop is in the order of 300 Pa for all cases. The comparison of Cases C10 and C10C shows the sensitivity of the numerical solution to the grid size. Whenthe grid size is reduced by half the pressure drop increases by about 8% . Cases C10 and C10U show the difference between a lower order scheme (i.e. the first order upwind difference) and a higher order scheme (QUICK). It is expected that with the same grid the higher order scheme should give more accurate results; a difference of about 7% is observed between the two.

The drop in the static pressure in the system was also calculated. The mass-weighted static pressure drops are: 110.1, -13.0, 91.4, 101.6, and 104.6 Pa for cases C10, C10C, C10U,

C11, and C10R, respectively. The area-weighted values were approximately the same as those of the mass-weighted ones. These results show that static pressure drop is very sensitive to the grid, and numerical scheme. It is recommended that the mass weighted total pressure drops are used as a measure of the overall system pressure drop.

Effect of wall roughness:

The walls of the residence chamber is to be constructed from commercial brick. An equivalent wall roughness height was selected using the values for concrete as a guide. A conservative value of , k=5.35 mm (0.216 inches) is used uniformly for all walls. To our surprise the inclusion of the roughness in the flow calculations did not change the system pressure drop significantly. The increase in the pressure drop due to wall roughness was about 5 Pa (see Table 2).This is most probably because the dimensionless roughness, $k+ = k u_* / \nu$, (here k is the roughness height, u_* is the friction velocity, and ν is the kinematic viscosity) was in the lower range of $k+ < 15$ over most of the wall surface such that the flow is in the so called "hydraulically smooth" regime (see White, 1991). When the flow is in the hydraulically smooth regime the velocity profiles near the wall are approximately the same as those of "smooth" walls. Hence the influence of the wall roughness would be negligible.

Table 1 Operating conditions

Mass flow rate:	1.0 kg/s (1751 scfm) of air
Pressure:	1.0 atm.
Temperature:	1694 K (1590 °F) isothermal flow conditions
Density	0.2057 kg/m^3
Wall roughness:	5.35 mm (0.216 inches) ; for Case C10R only
Geometry:	New residence chamber with vortex finder

Table 2 Predicted pressure drop* for the conditions of Table 1

Case #	mass averaged pressure drop (Pa)	area averaged pressure drop (Pa)	comments
C10	300	248	symmetry cells at the centerline
C10C	275	224	coarse grid version of Case C10
C10U	321	321	Same grid as Case C10 with QUICK scheme
C11	300	248	Same grid as Case C10 with "axis" option
C10R	304	305	Same grid as Case C10 with wall roughness

* The pressure drop is calculated using the total pressure not the static pressure.

Gas-Residence Time Calculations:

Gas-residence calculations are performed using several methods. Sample fluid particles of five micron size are tracked through the chamber after they are injected at the inlet using first the mean fluid motion as input, and then the instantaneous fluid motion as input. The later involves a random selection of fluid velocity from a prescribed probability distribution function to represent the turbulent nature of the flow. This approach is referred to as the

random walk method. The residence time is also calculated using the flow-through curve (FTC) method as explained in the previous quarterly report. Here some amount of marked fluid is injected into the reactor instantaneously (approximately of 0.1 sec duration for the present study). The time variation of the mean, outlet concentration of that scalar is tracked in time (see Figure 3.6). This curve is then used to calculate certain time scales to be used as indicator of the gas-residence time.

Figure 3.5(a) shows the trajectory of a sample fluid particle released at the inlet. Note that the sign convention for the particle calculations is not the same as the flow field calculations. Hence the particle trajectories exhibit a clockwise swirl as opposed to the counterclockwise motion seen in Figure 3.(a)-(d). It is interesting to note that this particular particle first travels upward then downward while swirling around the inner tube. Near the middle section of the chamber the particle almost levitates. It even moves upward (towards the recuperator) momentarily, then escapes this trap and finally enters into the inner tube at the bottom. Inside the inner tube (the vortex finder) the particle has very little swirl velocity, hence it travels along a relatively straight trajectory to the outlet of the chamber. Another particle trajectory with a short residence time is shown in Figure 3.5(b). It is observed that the particles spend relatively short time inside the vortex finder. This can be enhanced by allowing the fluid enter the vortex finder tube tangentially rather than radially as is the case in the present design.

Figure 3.6 shows the flow through curve (FTC) for the new geometry using 3D isothermal flow calculations. It takes 2.73 seconds for 50% of the mass injected to pass through the residence chamber. Peak concentration passes through the outlet after about 2.0 seconds. The average residence time calculated using the first area moment is 3.28 seconds. A summary of the calculated residence times is given in Table 3. This table clearly shows that in all cases the gas-residence time is greater than or equal to 2.0 seconds. The random walk method yields in general larger residence times. Preliminary calculations with heat loss seem indicate a slight increase in residence time. The average residence time calculated from the flow through curve which is 3.28 sec is recommended for design purposes. It is interesting to note that the old geometry also gives a residence time of about 2.0 seconds.

Table 3. Summary of calculated average residence times

	Case Description	Based on :	# of Particles Used	Residence Time
1	Isothermal, OLD 3D geometry	mean velocity	16	2.34 sec
2	(same as #1)	3 step random walk	3 x 16	3.57 sec
3	Isothermal, NEW 3D geometry	mean velocity	32	1.99 sec
4	(same as #3)	3 step random walk	3 x 32	2.49 sec
5	NEW 3D geometry with heat loss	mean velocity	32	2.27 sec
6	(same as #5)	3 step random walk	3 x 32	2.41 sec
7	(same as #3)	fist moment of FTC	--	3.28 sec

Influence of Wall Heat Loss:

A total heat loss of 285,000 Btu/hr (83,520 J/s) is applied to the new geometry. The heat loss is uniformly distributed over the outer walls of the residence chamber at a rate of 2440 W/m^2. Preliminary results (Figure 3.7) indicate that there is a temperature drop of about 70 K from the inlet to the exit. The minimum temperature observed inside the chamber is about 1150 K localized to small region. It should be emphasized that these results with the heat loss are preliminary. More accurate results will be obtained, and the consequences of these on the species concentrations will be investigated further.

6.4 PCB Kinetic Rate Data

The flue gas composition distribution as it enters the residence chamber is shown in Table 4. The total PCB concentration is about 175 PPM. As a first order approximation we intend to represent all PCB by a single component which will be selected in consultation with Vortec engineers. A compound which is difficult to destroy is Methyl Chloride. This can be considered for further study. According to the data of Lee et. al. (1982) a temperature of 1514 ^0F (1096 K) is necessary at 2.0 seconds residence time to obtain 99.99% conversion compared to 1372 ^0F (1017 K) for Chlorobenzene. If Chlorobenzene is used as a single PCB compound to represent all the others it is seen that the mass fraction of PCB compounds constitutes about 0.2% of the flue gas on mass bases. The organic compounds that will be targeted are listed in Table 5 along with the available reaction rate data obtained from the literature (see e.g. Lee at al., 1982). For the compounds given in this table without reaction rate we have information that could be used implicitly to obtain reaction rates. Currently we are in the process of completing this table while running a case with heat loss including Chlorobenzene conversion.

The PCB reaction rate data is based on a first order Arrhenius type reaction mechanism for an over all reaction of the following form

$$C_aH_bCl_d + [a + (b-d)/4\ ]\ O_2 \Longrightarrow a\ CO_2 + d\ HCl + [(b-d)/2]\ H_2O \qquad (6.3.1)$$

HCl is known to be stable at fairly high temperatures but the following reaction can also be considered at very high temperatures:

$$2HCl + 1/2\ O_2 \quad <\Longrightarrow \quad Cl_2 + H_2O \qquad (6.3.2)$$

In order to investigate NO_x formation the well known Zel'dovich mechanism can be used. More up-to-date reaction rates are available for NOx formation in Rizk and Mongia (1995). In addition to the above soot formation should also be considered. The relevant reactions for this are(VanDell and Shadoff, 1984):

$$C_aH_bCl_d + [a + (b-d)/4\ ]\ O_2 \Longrightarrow a\ C(s) + d\ HCl + [(b-d)/2]\ H_2O \qquad (6.3.3)$$

$$C(s) + O_2 \quad \Longleftrightarrow \quad CO_2 \qquad (6.3.4)$$

If there is considerable amount of H2 in the flue gas then the Following reactions should be considered (Ritter and Bozzelli, 1990)

Dichlorobenzene:

$$C_6H_4Cl_2 + H_2 \Longrightarrow \quad C_6H_5Cl \quad + \quad HCl \qquad (6.3.5)$$

Chlorobenzene:

$$C_6H_5Cl + H_2 \Longrightarrow \quad C_6H_6 \quad + \quad 2HCl \qquad (6.3.5)$$

The global reaction of benzene, C_6H_6, is to be followed by Equation 6.3.1

Table 4.0 Mass fractions of exhaust gas entering the residence chamber

Compound	mass (kg/s)	mass fraction
CO_2	.1916	.1915
H_2O	96.56e-3	99.59e-3
N_2	.6519	.6514
O_2	26.84e-3	26.82e-3
SO_2	0	0
Particulate Mass (PM)	14.11e-3	14.10e-3
C_6H_5Cl	19.69e-3	19.68e-3

note: C_6H_5Cl is calculated from the given concentration of 175 PPM PCB present in the flue gas. C_6H_5Cl was assumed to represent the whole mixture of PCB compounds.

Table 5. Thermal oxidation parameters for selected hydrocarbons (Incomplete Table)

Formula	Compound	A (1/sec)	E cal/g-mole	Lower Limiting Temp (F)	Auto-Ignition Temp (F)
C_6H_6	Benzene	7.43e21	95900	1275	1044
C_6H_5Cl	Chlorobenzene	1.34e17	76600	1350	1180
$C_6H_4Cl_2$	m-Dichlorobenzene*	2.10e12	62570		
$C_2H_4Cl_2$	1,2-Dichloroethane	4.82e11	45600	1050	775
CH_4	Methane	1.68e11	52100	1200	999
CH_3Cl	Methyl Chloride	7.34e08	40900	1500	1170
CH_2Cl_2	Dichloromethane	1.38e08	41730		
$CHCl_3$	Trichloromethane	5.47e11	46040		
CCl_4	Tetrachloromethane	1.48e08	35280		
$C_{10}H_{18}$	Naphthalene	---	---		

* Dichlorobenzene reaction is in H_2

7.0 CONCLUSIONS (*for the current period of performance*)

The computer simulations of the three-dimensional, turbulent, isothermal flow inside the residence chamber with the vortex finder showed that the system pressure drop in the total pressure is about 300 Pa. The gas-residence time calculated in several ways is greater or equal to 2.0 seconds. Recirculation zones are detected inside the outer tube which act as a trap for the scalar quantities and particulate matter. This increases the residence time, but may be not so desirable when particle deposition is considered. The swirl inside the vortex finder tube is relatively weak. Introducing the flow tangentially into the vortex finder tube can increase the residence time further. The wall roughness does not seem to have a significant effect on the overall flow structure nor on the system pressure drop. Preliminary results with about 4% heat loss from the walls of the residence chamber indicate a temperature drop of about 70 K from the inlet to the outlet. This shall be investigated closely in the feature. PCB reaction rate data compilation is near completion. Conversion rates will be calculated for some critical compounds in the next quarterly period.

8.0 WORK PLANNED FOR NEXT PERIOD

Mainly due to the new geometry selected by the Vortec engineers the schedule for completing the analysis of the recuperator base (i.e. residence chamber) had to be extended. Also it was requested by Vortec that the analysis of the recuperator be performed prior to that of the reservoir/separator. The changes in time schedule is partly due to the fact that we had to perform three-dimensional calculations based on our findings as reported in the previous quarterly period. Three-dimensional calculations are very difficult in that the computer time and storage needed increases exponentially leading to serious convergence problems and significantly long turn around times. The changes are reflected in the following new tasks order and time schedule planned. In the new schedule the old Tasks 4 and 5 are interchanged.

Task 1. Information required for the National Environmental Policy Act

Task 2. *(1 month)* Gathering of system specific-information, e.g. geometry, gas composition, conceptual design criteria etc., in consultation with Vortec.

Task 3. (*6 months*) Analysis of the recuperator base

Task 4. (*1.5 months*) Analysis of the recuperator (***old Task 5***)

Task 5. (*2.5 months*) Analysis of the separator/reservoir (***old Task 4***)

Task 6. (*1 month*) Analysis of the results for the whole system and preparation of the final report.

In the next quarterly period Tasks 3 and 5 will be completed. The research will focus on calculation of destruction efficiency for selected PCB compounds.

APPENDIX

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White, F. M. (1991) Viscous Fluid Flow, Chap. 6, McGraw-Hill, Inc. New York

FIGURES

VORTEC'S CMS SYSTEM

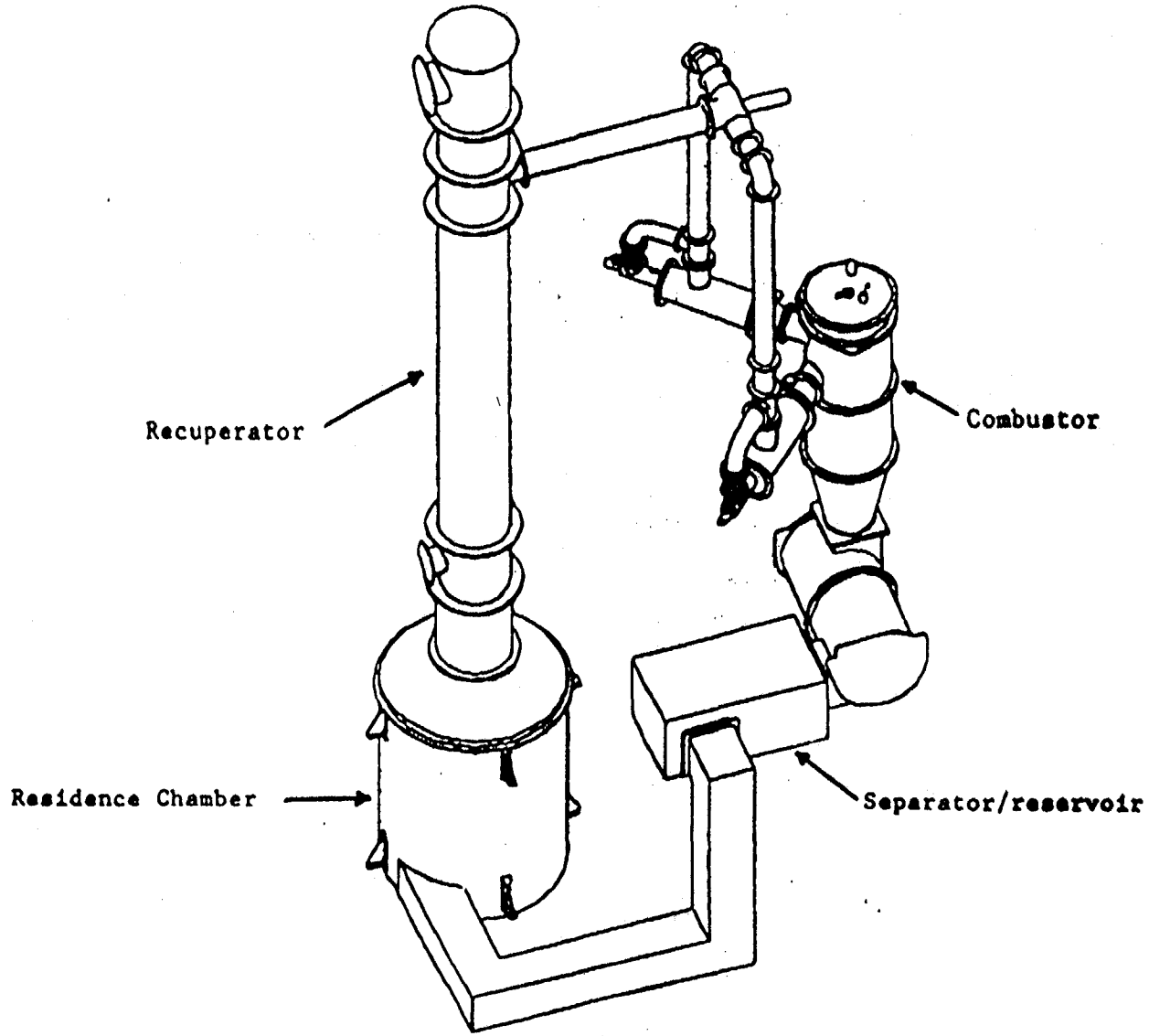
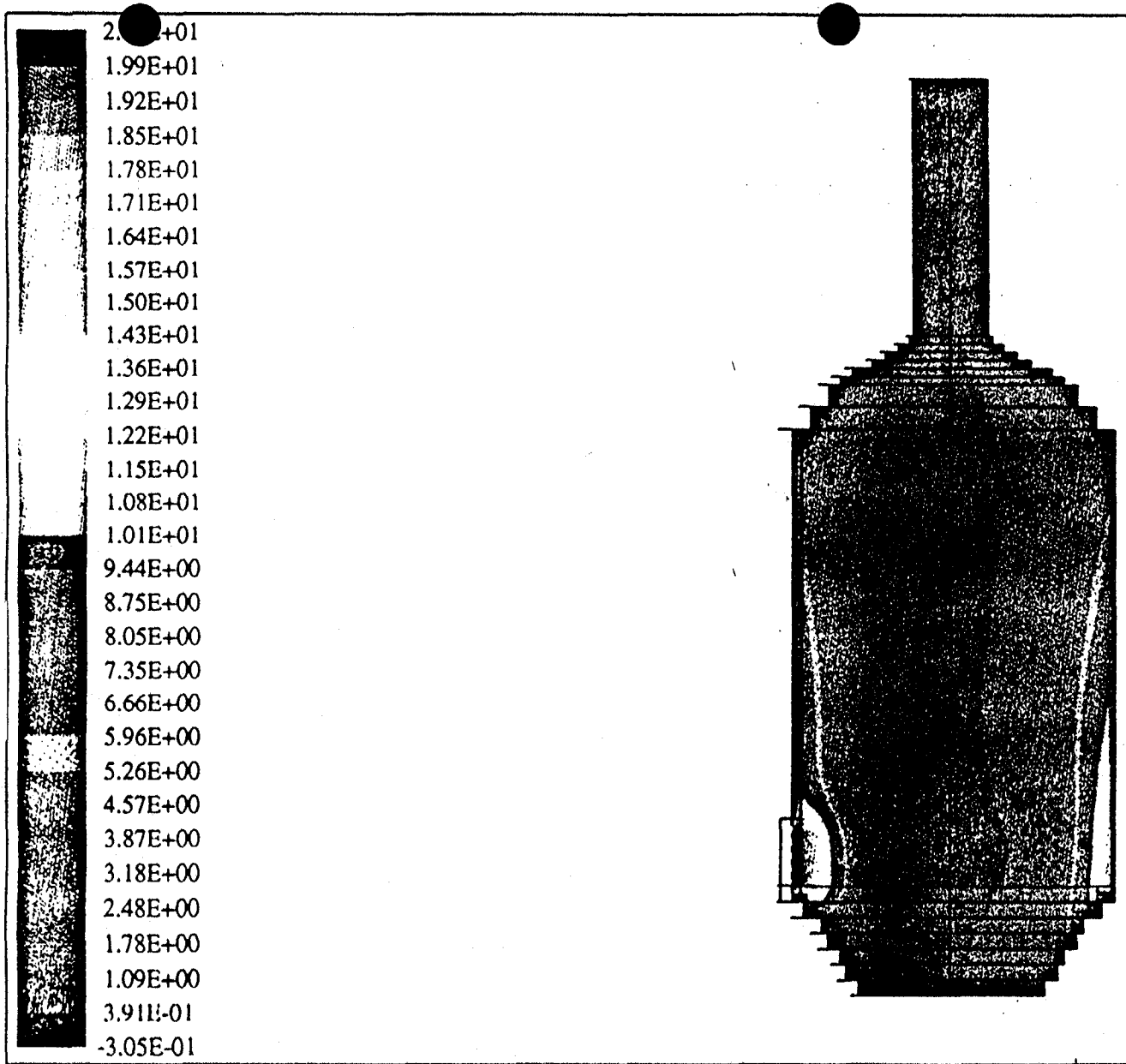


Figure 1. Vortec CMS™ System Sketch

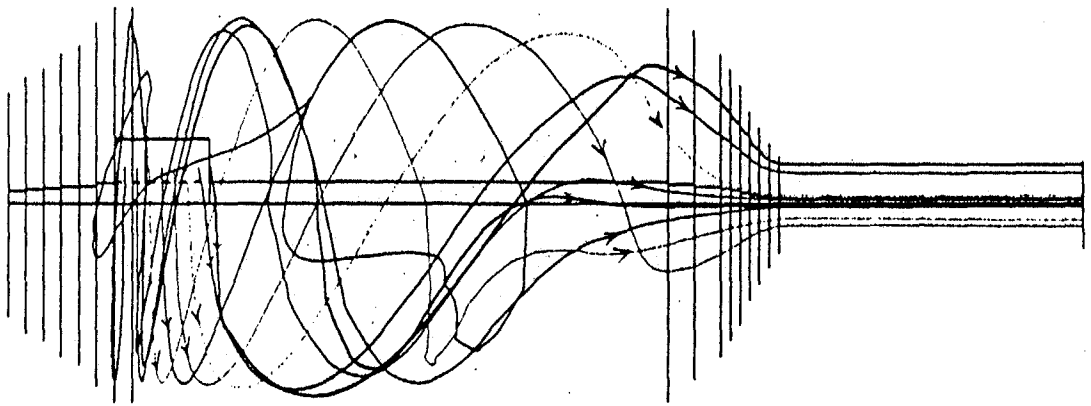


L8

X
Y Z

VORTEC RESIDENCE CHAMBER: 3D
Figure 2.1 Swirl Velocity Contours (m/s) (w velocity)
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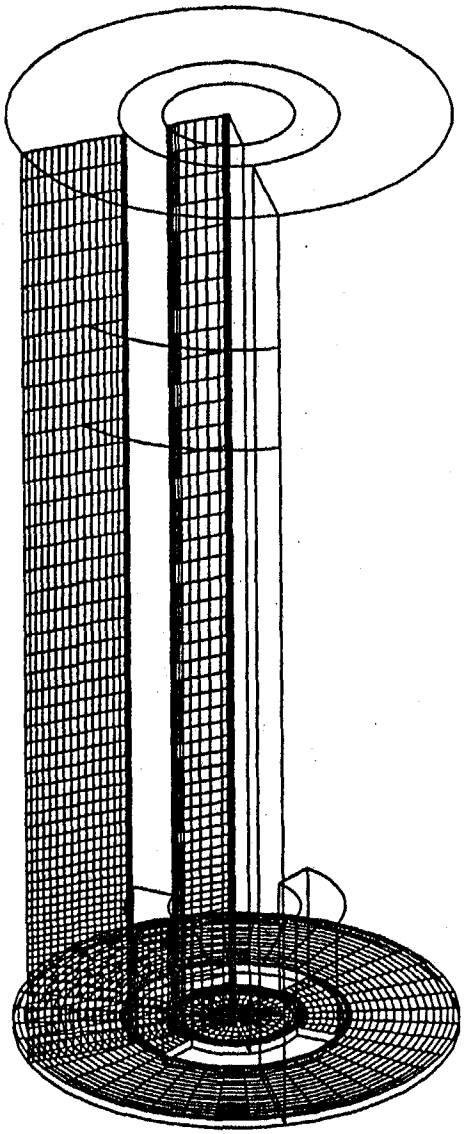
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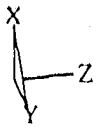


VORTEC RESIDENCE CHAMBER: 3D (Old geometry)

Figure 2.2 Particle trajectories for particles A-H

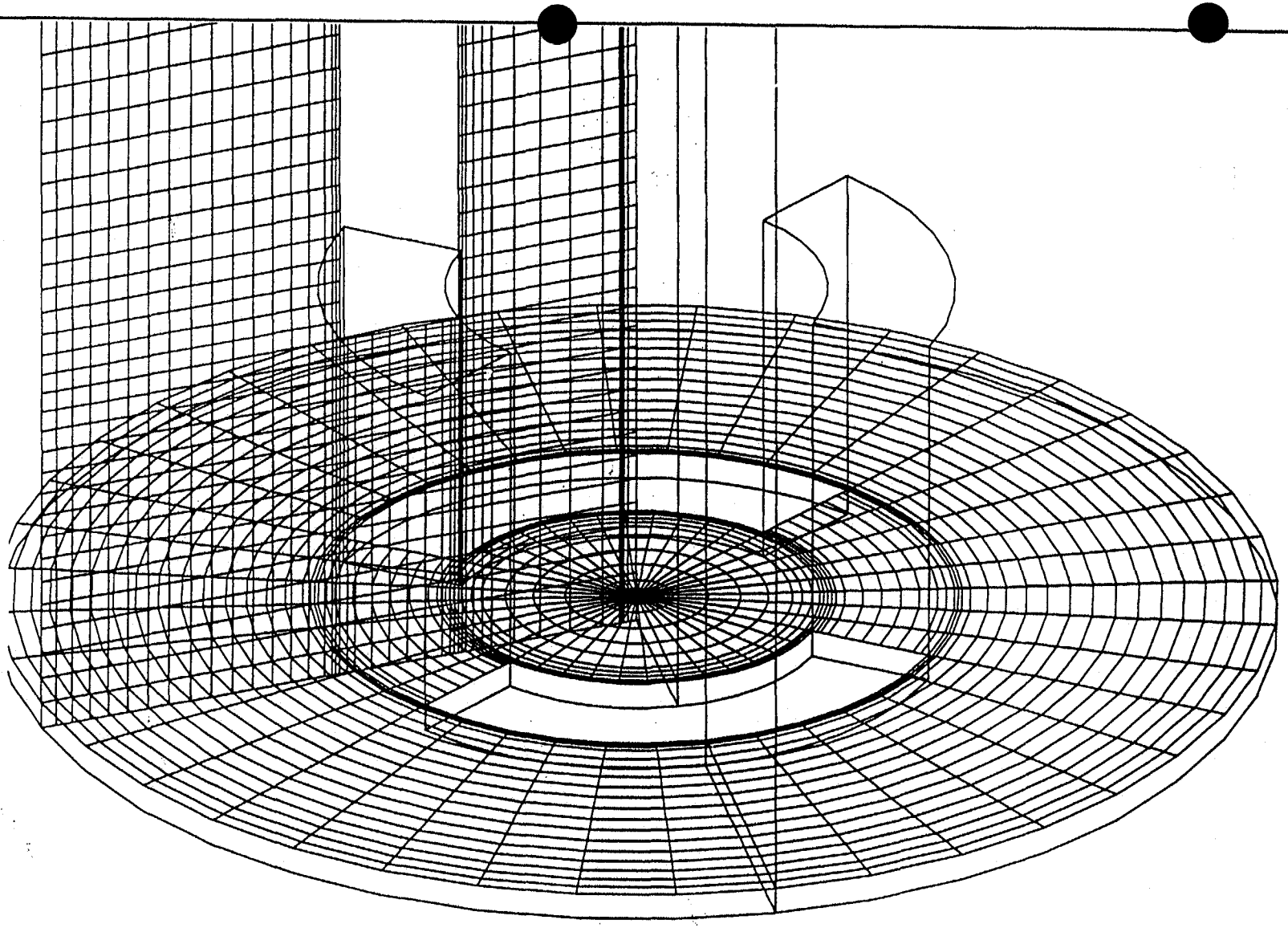
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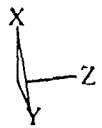




VORTEC RECUPERATOR BASE NEW 3D GEOMETRY
Figure 3.0a Grid Profile (41 X 53 X 61)
Slices: K=2, I=1

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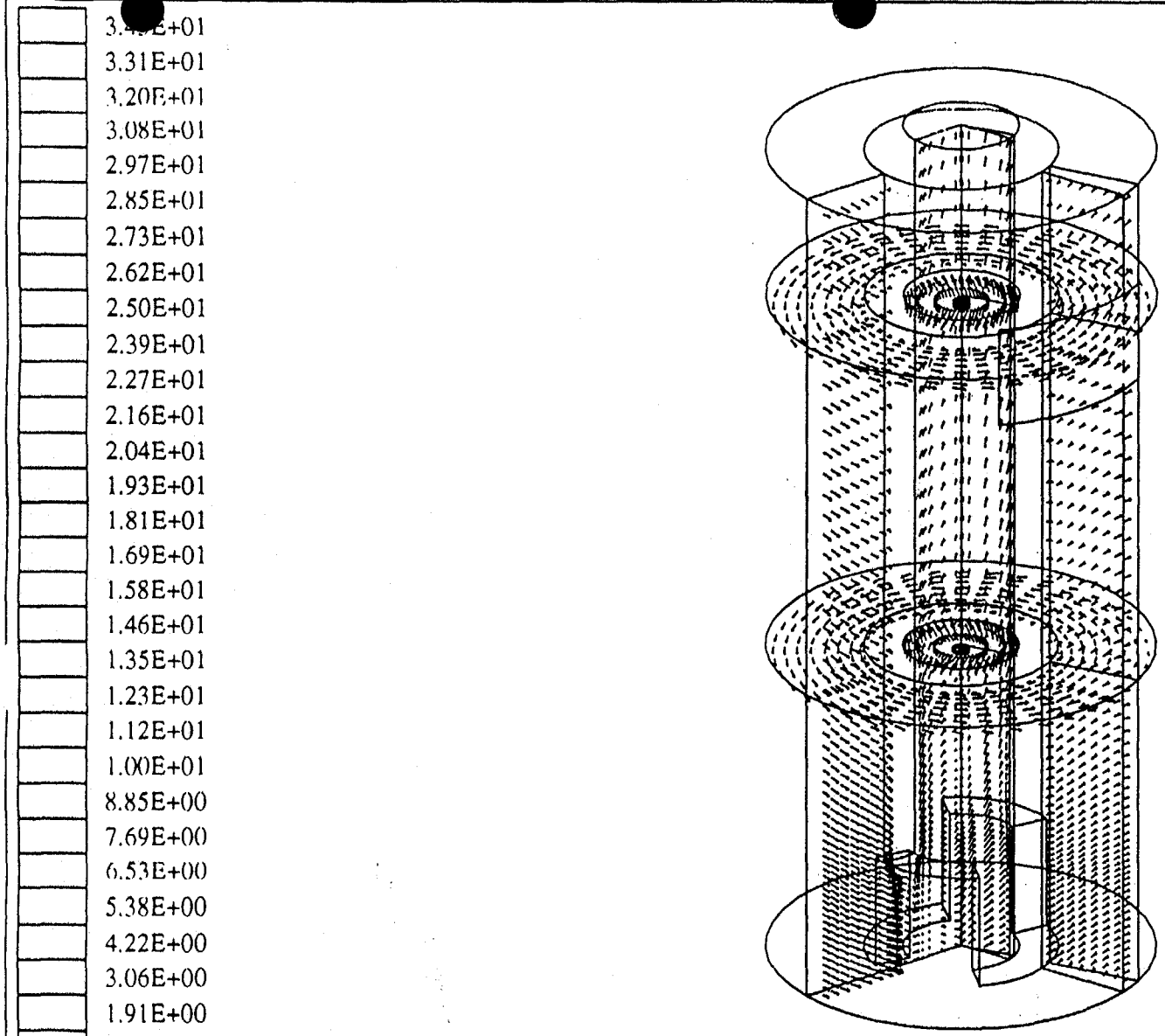


VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.0b Enlarged View of Grid Profile (41 X 53 X 61)

Slices: K=2, I=1

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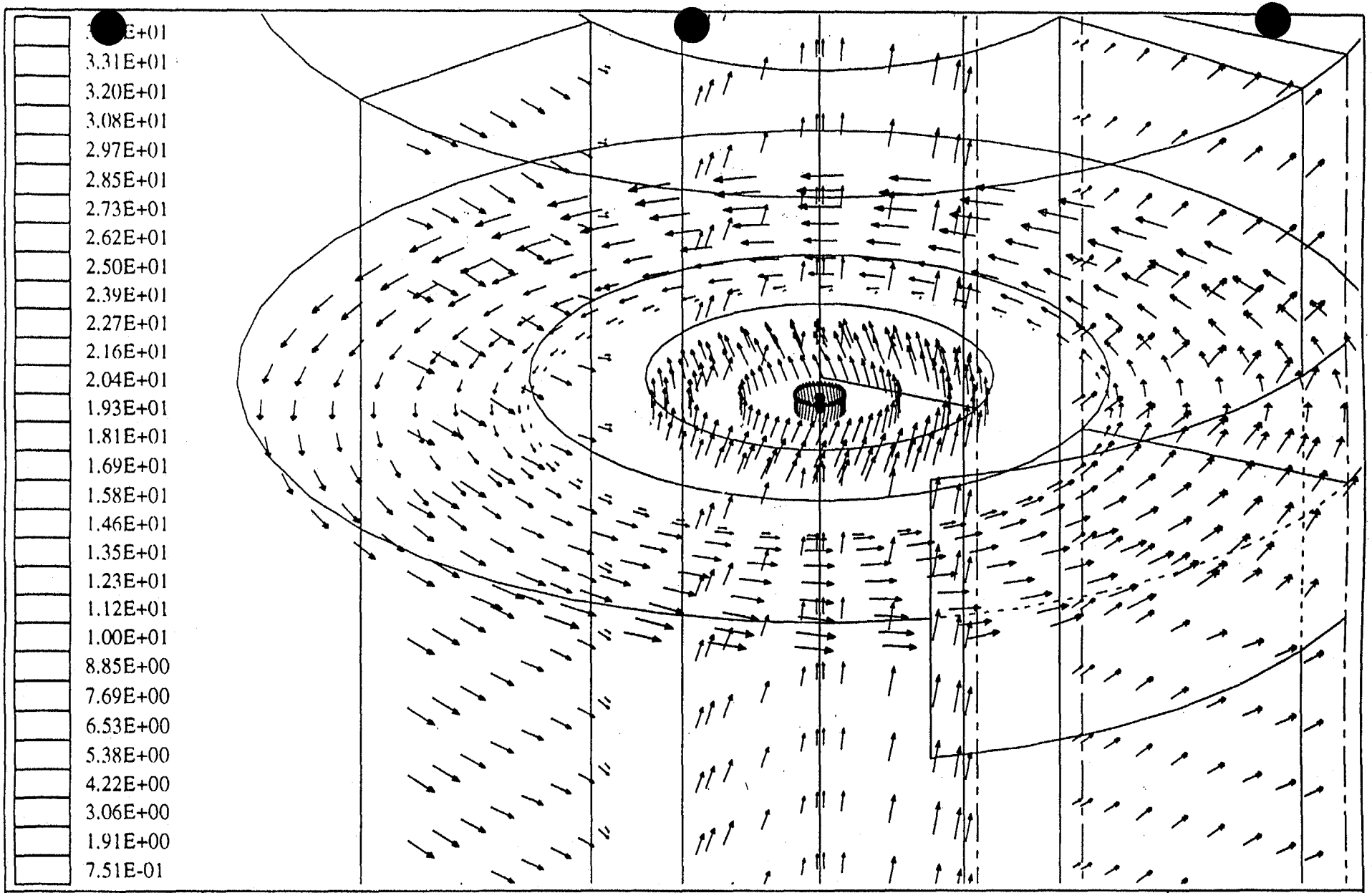


VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.1a Velocity vectors (m/s) at k=36 and 54 planes

Lmax = 3.429E+01 Lmin = 7.513E-01

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7b



VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

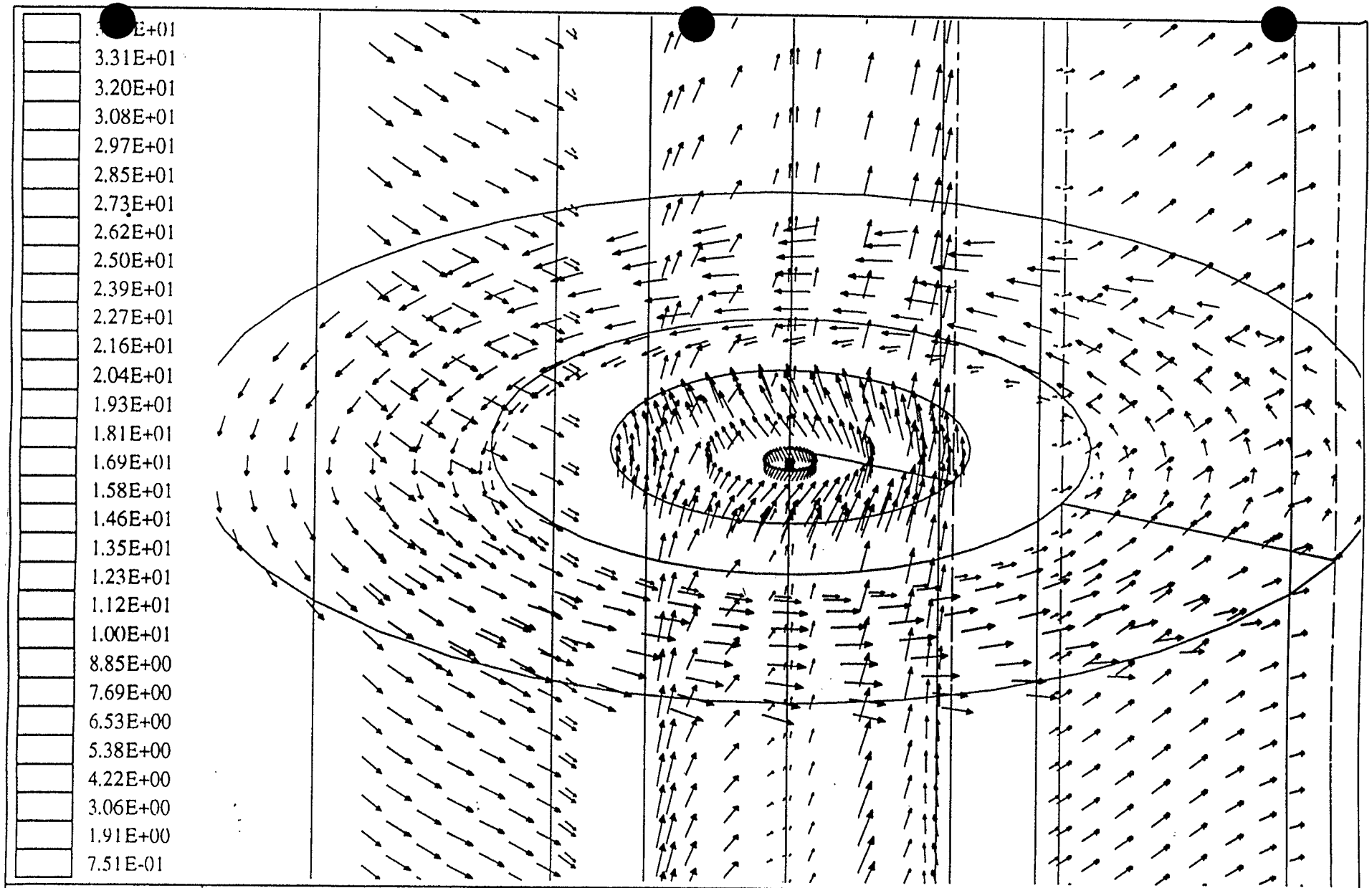
Figure 3.1b Velocity vectors (m/s) at k=36 and 54 planes (Enlarged view)

Lmax = 3.429E+01 Lmin = 7.513E-01

Jun 17 1996

Fluent 4.32

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VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

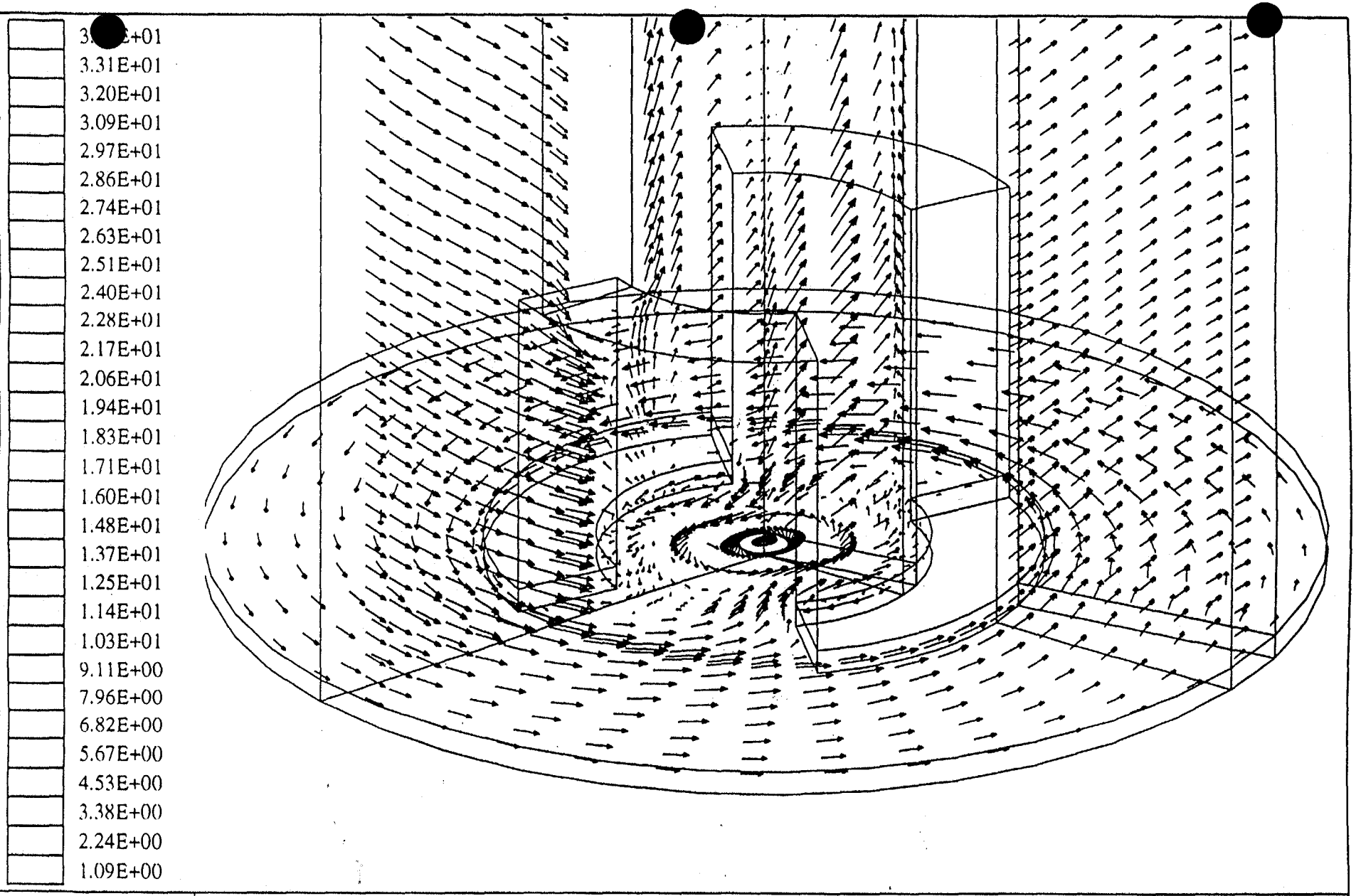
Figure 3.1c Velocity vectors (m/s) at k=36 and 54 planes (Enlarged view)

Lmax = 3.429E+01 Lmin = 7.513E-01

Jun 17 1996

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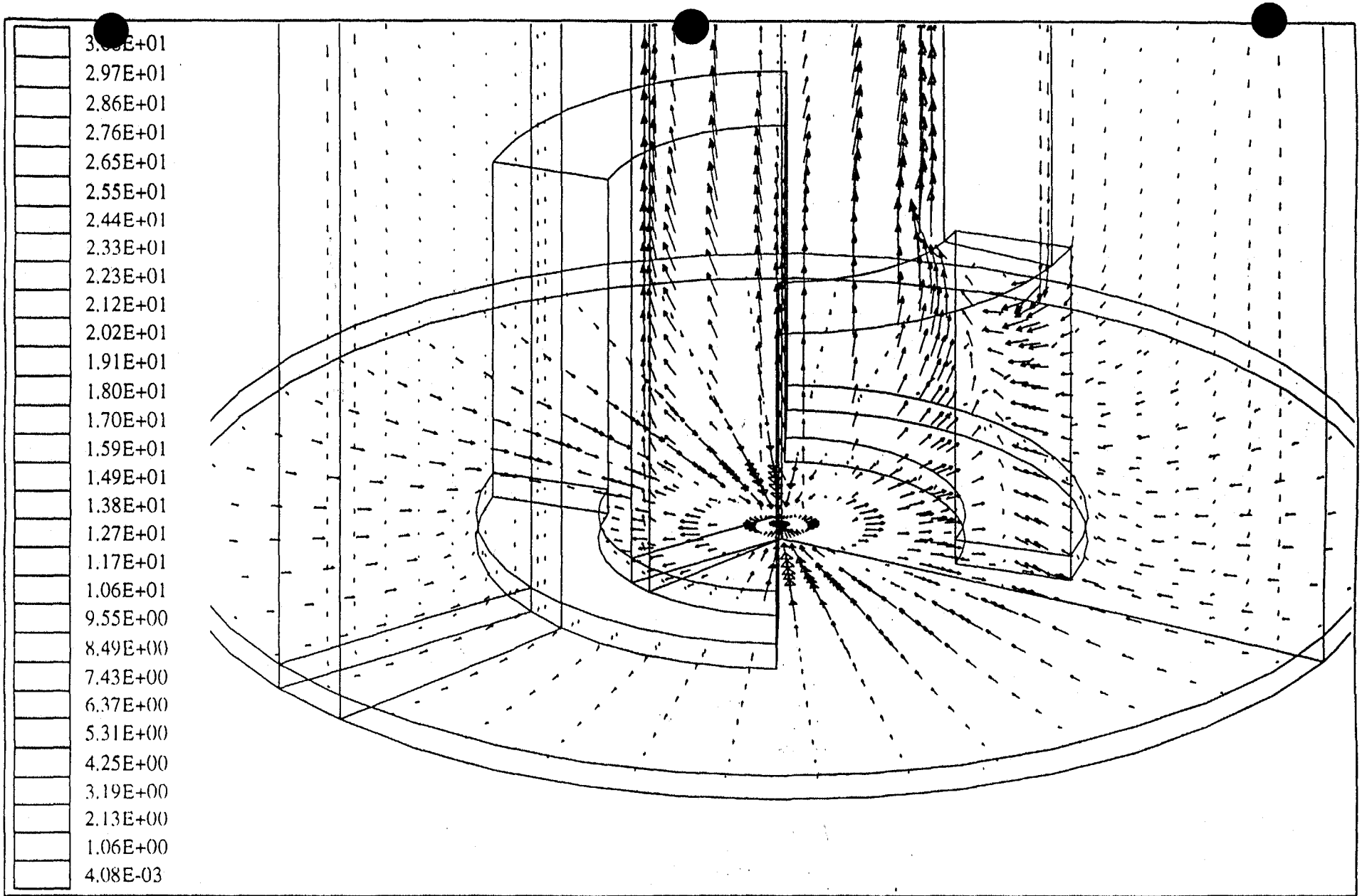


VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.1d Velocity vectors (m/s) (Enlarged view of the base)

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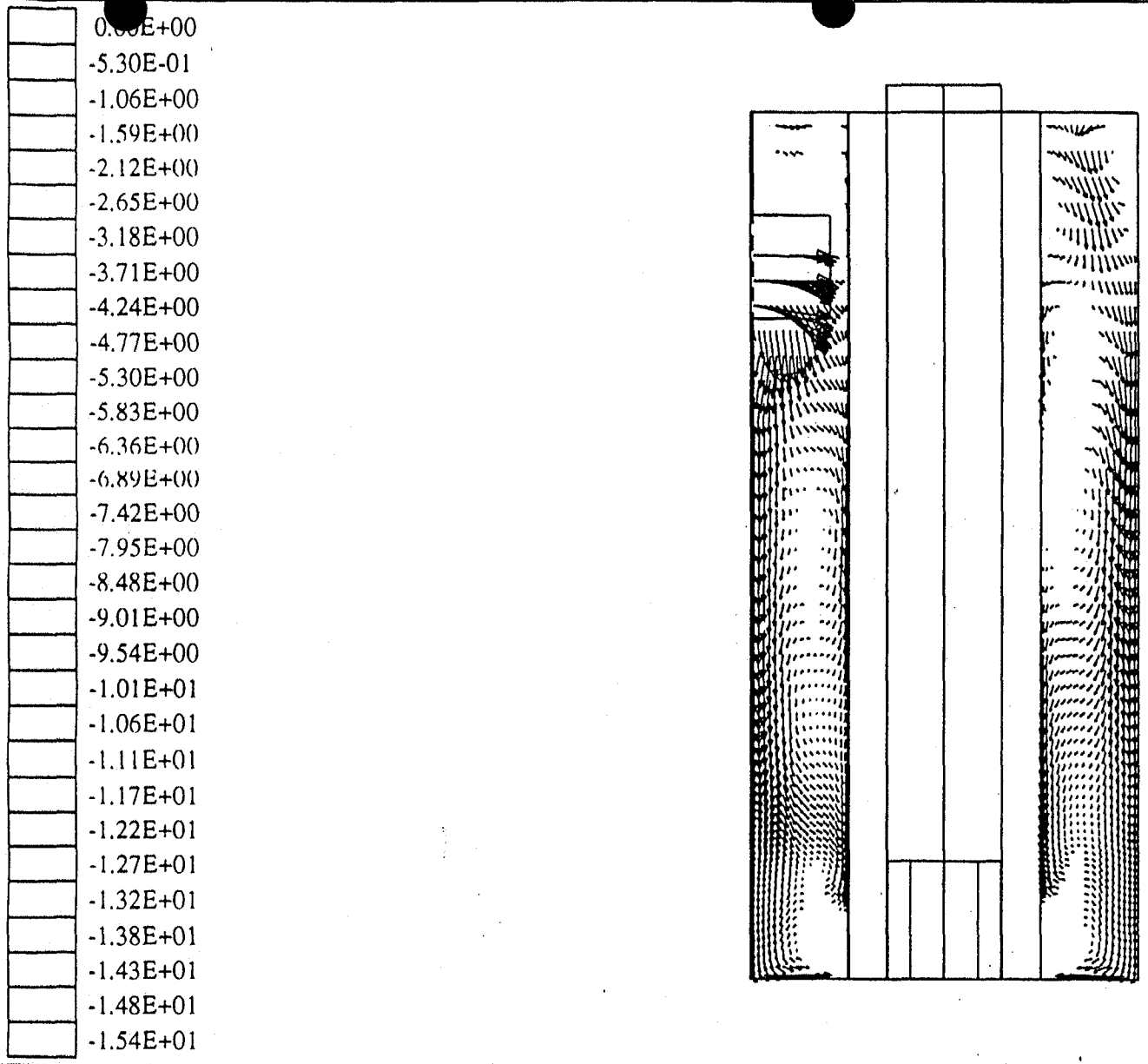


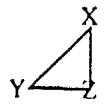
VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.2a Velocity vectors (u & v) [Enlarged view of base]

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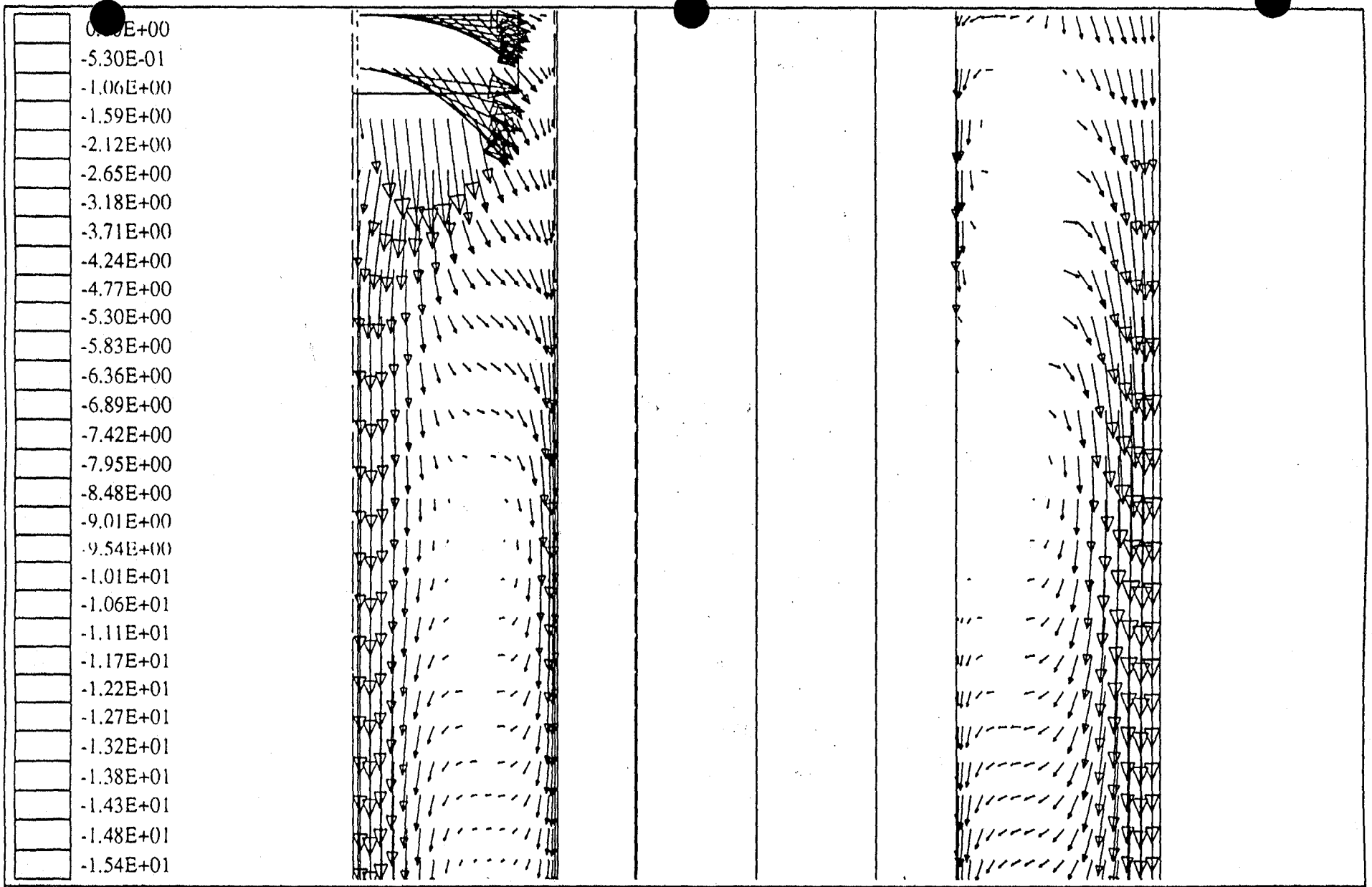


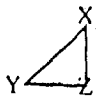
VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.2b Velocity vectors (m/s) (u & v components)

Colorbar is adjusted to show recirculation zones in the flow

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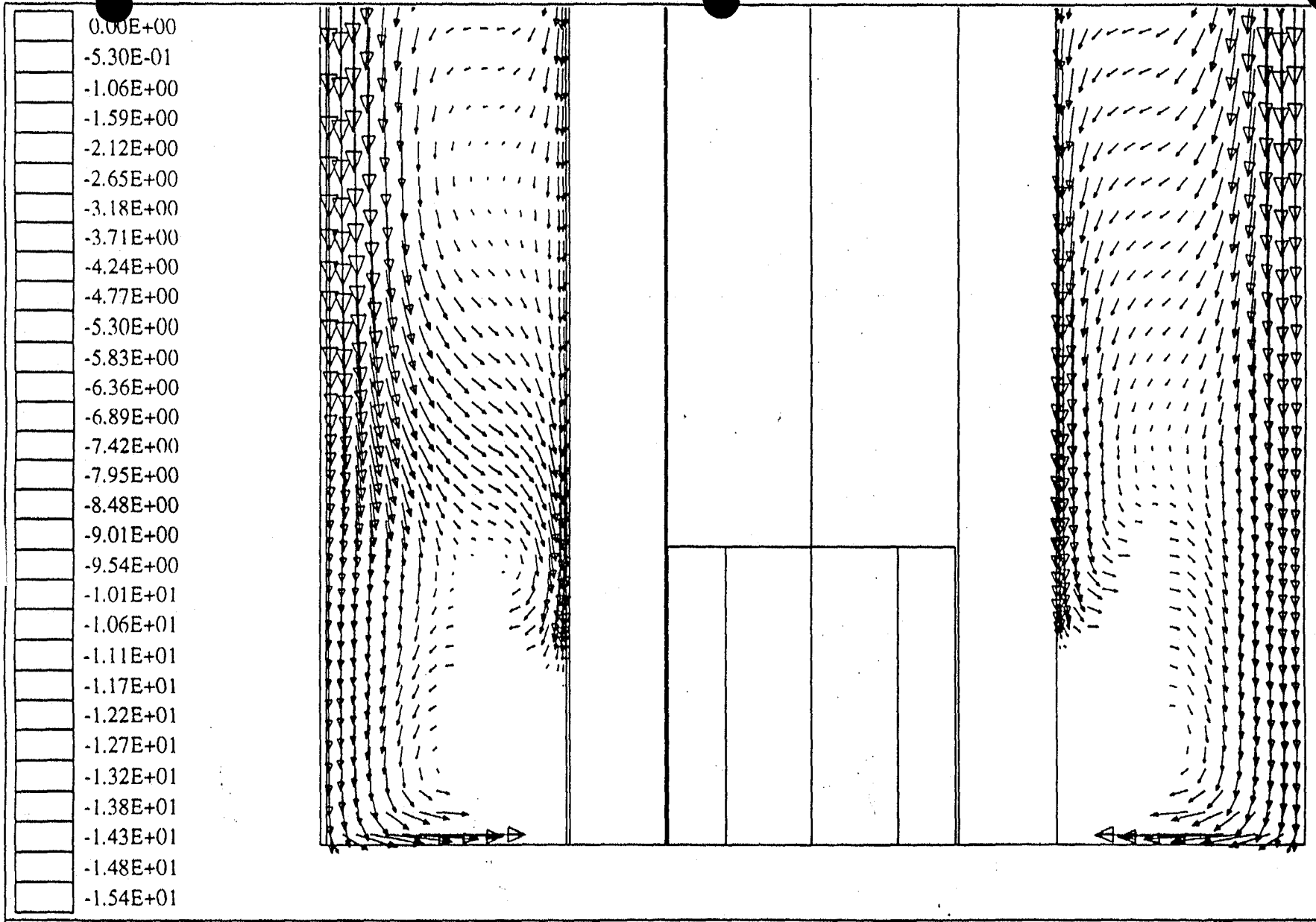


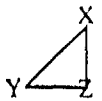
VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.2c Velocity vectors (m/s) (u & v components)

Colorbar is adjusted to show recirculation zones in the flow

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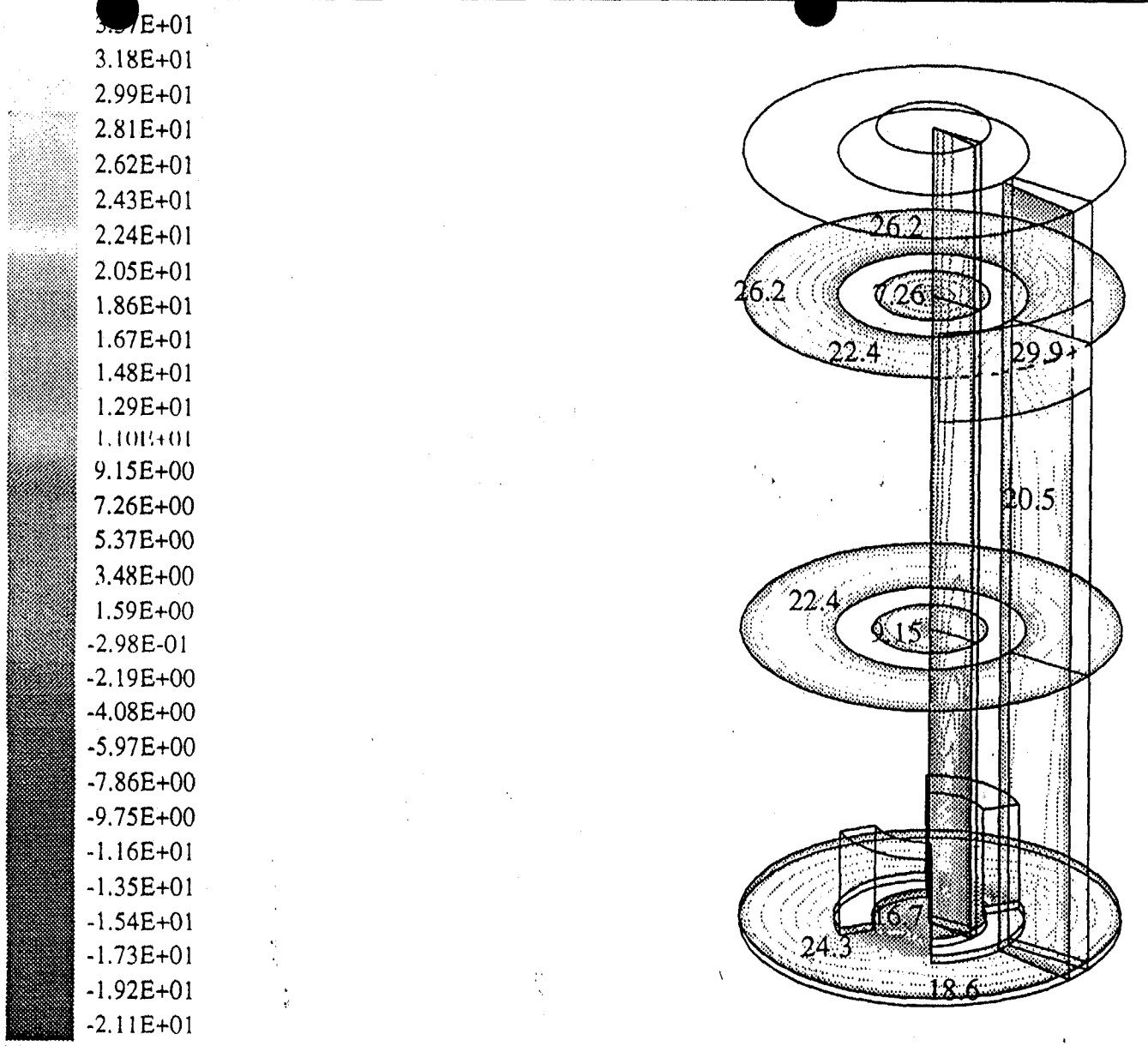


VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.2d Velocity vectors (m/s) (u & v components)

Colorbar is adjusted to show recirculation zones in the flow

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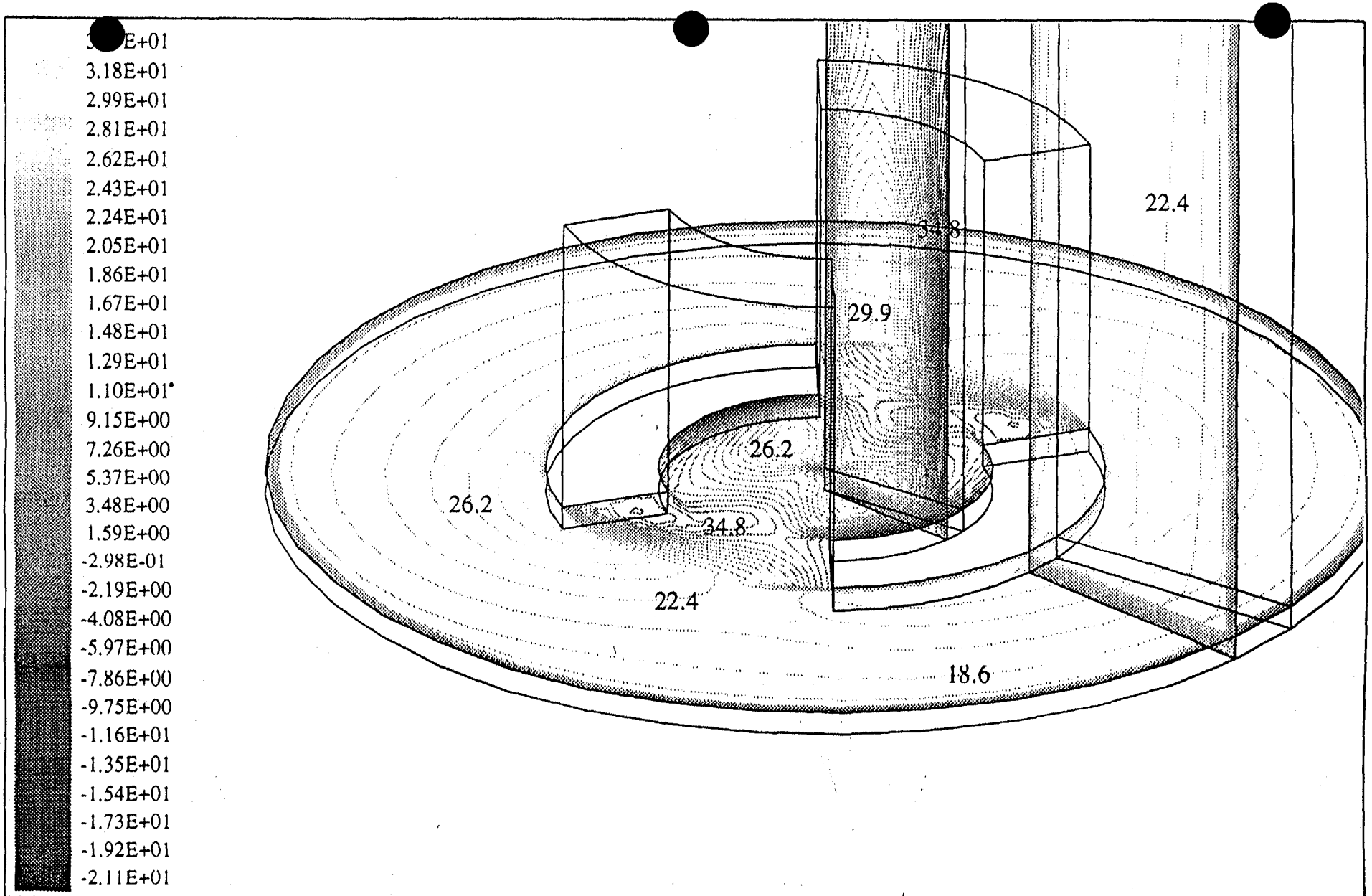
X
Z
Y

VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.3a Swirl velocity (m/s) contours

Lmax = 3.373E+01 Lmin = -2.109E+01

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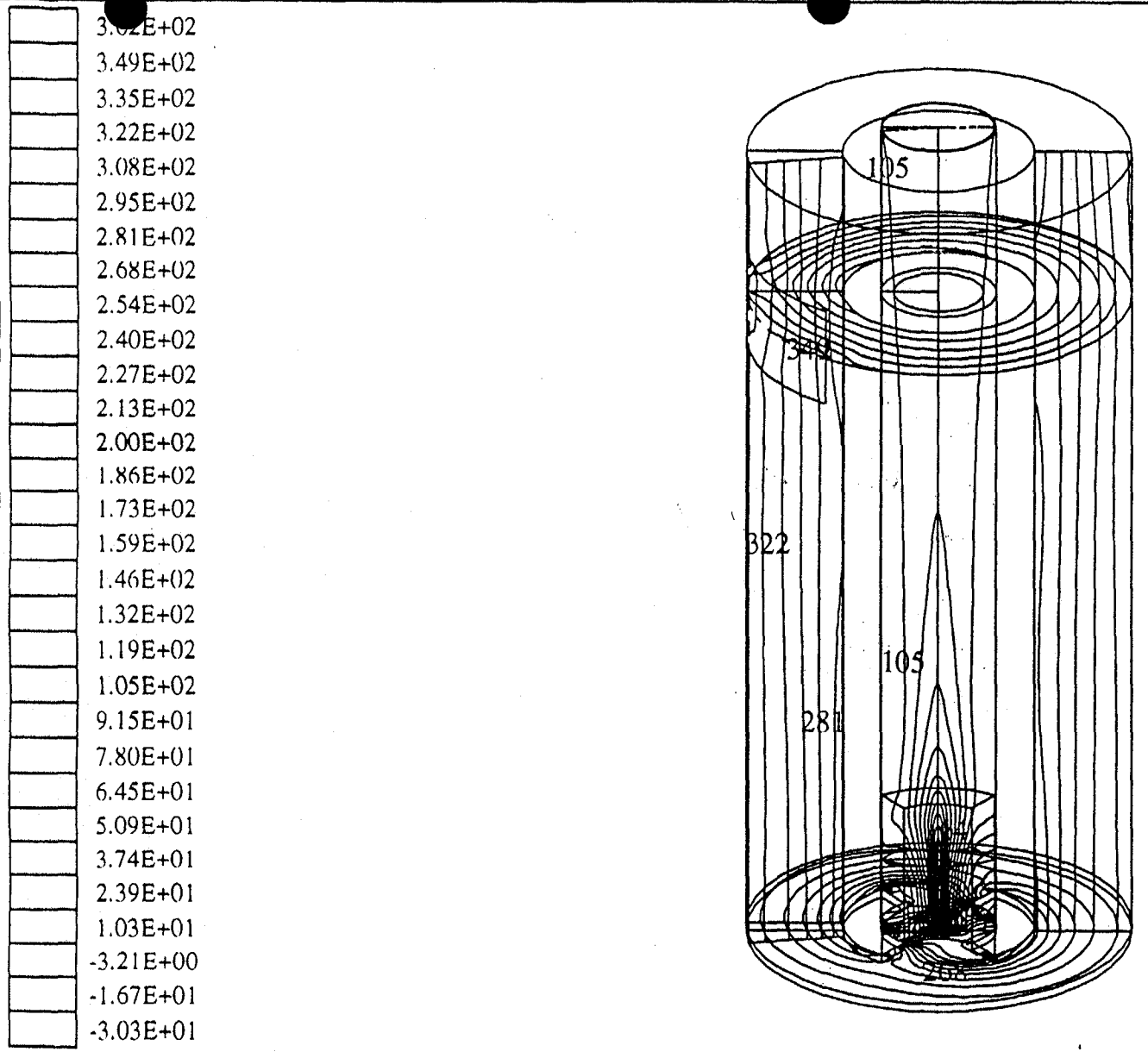
X
Z
Y

VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.3b Swirl velocity (m/s) contours (Enlarged view of k=2

Lmax = 3.373E+01 Lmin = -2.109E+01

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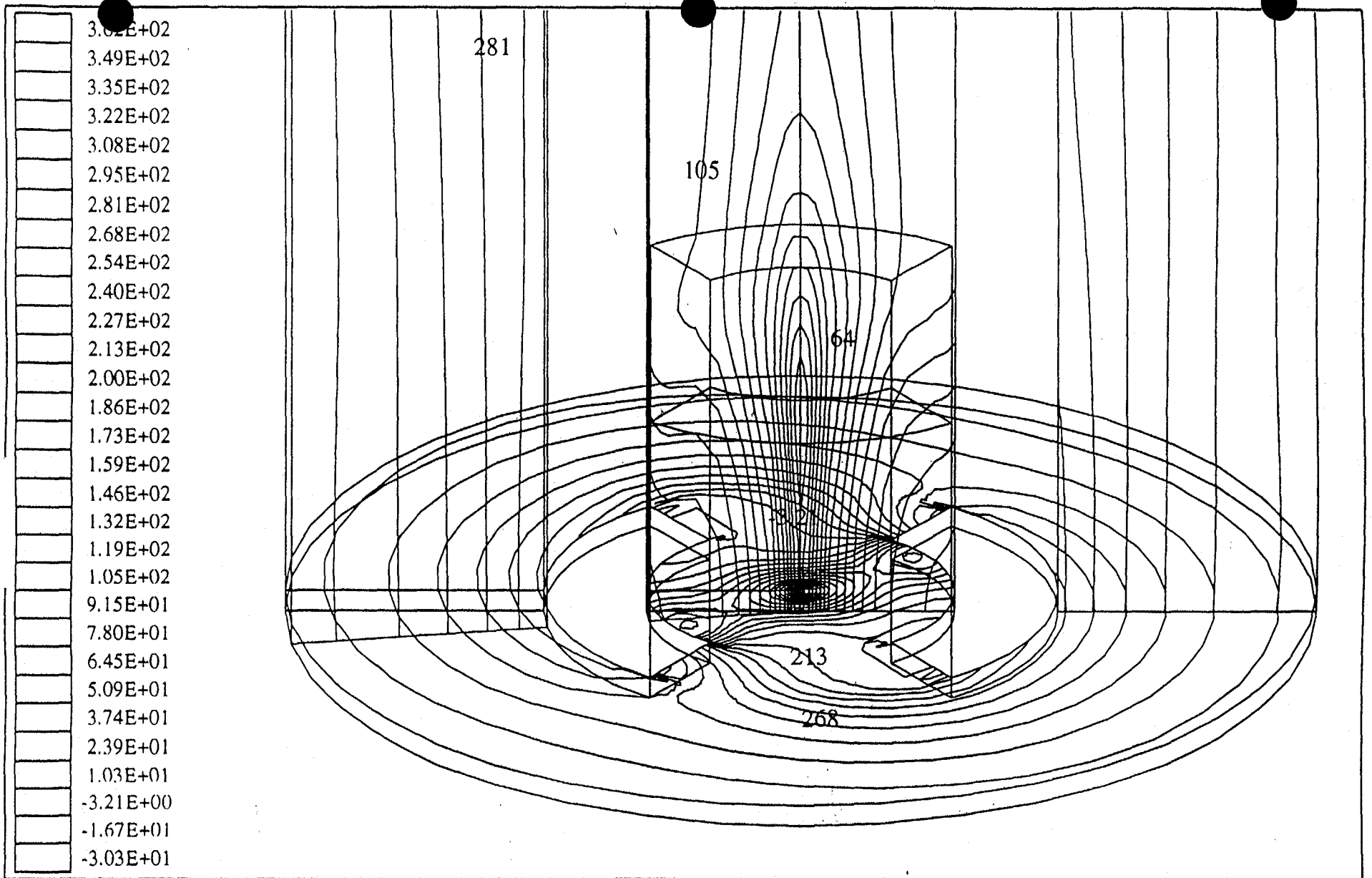


VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.4a Relative Static Pressure (Pa) Contours

Lmax = 3.623E+02 Lmin = -3.029E+01

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Fluent Inc.

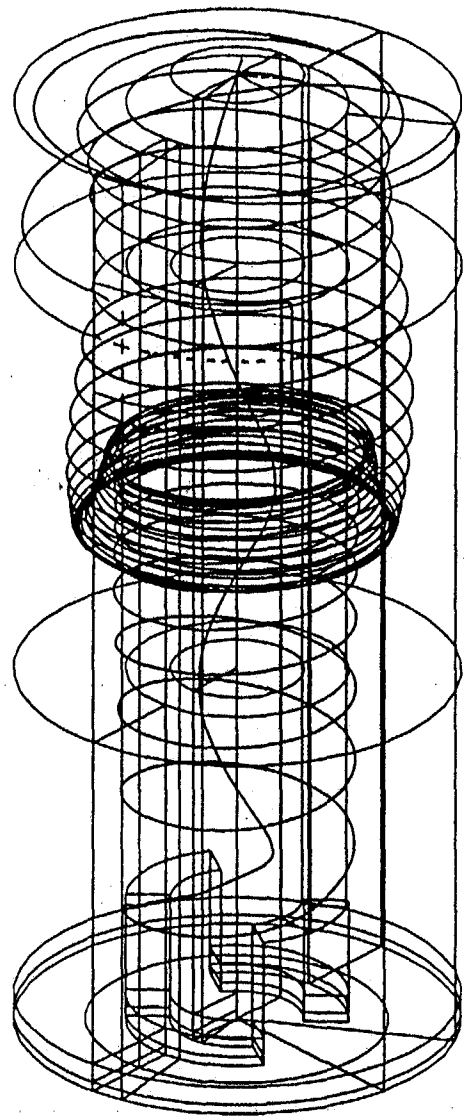


VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.4b Relative Static Pressure (Pa) Contours

Lmax = 3.623E+02 Lmin = -3.029E+01

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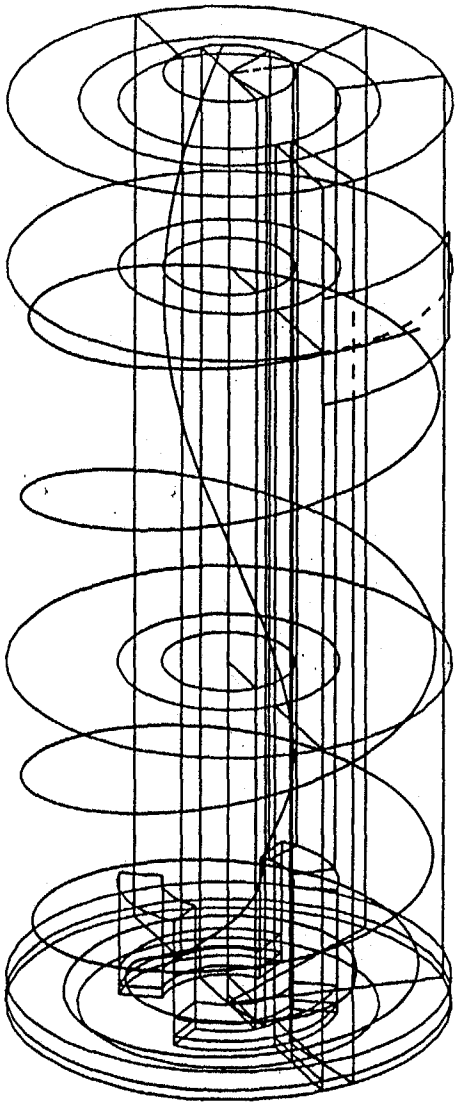




VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.5a Particle trajectory plot for particle A

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VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.5b Particle trajectory plot for particle C

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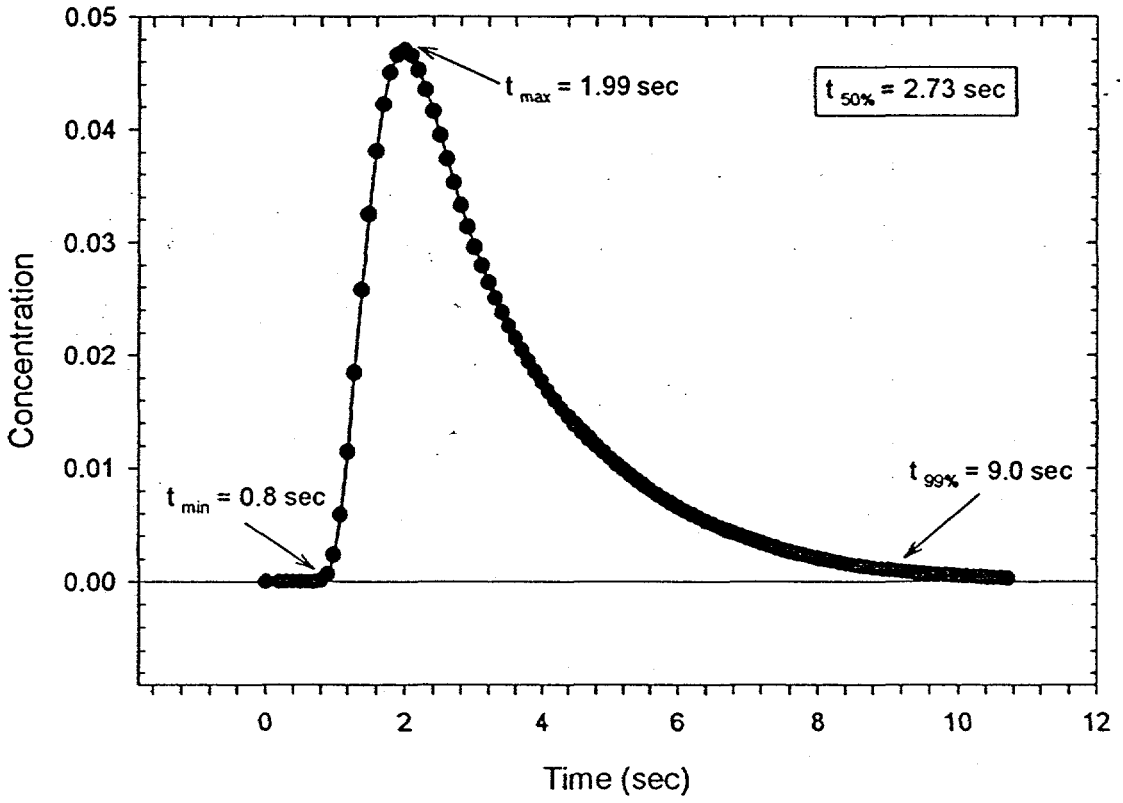
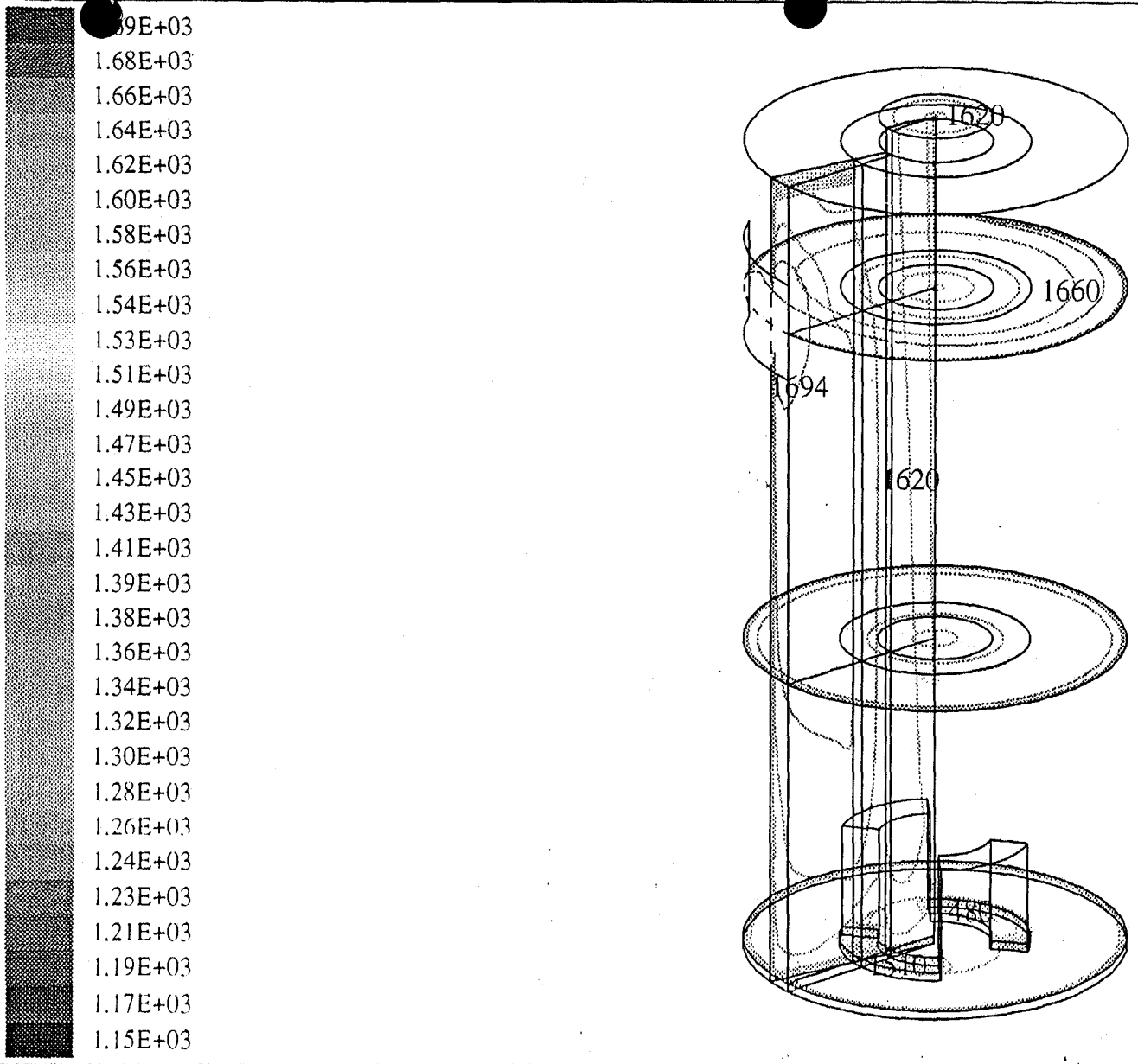


FIGURE 3.6 Flow through curve of a unit pulse of 0.1 sec duration at the inlet: Variation of outlet concentration with time.



VORTEC RECUPERATOR BASE NEW 3D GEOMETRY

Figure 3.7 Temperature (K) Contours

Lmax = 1.694E+03 Lmin = 1.150E+03

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SITE REMEDIATION TECHNOLOGIES

DRAIN-ENHANCED SOIL FLUSHING (DESF) FOR ORGANIC CONTAMINANTS REMOVAL

TASK 1.2

Quarterly Report XV for Period
April 1 through June 30, 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

Principle Investigator:

M. A. Gabr, Ph.D., P.E.

Research Assistants:
Doug Szabo
Mike Sabodish
Alan Williamson

Department of Civil Engineering
West Virginia University
Morgantown, West Virginia 26505-6101

June 1996

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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 equivalent 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

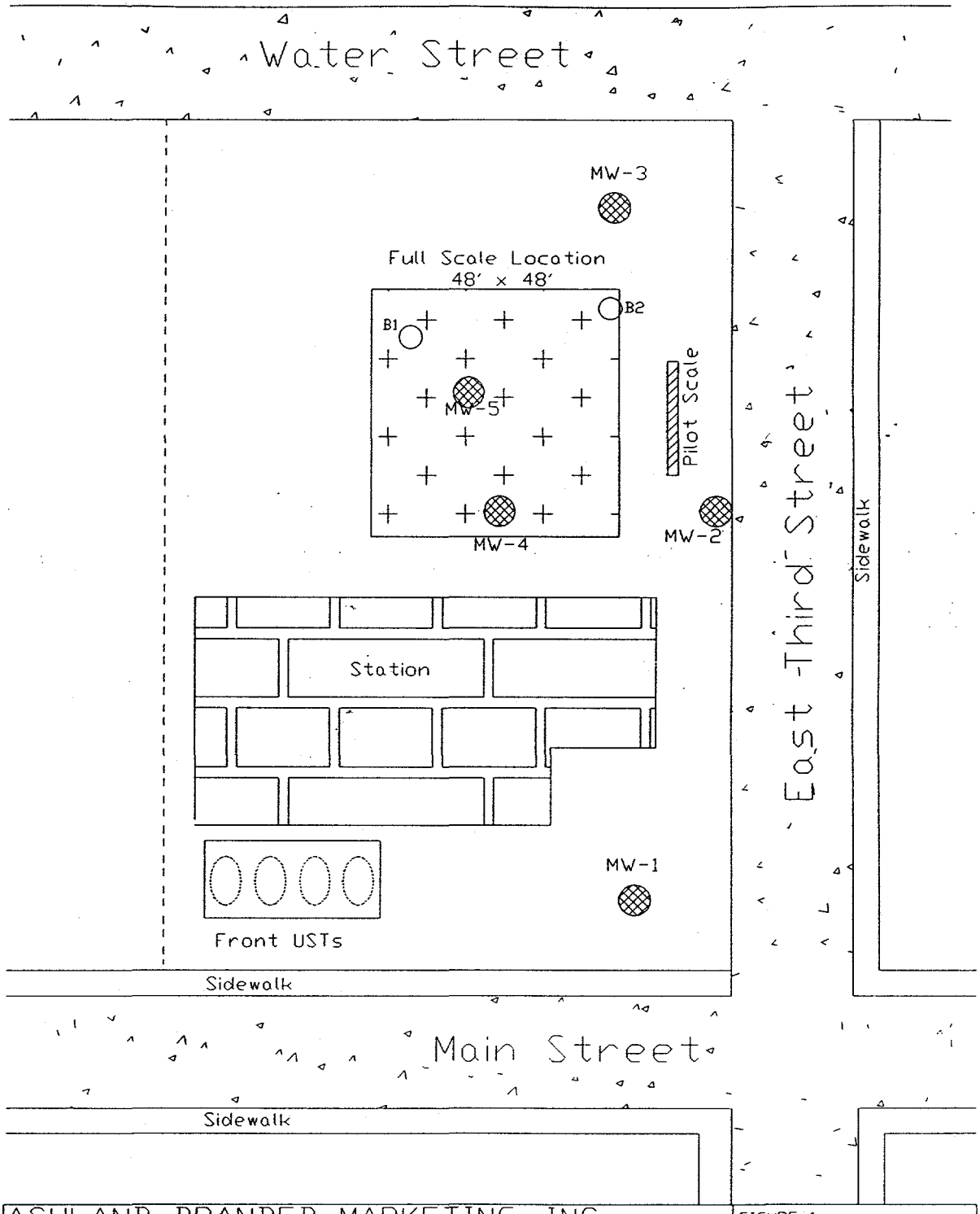
Five tasks were performed during this reporting period, 1) Site assessment including drilling and collection of split spoon and shelby tube samples, 2) Soil testing including perm tests, BTEX tests, and basic engineering soil index tests, 3) Underground Storage Tank removal by private contractor, 4) The selection of a surfactant based on bench scale testing, 5) Permitting and Planning of field site located in Weston W.V. The details of these tasks will discussed below.

Site Assessment

Southeastern Environmental was employed to take samples at the site on May 16, 1996. These samples included six split spoons at depths of 2.5', 7.5', and 12.5'. Shelby tubes were also taken at 5, 10, and 15 foot depths. Figure 1, plan view of the Ashland facility, shows sampling locations. Figure 2 shows pictorially the soil sampling operation.

Soil Testing

Engineering properties were found on the samples collected at the site by the methods described above. These tests included Atterberg Limits (ASTM D4318), Grain Size Analysis (ASTM D422), Specific Gravity (ASTM D854), and Permeability Tests (ASTM D5084). Also, The National Research Center for Coal and Energy was employed to perform BTEX testing on the



ASHLAND BRANDED MARKETING, INC. FACILITY #289-020 257 Main Street Weston, West Virginia	FIGURE 1 DESF PROJECT LOCATION Scale: 1" = 30'
West Virginia University Department of Civil and Environmental Engineering P.O. Box 6103 Morgantown, West Virginia 26506	Drafted by: Alan Williamson 6/4/96

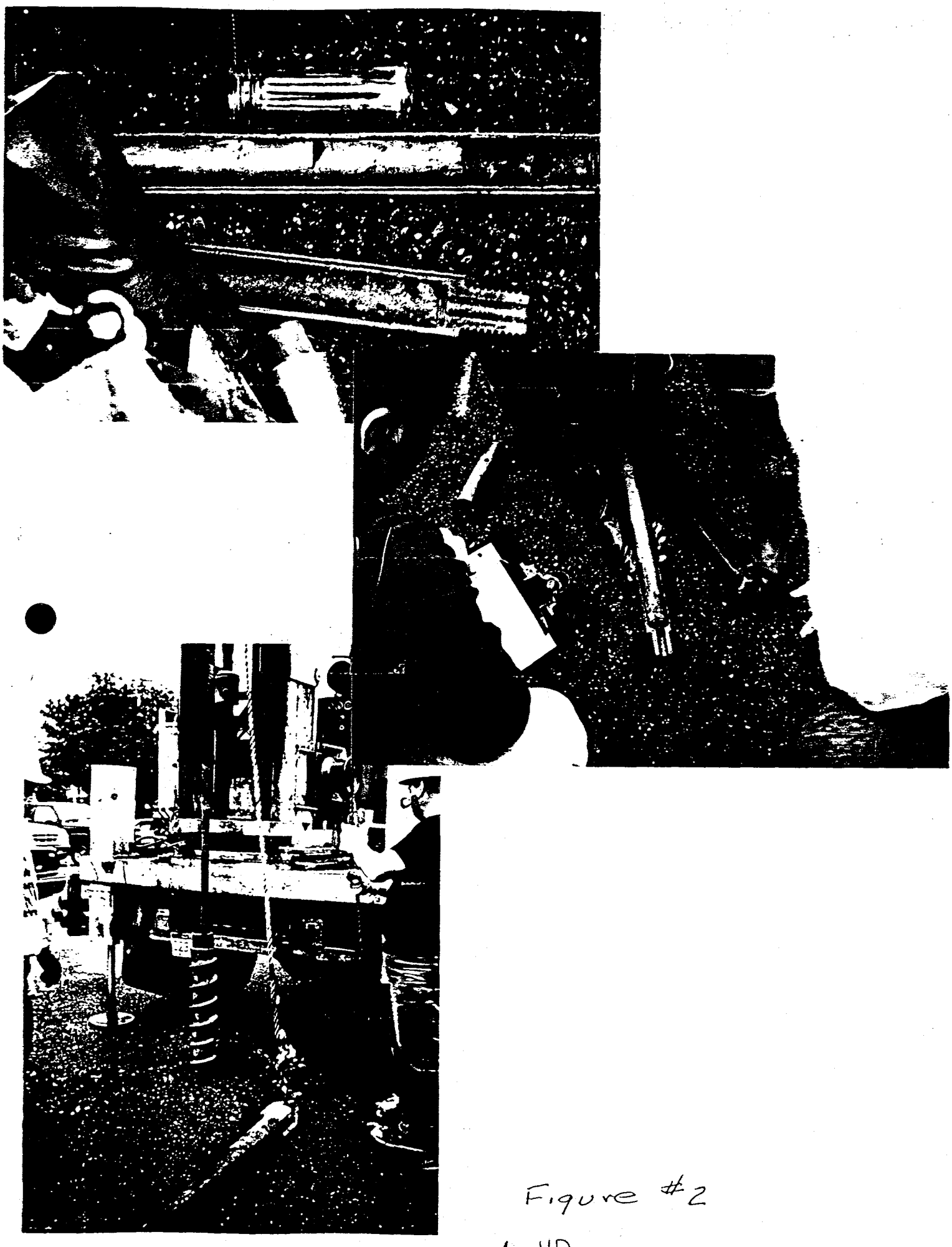


Figure #2

soil samples.

Tank Removal

Tanks were removed by a private contractor, Barnett Builders, on June 26, 1996. This operation was overseen by Ryan Environmental, and Art Loder from WVDEP. There were four tanks removed from the Ashland site, each with a capacity of four thousand gallons. Figure 3 contains pictures taken during removal of the storage tanks.

Selection of Surfactant

A surfactant was selected based on a literature review. (Tergitol TM - 10)

Permitting and Planning

A letter was drafted to Mr. Mike Sutphen from WVDEP Office of Waste Management. This letter is included in Attachment A.

Pilot Scale Test

A Pilot Scale test has been designed to be performed onsite. The layout of this test is shown in Figures 4 and 5. This test will give information pertaining to estimation of extraction flow rates and the feasibility of extraction using PVDs. The pilot test area will consist of a twenty foot strip, with the PVDs installed in one row and spaced every two feet. From the results of this test, we will be able to determine the air and water volumes as well as the zone of influence of the extraction process. A finite element computer program was utilized to predict drawdown of the water table as a direct result of fluid extraction from the PVDs. This program, SEEP\W; Geoslope International, models the flowrates and head values associated with the system. Figure 6 shows a layout of the grid. This program will aide in the determination of a pump system to be used in the pilot scale. If this method of determining pump size is accurate, it will be employed for the full scale test.

Cost Analysis

A cost analysis was performed to determine an overall cost for conducting the pilot scale test. Figure 7 outlines equipment and tests needed to complete the pilot scale test. From these findings an overall cost of $4,455 was determined.

Full Scale Test Design





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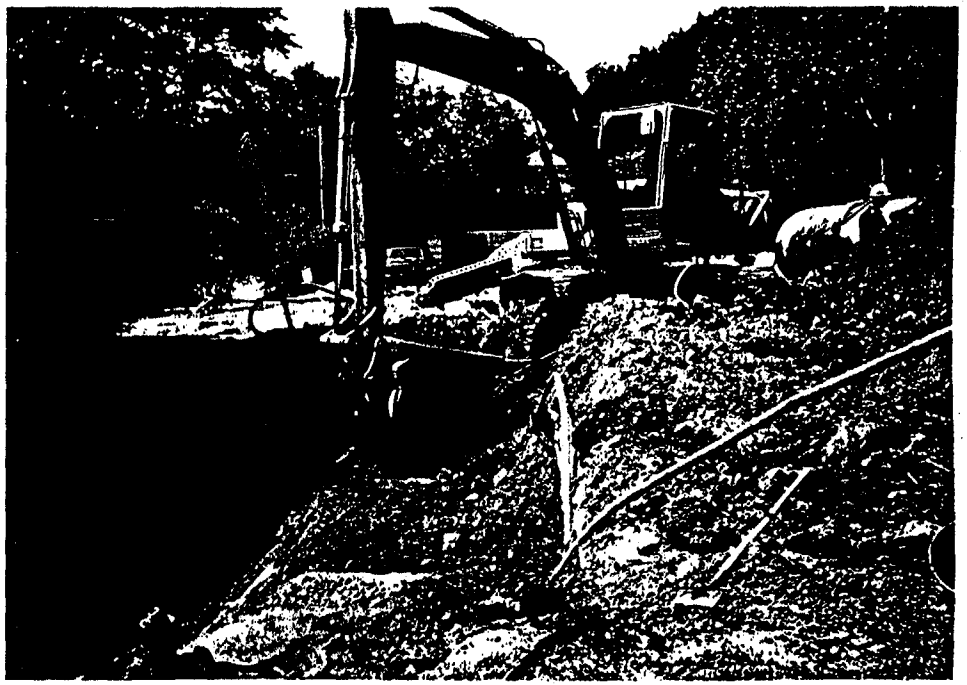
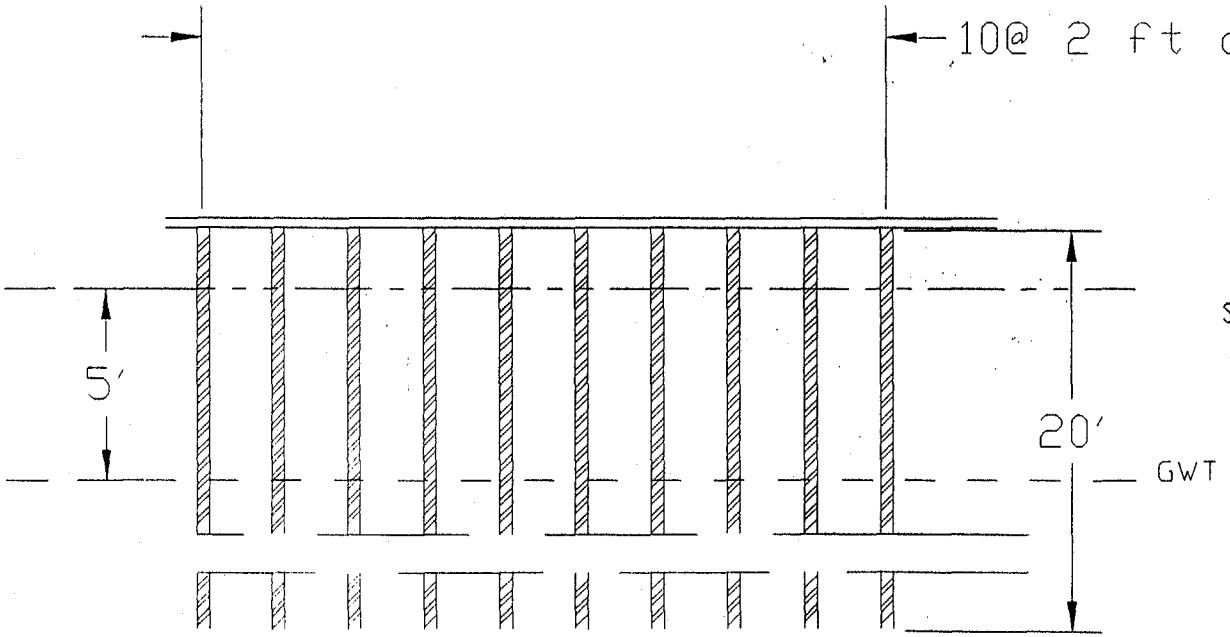
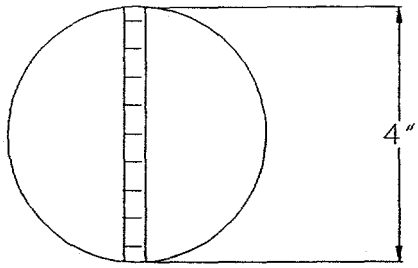


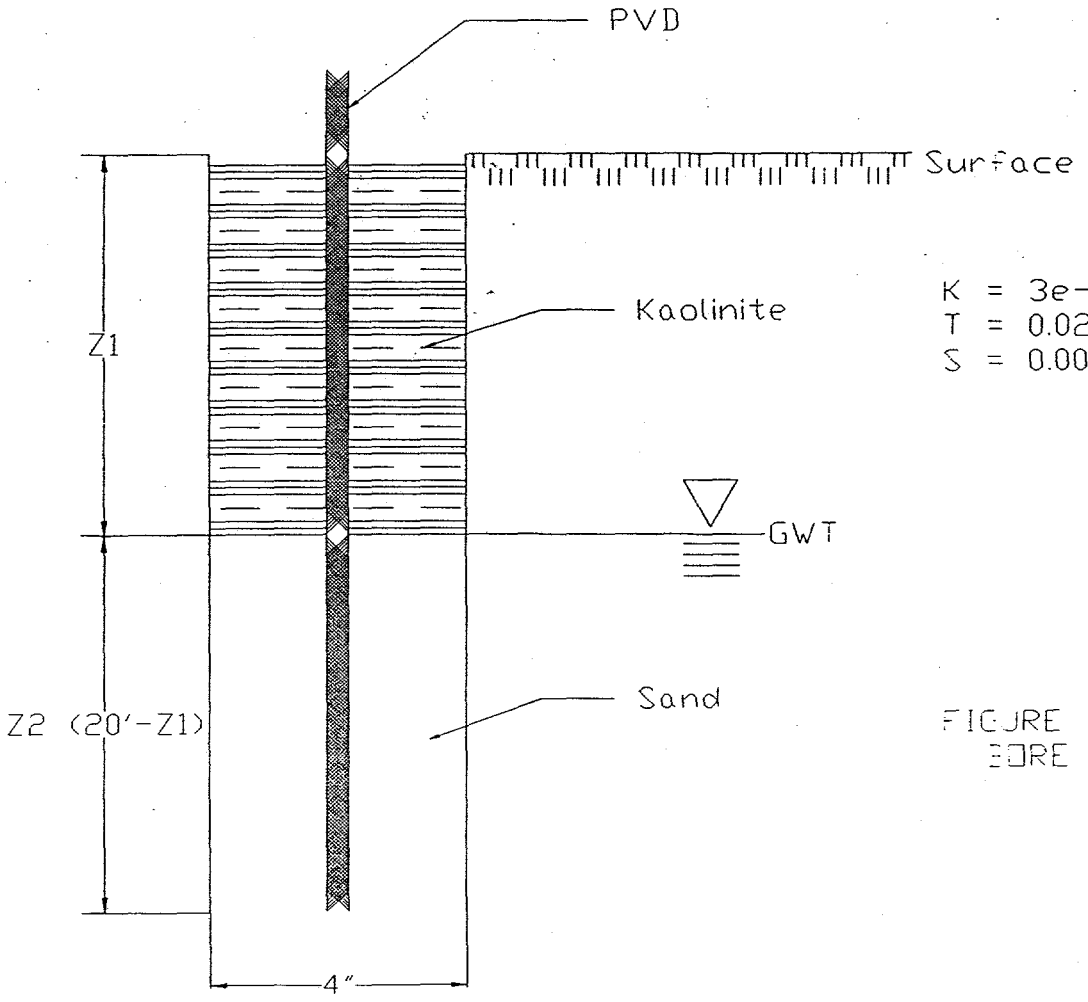
Figure # 3



Soil:
K = 3e-7' cm/s
T = 0.02079 sq. ft/min.
S = 0.0002873

FIGURE #4 : PILOT SCALE, ELEVATION VIEW





K = 3e-7 cm/s
T = 0.02079 sq. ft/min.
S = 0.0002873

FIGURE #5 :
BORE HOLE

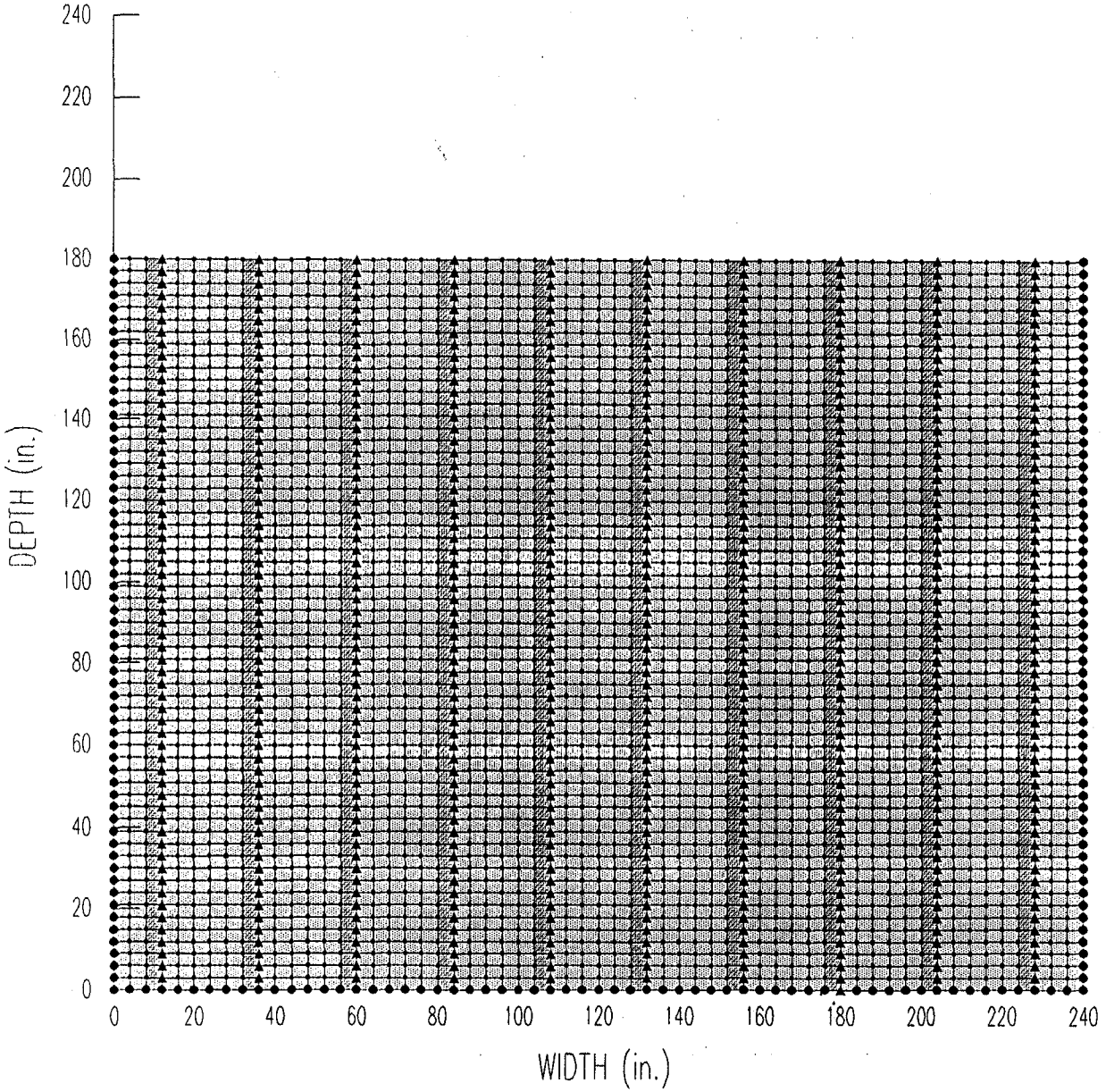


FIGURE #6 Finite Element Mesh

PILOT SCALE TEST

PUMP *(as per last conversation with Rick Stratton)* Southeastern Environmental: 304-824-5744 ○ Borings - 10 borings @ 20 feet deep - $5/foot ○ High Air Volume Vacuum Pump - cost includes man to run equipment - $ 600./day	$ 1000. $ 3000
TESTS Sturm Environmental Services: 304-623-6549 (BTEX test on grab samples => liquid) ○ $ 10/ per sample based on the following sampling scedule day 1 - 1 sample per hour days 2 and 3 - 1 sample every two hours days 4 and 5 - 1 sample every four hours	$ 420
MISCELLANEOUS Hoy Redi Mix: 304-363-4000 ○ 600 lb. of brown river sand - $16/ ton - delivery extra Lowe's : 304-983-3100 ○ PVC Materials - 40 feet, 3" I.D. - couplers - end cap - elbows ○ PVD Connection - band clamps (2 per PVD) - silicone caulk (10 tubes) - Duct tape (10 rolls)	$ 35. $ 300.
TOTAL	$ 4,455

Figure #7

Figure 1 shows a plan view of the proposed area to be remediated using the PVD system. Figure 8 shows this system in detail as it will be applied in the field. Alternating lines of injection and extraction will be used to flush the contaminants from the soil mass.

5.0 EXPERIMENTAL RESULTS AND DISCUSSION

Soil Testing

Results of the engineering properties tests performed on the soil samples collected in the field are shown in Attachment B. These results indicate the following properties:

1) Atterberg Limits (D4318) LL, and PL varied with depth, as shown in Attachment B.
2) Grain Size Distribution (D422) indicated that the soil contained primarily fine particles, this distribution is shown in Attachment B.
3) Specific Gravity (D854) gave a specific gravity of 2.65 for the soil.
4) Permeability Tests (D5084) showed an average hydraulic conductivity for the soil of 3.0×10^{-7} cm/s. The results of these tests can be found in Attachment B.
5) BTEX tests were performed on the samples taken in the field, results of this testing indicate the presence of Benzene, Toluene, Ethylbenzene, and Xylene in the groundwater table. The results of this testing can be found in Attachment C.

Finite Element Model

Figure 9 shows the results of the finite element model performed using data pertaining to pilot scale test. This figure indicates the groundwater table at steady state. It is evident that a drawdown of five feet can be expected. This model will be checked against the actual water levels monitored during the pilot scale test.

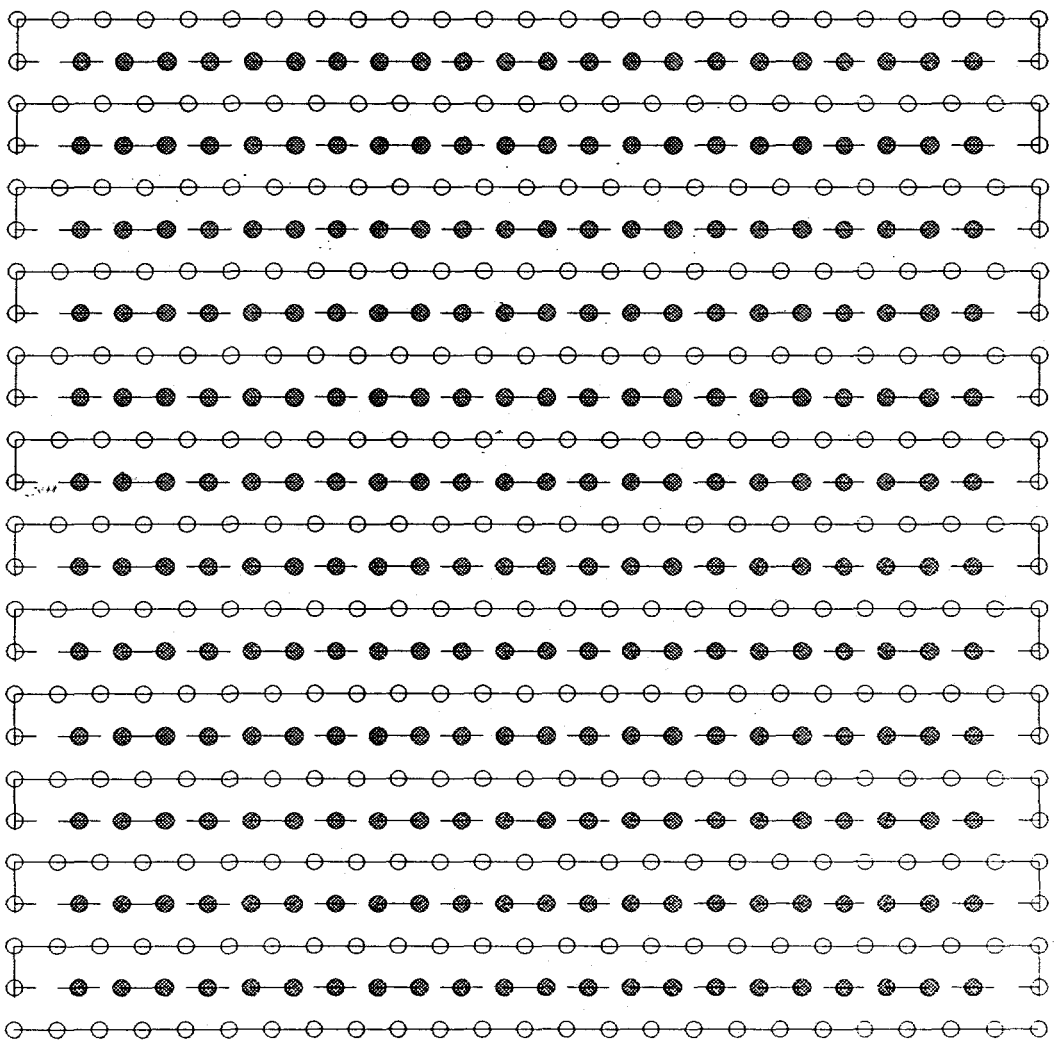
6.0 CONCLUSIONS

This report indicates all of the engineering properties for the soil located at the field site. Design of the pilot scale has been completed and will be implemented in the very near future.

7.0 WORK PLANNED FOR NEXT PERIOD

Tasks to be performed for the next reporting period include: implementation of the pilot scale test, gradient ratio test, and layout of the full scale system. The layout will include placement of the PVDs by the NILEX corp.

FIGURE # 8 : Full Scale Plan View



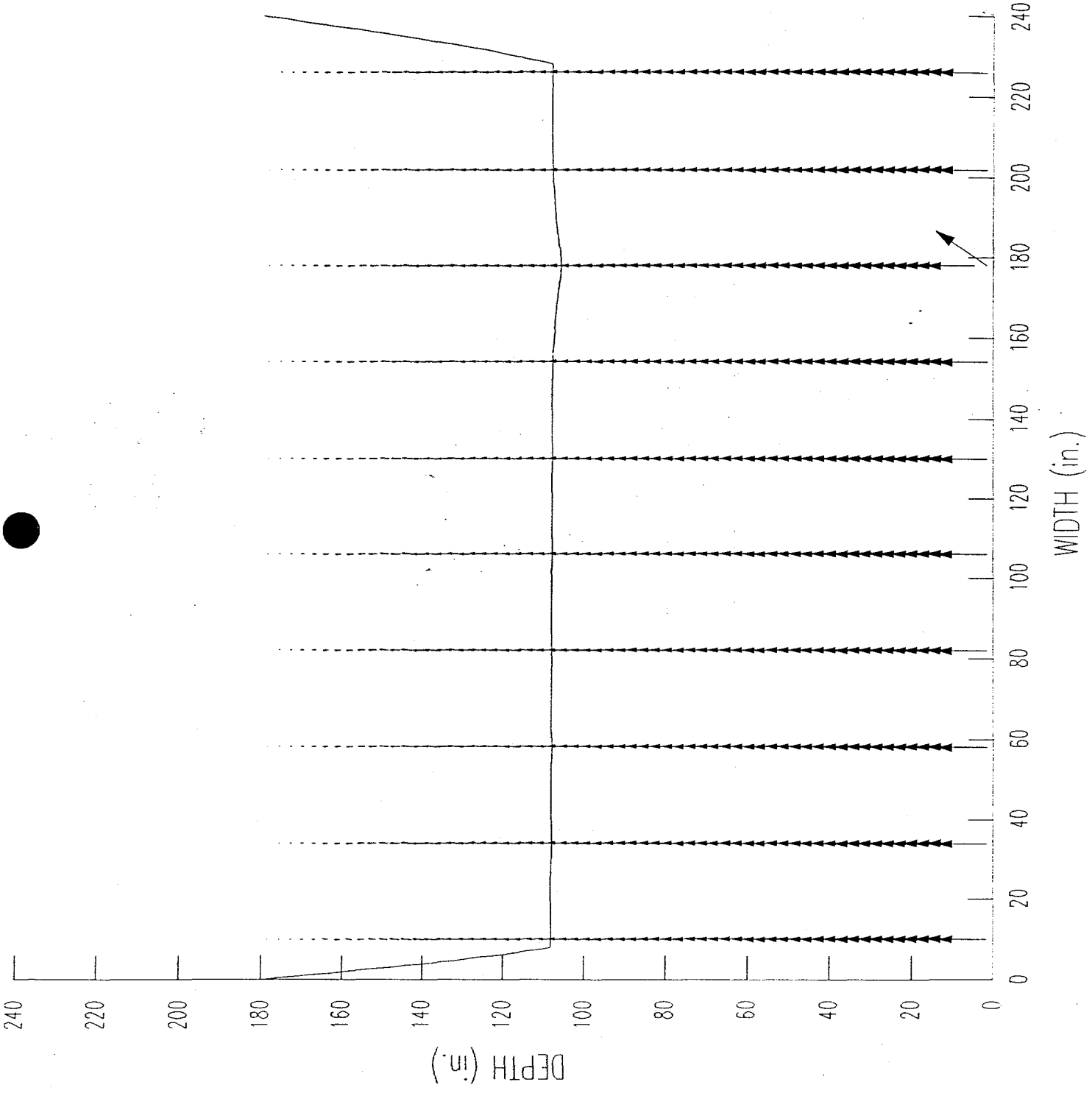


FIGURE # 9: FINITE ELEMENT RESULTS

ATTACHMENT A

Department of Civil & Environmental Engineering :: College of Engineering
West Virginia University

June 3, 1996

Mr. Mike Sutphen
WV Department of Environmental Protection
Office of Waste Management
Leaking Underground Storage Tanks
7356 Hansford St.
Charleston, W.V. 25301

Subject: Proposed Action and Technical Review, Weston, W.V.
W.V. ID #2102643, Leak #91-9918-L21

Dear Mike:

As we discussed over the phone, we have developed here at WVU a new technology for the enhanced flushing of BTEX from fine-grained soils and groundwater. The research in the laboratory has been completed and we are ready to conduct a field demonstration of the technology at the Ashland gas station in Weston (W.V. ID #2102643, Leak #91-9918-L21.) .

In a nutshell, the technology is similar to the "pump and treat systems". However, instead of using drilled wells, we are planing to use prefabricated drains (PVDs) that are 4" wide (a sample is included). A network of PVDs is installed on a closed spacing (typically 2-4 ft). This close spacing results in shortening the drainage path of the flow and therefore expediting the soil flushing process. The installation process of PVDs is relatively simple and inexpensive and requires no drilling. In addition, installing the PVDs on close spacing provides redundancy to capture the contaminant plumes. An overview of the Prefabricated Vertical Drains (PVD's), their working principle, and how the drains are installed is included in Attachment A.

The field study we are proposing at the Weston site will consist of two phases. First, a pilot scale test will be conducted to estimate the extracted flow rates and the feasibility of extraction using the PVDs. The pilot test area will consist of a 20 foot strip, with the PVD's installed in one row and spaced every two feet. The PVDs will be connected to a 3" in diameter PVC pipe and vacuum will be applied to the system. From the results of this test, we will be able to determine the air and water volumes as well as the zone of influence of the extraction process. Second, a full scale study will be conducted on a 48 ft. x 48 ft. square area. In this phase, one row of the PVDs will be used for extraction of BTEX and another row will be used for the injection of water or surfactant to desorb BTEX from the soil and transport it to the extraction

PVDs. Presently, laboratory flushing tests are being conducted using three permeants: water, sodium dodecylsulfate, and Tergitol. As soon as these tests are completed we will inform of the results and explore the issue of surfactant injection.

The description of the site area, the types and levels of contamination found at the site, a summary of the pilot scale test, and an overview of the test plan are presented in Attachment B. After meeting with representatives from Ashland Branded Marketing, Inc. and Delta Environmental Consultants, Inc., the following schedule is proposed:

Task	Deadline
WVU PVDs pilot study	July 14
WVU data reduction	August 1
equipment moblization	October 15
PVDs install/startup	December 15

We understand that Ashland have already submitted a CAP for the subject site in which they are proposing the use of the Dual Phase Extraction system. This will provide us with the opportunity to compare the performance of both flushing systems. We also understand that Ashland is committed to the clean-up of our test area if our proposed technology is unsuccessful. Thank you for your consideration. If you have any questions, the following is a list of contacts:

Rich Freeman (Ashland)	ph:(606)329-4131 fax: (606)329-3920
Mo Gabr (WVU) Doug Szabo Michael Sabodish Jr. Alan Williamson Jr.	ph:(304)293-3031 fax: (304)293-7109
Mark Vollmer (Delta)	ph:(412)487-7700 fax: (412)487-9786

Sincerely,

MA Gabr

M. A. Gabr, Ph.D., P.E.
Associate Professor

xc: Ashland, Delta, Bud Cook

ATTACHMENT A

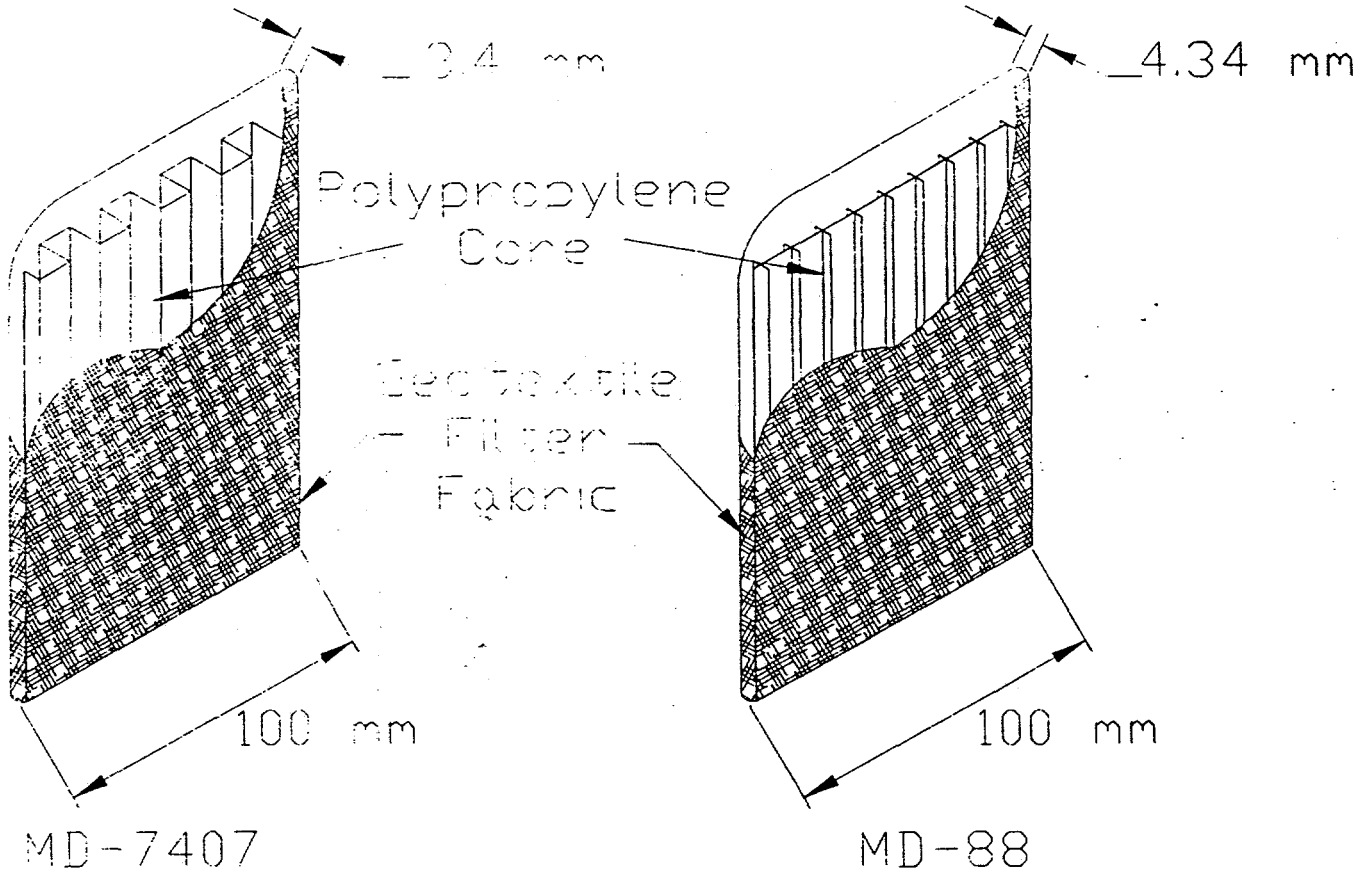
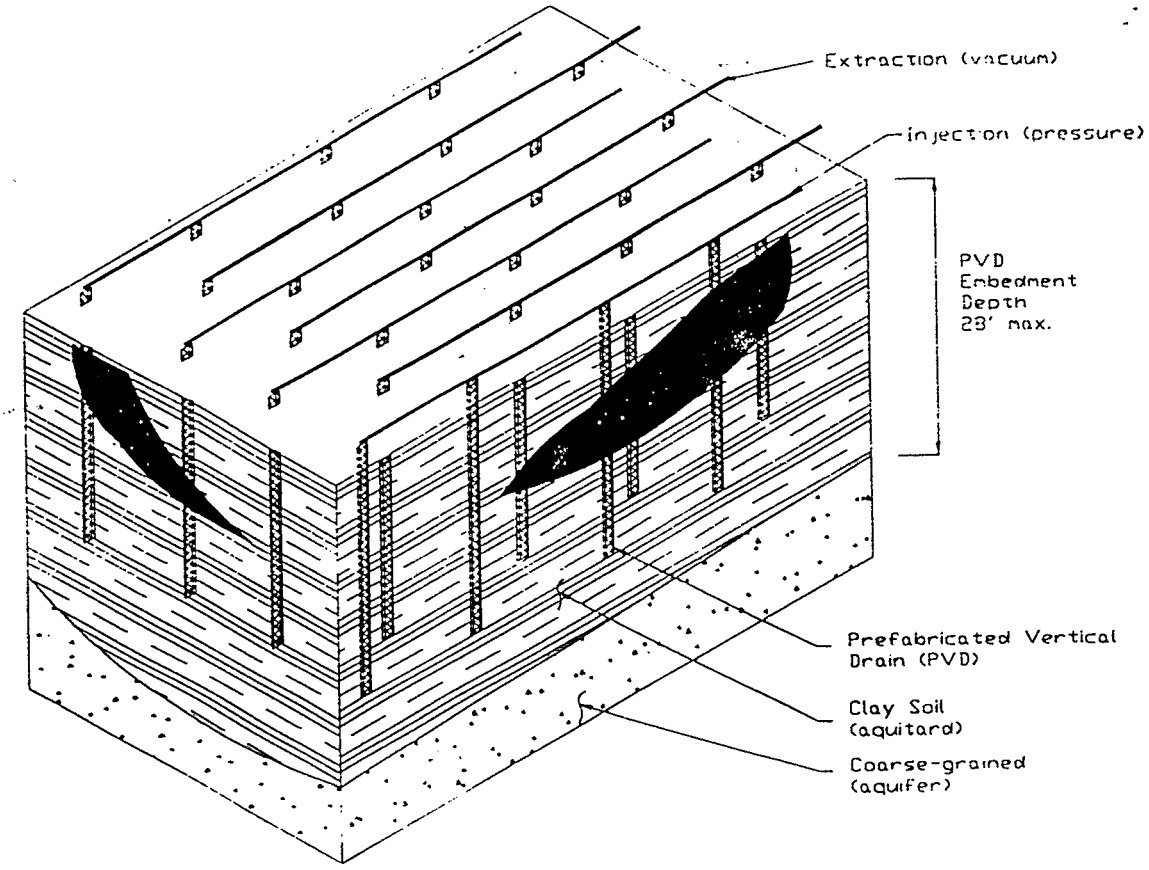

4.34 mm
Polypropylene
Core
Geotextile
Filter
Fabric
100 mm
MD-7407
4.34 mm
100 mm
MD-88

FIGURE A1

FIGURE A2



File: CROSS2

DRAIN ENHANCED SOIL FLUSHING

The concept of using Prefabricated Vertical Drains (PVDs) for remediation of contaminated sites with fine-grained soils has recently been investigated in a lab setting at WVU. The PVD materials used in this research are constructed of a composite system consisting of a inner core and an outer filter jacket. Figure A1 shows a typical NILEX Corporation brand PVD measuring 100 mm in width x 4 mm in thickness (NILEX, 1993). The flexible core is constructed of extruded polypropylene with formed flow path grooves on both sides along its length. The jacket serves as an outer skin to maintain the core's cross-sectional shape and hydraulic capacity of the flow path grooves. The jacket is constructed of a durable, non-woven polypropylene geotextile which functions as a filter to allow passage of groundwater into the drain core while preventing piping of fines from the adjoining soil.

The PVDs are installed in the field using a crane mounted mandrel. The PVDs are driven with anchor plates that secure the drains when the mandrel is removed. Various methods of mandrel driving include: cable pull powered by a conventional crane, vibratory head attached directly to the mandrel, and a hydraulic cylinder powered by the hydraulics of an excavator.

PVDs have been used for soil improvement, consolidation, purposes for several years with great success. In fact, PVDs have come to replace sand drains in certain situations. The primary reasons for this are: 1) the ease with which the PVDs may be handled and field delivered, and 2) lower material and total installation costs. This is true even though more PVDs are typically needed for soil improvement compared to sand drains. The application of PVDs for use as a mechanism to enhance in situ soil flushing is based on the same design and performance requirements as for soil improvement.

The research concept here is to use PVDs as a component in the "treatment train" for a soil flushing remediation. The PVDs will be used for injection of a flushing solution into the in situ soil and groundwater, and for the extraction and subsequent treatment of the flushing solution. Groundwater extraction will be performed by applying an air vacuum to the PVDs using a piping network. The contaminated fluid extracted with the PVDs may be recovered via a cyclone apparatus. Fluid injection may be performed by direct injection of the liquid using either a positive pressure pump or a standing head system.

Figure A2 is a conceptual layout of a field installation using a triangular grid pattern with

alternating off-set rows of injection and extraction PVDs. The PVDs are tied into collector piping for application of the air vacuum system and introduction of the surfactant solution. After installation of the PVDs and collector piping, the entire field site would be covered with a flexible PVC sheeting to minimize air infiltration and vacuum losses. A mass balance of the injection and extraction fluids is intended so that there is no consolidation of the soil during the flushing process. Any consolidation would reduce the soil porosity and therefore cause a reduction in the soil hydraulic conductivity requiring longer clean-up times. One of the main advantages of this type of flushing system is that the fluid being injected will desorb the contaminant from fine grained soils.

ATTACHMENT B

SITE LOCATION

Ashland Branded Marketing, Inc. Facility #289-020 at 257 Main Street, Weston, West Virginia is the location of the PVD project. The facility is a closed-down gasoline station. The proposed area for the 48 ft. x 48 ft. PVD network is located in the back lot of the facility(Refer to Figure B1). There is approximately a four inch layer of asphalt in the rear of the facility. The back lot is currently being used as a parking lot for people working in the area. From surface elevation, there is a small gradient sloping towards the top right corner of the lot (See Figure B1). This slope leads to the West Fork River located behind Water Street. The Underground Storage Tanks (USTs) placed in the front of the building are scheduled to be removed along with the demolition of the building.

SOILS AND CONTAMINANTS

The site consists primarily of a silty clay, and is relatively medium stiff. The groundwater table is at an average depth of seven feet across the area of the site. The hydraulic conductivity of the soil was found to be approximately 10^{-6} cm/s. From other soil properties tests, the moisture content is an average of 20%, and the specific gravity of the solids is 2.65. The site was tested for several contaminants by the NPTC. Figure B2 shows the locations of the monitoring wells installed by Ashland. This figure also indicates the approximate extent of the contaminated groundwater. Table B1 shows a list of the PAH concentrations on the site as of July 30, 1995. Some of the largest concentrations are outlined in Table 1. Figure B1 outlines the area with which this project will focus on. This area encompasses monitoring wells 4 and 5 which have been indicating the presence of free product.

PILOT SCALE

The pilot scale will be used to approximate airflow and fluid flowrates to be used for the design of the full scale system. This test will be helpful in determining the effectiveness of this technology in a field setting. Ten PVDs are to be used in the pilot scale at two foot spacing, yielding a total length of a twenty foot section of collector pipe. The location of the pilot scale is near MW-2(See Figure B1). In contrast to typical installation methods discussed in Attachment A, the PVDs in the pilot scale test will be placed in pre-drilled bore holes. These bore holes have a diameter of 4" and will approximately be twenty feet deep.

TABLE 1: Groundwater Analytical Summary Table
Ashland Branded Marketing Facility # 289-020
[redacted], Lewis County, West Virginia

		Benzene	Toluene	Ethylbenzene	Xylene	Total BTEX	TPH (GRO)	TPH (418.1)
MW-1	Jul 30, 1995	1.090	0.260	0.460	0.690	2.500	4.360	NS
	Nov 91 - Apr 92	1.100	0.059	0.450	0.839	2.448	NS	3.36
MW-2	Jul 30, 1995	0.120	0.010	0.340	0.300	0.770	2.170	NS
	Nov 91 - Apr 92	0.230	< 0.100	1.640	2.820	< 4.790	NS	5.30
MW-3	Jul 30, 1995	NS	NS	NS	NS	NS	NS	NS
	Nov 91 - Apr 92	NS	NS	NS	NS	NS	NS	NS
MW-4	Jul 30, 1995	NS	NS	NS	NS	NS	NS	NS
	Nov 91 - Apr 92	NS	NS	NS	NS	NS	NS	NS
MW-5	Jul 30, 1995	NS	NS	NS	NS	NS	NS	NS
	Nov 91 - Apr 92	0.032	0.017	0.215	0.199	0.463	NS	6.90
MW-6	Jul 30, 1995	0.002	< 0.001	< 0.001	0.022	< 0.026	0.500	NS
	Nov 91 - Apr 92	< 0.005	0.010	0.140	0.550	< 0.705	NS	< 0.200
EB-6A	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.200	NS
[redacted]-7	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	1.42
MW-8	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-9	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-10	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-11	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-12	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-13	Jul 30, 1995	1.580	0.810	1.980	3.330	7.700	16.90	NS
	Nov 91 - Apr 92	1.200	2.700	1.500	5.100	10.500	NS	3.31
MW-14	Jul 30, 1995	2.300	1.440	0.450	1.480	5.670	10.30	NS
	Nov 91 - Apr 92	9.700	9.800	2.800	13.500	35.800	NS	16.90

NOTES:
mg/L denotes milligrams per liter.
[redacted]H (GRO) denotes anlytical method 8015 total petroleum hydrocarbons (gasoline range organics).
MW-3, MW-4, MW-5 not sampled due to presence of free product.
Outlined BTEX results exceed either 0.005 mg/L benzene and/or Federal Drinking Water Maximum Contaminant Levels (MCLs) for toluene (1 mg/L), ethylbenzene (0.7 mg/L), and xylenes (10 mg/L).

h:\users\marcy\ashland\westongw.wq1

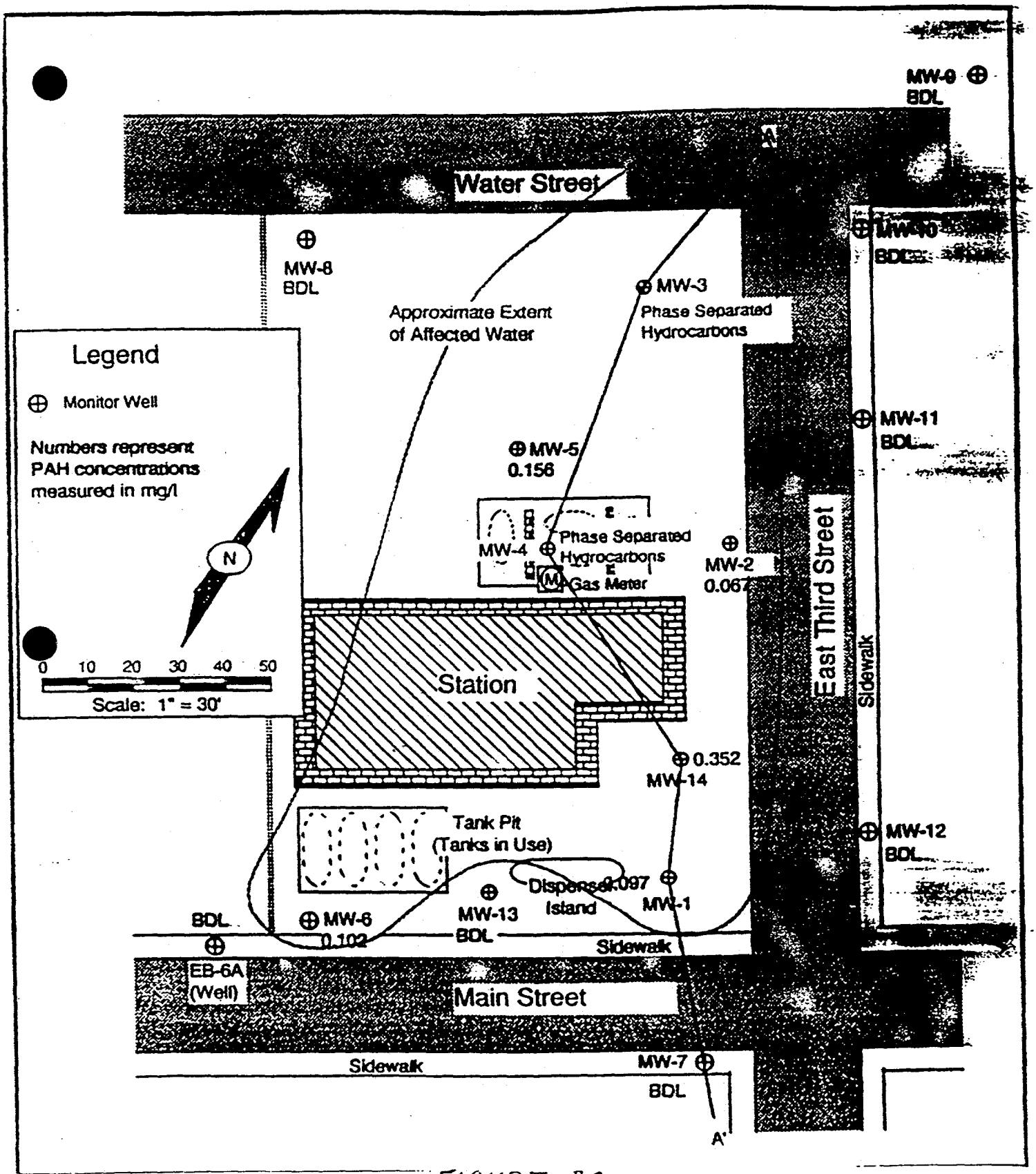

MW-9
BDL
Water Street
MW-8
BDL
Approximate Extent
of Affected Water
MW-3
Phase Separated
Hydrocarbons
MW-10
BDL
Legend
Monitor Well
Numbers represent
PAH concentrations
measured in mg/l
MW-11
BDL
MW-5
0.156
N
MW-4
Phase Separated
Hygrocarbons
MW-2
0.067
Gas Meter
East Third Street
Sidewalk
0 10 20 30 40 50
Scale: 1" = 30'
Station
0.352
MW-14
Tank Pit
(Tanks in Use)
MW-12
BDL
Dispenser
Island
0.097
MW-1
MW-13
BDL
MW-6
0.102
BDL
BDL
Sidewalk
EB-6A
(Well)
Main Street
Sidewalk
MW-7
BDL
A'

FIGURE B2

ATTACHMENT B

Ashland Site Soil Tests Results								
			Boring 1				Boring 2	
Test		*Trial 1*	*Trial 2*	*Average*		*Trial 1*	*Trial 2*	*Average*
	2.5 feet	23.6	21.1	22.4		23.7	22.6	23.2
Water Content (%)	7.5 feet	18.7	12.1	15.4		19.9	17.8	18.9
NR- no recovery	12.5 feet	NR	NR	NR		21.3	16.4	18.9
	2.5 feet	2.6	2.58	2.59		2.68	2.68	2.68
Specific Gravity	7.5 feet	2.7	2.68	2.69		2.72	2.72	2.72
IA- insufficient amount	12.5 feet	---	---	---		2.65	IA	2.65
	15.0 feet	2.69	2.65	2.67				
Atterberg Limits								
	LL	37	39	38		42	40	41
2.5 feet	PL	22	20	21		21	22	22
	PI	15	19	17		21	18	19
	LL	30	30	30		28	28	28
7.5 feet	PL	17	19	18		16	18	17
	PI	13	11	12		12	10	11
	LL	---	---	---		25	25	25
12.5 feet	PL	---	---	---		15	17	16
	PI	---	---	---		10	8	9
	LL	27	27	27		---	---	---
15.0 feet	PL	15	17	16		---	---	---
	PI	12	10	11		---	---	---
Hydrometer Tests --- See Data Sheets								
(D)								

MOISTURE CONTENT

West Virginia University — Department of Civil Engineering

MOISTURE CONTENT DATA SHEET

Project: Ashland Site — Name: Michael Sabodish & Alan Williamson

Comments: B1 - boring #1; B2 - boring #2 — Date: 5/17/96 - 5/18/96

Identification	B1-A 2.5'	B1-B 2.5'	B1-A 7.5'	B1-B 7.5'	B2-A 2.5'
Can Number					
Wet Wt. + Tare	30.91 g	36.45g	27.88 g	27.76 g	29.57 g
Dry Wt. + Tare	28.29 g	33.84 g	26.19 g	26.66 g	27.23 g
Weight of Water	2.62 g	2.61 g	1.69 g	1.10 g	2.34 g
Tare Weight	17.18 g	21.48 g	17.16 g	17.58 g	17.35 g
Dry Weight	11.11 g	12.36 g	9.03	9.08	9.88 g
Moisture Content	23.6%	21.1%	18.7%	12.1%	23.7%

Identification	B2-B 2.5'	B2-A 7.5'	B2-B 7.5'	B2-A 12.5'	B2-B 12.5'
Can Number					
Wet Wt. + Tare	31.35 g	40.24 g	36.87 g	41.41 g	41.65 g
Dry Wt. + Tare	28.63 g	37.15 g	33.97 g	37.98 g	39.81 g
Weight of Water	2.72 g	3.09 g	2.9 g	3.53 g	2.84 g
Tare Weight	16.58 g	21.66 g	17.70 g	21.30 g	21.53 g
Dry Weight	12.05 g	15.49 g	16.27	16.58 g	17.28 g
Moisture Content	22.6%	[illegible]%	17.8%	21.3%	16.4%

Identification					
Can Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Weight of Water					
Tare Weight					
Dry Weight					
Moisture Content					

B1 - 2.5' → 22.4%
B1 - 7.5' → 15.4%
B2 - 2.5' → 23.2%
B2 - 7.5' → 12.9%
B2 - 12.5' → 18.9%

SPECIFIC GRAVITY

West Virginia University

Department of Civil Engineering

SPECIFIC GRAVITY TEST

Project DESF Ashland Site Operator Michael SABOURIN

Soil B-1 2.5' Date 5/20/96

Comments _____

$$G_s = \frac{W_d}{W_1 + W_d - W_2}$$

where: W_d is the oven dry weight of soil

W_1 is the weight of the pycnometer full of water

W_2 is the weight of the pycnometer full of water and soil

Test Number	#1	#2			
Soil Description					
Nominal Pyc. Volume	200mL	200mL			
W_d	25g	25g			
W_1	279.19g	288.12g			
Temperature for W_1	29°C	29°C			
W_2	294.60	303.46			
Temperature for W_2	28°C	28°C			
G_s Temp Corrected	2.60	2.58			
Container Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Tare					
Moisture Content	22.4%	22.4%			

West Virginia University — Department of Civil Engineering

SPECIFIC GRAVITY TEST

Project DESF Ashland Site — Operator M. K. SABOOSH & ALAN WILLIAMSON

Soil B1 - 7.5' — Date 5/21/96

Comments _____

$$G_s = \frac{W_d}{W_1 + W_d - W_2}$$

where: W_d is the oven dry weight of soil

W_1 is the weight of the pycnometer full of water

W_2 is the weight of the pycnometer full of water and soil

Test Number	#1	#2			
Soil Description					
Nominal Pyc. Volume	200 ml	200 ml			
W_d	50.1 g	50.16 g			
W_1	279.04 g	287.93 g			
Temperature for W_1	30°C	30°C			
W_2	310.62 g	319.41 g			
Temperature for W_2	26°	26°			
G_s Temp. Corrected	2.70	2.68			
Container Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Tare					
Moisture Content	15.4%	15.4%			

Avg

West Virginia University — Department of Civil Engineering

SPECIFIC GRAVITY TEST

Project DESF ASHLAND SITE — Operator M.16 SABOLISH JR

Soil B1 - 15' — Date 5/21/96

Comments SAMPLE FROM CUTTINGS

$$G_s = \frac{W_d}{W_1 + W_d - W_2}$$

where: W_d is the oven dry weight of soil

W_1 is the weight of the pycnometer full of water

W_2 is the weight of the pycnometer full of water and soil

Test Number	#1	#2			
Soil Description					
Nominal Pyc. Volume	200 mL	200mL			
W_d	50.0 g	50.0g			
W_1	279.34g	288.39g			
Temperature for W_1	26°C	26°C			
W_2	310.76g	319.54g			
Temperature for W_2	25°C	25°C			
G_s Temp Corrected	2.69	2.65			
Container Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Tare					
Moisture Content	19%	19%			

West Virginia University — Department of Civil Engineering

SPECIFIC GRAVITY TEST

Project DESF Ashland Site — Operator MS AW

Soil B2 - 2.5' — Date 5/31/96

Comments

$$G_s = \frac{W_d}{W_1 + W_d - W_2}$$

where: W_d is the oven dry weight of soil

W_1 is the weight of the pycnometer full of water

W_2 is the weight of the pycnometer full of water and soil

Test Number	#1	#2			
Soil Description					
Nominal Pyc. Volume	200 ml	200 mL			
W_d	50.04 g	50.10 g			
W_1	279.37 g	288.26 g			
Temperature for W_1	25°C	25°C			
W_2	310.75 g	319.65 g			
Temperature for W_2	25°C	25°C			
G_s	2.68	2.68			
Container Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Tare					
Moisture Content					

West Virginia University — Department of Civil Engineering

SPECIFIC GRAVITY TEST

Project DESF ASHLAND SITE — Operator Mike Sabbaish Jr

Soil BZ- 7.5' — Date ~~5/30/96~~ 6/3/96

Comments _____

$$G_s = \frac{W_d}{W_1 + W_d - W_2}$$

where: W_d is the oven dry weight of soil

W_1 is the weight of the pycnometer full of water

W_2 is the weight of the pycnometer full of water and soil

Test Number	#1	#2			
Soil Description					
Nominal Pyc. Volume	200 ml	200ml			
W_d	50.45	50.56g			
W_1	279.44g	288.43g			
Temperature for W_1	23	24			
W_2	311.39g	320.39g			
Temperature for W_2	24	24			
G_s	2.72	2.72			
Container Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Tare					
Moisture Content					

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SPECIFIC GRAVITY TEST

Project DESF Ashland Site Operator Mike Sabourin JR

Soil B2 - 12.5' Date 6/3/96

Comments - only Ran 1 trial due to sample size.

*

$$G_s = \frac{W_d}{W_1 + W_d - W_2}$$

where: W_d is the oven dry weight of soil

W_1 is the weight of the pycnometer full of water

W_2 is the weight of the pycnometer full of water and soil

Test Number	#1	#2*			
Soil Description					
Nominal Pyc. Volume	200ml				
W_d	25g				
W_1	288.39g				
Temperature for W_1	24°C				
W_2	303.95				
Temperature for W_2	24°C				
G_s	2.65				
Container Number					
Wet Wt. + Tare					
Dry Wt. + Tare					
Tare					
Moisture Content					

* - Not enough sample to run a second trial

HYDROMETER ANALYSIS

West Virginia University

Department of Civil Engineering

TRIAL #1

DATA FORM FOR HYDROMETER ANALYSIS

Operator: Michael Sabodish & Alan Williamson Date: 5/20/96 - 5/21/96 Project: DESF Ashland Site

Soil: B1 - 2.5' G_s: 2.58 & 2.60 Avg 2.59 Hydrometer No. 152H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
5/20 11:47	0								
11:49	2	33	29	0.01249	1.01		65.9	10.9	0.02916
11:52	5	31	29	0.01249	1.01		61.9	11.2	0.01869
12:02	15	27	29	0.01249	1.01		53.9	11.9	0.01112
12:17	30	24	29	0.01249	1.01		47.9	12.4	0.00803
12:47	60	21	28	0.01264	1.01		41.9	12.9	0.00586
4:57	310	16	29	0.01249	1.01		31.9	13.7	0.00262
5/21 11:47	1440	13	26	0.01261	1.01		25.9	14.2	0.00125

137

50.41 - MOIST

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TRIAL #2

DATA FORM FOR HYDROMETER ANALYSIS

Operator: MIKE S. + ALAN W Date: 5/20/96 - 5/21/96 Project: DESF / ASHLAND SITE

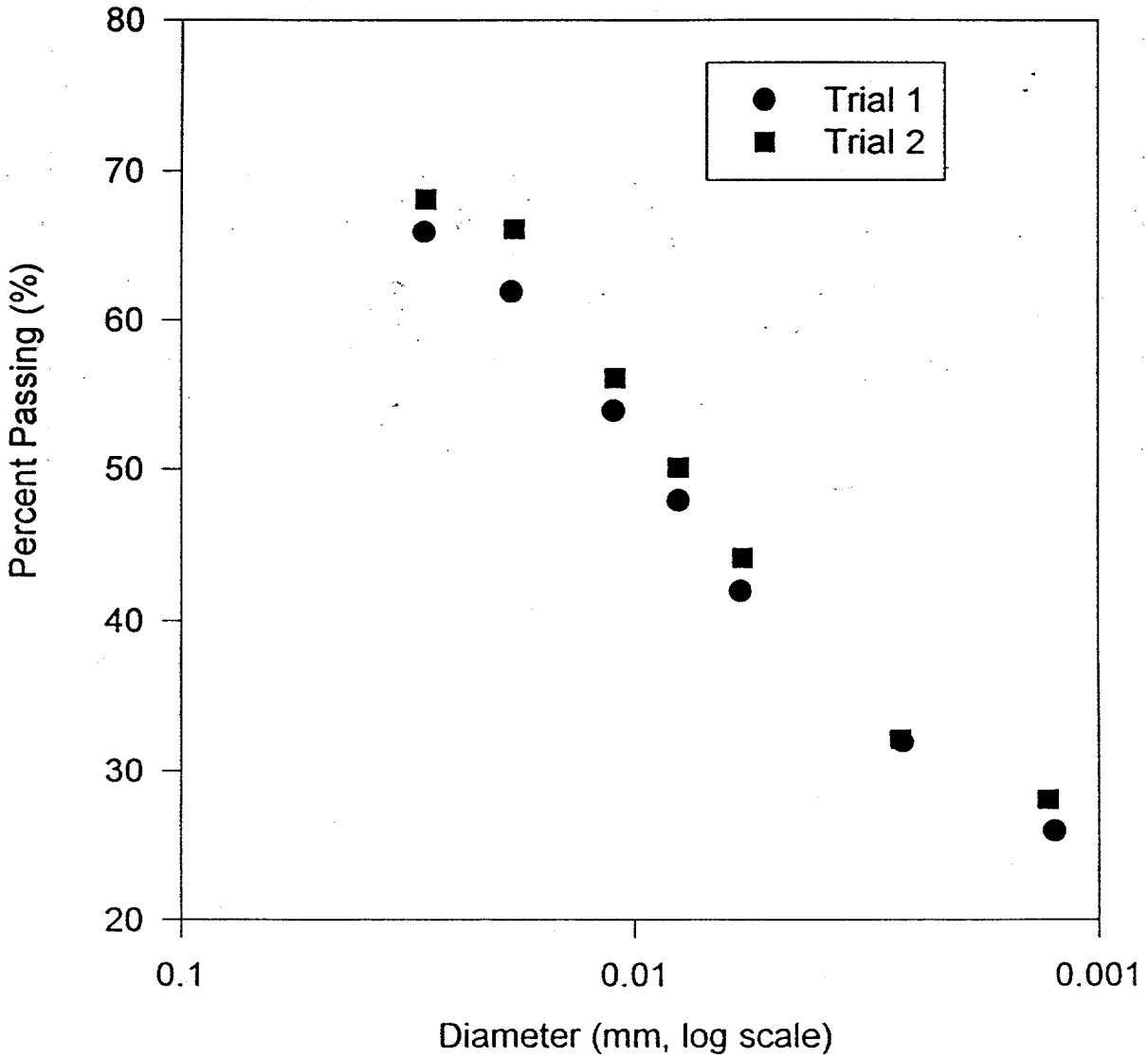
Soil: 81 - 2.5' G_s: 2.58 & 2.66 Hydrometer No. 152 H

Avg 2.59

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
	2	34	29	.0125	1.01	2.6	68.1	10.7	.02891
	5	33	29	.0125	1.01	2.6	66.1	10.9	.01845
	15	28	29	.0125	1.01	2.6	56.1	11.7	.01103
	30	25	28	.0126	1.01	2.6	50.1	12.2	.00803
	60	22	28	.0126	1.01	2.6	44.1	12.7	.00580
	310	16	28	.0126	1.01	2.6	32.1	13.7	.00265
	1440	14	25	.0131	1.01	3.5	28.0	14.0	.00129

138

Ashland Site
Boring 1; 2.5 feet



West Virginia University

$m_{DRY} = 50.0$ g

Department of Civil Engineering

DATA FORM FOR HYDROMETER ANALYSIS

Operator: M.G. SAYOOD, S.H. YAN, I. WILLIAMSON **Date:** 5/21/96 - 5/22/96 **Project:** DESF ASHLAND SITE

Soil: B1 - 7.5' **G_s:** 2.69 Avg ≈ 2.70 **Hydrometer No.** 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
5/21 12:15	0								
12:17	2	17	26	.0125	.99	3.2	54.0	11.8	.03036
12:20	5	16	26	.0125	.99	3.2	50.8	12.1	.01944
12:30	15	13	26	.0125	.99	3.2	41.3	12.9	.01159
12:45	30	12	26	.0125	.99	3.2	38.1	13.1	.00826
1:15	60	11	26	.0125	.99	3.2	34.9	13.4	.00591
4:25	250	8	25	.0127	.99	3.5	25.4	14.2	.00303
5/22 12:15	1440	7	24	.0128	.99	3.8	22.2	14.4	.00128

1440

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Mass = 50.0 g

Department of Civil Engineering

DATA FORM FOR HYDROMETER ANALYSIS

NAK

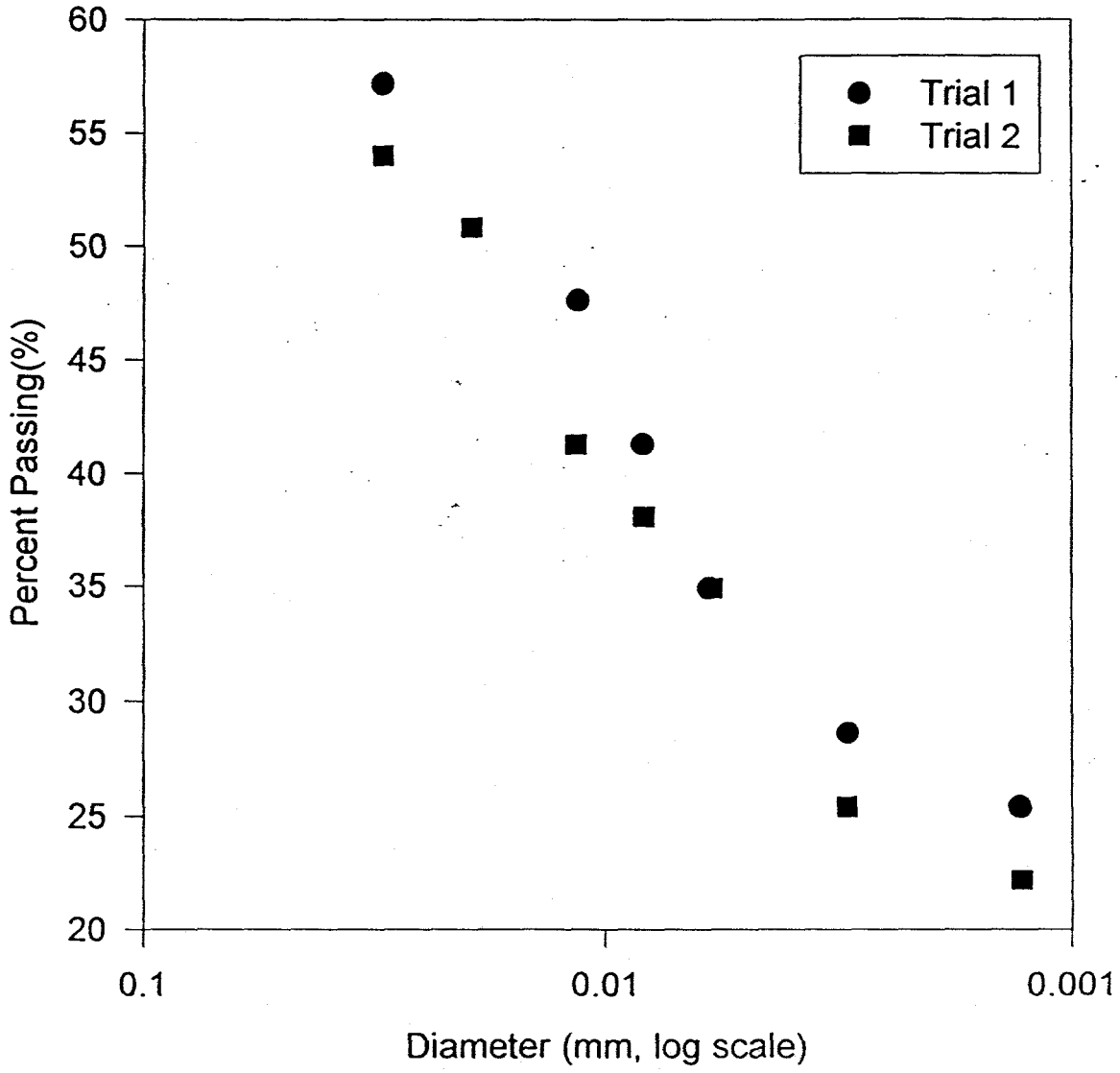
Operator: Mike Sabovish & Alan Williamson Date: 5/21/96 - 5/22/96 Project: DESF Ashland Site

Soil: B1 - 7.5' G_s: 2.69 - Avg ≈ 2.70 Hydrometer No. 151H

	Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
5-21	12:15	0								
	12:17	2	18	25	.0127	.99	3.5	57.2	11.5	.03045
	12:20	5	18	25	.0127	.99	3.5	57.2	11.5	.03045
	12:30	15	15	25	.0127	.99	3.5	47.6	12.3	.01150
	12:45	30	13	25	.0127	.99	3.5	41.3	12.9	.00833
	1:15	60	11	25	.0127	.99	3.5	34.9	13.4	.00600
	4:25	250	9	24	.0128	.99	3.8	28.6	13.9	.00302
5-22	12:15	1440	8	23	.0130	.99	4.1	25.4	14.2	.00129

151H

Ashland Site
Boring 1; 7.5 feet



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$M_{dry} = 50.0g$

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DATA FORM FOR HYDROMETER ANALYSIS

Operator: Mike Saboonsh Date: 5/22/96 - 5/23/96 Project: DESF Ashland Site

Soil: B2 - 15' G_s: 2.65 Hydrometer No. 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
5/22 9:43	0								
9:45	2	17	24°	.01301			54.6	11.8	.03160
9:48	5	15	24°	.01301			48.2	12.3	.02041
9:58	15	14	24°	.01301			45.0	12.6	.01192
10:13	30	13	24°	.01301			41.8	12.9	.00853
10:43	60	12	24°	.01301			38.5	13.1	.00608
1:53	250	10	25°	.01286			32.1	13.7	.00301
5/23 9:43	1440	8	22°	.01332			25.7	14.2	.00132

143

$m_{dry} = 2.09$

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3212.12

DATA FORM FOR HYDROMETER ANALYSIS

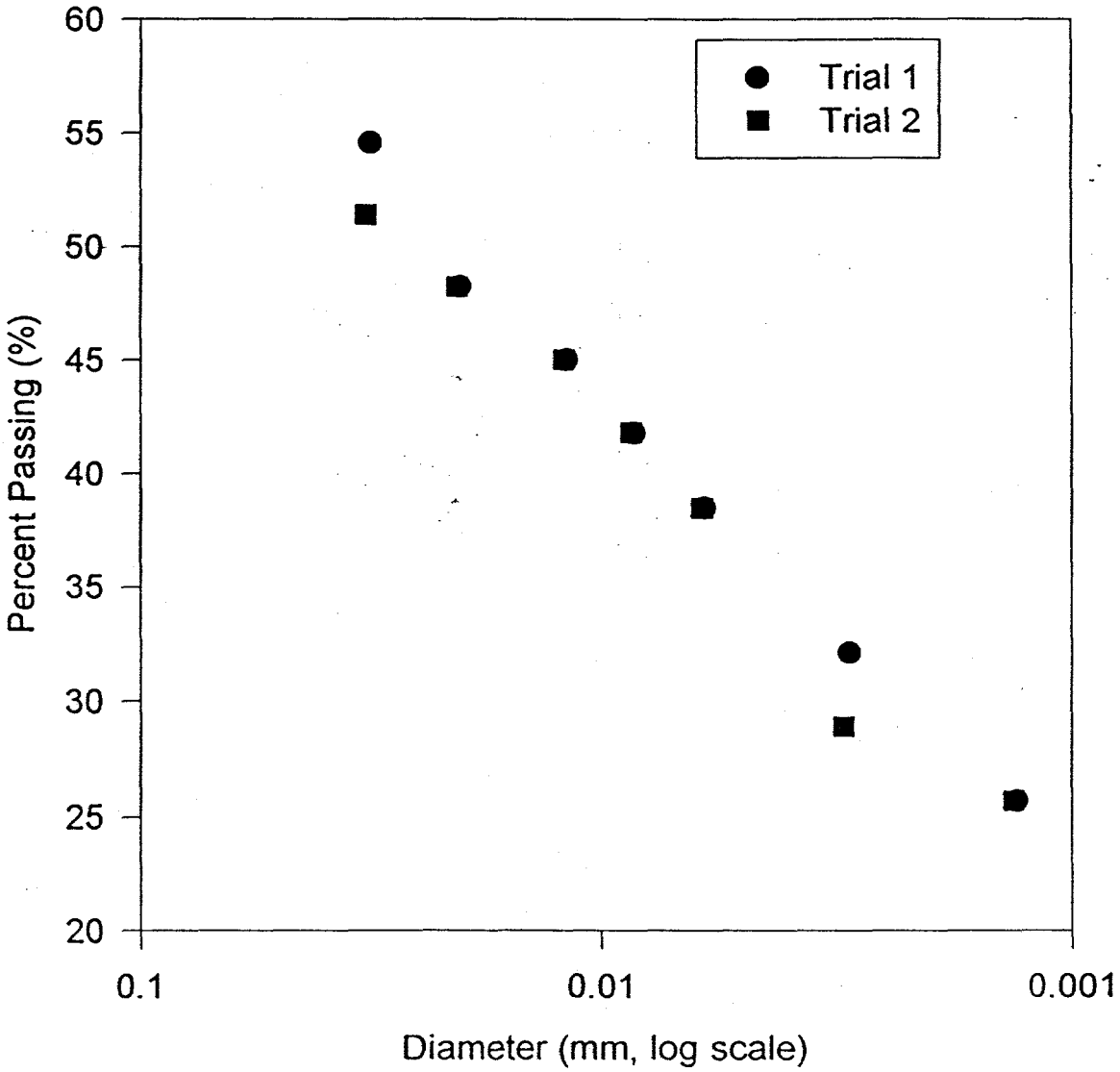
Operator: Nikolas A Kamaradas / Milo Shaboon II — Date: 5/22/96 - 5/23/96 — Project: DESF Ashland Site

Soil: B1 - 15' — G_s: 2.65 — Hydrometer No. 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
5-22 9:43	0								
9:45	2	16	23	.01317			51.4	12.1	.03239
9:48	5	15	23	.01317			48.2	12.3	.02066
9:58	15	14	23	.01317			45.0	12.6	.01207
10:13	30	13	23	.01317			41.8	12.9	.00864
10:43	60	12	23	.01317			38.5	13.1	.00615
1:53	250	9	24	.01301			28.9	13.9	.00310
5-23 9:43	1440	8	21	.01348			25.7	14.2	.00134

TH1

Ashland Site
Boring 1; 15 feet



$m_D = .01$

West Virginia University — Department of Civil Engineering

3124.1

DATA FORM FOR HYDROMETER ANALYSIS

Operator: Mike Sabodish JR. Date: ~~6/5/96~~ 6/4/96 Project: DESF Ash/Army Site

Soil: B2 - 2.5' G_s: 2.68 Hydrometer No. 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
6/4 11:45	0								
11:47	2	25	25	.01267			79.6	9.7	.02790
11:50	5	24	25	.01267			76.4	10.0	.01792
12:00	15	18	25	.01267			57.3	11.5	.01109
12:15	30	16	25	.01267			50.9	12.1	.00805
6/4 12:45	60	14	24	.01282			44.6	12.6	.00587
3:55	250	12	23	.01297			38.2	13.1	.00297
6/5 11:45	1440	10	20	.01344			31.8	13.7	.00131

3190.5

$h_D = 10.5$

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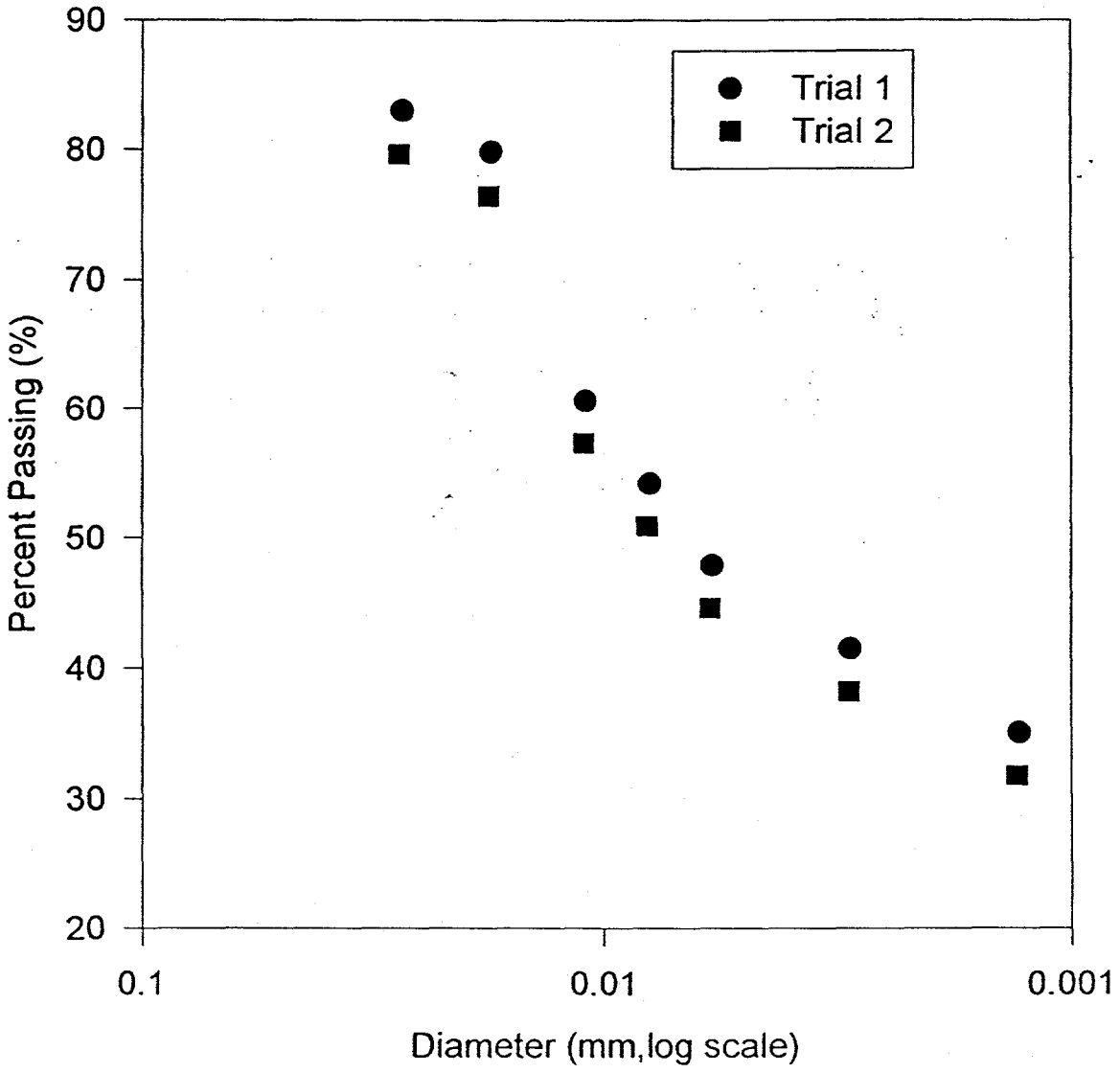
DATA FORM FOR HYDROMETER ANALYSIS

Operator: Mike Sabolish JR Date: ~~6/5/96~~ 6/4/96 Project: DESF Ashland Site

Soil: B2 - 2.5' G_s: 2.68 Hydrometer No. 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
6/4 11:45	0								
11:47	2	26	25	.01267			83.0	9.4	.02747
11:50	5	25	25	.01267			79.8	9.7	.01765
12:00	15	19	25	.01267			60.6	11.3	.01100
12:15	30	17	25	.01267			54.2	11.8	.00795
12:45	60	15	24	.01282			47.9	12.3	.00580
3:55	250	13	23	.01297			41.5	12.9	.00295
6/5 11:45	1440	11	20	.01344			35.1	13.4	.00130

Ashland Site
Boring 2; 2.5 feet



3/L 2.71

$M_D = 50.09$

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DATA FORM FOR HYDROMETER ANALYSIS

Operator: Mike Saboish Jr Date: 6/5/96 Project: DESF Ashland Site

Soil: 132-7.5' G_s: 2.72 Hydrometer No. 151 H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
6/5 12:00	0								
12:02	2	21	22	.01312			66.4%	10.7	.03035
12:05	5	18	22	.01312			56.9%	11.5	.01990
12:15	15	14	22	.01312			44.3%	12.6	.01202
12:30	30	12	22	.01312			38.0%	13.1	.00867
1:00	60	10	22	.01312			31.6%	13.7	.00627
4:10	250	8	23	.01297			25.3%	14.2	.00310
6/6 12:00	1440	6	22	.01312			19.0%	14.7	.00133

1479

3142.77

West Virginia University

MD = 11.09

Department of Civil Engineering

DATA FORM FOR HYDROMETER ANALYSIS

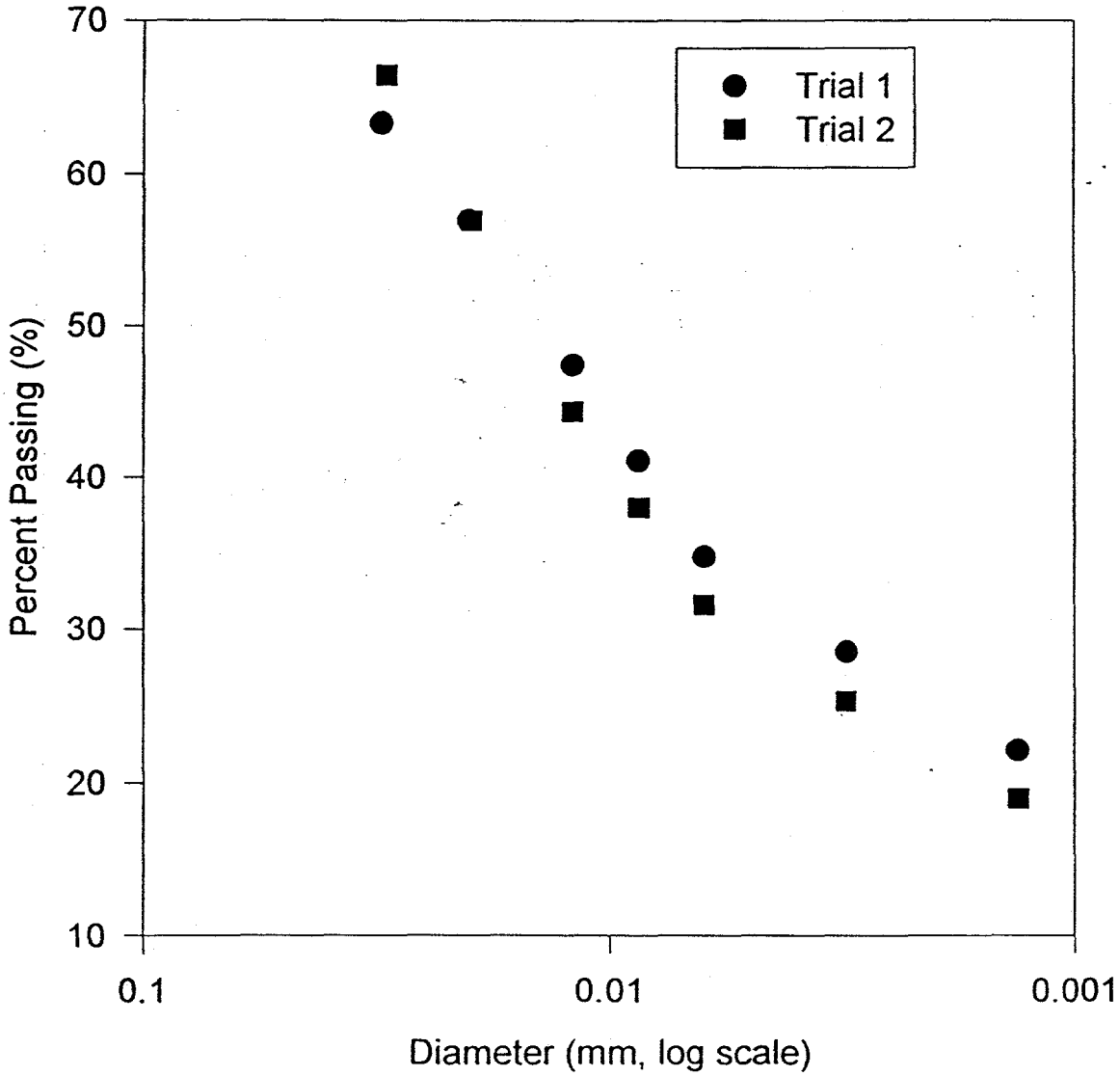
Operator: Michael SABOLICH JR Date: 6/5/96 Project: DESF Ashland Site

Soil: B2 - 7.5' G_s: 2.72 Hydrometer No. 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
6/5 12:00	0								
12:02	2	20	21	.01328			63.3%	11.0	.03114
12:05	5	18	21	.01328			56.9%	11.5	.02014
12:15	15	15	21	.01328			47.4%	12.3	.01203
12:30	30	13	21	.01328			41.1%	12.9	.00871
1:00	60	11	21	.01328			34.8%	13.4	.00628
4:10	250	9	22	.01312			28.5%	13.9	.00309
6/6 12:00	1440	7	21	.01328			22.1%	14.4	.00133

50

Ashland Site
Boring 2; 7.5 feet



3211.47

$M_D = .001g$

West Virginia University

Department of Civil Engineering

DATA FORM FOR HYDROMETER ANALYSIS

Operator: Mike Sabodish III Date: 6/6/96 Project: DESF Ashland Site

Soil: B2 - 12.5' G_s: 2.65 Hydrometer No. 151H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
6/6 12:07	0								
12:09	2	16	25	.01286			51.4%	12.1	.03163
12:12	5	15	26	.01272			48.2%	12.3	.01995
12:22	15	13	26	.01272			41.7%	12.9	.01180
12:37	30	11	25	.01286			35.3%	13.4	.00859
1:07	60	10	25	.01286			32.1%	13.7	.00615
4:17	250	7	26	.01272			22.5%	14.4	.00305
6/7 12:07	1440	6	26	.01272			19.3%	14.7	.00129

152

3 22.5

$M_D = 4.67_5$

West Virginia University

Department of Civil Engineering

DATA FORM FOR HYDROMETER ANALYSIS

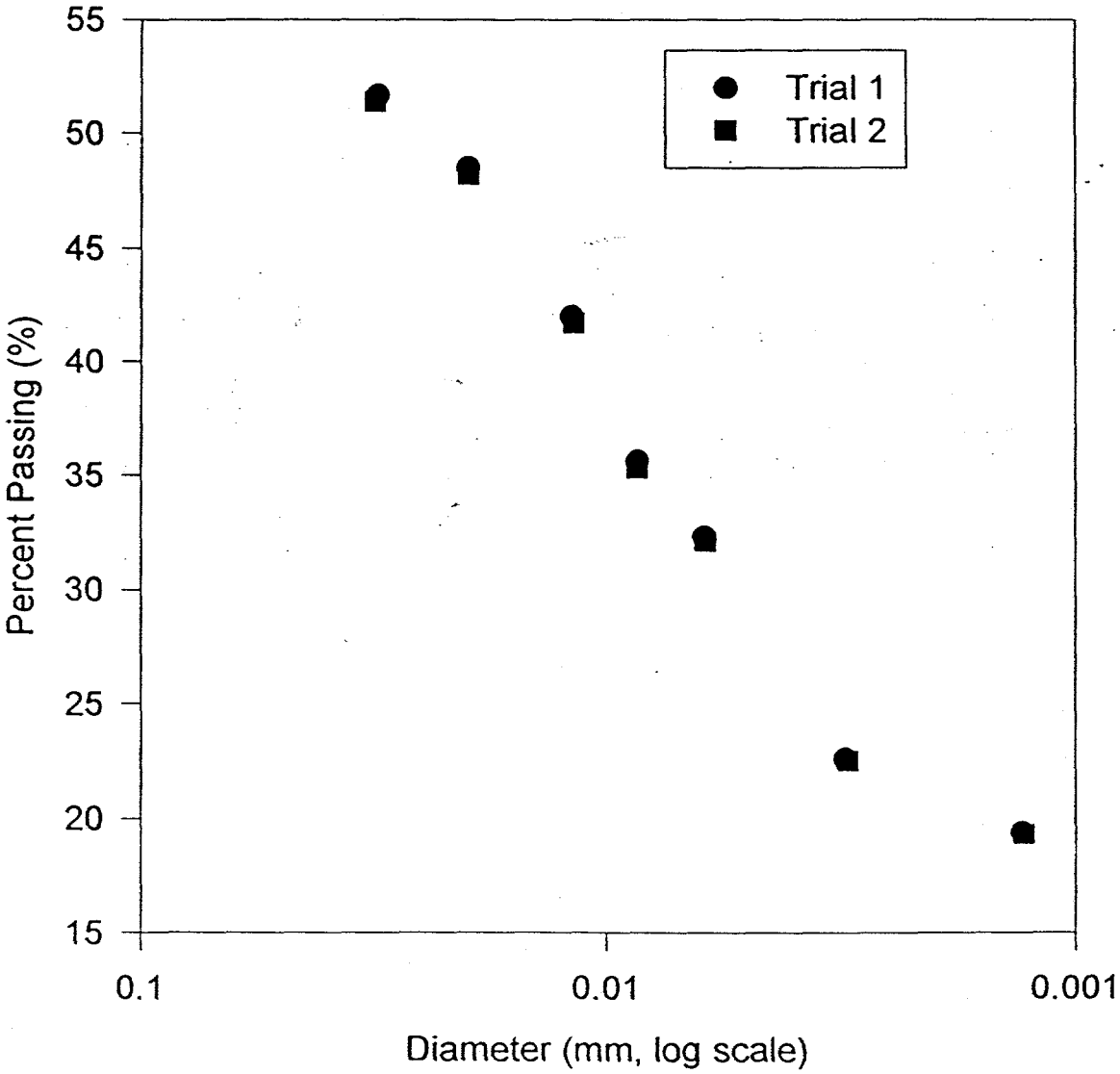
Operator: Mike Sadovich Jr. Date: 6/6/96 Project: DESF Ashland Site

Soil: B2-12.5' G_s: 2.65 Hydrometer No. 151 H

Time	Elapsed Time (min)	Hydrometer Reading (R)	Temperature (°C)	K (Table 2)	a (Table 3)	b (Table 4)	Percent Finer (Eq. 7)	Effective Depth (cm) (Eq. 5)	Particle Diameter (mm) (Eq. 6)
6/6 12:07	0								
12:09	2	16	26	.01272			51.7%	12.1	.03129
12:12	5	15	26	.01272			48.5%	12.3	.01995
12:22	15	13	25	.01286			42.0%	12.9	.01193
12:37	30	11	25	.01286			35.6%	13.4	.00859
1:07	60	10	25	.01286			32.3%	13.7	.00615
4:17	250	7	25	.01286			22.6%	14.4	.00309
6/7 12:07	1440	6	25	.01286			19.4%	14.7	.00130

53

Ashland Site
Boring 2; 12.5 feet



ATTERBERG LIMITS

5.0 ATTERBERG LIMITS

Name M.16 SAB DISH Nikolas A. Kamarados

Date 5/28/96 Comments B1 - 2.5'

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.	6	7	8	9		
Wet Wt. + Tare	26.8	29.47	27.92	24.38		
Dry Wt. + Tare	24.71	27.46	26.27	22.50		
Wt. of Water	2.09g	2.01	1.65	1.88		
Tare Wt.	17.68	21.72	21.92	17.59		
Dry Wt.	7.03g	5.74	4.35	4.91		
Moisture Content	29.7%	35.0%	37.9%	38.3%		
No. of Blows	150	29	25	21		
LL	36.9	35.6	37.9	37.5	Avg = 37	

PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	X					
Wet Wt. + Tare	47.52					
Dry Wt. + Tare	42.09					
Wt. of Water	5.43					
Tare Wt.	17.37g					
Dry Wt.	24.72					
Moisture Content	22.0%					
Plastic Limit	22					

Liquid Limit = 37

Plastic Limit = 22

Plasticity Index = 15

	Test 1	Test 2
LL	37	39
PL	22	20
PI	15	19

w_c vs N
y x
Arith. scale log scale

Avg LL PL PI
38 21 55 17

5.0 ATTERBERG LIMITS

Name Michael Sesodish Nikolas A Kamaradas

Date 5/28/96 Comments B1 - 2.5'

2 pm 5-28-96

11 am 5-29-96

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.		2	3	4	5	
Wet Wt. + Tare	25.29g	30.49g	27.29g	33.86	—	
Dry Wt. + Tare	23.38g	28.08g	24.58g	30.45g	—	
Wt. of Water	1.91g	2.41g	2.71g	3.41g	—	
Tare Wt.	17.33g	21.55g	17.36g	21.68g	~~16.73g~~	
Dry Wt.	6.05g	6.53g	7.22g	8.77g	—	
Moisture Content	31.6%	36.9%	37.5%	38.9%	—	
No. of Blows	147	35	31	23	—	
LL	39.2	38.4	38.5	38.5	Avg = 38.7	

PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	7					
Wet Wt. + Tare	48.79					
Dry Wt. + Tare	43.56g					
Wt. of Water	5.14g					
Tare Wt.	17.37g					
Dry Wt.	26.13					
Moisture Content	19.7%					
Plastic Limit	20					

Liquid Limit = 39

Plastic Limit = 20

Plasticity Index = 19

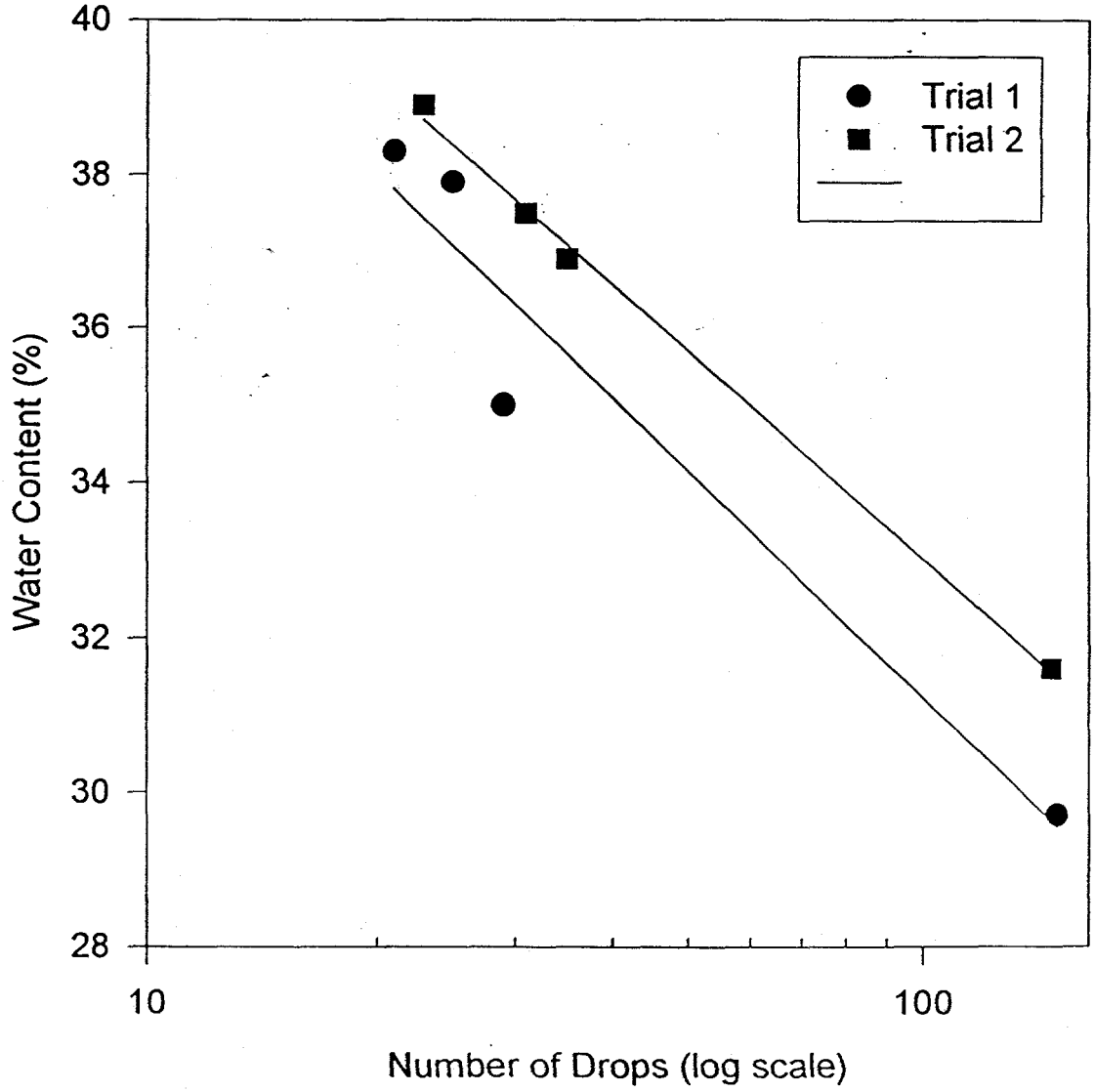
w_c vs N

y x

arith. scale log scale

$$LL = w_N \left(\frac{N}{25}\right)^{.121}$$

Ashland Site
Boring 1; 2.5 feet



5.0 ATTERBERG LIMITS

Name Michael SABOOISH JR

Date 5/29/96 Comments B2 - 7.5'

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.	1	2	3	4		
Wt. Wet + Tare	21.41g	28.45	26.35	30.48		
Wt. Dry + Tare	20.53g	26.92	24.34	28.49g		
Wt. of Water	.88	1.53	2.01	1.99		
Tare Wt.	17.37	21.64	17.37	21.77		
Dry Wt.	3.16	5.28	6.97	6.72		
Moisture Content	27.8	29.0%	28.8%	29.6%		
No. of Blows	65	22	32	28		
LL	31.2	28.6	29.7	30.0	Avg = 29.9	

PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	M					
Wt. Wet + Tare	50.23g					
Wt. Dry + Tare	45.51g					
Wt. of Water	4.72					
Tare Wt.	18.28					
Dry Wt.	27.23					
Moisture Content	17.33					
Plastic Limit	17.3					

Liquid Limit = 30

Plastic Limit = 17

Plasticity Index = 13

	Test 1	Test 2
LL	30	30
PL	17	19
PI	13	11

158 Avg LL PL PI

30 15 12

5.0 ATTERBERG LIMITS

Name Michael Sabodish Jr Nikolas A. Kamarado

Date 5/29/96 Comments B1 - 7.5'

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.	6	7 MS #3	8	9		
Wt. Wet + Tare	23.96	30.71	28.65	24.77		
Wt. + Tare	22.62g	28.7g	27.15	23.11g		
Wt. of Water	1.34	2.01	1.5	1.66		
Tare Wt.	17.69	21.73	21.89	17.60		
Dry Wt.	4.93	6.97	5.26	5.51		
Moisture Content	27.2%	28.8%	28.5%	30.1%		
No. of Blows	60	40	33	20		
LL	30.2	30.5	29.5	29.3	Avg = 29.9	

PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	N					
Wt. Wet + Tare	48.94					
Wt. + Tare	44.13					
Wt. of Water	4.81					
Tare Wt.	18.33					
Dry Wt.	25.8					
Moisture Content	18.6					
Plastic Limit	19					

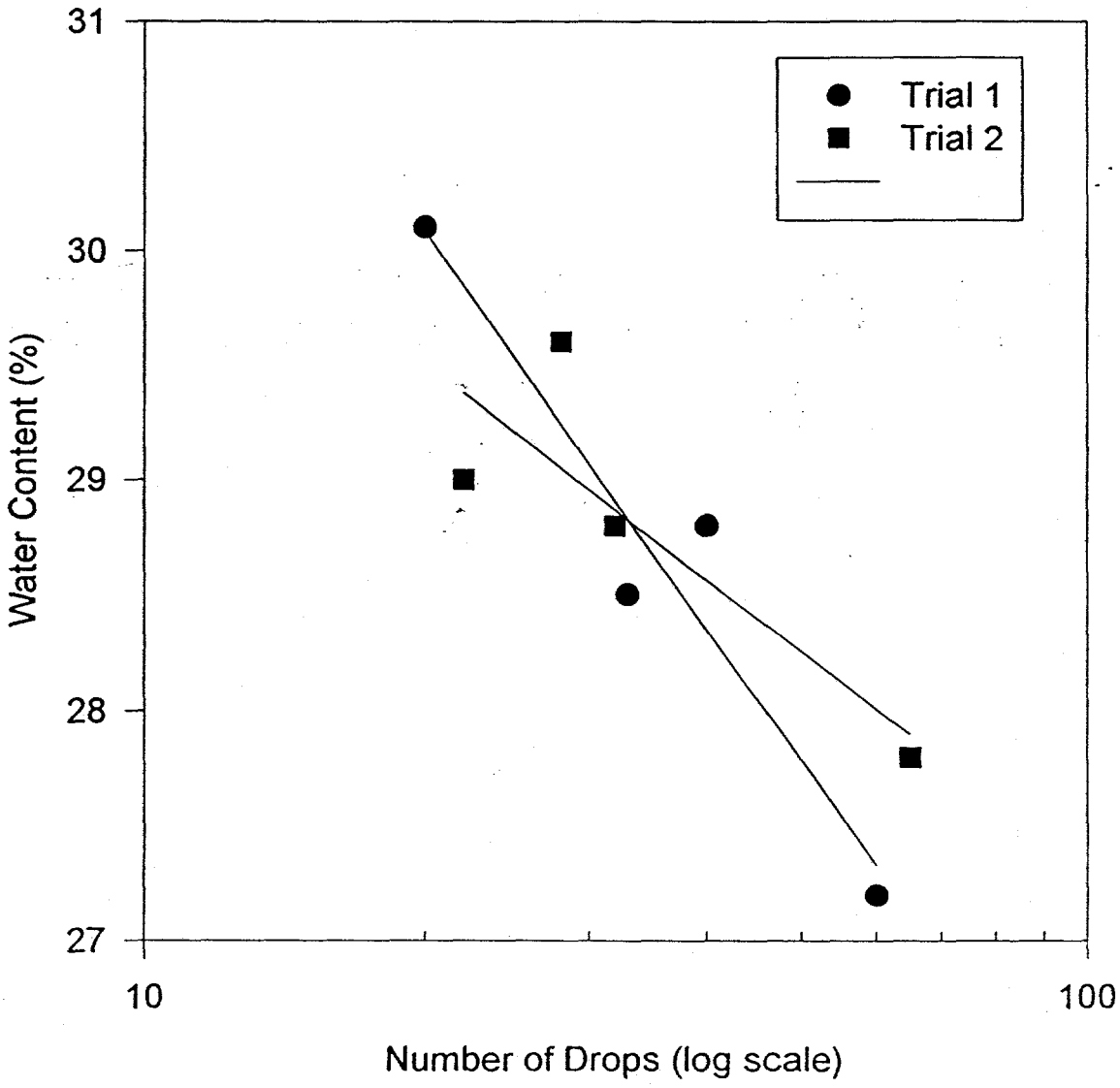
Liquid Limit = 30

Plastic Limit = 19

Plasticity Index = 11

$LL = w_N \left(\frac{N}{25}\right)^{.121}$

Ashland Site
Boring 1; 7.5 feet



5.0 ATTERBERG LIMITS

Name Mike Sabodish Jr Nikolas A. Komarados

Date 5/30/96 Comments B2 - 15.0'

LIQUID LIMIT

Run No.	1	2	3	4	5	6
Container No.	1	2	3	4		
Wet + tare	26.87	28.62	26.91	31.94		
Dry + tare	25.08	27.23	24.99	29.68		
Tare	1.79	1.39	1.92	2.26		
Dry W	17.35	21.57	17.37	21.69		
Water W	7.73	5.66	7.62	7.99		
Moisture Content	23.16%	24.56%	25.20%	28.29%		
No. of Blows	64	46	41	22		

WET
DRY

LL 25.9 26.4 27.1 27.8 AVG = 27

PLASTIC LIMIT

Run No.	1	2	3	4	5	6
Container No.	B					
Wet + tare	47.61					
Dry + tare	43.65					
Tare	3.96					
Dry W	17.38					
Water W	26.27					
Moisture Content	15.07%					
Plastic Limit	15					

Liquid Limit = 27

Plastic Limit = 15

Plasticity Index = 12

	Trial 1	Trial 2
LL	27	27
PL	15	17
PI	12	10

$LL = N\left(\frac{w_N}{25}\right)^{.121}$

Avg IGP	LL	PL	PI
	27		

NAK

5.0 ATTERBERG LIMITS

Name Michael Sabourin Jr Nikolas A Kamarados

Date 5/30/96 Comments B2 - 15'

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.	6	7	8	9		
Wet Wt. + Tare	28.94	29.35	27.78	23.27		
Dry Wt. + Tare	26.85	27.84	26.59	22.02		
Wt. of Water	2.09	1.51	1.19	1.25		
Tare Wt.	17.69	21.72	21.89	17.59		
Dry Wt.	9.16	6.12	4.7	4.43		
Moisture Content	22.82%	24.67%	25.32%	28.22%		
No. of Blows	74	52	42	17		
LL	26	27	27	27	AVG = 27	

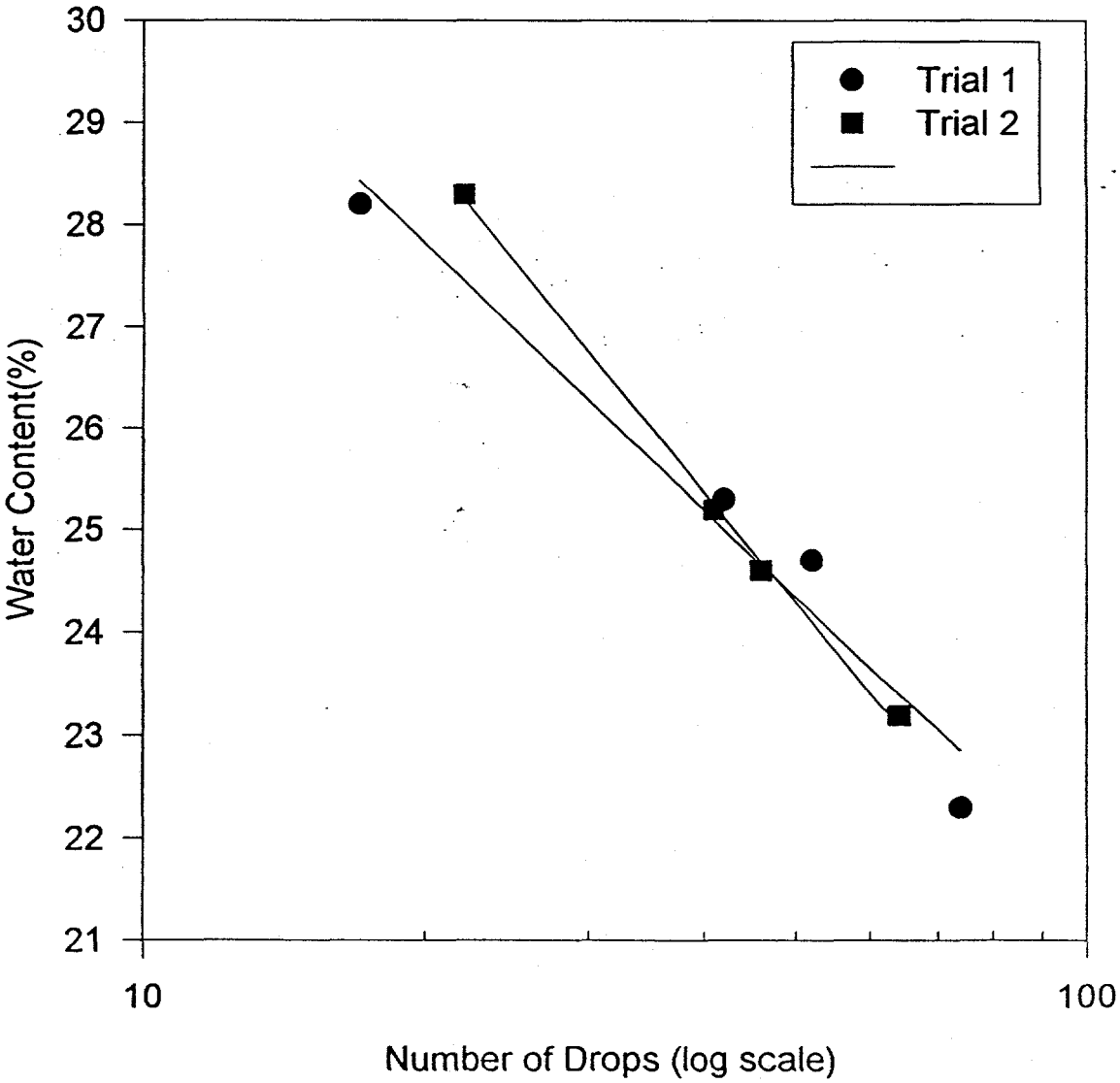
PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	A					
Wet Wt. + Tare	48.50					
Dry Wt. + Tare	44.08					
Wt. of Water	4.42					
Tare Wt.	17.39					
Dry Wt.	26.69					
Moisture Content	16.56%					
Plastic Limit	17					

Liquid Limit = 27

Plastic Limit = 17

Plasticity Index = 10

Ashland Site
Boring 1; 15 feet



5.0 ATTERBERG LIMITS

Name Michael Sabouish

Date 6/10/96 Comments B2 - 2.5' TRIAL 1

LIQUID LIMIT

Run No.	1	2	3	4	5	6
Container No.	1	2	3	4		
Wet + Tare	23.48	28.05	27.63	35.80		
Dry + Tare	21.80	26.28	24.68	31.59		
Water	1.68	1.77	2.95	4.21		
Tare Wt.	17.33	21.57	17.36	21.69		
Dry Wt	4.47	4.71	7.32	9.90		
Moisture Content	38%	38%	40%	43%		
No. Blows	48	36	24	17		
LL	41	40	40	46	Avg = 42	

PLASTIC LIMIT

Run No.	1	2	3	4	5	6
Container No.	B					
Wt. Wet + Tare	48.13					
Wt. Dry + Tare	42.86					
Wt. Water	5.27					
Tare Wt.	17.38					
Dry Wt.	25.48					
Moisture Content	21%					
Plastic Limit	21					

Liquid Limit = 42

Plastic Limit = 21

Plasticity Index = 21

	Trial 1	Trial 2
LL	42	40
PL	21	22
PI	21	18

$LL = w_{no} \left(\frac{N}{25}\right)^{.121}$

Avg 164 LL PL PI

5.0 ATTERBERG LIMITS

Name Mike SABOOISH JR Nikolas A. Kamarades

Date 6/16/96 Comments B2 - 2.5' TRIAL 2

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.	6	7	8	9		
Wt. Soil + Tare	20.77	23.42	25.41	23.26		
Wt. Dry + Tare	19.94	22.96	24.39	21.54		
Wt. Water	.83	.46	1.02	1.72		
Tare Wt.	17.72	21.72	21.89	17.62		
Dry Wt.	2.22	1.24	2.50	3.92		
Moisture Content	37%	37%	41%	44%		
No. of Blows	40	36	25	18		
	39	39	41	42	AVG =	40

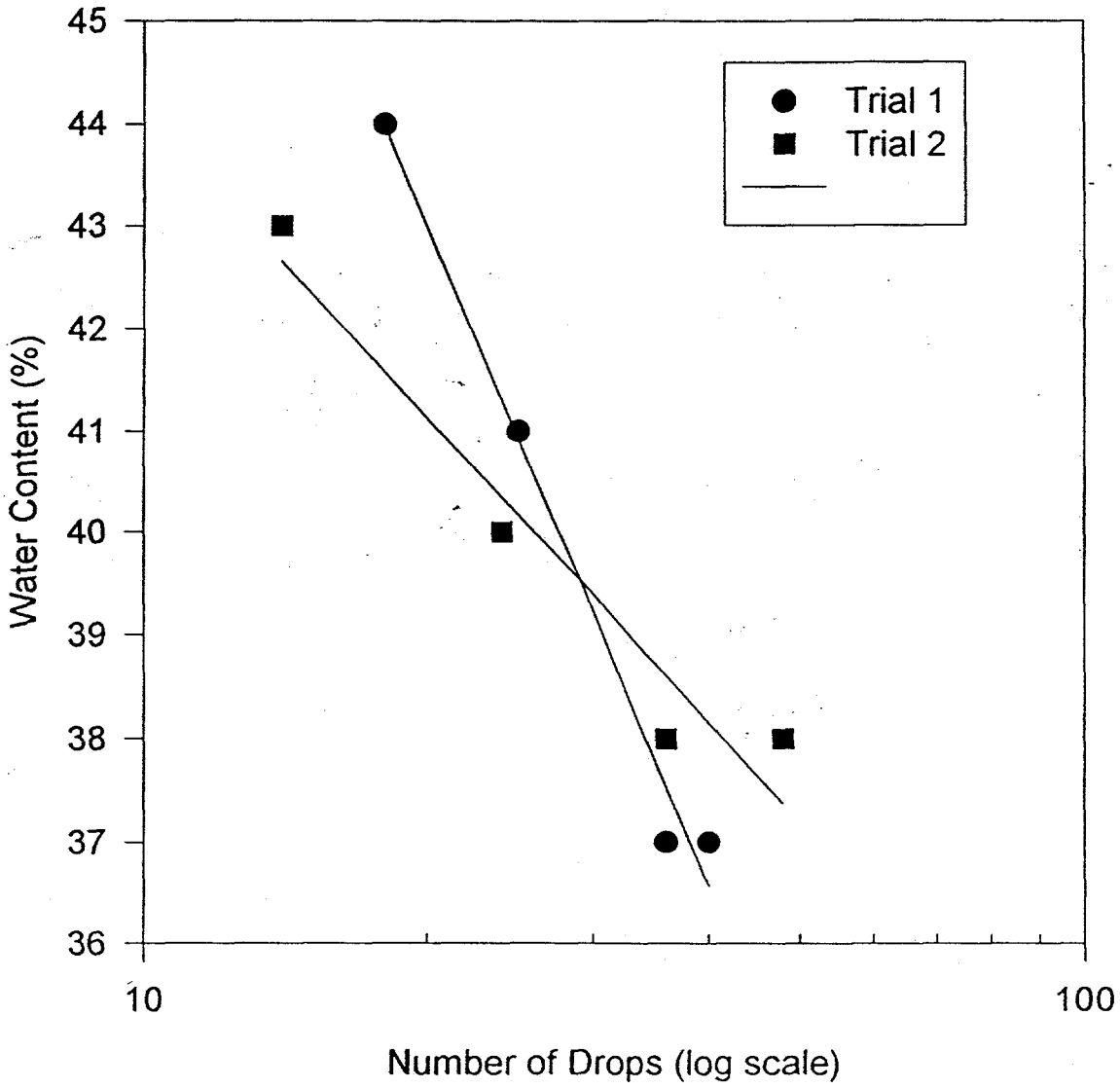
PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	A					
Wt. Wet + Tared	48.07					
Wt. Dry + Tare	42.55					
Wt. Water	5.52					
Tare Wt.	17.37					
Dry Wt.	25.18					
Moisture Content	22%					
Plastic Limit	22					

Liquid Limit = 40

Plastic Limit = 22

Plasticity Index = 18

Ashland Site
Boring 2; 2.5 feet



5.0 ATTERBERG LIMITS

Name Michael S Jacovish JR NAK Trial # 1

Date 6/11/96 Comments B2 - 7.5' ASHLAND SITE

LIQUID LIMIT

Run No.	1	2	3	4	5	6
Container No.	1	2	3	4		
Wet + Tare	27.42	30.93	33.52	33.84		
Dry + Tare	25.16	28.93	30.06	31.06		
Water	2.26	2.00	3.46	2.78		
Tare Wt.	17.33	21.56	17.35	21.68		
Dry Wt.	7.83	7.37	12.71	9.38		
Moisture Content	29%	27%	27%	30%		
No. of Blows	19	32	23	11		
LL	28	28	27	27		Avg 28

PLASTIC LIMIT

Run No.	1	2	3	4	5	6
Container No.	A					
Wet + Tare	49.48					
Dry + Tare	44.97					
Water	4.51					
Tare Wt.	17.36					
Dry Wt.	27.61					
Moisture Content	16%					
Plastic Limit	16					

Liquid Limit = 28

Plastic Limit = 16

Plasticity Index = 12

	Trial 1	Trial 2
LL	28	28
PL	16	18
PI	12	10

Avg LL PL PI

28 167 17 11

5.0 ATTERBERG LIMITS

Name Michael S Sabodish Jr Nicholas Kyriakides Trial #2

Date 6/11/96 Comments B2 - 7.5' Ashland Site

LIQUID LIMIT

Run No.	1	2	3	4	5	6
Container No.	6	7	8	9		
wet + TARE	24.59	28.44	27.35	24.28		
Dry + TARE	23.07	27.0	26.18	22.72		
wt of H_2O	1.52	1.44	1.17	1.56		
TARE wt	17.68	21.69	21.87	17.60		
Dry wt	5.39	5.31	4.31	5.12		
Moisture Content	28%	27%	27%	30%		
No. Blows	17	26	38	14		
LL	27	27	28	28		Avg = 28

PLASTIC LIMIT

Run No.	1	2	3	4	5	6
Container No.	B					
Wet + Tare	47.97					
Dry + Tare	43.28					
Wt. Water	4.69					
Tare Wt.	17.36					
Dry Wt.	25.92					
Moisture Content	18%					
Plastic Limit	18					

Liquid Limit = 28

Plastic Limit = 18

Plasticity Index = 10

ATTACHMENT B

SITE LOCATION

Ashland Branded Marketing, Inc. Facility #289-020 at 257 Main Street, Weston, West Virginia is the location of the PVD project. The facility is a closed-down gasoline station. The proposed area for the 48 ft. x 48 ft. PVD network is located in the back lot of the facility(Refer to Figure B1). There is approximately a four inch layer of asphalt in the rear of the facility. The back lot is currently being used as a parking lot for people working in the area. From surface elevation, there is a small gradient sloping towards the top right corner of the lot (See Figure B1). This slope leads to the West Fork River located behind Water Street. The Underground Storage Tanks (USTs) placed in the front of the building are scheduled to be removed along with the demolition of the building.

SOILS AND CONTAMINANTS

The site consists primarily of a silty clay, and is relatively medium stiff. The groundwater table is at an average depth of seven feet across the area of the site. The hydraulic conductivity of the soil was found to be approximately 10^{-6} cm/s. From other soil properties tests, the moisture content is an average of 20%, and the specific gravity of the solids is 2.65. The site was tested for several contaminants by the NPTC. Figure B2 shows the locations of the monitoring wells installed by Ashland. This figure also indicates the approximate extent of the contaminated groundwater. Table B1 shows a list of the PAH concentrations on the site as of July 30, 1995. Some of the largest concentrations are outlined in Table 1. Figure B1 outlines the area with which this project will focus on. This area encompasses monitoring wells 4 and 5 which have been indicating the presence of free product.

PILOT SCALE

The pilot scale will be used to approximate airflow and fluid flowrates to be used for the design of the full scale system. This test will be helpful in determining the effectiveness of this technology in a field setting. Ten PVDs are to be used in the pilot scale at two foot spacing, yielding a total length of a twenty foot section of collector pipe. The location of the pilot scale is near MW-2(See Figure B1). In contrast to typical installation methods discussed in Attachment A, the PVDs in the pilot scale test will be placed in pre-drilled bore holes. These bore holes have a diameter of 4" and will approximately be twenty feet deep.

TABLE 1: Groundwater Analytical Summary Table
Ashland Branded Marketing Facility # 289-020
Weston, Lewis County, West Virginia

		Benzene	Toluene	Ethylbenzene	Xylene	Total BTEX	TPH (GRO)	TPH (418.1)
MW-1	Jul 30, 1995	1.090	0.260	0.460	0.690	2.500	4.360	NS
	Nov 91 - Apr 92	1.100	0.059	0.450	0.839	2.448	NS	3.36
MW-2	Jul 30, 1995	0.120	0.010	0.340	0.300	0.770	2.170	NS
	Nov 91 - Apr 92	0.230	< 0.100	1.640	2.820	< 4.790	NS	5.30
MW-3	Jul 30, 1995	NS	NS	NS	NS	NS	NS	NS
	Nov 91 - Apr 92	NS	NS	NS	NS	NS	NS	NS
MW-4	Jul 30, 1995	NS	NS	NS	NS	NS	NS	NS
	Nov 91 - Apr 92	NS	NS	NS	NS	NS	NS	NS
MW-5	Jul 30, 1995	NS	NS	NS	NS	NS	NS	NS
	Nov 91 - Apr 92	0.032	0.017	0.215	0.199	0.463	NS	6.90
MW-6	Jul 30, 1995	0.002	< 0.001	< 0.001	0.022	< 0.026	0.500	NS
	Nov 91 - Apr 92	< 0.005	0.010	0.140	0.550	< 0.705	NS	< 0.200
EB-6A	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.200	NS
MW-7	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	1.42
MW-8	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-9	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-10	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-11	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-12	Jul 30, 1995	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	< 0.100	NS
	Nov 91 - Apr 92	< 0.001	< 0.001	< 0.001	< 0.001	< 0.004	NS	< 0.200
MW-13	Jul 30, 1995	1.580	0.810	1.980	3.330	7.700	16.90	NS
	Nov 91 - Apr 92	1.200	2.700	1.500	5.100	10.500	NS	3.31
MW-14	Jul 30, 1995	2.300	1.440	0.450	1.480	5.670	10.30	NS
	Nov 91 - Apr 92	9.700	9.800	2.800	13.500	35.800	NS	16.90

NOTES:
mg/L denotes milligrams per liter.
TPH (GRO) denotes anlytical method 8015 total petroleum hydrocarbons (gasoline range organics).
MW-3, MW-4, MW-5 not sampled due to presence of free product.
Outlined BTEX results exceed either 0.005 mg/L benzene and/or Federal Drinking Water Maximum Contaminant Levels (MCLs) for toluene (1 mg/L), ethylbenzene (0.7 mg/L), and xylenes (10 mg/L).

h:\users\marcy\ashland\westongw.wq1

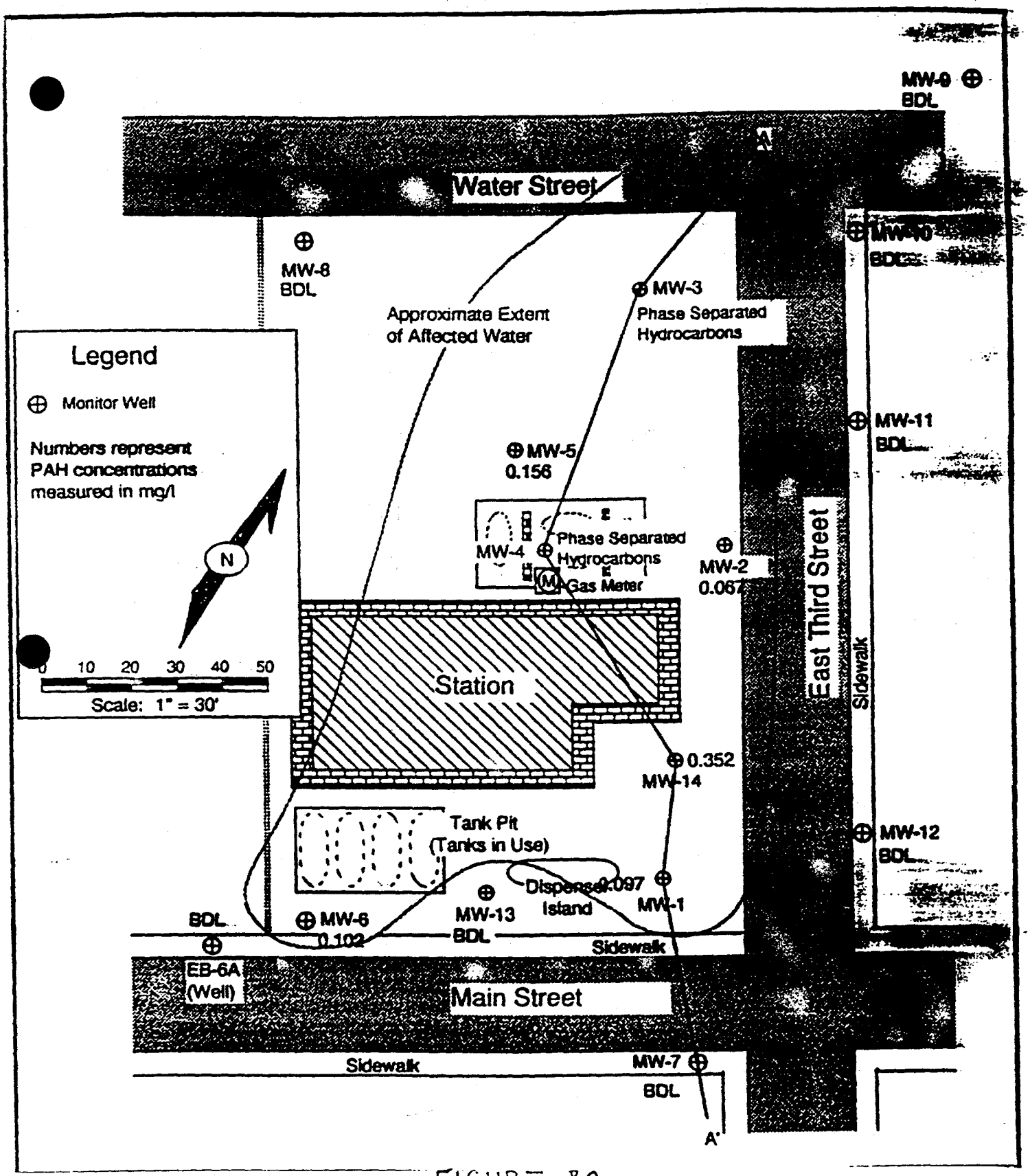
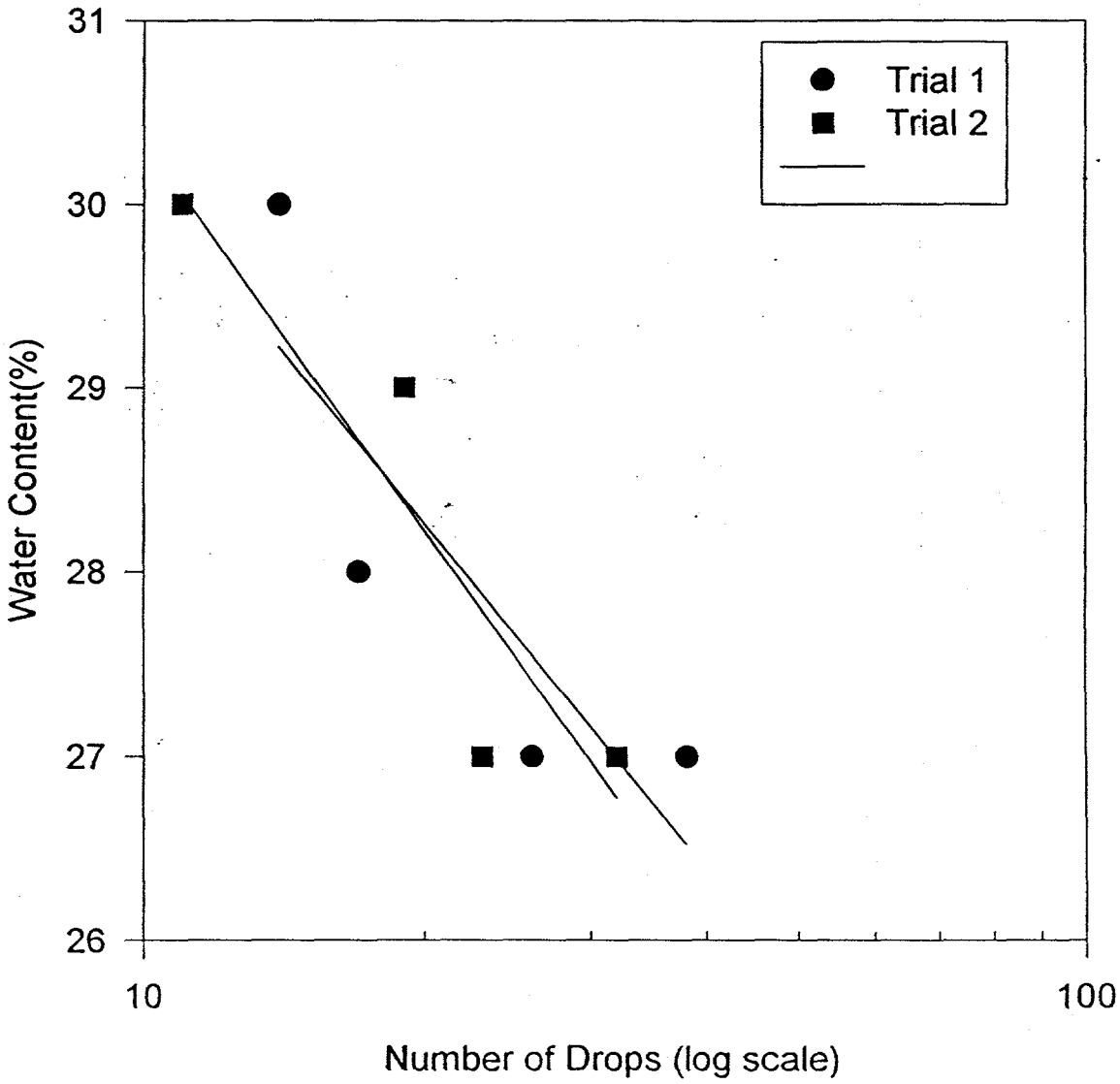

MW-9
BDL
Water Street
MW-8
BDL
Approximate Extent
of Affected Water
MW-3
Phase Separated
Hydrocarbons
MW-10
BDL
MW-11
BDL
Legend
Monitor Well
Numbers represent
PAH concentrations
measured in mg/l
MW-5
0.156
MW-4
Phase Separated
Hydrocarbons
Gas Meter
MW-2
0.067
East Third Street
Sidewalk
N
0 10 20 30 40 50
Scale: 1" = 30'
Station
0.352
MW-14
Tank Pit
(Tanks in Use)
MW-12
BDL
Dispenser Island
0.097
MW-1
MW-13
BDL
BDL
MW-6
0.102
Sidewalk
EB-6A
(Well)
Main Street
Sidewalk
MW-7
BDL
A'

FIGURE B2

Ashland Site
Boring 2; 7.5 feet



5.0 ATTERBERG LIMITS

Name Michael SABODISH JR NAK Trial #1

Date 6/12/96 Comments B2 - 12.5'

LIQUID LIMIT

Run No.	1	2	3	4	5	6
Container No.	1	2	3	4		
Wt. + Tare	27.36	37.35	28.09	33.17		
Wt.	25.35	34.20	25.88	30.68		
Wt. Water	2.01	3.15	2.21	2.49		
Wt. W	17.33	21.56	17.35	21.67		
Wt. Wet	8.02	12.64	8.53	9.01		
Moisture Content	25%	25%	26%	28%		
No. Blows	38	26	19	9		
LL	26	25	25	25		Avg = 25

PLASTIC LIMIT

Run No.	1	2	3	4	5	6
Container No.	B					
Wt. + Tare	48.18					
Wt.	44.18					
Wt. Water	4.0					
Wt. W	17.37					
Wt. W	26.81					
Moisture Content	15%					
Plastic Limit	15					

Liquid Limit = 25

Plastic Limit = 15

Plasticity Index = 10

	Trial 1	Trial 2
LL	25	25
PL	15	17
PI	10	8

Avg	LL	PL	PI
173	25	16	9

5.0 ATTERBERG LIMITS

Name Michael Saboda JR Nikolas A. Kapanka TRial # 2

Date 6/12/96 Comments B2 - 12.5'

LIQUID LIMIT						
Run No.	1	2	3	4	5	6
Container No.	6	7	8	9		
Wt. Soil + Tare	22.30	25.75	27.18	23.84		
Wt. Dry Soil + Tare	21.38	24.94	26.07	22.46		
Wt. Water	.92	.81	1.11	1.38		
Tare Wt.	17.59	21.73	21.87	17.63		
Dry Wt. Soil	3.79	3.21	4.20	4.83		
Moisture Content	24%	25%	26%	29%		
No. Blows	35	25	19	10		
LL	25	25	25	26	Avg = 25	

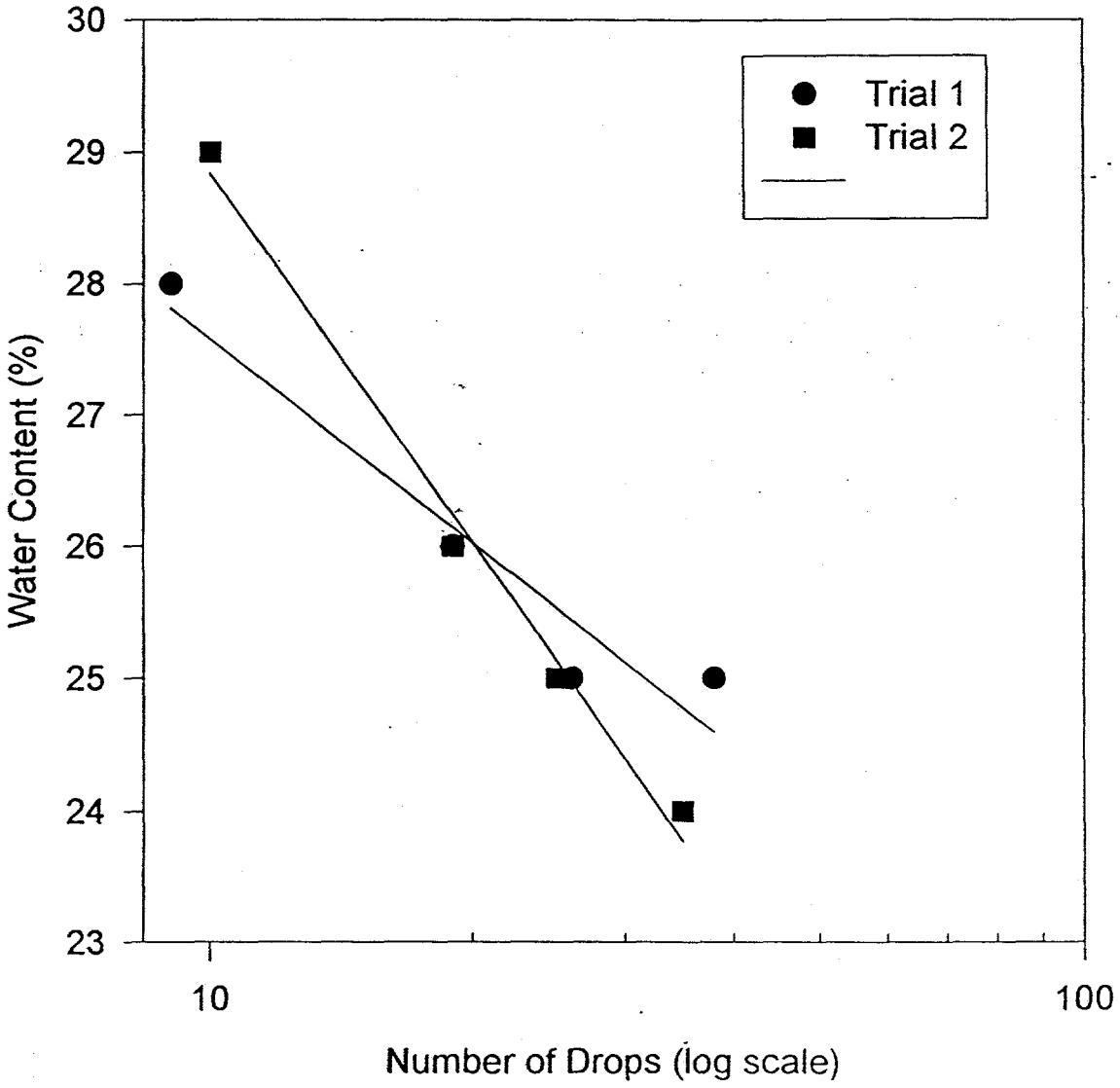
PLASTIC LIMIT						
Run No.	1	2	3	4	5	6
Container No.	A					
Wt. Soil + Tare	48.98					
Wt. Dry Soil + Tare	44.47					
Wt. Water	4.51					
Tare Wt.	17.35					
Dry Wt. Soil	27.12					
Moisture Content	17%					
Plastic Limit	17					

Liquid Limit = 25

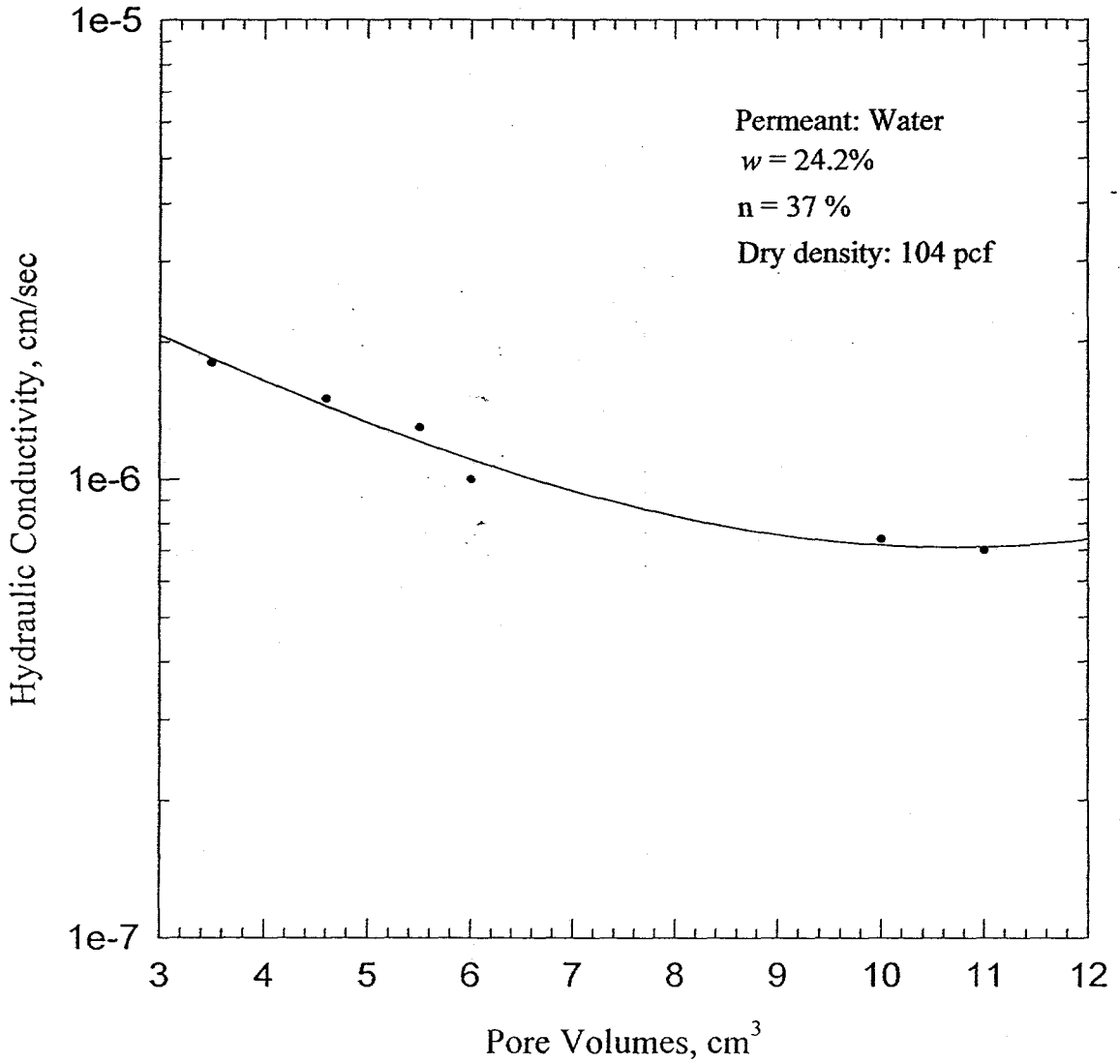
Plastic Limit = 17

Plasticity Index = 8

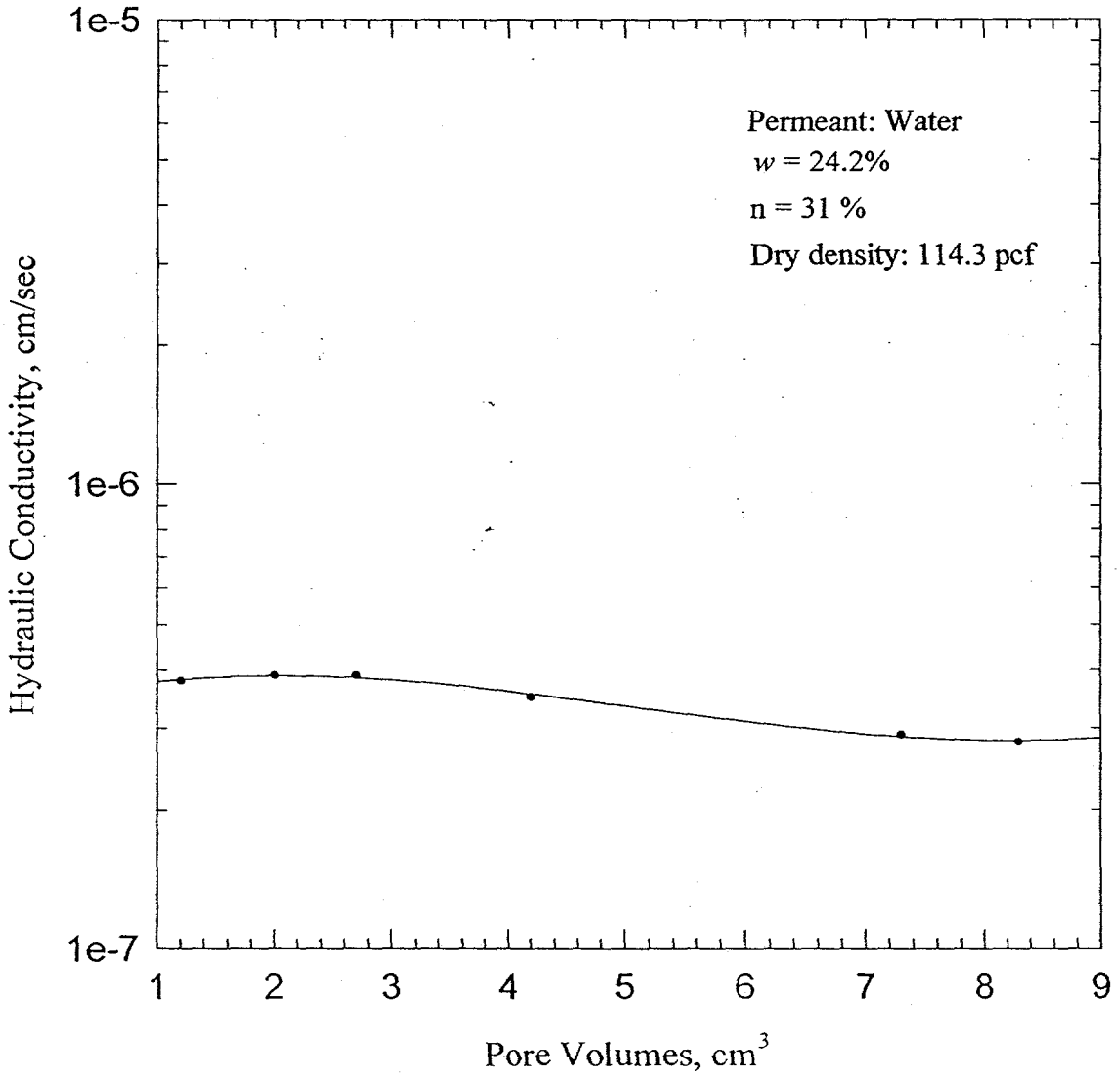
Ashland Site
Boring 2; 12.5 feet



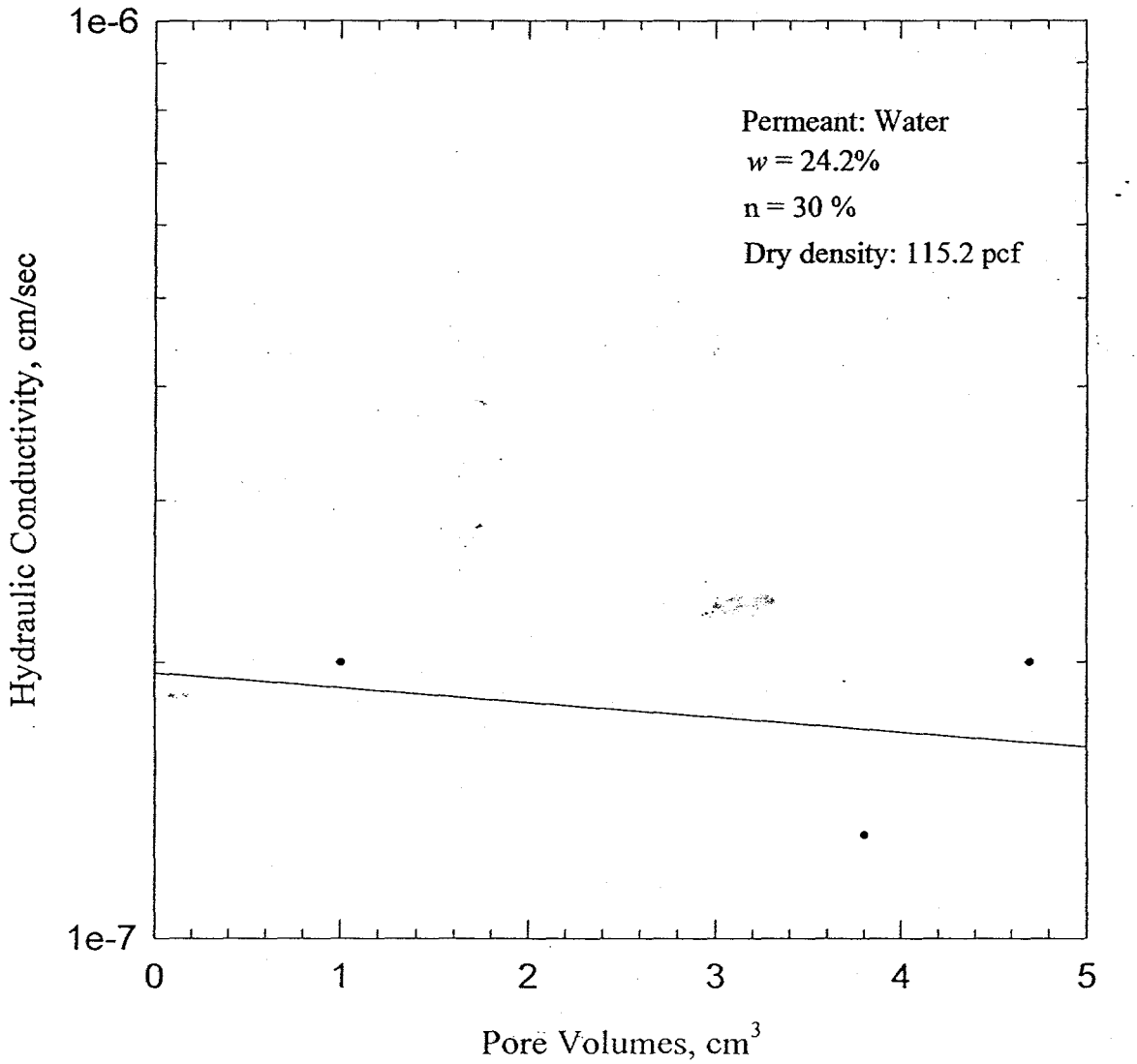
Sample A-1, BTEX-1, Ashland



Sample B-1, BTEX-3, Ashland



Sample C-1, BTEX-2, Ashland



ATTACHMENT C

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 13, 1996
Report No.: 199606130003
PKC #: 060596-01
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: 10.0'
Station Number: B-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/10/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 13, 1996
Report No.: 199606130004
PKC #: 060596-02
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: 5.0'
Station Number: B-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/10/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 13, 1996
Report No.: 199606130005
PKC #: 060596-03
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: 5.0'
Station Number: B-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/10/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/10/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 13, 1996
Report No.: 199606130006
PKC #: 060596-04
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: 10'
Station Number: B-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/12/96	JB

Comments:

Approved by

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 13, 1996
Report No.: 199606130007
PKC #: 060596-05
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: 15'
Station Number: B-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/12/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
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Westover, WV 26502

(304) 291-5961
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Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 13, 1996
Report No.: 199606130008
PKC #: 060596-06
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: 15'
Station Number: B-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Toluene	8020	5.00	13.47	ug/kg	06/12/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/12/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/12/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
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(304) 291-5961
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Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606060001
PKC #: 060596-07
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: A-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/05/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606060002
PKC #: 060596-08
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: A-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/05/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3[illegible]3 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606060003
PKC #: 060596-09
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: A-3
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/05/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/05/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606060004
PKC #: 060596-10
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: B-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	66.77	ug/kg	06/05/96	JB
Toluene	8020	5.00	41.68	ug/kg	06/05/96	JB
Ethylbenzene	8020	5.00	295.47	ug/kg	06/05/96	JB
Xylene	8020	15.00	408.58	ug/kg	06/05/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3012 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100005
PKC #: 060596-11
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: B-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Toluene	8020	5.00	5.73	ug/kg	06/06/96	JB
Ethylbenzene	8020	5.00	52.92	ug/kg	06/06/96	JB
m,p-Xylene	8020	10.00	<10.00	ug/kg	06/06/96	JB
o-Xylene	8020	5.00	12.82	ug/kg	06/06/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3[redacted] Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100006
PKC #: 060596-12
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: B-3
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Toluene	8020	5.00	14.99	ug/kg	06/06/96	JB
Ethylbenzene	8020	5.00	20.27	ug/kg	06/06/96	JB
Xylene	8020	15.00	38.42	ug/kg	06/06/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
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Westover, WV 26502

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Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100007
PKC #: 060596-13
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: C-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/06/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
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Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100008
PKC #: 060596-14
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: C-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Ethylbenzene	8020	5.00	27.89	ug/kg	06/06/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/06/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
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Westover, WV 26502

(304) 291-5961
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Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100009
PKC #: 060596-15
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: C-3
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/06/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/06/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

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Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100010
PKC #: 060596-16
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: D-1
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/07/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3[redacted] Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100011
PKC #: 060596-17
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: D-2
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Ethylbenzene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Xylene	8020	15.00	<15.00	ug/kg	06/07/96	JB

Comments:

Approved by:

PKC ENVIRONMENTAL SERVICES

3023 Greenbag Road
P.O. Box 2400
Westover, WV 26502

(304) 291-5961
Fax (304) 291-5963

Laboratory Report

Customer: National Research Center for Coal and Energy
P.O. Box 6064, Evansdale Drive
Morgantown WV 26506

Attention: Shawn Keslar

Date: June 10, 1996
Report No.: 199606100012
PKC #: 060596-18
COC #: 96F0006
Received: 06/05/96 at 15:30 by John Brown

Site Name: Ashland
Station Location: n/a
Station Number: D-3
Sample Collected: 01/01/00 at 00:00 by n/a

Sample Matrix: Soil
Sampling Method: Grab
Other Information: n/a

Analyte	Method	MQL	Concentration	Units	Date	Analyst
Benzene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Toluene	8020	5.00	<5.00	ug/kg	06/07/96	JB
Ethylbenzene	8020	5.00	44.38	ug/kg	06/07/96	JB
m,p-Xylene	8020	10.00	<10.00	ug/kg	06/07/96	JB
o-Xylene	8020	5.00	13.42	ug/kg	06/07/96	JB

Comments:

Approved by:

Quality Control Batch Summary

Batch Number: 1996157-001 **Category:** Organics **Method:** 8020
Batch Date: 06/05/96 **Test:** BTEX (P&T/GC/PID) **Matrix:** Soil

Ethylbenzene	10	200	ug/kg	220.01	06/06/96	JB	110.0
m,p-Xylene	10	400	ug/kg	447.92	06/06/96	JB	112.0
o-Xylene	10	200	ug/kg	224.27	06/06/96	JB	112.1
Xylene	10	600	ug/kg	672.19	06/06/96	JB	112.0
Benzene	17	200	ug/kg	221.34	06/07/96	JB	110.7
Toluene	17	200	ug/kg	216.18	06/07/96	JB	108.1
Ethylbenzene	17	200	ug/kg	222.83	06/07/96	JB	111.4
m,p-Xylene	17	400	ug/kg	452.42	06/07/96	JB	113.1
o-Xylene	17	200	ug/kg	229.57	06/07/96	JB	114.8
Xylene	17	600	ug/kg	681.99	06/07/96	JB	113.7
Benzene	22	200	ug/kg	210.75	06/10/96	JB	105.4
Toluene	22	200	ug/kg	206.25	06/10/96	JB	103.1
Ethylbenzene	22	200	ug/kg	209.25	06/10/96	JB	104.6
m,p-Xylene	22	400	ug/kg	423.39	06/10/96	JB	105.8
o-Xylene	22	200	ug/kg	214.6	06/10/96	JB	107.3
Xylene	22	600	ug/kg	637.99	06/10/96	JB	106.3
Benzene	27	200	ug/kg	209.91	06/12/96	JB	105.0
Toluene	27	200	ug/kg	202.06	06/12/96	JB	101.0
Ethylbenzene	27	200	ug/kg	203.9	06/12/96	JB	102.0
m,p-Xylene	27	400	ug/kg	413.91	06/12/96	JB	103.5
o-Xylene	27	200	ug/kg	213.33	06/12/96	JB	106.7
Xylene	27	600	ug/kg	627.24	06/12/96	JB	104.5
Benzene	32	200	ug/kg	211.76	06/13/96	JB	105.9
Toluene	32	200	ug/kg	205.53	06/13/96	JB	102.8
Ethylbenzene	32	200	ug/kg	210.45	06/13/96	JB	105.2
m,p-Xylene	32	400	ug/kg	428.17	06/13/96	JB	107.0
o-Xylene	32	200	ug/kg	216.06	06/13/96	JB	108.0
Xylene	32	600	ug/kg	644.23	06/13/96	JB	107.4

Matrix Spike and Matrix Spike Duplicates

Analyte	Sample	Conc.	Units	Date	Spike Conc.	MS Que	MS Conc.	MS Date	MS Anal.	MS % R	MSD Que	MSD Conc.	MSD Date	MSD Anal.	MSD RPD
Benzene	060596-07	0	ug/kg	06/13/96	200	3	211.9	06/13/96	JB	105.9	4	220.7	06/13/96	JB	4.11
Toluene	060596-07	0	ug/kg	06/13/96	200	3	208.3	06/13/96	JB	104.2	4	211.0	06/13/96	JB	1.28
Ethylbenzene	060596-07	0	ug/kg	06/13/96	200	3	213.6	06/13/96	JB	106.8	4	216	06/13/96	JB	1.09
m,p-Xylene	060596-07	0	ug/kg	06/13/96	400	3	432.8	06/13/96	JB	108.2	4	438.8	06/13/96	JB	1.37
o-Xylene	060596-07	0	ug/kg	06/13/96	200	3	216.2	06/13/96	JB	108.1	4	222.4	06/13/96	JB	2.83
Xylene	060596-07	0	ug/kg	06/13/96	600	3	649	06/13/96	JB	108.2	4	661.2	06/13/96	JB	1.86

Quality Control Batch Summary

Batch Number: 1996157-001 **Category:** Organics **Method:** 8020
Batch Date: 06/05/96 **Test:** BTEX (P&T/GC/PID) **Matrix:** Soil

Blanks

Analyte	Que	Result	Units	Date	Analyst
Benzene	1	<5.00	ug/kg	06/05/96	JB
Toluene	1	<5.00	ug/kg	06/05/96	JB
Ethylbenzene	1	<5.00	ug/kg	06/05/96	JB
m,p-Xylene	1	<10.00	ug/kg	06/05/96	JB
o-Xylene	1	<5.00	ug/kg	06/05/96	JB
Xylene	1	<15.00	ug/kg	06/05/96	JB
Benzene	9	<5.00	ug/kg	06/06/96	JB
Toluene	9	<5.00	ug/kg	06/06/96	JB
Ethylbenzene	9	<5.00	ug/kg	06/06/96	JB
m,p-Xylene	9	<10.00	ug/kg	06/06/96	JB
o-Xylene	9	<5.00	ug/kg	06/06/96	JB
Xylene	9	<15.00	ug/kg	06/06/96	JB
Benzene	16	<5.00	ug/kg	06/07/96	JB
Toluene	16	<5.00	ug/kg	06/07/96	JB
Ethylbenzene	16	<5.00	ug/kg	06/07/96	JB
m,p-Xylene	16	<10.00	ug/kg	06/07/96	JB
o-Xylene	16	<5.00	ug/kg	06/07/96	JB
Xylene	16	<15.00	ug/kg	06/07/96	JB
Benzene	21	<5.00	ug/kg	06/10/96	JB
Toluene	21	<5.00	ug/kg	06/10/96	JB
Ethylbenzene	21	<5.00	ug/kg	06/10/96	JB
m,p-Xylene	21	<10.00	ug/kg	06/10/96	JB
o-Xylene	21	<5.00	ug/kg	06/10/96	JB
Xylene	21	<15.00	ug/kg	06/10/96	JB
Benzene	26	<5.00	ug/kg	06/12/96	JB
Toluene	26	<5.00	ug/kg	06/12/96	JB
Ethylbenzene	26	<5.00	ug/kg	06/12/96	JB
m,p-Xylene	26	<10.00	ug/kg	06/12/96	JB
o-Xylene	26	<5.00	ug/kg	06/12/96	JB
Xylene	26	<15.00	ug/kg	06/12/96	JB
Benzene	31	<5.00	ug/kg	06/13/96	JB
Toluene	31	<5.00	ug/kg	06/13/96	JB
Ethylbenzene	31	<5.00	ug/kg	06/13/96	JB
m,p-Xylene	31	<10.00	ug/kg	06/13/96	JB
o-Xylene	31	<5.00	ug/kg	06/13/96	JB
Xylene	31	<15.00	ug/kg	06/13/96	JB

Check Standards

Analyte	Que	CS Conc.	Units	CS Result	Date	Anal.	% R
Benzene	2	200	ug/kg	221.19	06/05/96	JB	110.6
Toluene	2	200	ug/kg	212.78	06/05/96	JB	106.4
Ethylbenzene	2	200	ug/kg	215.79	06/05/96	JB	107.9
m,p-Xylene	2	400	ug/kg	432.48	06/05/96	JB	108.1
o-Xylene	2	200	ug/kg	219.82	06/05/96	JB	109.9
Xylene	2	600	ug/kg	652.3	06/05/96	JB	108.7
Benzene	10	200	ug/kg	222.1	06/06/96	JB	111.1
Toluene	10	200	ug/kg	216.05	06/06/96	JB	108.0

PERFORMANCE AND CHARACTERISTICS EVALUATION OF ACRYLATES AS GROUT BARRIERS

METC Task No. 1.3
(Chemical Grout Barriers)

PROGRESS REPORT
Reporting Period: March 16, 1996-June 15, 1996

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

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

Department of Civil and Environmental Engineering
West Virginia University
Morgantown, WV 26506

Evaluation of Acrylate 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 (Duroseal™ 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, and c) Grout Testing Chamber. 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 involves the design and construction of the Grout Testing Chamber (GTC) (essentially a 91.4 cm flexible-wall permeameter) and manufacture of a sand rain device to prepare uniform specimens for the GTC. 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. It is currently being calibrated.

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

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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. Though these techniques are fully capable of preventing lateral migration of contaminants in soil and water, longitudinal migration of contaminants is generally 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 which is defined as the process of filling small interstitial voids and fissures in rock or soil (Karol 1990). If permeation grouting is proven to be preventative measure (i.e., secondary containment), as well as a post-release alternative, it could potentially be utilized at numerous sites (Superfund and RCRA) throughout the country.

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. 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)

Grout Development involves the identification of the grout mix ratio which exhibits the optimum properties for use as a subsurface barrier. Performance Testing utilizes 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 is also evaluated by performing immersion/strength testing (triaxial and unconfined compression) and permeability testing on samples collected from the grouted-sand bulb. Task III involves the design and construction of the Grout Testing Chamber (GTC), essentially a large-scale flexible wall permeameter with 3 feet diameter specimens which will be capable of simulating in-situ stress conditions. A sub-task was the development of a device and method for preparing specimens of a uniform density which can be accomplished through the use of a sand rain device.

2.0 EVALUATION OF A URETHANE GROUT FOR CONTAINMENT OF WASTES

2.1 Purpose

This research presented in this section was performed to successfully fulfill the requirements of Task I (Grout Development) and Task II (Performance Testing). Only urethane grout is performance is currently being pursued. The objectives of this research program are to establish grout testing protocol, evaluate grout performance, and determine grout characteristics for several injection strategies.

2.2 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. Past field studies (May et al. 1986, Dwyer 1994, Moridis 1995) conducted to evaluate subsurface barrier characteristics have 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.

The urethane grout evaluated in this research was supplied by the 3M Company under the trade name Scotch-Seal (TM) Brand Chemical Grout 5610 (Gel). This was chosen after reviewing the product literature and past studies as well as discussing the grout's capabilities with various distributors and manufacturers with research objectives in mind. Furthermore, 3M defines Scotch-Seal (TM) as groutable. The 5610 gel is a hydrophilic material most commonly used for sewer and water line rehabilitation projects.

2.3 Methodology

The experimental program of this investigation was performed to develop a standard testing protocol to evaluate the performance (i.e., durability, hydraulic conductivity, and strength) of permeation grouts. Experimental testing was implemented in two phases: a) Materials Testing Phase and b) Performance Testing Phase. The first phase consisted of testing material properties which included: moisture content (ASTM D 2216), specific gravity (ASTM D 1429), minimum and maximum densities (ASTM D 4254 83 and D 4253 83), and triaxial compression (ASTM D 2850). Additionally, the permeability the material was determined using a rigid wall permeameter conducted in accordance with ASTM Draft Standard Test Method for Measurement of Hydraulic Conductivity Using a Rigid Wall, Compaction-Mold Permeameter. Performance testing examined the injectability (groutability) of the grout in large diameter columns and Post-grout testing (permeability testing, immersion testing, and strength testing).

2.4 Work Performed this Period

Work performed during this period included the following tasks:

1. Viscosity tests on various urethane grout mixtures
2. Injection of urethane grout into large diameter (11.5" I.D.) columns
3. Flexible wall permeability tests on grout samples

During this period the process of optimizing the urethane grout was initiated. The first acceptance criteria used for the grout was a plot of viscosity versus time. By using a LVT model Brookfield Viscometer characteristics such as initial viscosity and gel time were determined. Once a mix achieved a geltime greater than 15 minutes, it was considered to be acceptable. Any acceptable mix was then injected into the large diameter columns which contained 20/30 Ottawa sand compacted to 50% relative density or 102 pcf.

After the grout cured for approximately 24 hours, samples were taken for flexible wall permeability tests, placed in a sealed container, and stored in a moisture room. The permeate used in the tests was water.

2.5 Results and Discussion

In the last progress report there was a discussion of permeability tests being performed in the large columns. From these tests, it was determined that there was no permeation of the 0.01M HCL or 0.01M NaOH through the grouted region. At the conclusion of the tests, samples were taken from the chemically saturated grout (upper region of grouted sand exposed to the chemicals) and placed in flexible wall permeameters for testing. The permeability tests yielded a hydraulic conductivity of 6.0E-9 cm/s.

2.6 Conclusion

The result of the flexible wall permeability tests were favorable for the 100% GTE mix when it comes to durability in HCL and the NaOH, but only when the thickness of the grouted region was entirely too thick (approximately 20cm - 25cm). The thickness of the grouted region needs to be reduced in order to measure the effects of the chemicals more accurately.

To this day the most extensive work performed with the urethane grout has been on a 10:1 mix with 100% of the activator being comprised of GTE. Testing of different mixes varying the activator components needs to be performed.

2.7 Work Planned for next Period

The major task for the next period is the further optimization of the urethane grout. This will be achieved primary by the results of the flexible permeability tests with different chemicals. Once the hydraulic conductivity of the different grout mixes is determined in water, three of the best ratios will be chosen and proceed to testing with harsher chemicals, such as TCLP #1 and TCLP #2 solutions.

3.0 SAND RAIN DEVICE

3.1 Purpose

The grout testing chamber (GTC) is to be used to test grout characteristics on a larger or meso-scale to reproduce field conditions. This is to observe the effects of multiple injection wells on barrier formation and grout performance in this environment. Obviously, a large soil sample is needed to execute such an experiment. The sand rain device will be able to deliver such a sample at a uniform and desired relative density.

3.2 Background

Hydraulic conductivity is the soil characteristic that is believed will most affect the grout's performance. Sand was chosen as the soil for grout performance testing since it has a very high hydraulic conductivity and represents the worst case scenario for barrier formation in non-fractured soil. Controlling the value of hydraulic conductivity can be done by fixing the relative density of the test specimen.

Fabricating such sand specimens, especially on a large scale, presents a few obstacles, because guaranteeing a homogenous sample on any scale is difficult without automation. ASTM offers methods for finding the maximum and minimum densities that are adequate for relatively small sand samples, but are both impractical and inaccurate for large scale samples. Therefore, testing grout performance on meso-scale sand specimens dictates the need for a device. This can be done by constructing an apparatus that is able to insure the following in large scale test specimens:

- they must have the requested relative density
- they must have properties that are reproducible independent of the operator
- they must be homogenous

Although such a device is not commercially available, success has recently been realized by a handful of researchers in creating a machine to produce large-scale, homogenous sand samples. The machine they designed is called a sand rain device.

3.3 Methodology

The most important considerations for the design process were cost, durability, and the practical limitations of the technician employed to perform the actual construction. With this in mind sand rain device was designed much like those in the literature. Normally the upper sand reservoir allows flow out through a stopcock and funnel assembly. The sand rain device at WVU has dual perforated plates in place of this assembly to better facilitate dispersion. A scale drawing of the final design can be seen in FIG 3.1.

3.4 Work Performed this Period

Work during this past quarter has been very progressive in the area of sand rain device research. The funnel platform has been completed. A locking mechanism was constructed by

SAND RAIN DEVICE

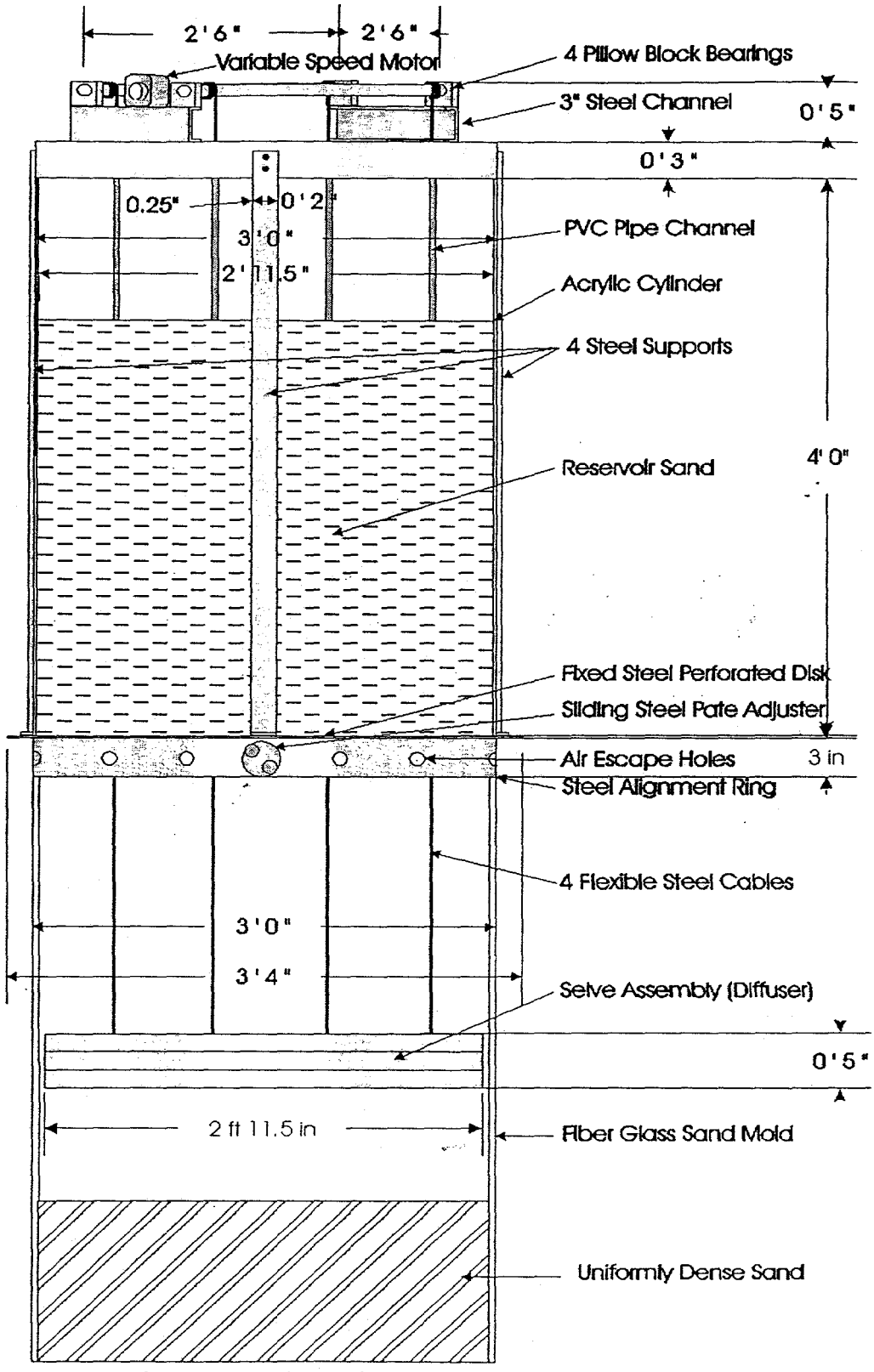


FIG 3.1. Scaled Drawing of the Sand Rain Device

by simply holding the two doors open by simple, 4-ton hydraulic jacks like those sold in auto parts stores. The doors are dropped by releasing the pressure in the jacks simultaneously which funnels the sand down and toward the front via a trough. The sand is allowed out by a sliding door so that the sand falls into a 5-gallon bucket placed at the end of the trough which are poured into the top of the sand rain device. With this procedure, testing time is reduced greatly when making full size samples (completely filling the sand mold) than by leaving the mold on the floor. On the floor, a significant amount of time is spent scooping out sand through the top of the mold with small shovels before the mold can be physically lifted to allow the remainder of the sand to pour out onto the floor to be shoveled into buckets and then poured again into the top of the sand rain device. The funnel base nearly eliminates shoveling altogether and significantly reduces loss onto the floor. Furthermore, it keeps the sand cleaner since it never reaches the floor. The funnel base was designed to hold the SRD while full of sand for storage purposes. It is not currently being used as such because it has been more convenient to rest it on two steel I-beams that became available. However, the funnel base is fully capable of holding the sand rain device while full if it became necessary in the future. Finally, the amount of time reloading the SRD has been reduced from three people with shovels taking approximately 1 hour 20 minutes to two people taking requiring less than 30 minutes. If the funnel base were to be placed on some other platform high enough to allow the trough to be above the top of the SRD, refilling the device could be further reduced to about five minutes.

The struts and PVC pipe were installed successfully as projected in the last report. Although the sand streams are still not quite centered over the sample, the strut assemble greatly reduced the diagonal effect mentioned in the last report. It remains to be seen if this is still a problem in the final product, but preliminary results seem to indicate acceptable results.

The speeds required of the electric motor have been narrowed so that the speeds needed can be achieved with the new sprocket design which was simply a matter of increasing the gear ratio to 4 to 1. With the installation of the new sprocket and new, smaller diameter cables for easier winding, the mechanics of raising the sieves at a constant rate are completed.

It became obvious for a need to keep the sand relatively clean because of the obvious need for a homogenous material, but more importantly to keep the sand rain device from clogging when the ports were opened only a small amount. In cases where one port was closed due clogging, the entire sample makeup was altered. Therefor, a large square sieve made from 2x4s, plastic reinforcing mesh, and windows screen was constructed to use when cleaning became necessary. Cleaning the entire supply of sand requires about 4 hours.

Radial density tests have been completed with the quality being quite good. Two series of tests have been performed with different volumes. Tests with these concrete testing cylinders have shown agreement to within less than 5%. Once acclimated to the tests, between 4 and 6 tests could be run in one day.

Vertical testing has also been nearly completed using the nuclear gage. Care was taken to insure that the readings would not be adversely affected by the close quarters of the boundary and it appears that the gage is adequate. Still, the readings by the nuclear gage have not been reasonable in reference to the concrete molds nor have they been constant with depth. Possible reasons for this is discussed below. This testing required raining the entire sample so no more than two could be completed in a day.

Perhaps the most important accomplishment was devising the new equipment needed as it

came up and developing testing protocol for the radial vertical tests for the quality of the samples. Both of these tests can be run with little difficulty and efficiently.

3.5 Results and Discussion

As was mentioned vertical testing results were not as good as expected. It appears at this point that a dense sample can be created with little difficulty and the longitudinal change in density is not great. However, in most samples the density increases with depth. The question is whether this increase is due to overburden stress or a flaw in the reading of the nuclear gage due to the near boundary. Tests made on two samples under the same conditions using both the cylinders and the gage for measuring seem to indicate that the readings are true since the gage agrees with the density calculated from the molds to within 1-5% while still showing the same increasing trend with depth. However not enough tests have been conducted to draw this conclusion for certain. If this were true, then it may not be possible to achieve low density samples using the current methods. Currently, tests are being conducted to measure the lower third of the sample with and without overburden to see if there is any change in the readings.

In a related matter, it was discovered that raining sand into the diffuser when it consisted of only the largest sieve and when it had the full compliment made almost no difference on the speed required for raising the sieves. This may indicate that the sieves are not performing properly and they may not be fine enough or the mass flow is too little. It would be worthwhile to explore those possibilities.

3.6 Conclusions

Much progress has been made over the past quarter and the sand rain device is nearing completion. Most of the unforseen problems have been worked out and it is both mechanically and structurally sound. Dense samples can already be made with a reasonable degree of accuracy while loose samples lose much homogeneity longitudinally. However, there is reason to believe that these things may be overcome with further testing.

3.7 Work Planned for next Period

Further radial and longitudinal uniformity testing will take place if needed and the exact nature of why low density samples will be explored.

3.8 Technical/Administrative Difficulties

There are no difficulties to report at this time.

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DEVELOPMENT OF STANDARD TEST PROTOCOLS AND DESIGN MODELS FOR DESICCATION BARRIERS
METC Task No. 1.4

Quarterly Technical Progress Report
Reporting Period: 04/01/96 - 06/30/96

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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, CO_2, 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.

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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-excavatible 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

A draft of the 'Project Operating Plan' has been completed and was submitted as per the "Process Safety Committee Handbook, part 6. Operating Permit: New Request, subpart f. Project Operating Plan."

A draft of the 'Operating Procedure' has been completed and was submitted as per the "Process Safety Committee Handbook, part 6. Operating Permit: New Request, subpart g. Operating Procedure." This includes (g-1) Safety Precautions, (g-2) Material List, (g-3) Pre-Run Procedures, (g-4) Start-up Procedures, (g-5) Operating Procedures, (g-6) Shut-down Procedures, (g-7) Emergency Procedures, and (g-8) Training Plan.

A draft of the 'Risk Assessment' has been completed and was submitted as per the "Process Safety Committee Handbook, part 6. Operating Permit: New Request, subpart I. Risk Assessment."

The CAB vessel assembly component parts were re-drawn to scale and these drawings were submitted as per the "Process Safety Committee Handbook, part 6. Operating Permit: New Request, subpart p. Drawings."

5.2 Task 2.1: Literature Review

A comprehensive literature review relative to CAB was conducted and completed during previous quarters and reported earlier.

Additional literature searches relative to procedures and instrumentation for measuring and monitoring air humidity, soil moisture, and permeability have been completed. 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/transmitters, electronic packages, and a data acquisition system have been selected, ordered, and received which adequately provide accurate data and also have application in the larger scaled experiments to be performed in the METC building B-17.

A comprehensive literature review relative to air-water mass transfer in porous media has been conducted. The results of literature review have established the foundation for interpretation of the results of the sand pack drying experiments.

5.3 Task 3: Laboratory Equipment and Preliminary Testing

With receipt of the completed CAB vessel assembly, several chambers have been calibrated and the previously determined methodologies for sand compaction have proceeded with these chambers. Compaction tests to determine the optimum water saturation for compaction of 20/30 mesh size sand and 30/40 mesh size sand have been completed.

An additional quantity of sand has been purchased and is currently being sieved which will yield 40/50, 50/70, 70/100, and 100/140 mesh sizes.

5.3.1 Sand Pack Assembly Characteristics Evaluation

The procedural and experimental configurations for determining sand pack porosity/permeability (Figure 1) and permeability/mass transfer (Figure 2) have been developed and a permanent air-flow manifold has been constructed. The 20/30 mesh size sand has been compacted at the optimum water saturation and porosity and permeability measurements (Figure 3) indicate that the compaction procedure is valid and repeatable.

The main portions of these experiments will be conducted at the METC building B-17, however, this series of preliminary experiments have been designed to evaluate the instrumentation and protocols for determining sand pack properties.

5.3.2 Sand Pack Drying Characteristics Determination

Experimental investigations for developing sand pack drying characteristics protocols has been initiated. The 20/30 mesh size sand has been compacted at the optimum water saturation. Drying tests were then performed by flowing laboratory air supply through the sand packs. The air flow rate has been varied from 1 to 15 liter per minute during these tests. Sand pack permeability has been measured throughout the drying test. The sand pack porosity has been also measured before and after drying tests. The main portions of these experiments will be conducted at the METC building B-17, however, this series of preliminary experiments have been designed to evaluate the instrumentation and protocols for determining sand pack drying characteristics.

6.0 RESULTS AND DISCUSSION

6.1 SARS Activity

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 were re-drawn to scale and the 'Operating Procedures' for the 'Operating Plan' were revised which enabled submission of a draft of the 'Operating Permit' for METC perusal and modification prior approval.

6.2 Sand Pack Assembly Characteristics Evaluation

The procedure and experimental setups for determining sand pack porosity and permeability have been developed and previously reported using a prototype experimental configuration. The measured porosity and permeability values based on the developed protocols have been found reasonable and repeatable.

The completion of a permanent air-flow manifold has enabled conducting these experiments with the CAB sand pack chambers and the results indicate that the procedures and instrumentation, with proper technique, generate highly accurate and quality data.

6.3 Sand Pack Drying Characteristics Determination

The results of the preliminary experiments are illustrated in Figure 4. As it can be seen as the air flow rate increases both the time required for drying and the water evaporation rate decline. The decline in water evaporation rate is more pronounced at higher flow rates. This can be mainly attributed to heat transfer effects as evidenced by the decline in exit air temperature with increasing air flow rate.

7.0 CONCLUSIONS

7.1 SARS Activity

The next phase of SARS activity is submission of the 'Operating Permit' and presentation to METC for approval. A modification of the 'Operating Plan' and several drawings may be necessary due to space limitations in Room 16 in METC Building B-17 requiring modifications in the air-flow manifold. Based on preliminary experimentation, these modifications will enhance the accuracy of the data gathering systems.

7.2 Sand Pack Assembly Characteristics Evaluation

The sand-pack tests have 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.

The incorporation of the CAB vessel sand pack chamber, coupled with the procured instrumentation, have enabled generation of high quality data.

The sand compaction tests for the 30/40 mesh sand indicate a higher water content than the 20/30 mesh sand. Compaction tests will be performed with assorted sand particle sizes to further evaluate this relationship. These compaction tests, coupled with porosity and permeability measurements, could provide baseline data for the larger scale experiments to be performed at METC building B-17.

7.3 Sand Pack Drying Characteristics Determination

The results of the preliminary drying tests indicate that the water evaporation process is significantly influenced by heat transfer between the air and the sand pack. The process is nearly isothermal at low air flow rates. However, as the air flow rate increases, the process approaches adiabatic conditions. The reduction in exit air temperature as flow rate increases verifies this aspect of the process.

8.0 WORK PLANNED FOR NEXT PERIOD

8.1 SARS Activity

Present 'Operating Permit' for METC approval in preparation to begin conducting experiments in METC building B-17.

Prepare 'Construction/Operating Permit' for larger scale experiments in METC Building B-17.

8.2 Sand Pack Assembly Characteristics Evaluation

Initiate experimentation in METC Building B-17.

8.3 Grain Size and Sorting Influence on Sand Pack Characteristics

Begin packing 40/50, 50/70, 70/100, and 100/140 mesh size sand as per modified 'Standard Ordinary Compaction Test', measuring porosity and permeability.

8.4 Sand Pack Drying Characteristics Determination

Continue drying tests on sand packs to evaluate the effect of grain size on drying process.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

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Porosity/Permeability Configuration

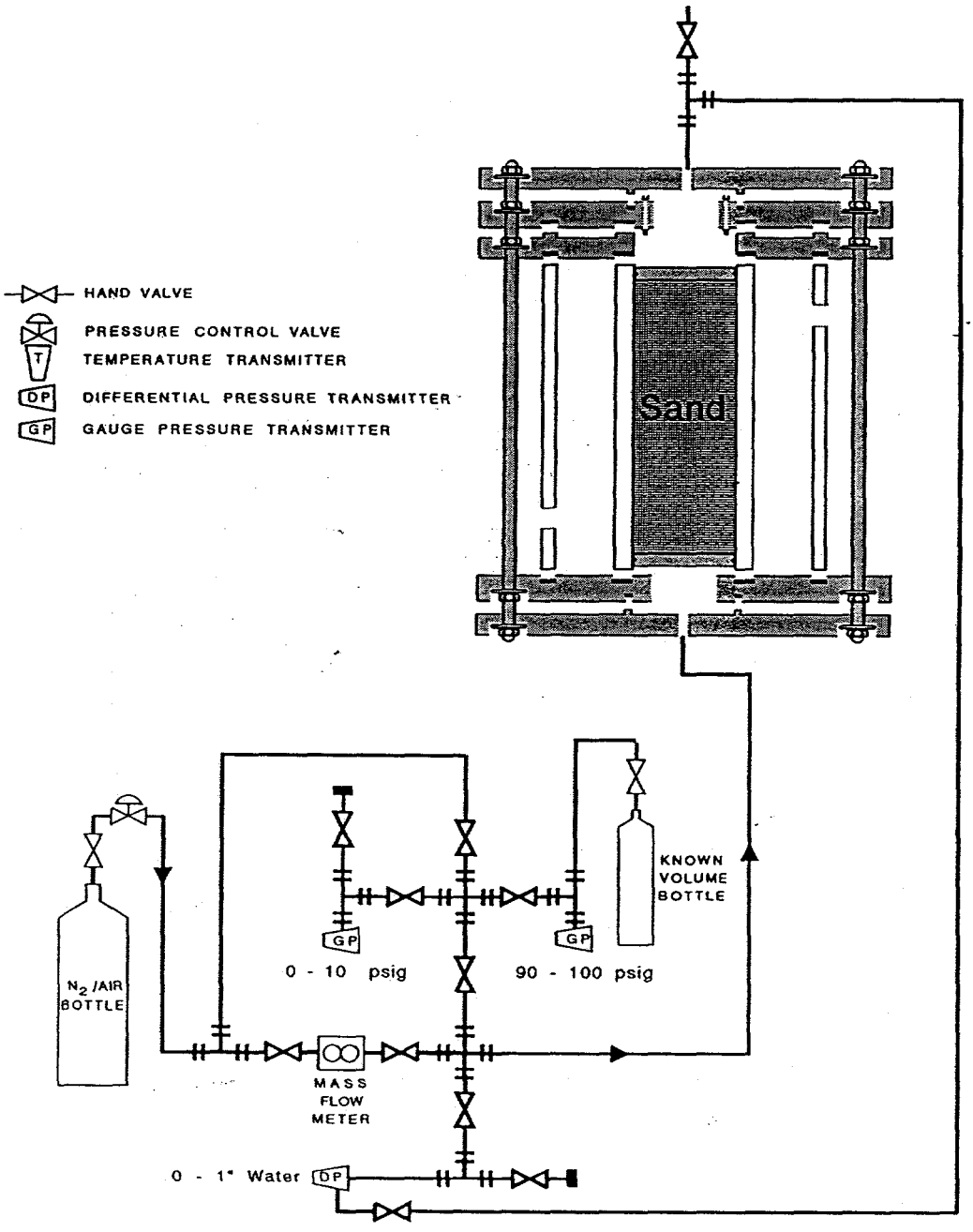


Figure 1: Porosity/Permeability Configuration

Permeability/Mass Transfer Configuration

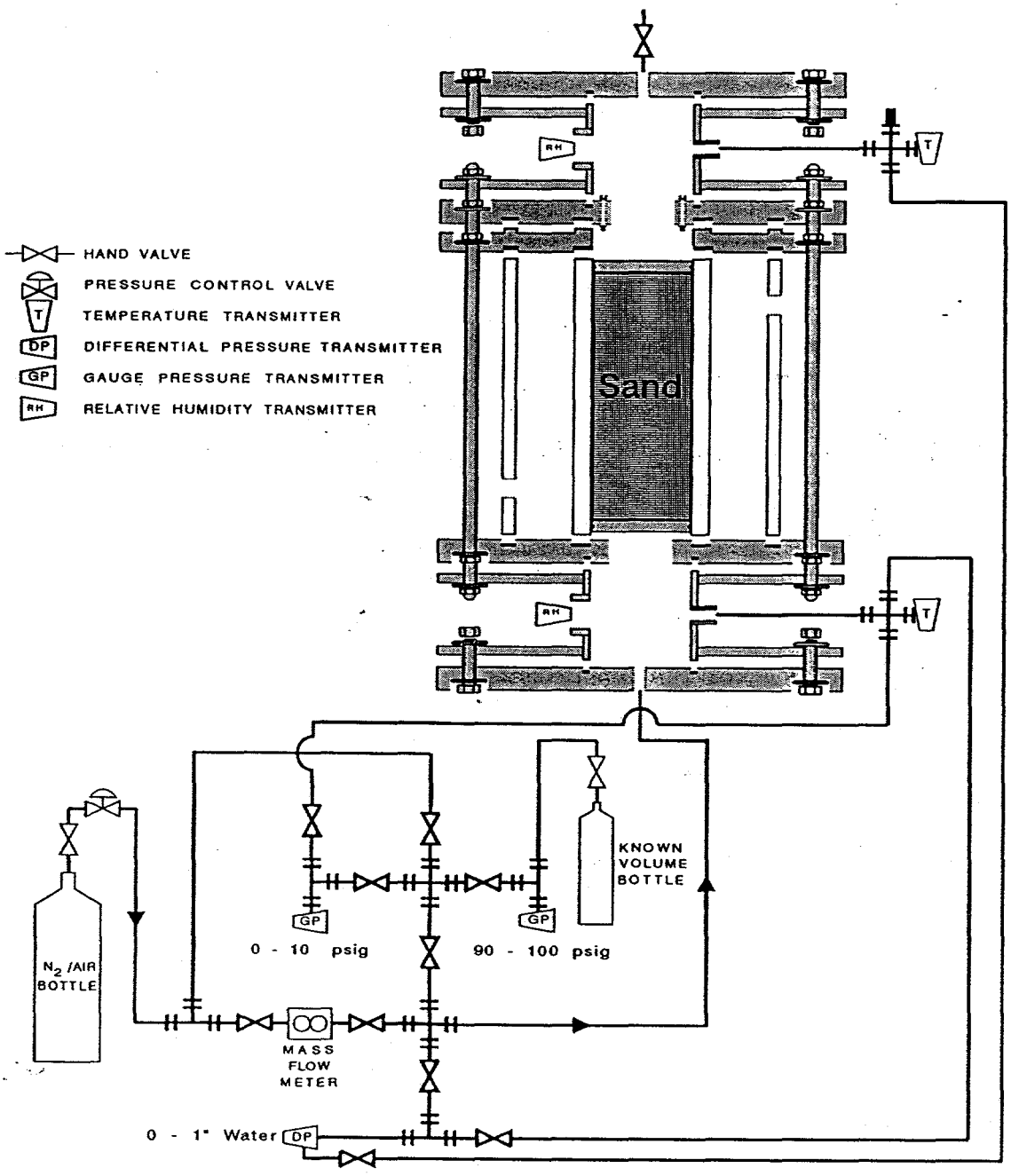


Figure 2: Permeability/Mass Transfer Configuration

Porosity/Permeability Results
For 20/30 Mesh Size Sand

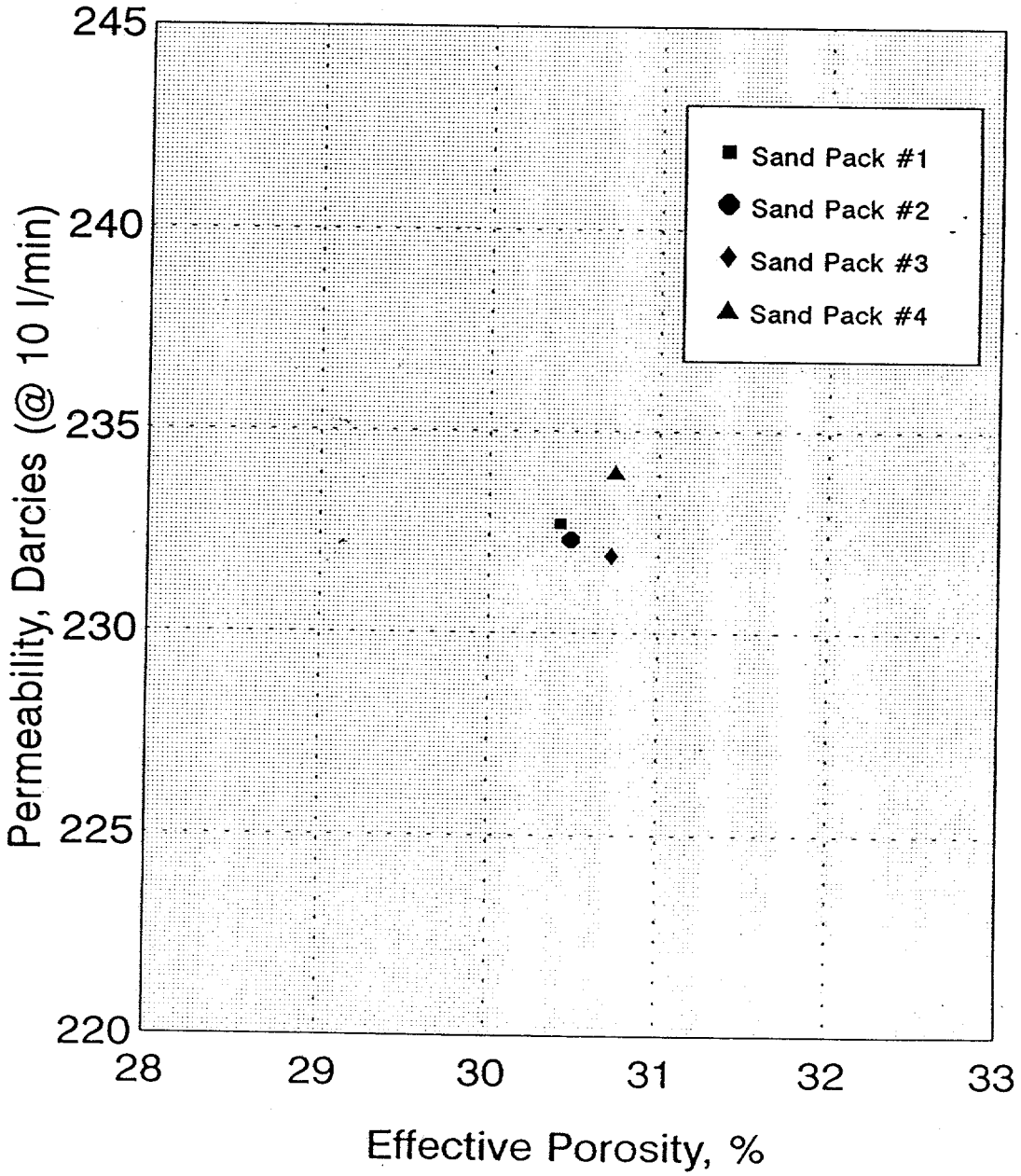


Figure 3: Porosity/Permeability Results for 20/30 Mesh Size Sand

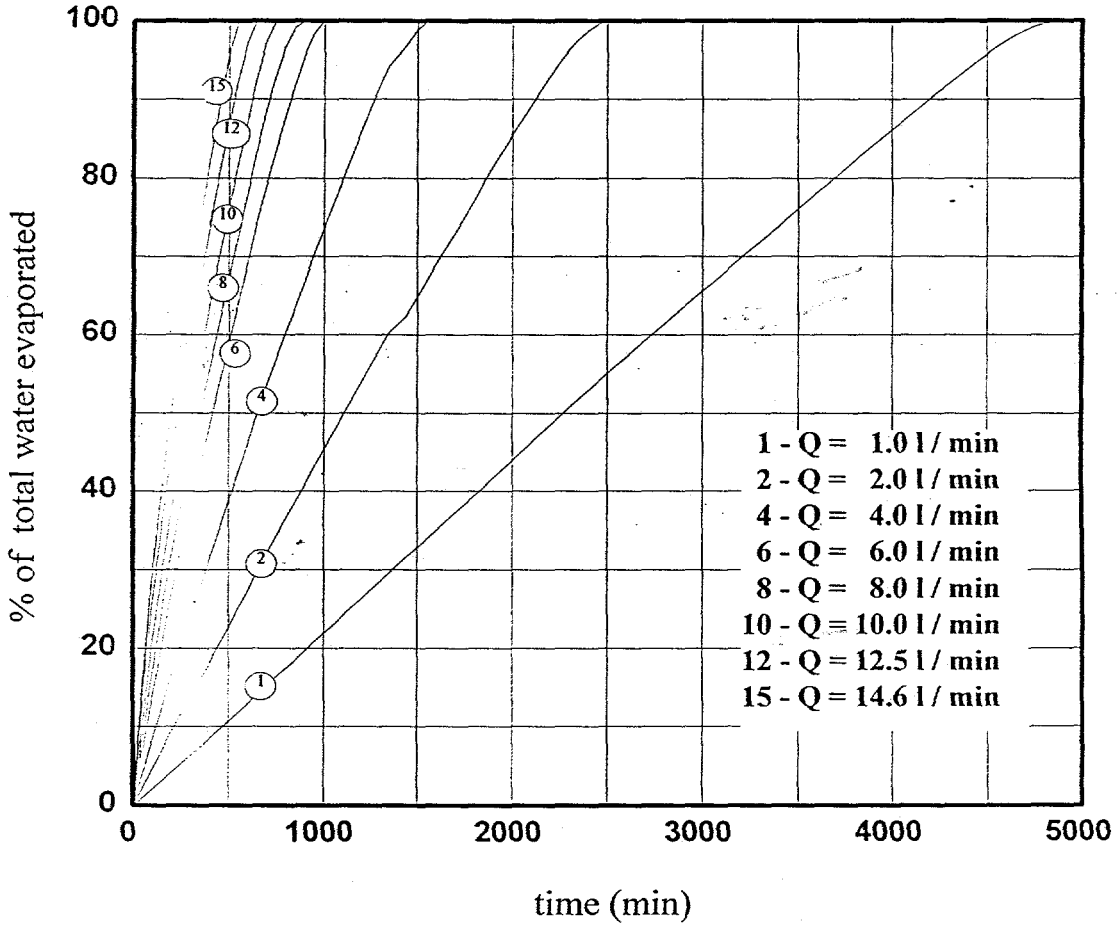


Figure 4: Results of the Drying Tests

TECHNICAL SUPPORT FOR DEVELOPMENT OF STANDARD TEST PROTOCOLS AND DESIGN MODELS FOR INSITU FORMED BARRIERS

Quarterly Technical Progress Report
Reporting Period:
April 1 to June 30, 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:
BDM Federal, Inc.
Morgantown, West Virginia

Abstract

This work is designed to support the on-going research at DOE/METC aimed at the development of standard test protocols for in-situ-formed barriers. The immediate support effort is directed toward establishing DOE/METC's B-17 building as a center for laboratory, bench-scale, and large-scale experiments needed to evaluate in-situ-formed barrier systems. Two systems are being evaluated initially: (1) a grout barrier system, and (2) a circulating air or desiccant barrier system. The grout and desiccant barrier systems currently being tested were identified previously by DOE researchers as high-potential alternatives for containing the movement of liquid contaminants which may have leaked from underground storage tanks existing at various DOE former weapon sites. Other barrier approaches are being independently evaluated under the DOE program, such as the freeze-wall systems and systems that totally encapsulate a leaking tank. The contractor will continue to monitor these programs for the development of standard test protocols in the B-17 facility. The goal is to establish the B-17 facility as the Focus Area Test and Evaluation Facility (FATE) for the entire DOE program.

The focus of the CY 1996 work is to (1) Support the operation of the circulating air barrier and grout laboratory experiments to be moved into the B-17 facility; (2) prepare for the scale-up of these experiments in 1996, and (3) support the planning for testing additional barrier systems in 1997 and beyond.

Documents will be developed for METC's Lab Safety Committee to obtain construction and/or operating permits for the B-17 experiments and will include, but are not limited to, line drawings and definitions of operating parameters. The contractor will plan and coordinate the installation of equipment and utilities needed to support the experimental work to be conducted in B-17, with a special focus on using the existing equipment for this research. The contractor will also assist principal investigators with the planning, hands on operation, and analysis of experimental operations.

In the conduct of this support, the contractor personnel will meet with the principal investigators and review the key design elements, operational procedures, quality assurance and control procedures, and initial design sketches for experimental equipment. After collecting the required supporting data, the contractor will prepare draft drawings and operational procedures for construction and subsequent operation of the test cells. Applications for construction permits and operating permits will be prepared and submitted to the DOE/METC Lab Safety Committee.

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Executive Summary

Details for installation of the CAB and Grout Barrier laboratory bench-scale test cells were worked out with DOE/METC and with the Principal Investigators and operating permit applications were completed, including the incorporation of modifications and additional details into the operating procedures for the test cells. Technical assistance and coordination of requirements for space, ventilation, utility, and logistics were provided for the CAB and Grout Barrier projects. Achievement of the operating permit milestones is contingent upon the completion of laboratory modifications by DOE/METC and minor test equipment construction/setup activities followed by inspections and safety committee approval of the CAB and Grout Barrier bench-scale operating permit applications.

A revised NEPA document to cover test operations on the CAB Large Laboratory Scale Unit was initiated during the quarter. A series of possible tests and equipment requirements were discussed with the Principal Investigators and are being outlined for this test unit.

The planning milestone to evaluate ways the B-17 facility can be used to support the DOE subsurface barriers program was achieved with the delivery of the draft report in May. The current DOE Barriers Program was reviewed and DOE/METC's B-17 Facility was evaluated as to how it could be best used to support the Plume Focus effort. For cost-effectiveness in utilizing the facilities in Building B-17 for barrier research, modifications to accommodate experiments should be kept to a minimum. The facility's original purpose was waste water treatment ; therefore, one of its best uses would be for testing the effectiveness of various types of reactive barrier materials for trapping and removing contaminant ions from waste water streams. The facility could easily be adapted to simulate either above-ground or in-situ removal of the contaminants that exist beneath DOE or other sites.

Humic Acid was identified from DOE research projects as a material with good potential for use in reactive barriers and/or pump-and-treat systems. Because of Humic Acid's favorable characteristics for adsorption of metals, radio nuclides, and organics, it may be possible to solve a number of complex contamination problems with a single step approach. The sludge filtration tanks in Building B-17 could be used as part of a system to evaluate the efficiency of humic acid and its derivatives or other compounds in removing contaminants from waste water or ground water.

Much of the focus during the quarter was on preparing for the movement of the bench-scale laboratory equipment from temporary facilities at West Virginia University to a suitable space at DOE/METC's B-17 building. Modifications to the building, revisions of the operating permit applications for the CAB and the Chemical Grout Barrier experiments, and a number of minor modifications to the project combined to create a number of activities which ranged from creating project identification signs to changing the final equipment installation site within Building B-17.

Minor delays were experienced that were associated with work order definition and general communication between the different project participants. Most delays were minimized by making an extra effort to communicate the needs of the project to those whose services or input were most urgently required.

1.0 Introduction

This work is designed to support the on-going research now underway at DOE/METC; research that is aimed at the development of standard test protocols for in situ formed barriers. The immediate support effort is directed to establishing the DOE/METC B-17 building as a center for laboratory bench-scale and large-scale experiments needed to evaluate in-situ formed barrier systems. Two systems being evaluated by researchers are identified as the initial systems to be tested in the facility: (1) a grout barrier system, and (2) a circulating air barrier system, also referred to as a desiccant barrier system .

2.0 Purpose

The focus of the CY 1996 work is to: (1) support the installation, permitting, and operation of the circulating air barrier and grout laboratory experiments in DOE/METC's B-17 facility; (2) prepare for the scale-up of these experiments in 1996, and (3) support the planning for testing additional barrier systems in 1997 and beyond.

3.0 Background

Subsurface barrier technology development is an important and growing part of the Department of Energy (DOE) environmental program. In support of this program, the contractor has, under separate contract since 1991, evaluated alternative barrier approaches. The grout and desiccant barrier systems currently being tested were identified by a team of DOE contract researchers as high-potential alternative approaches to contain the movement of liquid contaminants from underground storage tanks existing at various DOE former weapon sites.

The desiccant barrier concept is based on existing petroleum technology, but proof of concept is needed and will be provided in the B-17 facility. Specific variables being evaluated include: Vapor phase transport phenomena, effects of adiabatic cooling near injection points, and effects of changes in grain size, porosity, and permeability on sweep efficiency within the target subsurface interval.

Grout barriers are a more mature technology, but specific protocols are being developed in the B-17 facility for application to DOE sites. Specific variables include: Injectability of the grout (viscosity), setting time, immersion, durability, permeability, shear strength, compressibility, and toxicity of the cured injected material.

Other barrier approaches are being independently evaluated under the DOE program, and these approaches include freeze wall systems and systems that totally immerse a leaking tank. The contractor will continue to monitor these programs for the development of standard test protocols in the B-17 facility. The goal is to establish the B-17 facility as the Focus Area Test and Evaluation Facility (FATE) for the entire DOE program.

4.0 Methodology

The methodology involves the development of documents for DOE/METC's Lab Safety Committee that are needed to obtain construction and/or operating permits for the B-17 experiments. Installation of necessary equipment utilities is coordinated in support of the experimental work to be conducted in B-17, with a special focus on using the existing equipment for this research. Principal Investigators are assisted with the planning, hands on operation, and analysis of experimental operations.

In the conduct of this support, Contractor Personnel meet with the Principal Investigators and review the key design elements, operational procedures, quality assurance and control procedures, and initial design sketches for experimental equipment. After the required supporting data are collected, draft drawings and operational procedures for construction and subsequent operation of the test cells are prepared. Applications for construction permits and operating permits are prepared and submitted to the DOE/METC Lab Safety Committee with a goal of having permits returned approved within a 60 day period. This requires prioritized response by responsible DOE/METC Lab Safety Committee personnel, in order to keep the project on schedule and within budget.

5.0 Work Performed this Period

Milestones planned for this reporting period were as follows:

Task 0.0 - Planning and Technology Transfer

- Evaluation of the DOE subsurface barriers program and ways the B-17 facility can be used to support this program.

Task 1.0 - Circulating Air Barrier Test Protocol Development Support

- Obtain operating permits for CATC Bench Scale studies.
- Prepare quality assurance and quality control guidelines.

Task 2.0 - Grout Barrier Test Protocol Development Support

- Obtain operating permits for GTC Bench Scale studies.
- Prepare quality assurance and quality control guidelines.

The planning milestone was achieved with the delivery of the draft report in May, 1996, on DOE barrier and plume focus research and Building B-17's potential uses. No other milestones were reached, but significant progress was made. Operating permit applications (documents) have been completed, including the incorporation of modifications and additional details into the operating procedures for the test cells. Achievement of each of these milestones is contingent upon the completion of specific tasks by DOE/METC and by the completion of construction activities, inspections, and safety committee approval of the operating permit application. A detailed discussion of work performed follows in this section.

Task 0.0 Planning and Technology Transfer Support

Subtask 0.1 Planning and Analysis Support

The DOE Subsurface Barriers Program was reviewed and the DOE/METC B-17 Facility was evaluated relative to capabilities for support of Plume Focus Programs.

Subtask 0.2 Technology Transfer Support

No work was done on this task which is to assist the Principal Investigators and other researchers in development of reports and workshops for the transfer of technology developed during the research effort. Phase I research activities are still underway and results have not been completed.

Task 1.0 Circulating Air Barrier (CAB) Test Protocol Development Support.

Subtask 1.1 CAB Laboratory Bench-Scale Test Support

NEPA support (Subtask 1.1.1) and support for development of the construction permit for the bench scale testing (Subtask 1.1.2) was provided prior to CY 1996. Additional support was provided in developing the conceptual drawings and

operating procedures for the Operating Permit application for the CAB Bench-Scale testing during the past quarter.

Subtask 1.2 CAB Scale -Up to Large Laboratory Scale Unit

A revised NEPA document (Subtask 1.2.1) to cover test operations on the laboratory scale-up was initiated but not completed during the quarter.

A series of possible tests and equipment requirements have been discussed with the Principal Investigators and are being outlined for the CAB large laboratory scale test unit. (Subtask 1.2.2) Conceptual and constructional drawings were prepared for the CAB large laboratory scale test cell. (Subtask 1.2.3)

Subtask 1.3 CAB Demonstration Size Test

No work performed on this task this reporting period.

Task 2.0 Grout Barrier Test Protocol Development Support

Subtask 2.1 Grout Barrier Laboratory Bench-Scale Test Support

NEPA support completed prior to CY 1996; no additional NEPA support anticipated for this area at this time. (Subtask 2.1.1) Details for installation of the Grout Barrier Laboratory Bench-Scale Test Cell were worked out with DOE/METC and with the Principal Investigators. Technical assistance and coordination of space, ventilation, utility, and logistics (moving) requirements were provided (Subtask 2.1.2). Operating permit for the test unit was revised in accordance with review comments and is essentially ready for consideration by the cognizant DOE/METC safety committee. (Subtask 2.1.3).

Subtask 2.2 Grout Barrier Scale-Up to Large Scale Laboratory Test Unit

A revised NEPA document (Subtask 2.2.1) to cover test operations on the laboratory scale-up was initiated but not completed during the quarter.

Assistance was provided in arranging for and locating suitable space in DOE/METC's B-17 Facility for the large-scale Grout Barrier Test Cell (GTC) (Subtask 2.2.1). Safety Analysis and Review System (SARS) permitting documents have been initiated for the GTC. (Subtask 2.2.3)

Subtask 2.3 Grout Barrier Scale -Up to Demonstration Size Test

No work performed on this task this reporting period.

Task 3.0 Freeze Barrier Test Protocol Development Support.

No work performed on this task this reporting period.

Task 4.0 Dual Barrier System Test Protocol Development Support

No work performed on this task this reporting period.

6.0 Results and Discussion (Current Period)

The review of the current DOE Barriers Program and how DOE/METC's B-17 Facility can be best used to support the Plume Focus effort was completed and a draft report was submitted in May. The draft report discussed the need and desirability of modifying the waste water treatment facility located in the B-17 building at the DOE/METC Campus. Because of the cost associated with converting the individual components of the system to special purpose research facilities, the modifications should be kept to a minimum. For example, the cost to renovate one of the clarifier tanks to accommodate a large-scale CAB or similar experiment was estimated to exceed substantially the cost of the purchase of a new tank and would render the tank unusable for the purpose it was originally intended to serve. To the extent possible, the facility should be used for experiments that can use a piece of equipment for functions similar to its original intent. Because of the facility's original purpose as a waste water treatment facility, one of its best uses would be for testing the effectiveness of various types of reactive barrier materials to trap and remove contaminant ions from waste water streams. The facility could easily be adapted to simulate contaminated aquifers and the removal of the contaminants that exist beneath many DOE sites such as Oakridge, Savannah River, Portsmouth, Paducca, Fernald, etc.

A promising material that was identified from DOE research projects as having good potential for use in reactive barriers and/or pump-and-treat systems is Humic Acid. Humic Acid and derivative compounds have many favorable characteristics including large numbers of hydrogen donor sites for adsorption of metals and radio nuclides. Humic Acid also adsorbs organics making it possible to solve a number of complex contamination problems with a single step. Suggested designs for use of the sludge filtration tanks as part of a system to evaluate the efficiency of humic acid compounds were presented in the draft report.

Much of the focus during the quarter was on preparing for the movement of the bench-scale laboratory equipment from temporary facilities at West Virginia University to a suitable space at DOE/METC's B-17 building, including minor, but time-consuming modifications to the building itself and reviewing and incorporating revisions of the operating permit applications for the CAB and the Chemical Grout Barrier experiments. Meetings between the various cooperating entities in this project resulted in a number of minor modifications to the project which ranged from creating project identification signs to changing the final equipment installation site within Building B-17.

Some of the significant activities and events included the following:

The project area, and equipment dedicated to the circulating air barrier (CAB) and chemical grout (CG) projects were evaluated.

DOE/METC became actively involved to facilitate project equipment design and work order implementation.

Trailer 28 was re-established as an office area with phones and computers installed.

A more suitable project site was selected, a floor plan submitted, and the area revamped to accommodate the circulating air barrier (CAB) and chemical grout (CG) projects.

The CAB operating permit request was submitted to DOE/METC for a preliminary review, and a memo related to the document's content was returned. Comments and suggestions from the memo are being addressed.

The CAB equipment stands and cabinet, and fifty percent of the project operating equipment have been installed.

The CG vent-hood/bench is being fabricated and will be completed and installed in early July.

7.0 Conclusions (Current period)

For cost-effectiveness in utilizing the facilities in Building B-17 for barrier research, modifications to accommodate experiments should be kept to a minimum.To the extent possible, the facility should be used in a way and for a purpose similar to its original intent. The facility's original purpose was waste water treatment ; therefore, one of its best uses would be for testing the effectiveness of

various types of reactive barrier materials for trapping and removing contaminant ions from waste water streams. The facility could easily be adapted to simulate either above-ground or in-situ removal of the contaminants that exist beneath DOE or other sites.

Because of Humic Acid's favorable characteristics for adsorption of metals, radio nuclides, and organics, it may be possible to solve a number of complex contamination problems with a single step approach. The material appears to have good potential for use in reactive barriers and/or pump-and-treat systems.

8.0 Work Planned for Next Period

Tasks to be worked on next period include Task 0.0, "Planning and Technology Transfer Support;" Task 1.0, "Circulating Air Barrier (CAB) Test Protocol Development Support;" Task 2.0, "Grout Barrier Test Protocol Development Support;" and Task 3.0, "Freeze Barrier Test Protocol Development Support."

Specific objectives of the next quarter are to complete all activities necessary to obtain operating permits for the CAB and CG bench-scale laboratory experiments, complete QA/QC guidelines following the approval of the operating permits, complete activities necessary to prepare and submit construction permit applications for the large-laboratory-scale CATC and GTC units, and revamp project areas for installation of the large-scale units.

9.0 Technical/Administrative Difficulties (Current period only)

Delays were experienced that were associated with account funding, DOE/METC work order definition and implementation, and communication. Communication was the most significant problem and ranged from unclear or incomplete requests/ instructions to the inability of significant players to understand and visualize the overall project and the importance of their particular contribution at any given time. Most delays were minimized by making an extra effort to communicate the needs of the project to those whose services or input were most urgently required.

SITE REMEDIATION TECHNOLOGIES
IN SITU BIOREMEDIATION OF Chlorinated Solvents
METC TASK No. 1.6

Work Performed Under
Contract No.: DE-FC21-92M29467

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July 1996

Executive Summary

Chlorinated aliphatic hydrocarbons (CAHs) contamination in soils and groundwater is a wide-spread problem at Portsmouth Gaseous Diffusion Plant Site (PORTS) and many other DOE sites. These solvents often move downward through the soil profile and the groundwater accumulating as dense nonaqueous aqueous phase liquid (DNAPL) over an aquitard. Reliable and cost effective field technologies are needed to cleanup these sites. To date, when remedial measures are implemented to achieve source containment and/or plume containment at DNAPL sites, the measures nearly always include pump-and-treat. Approaches based on extracting contaminated groundwater with pumps and subsequently treating it above ground have proven ineffective for removing much of the immiscible DNAPL phase mass. To accomplish source mass reduction, another approach is to use surfactants to enhance the dissolution of DNAPLs followed by in situ bioremediation. In situ bioremediation of CAHs often involves amendments to enhance the degradation processes. These will include injection of primary substrate, nutrients, and electron acceptors into the plume after flushing of DNAPL zone to stimulate activity of natural microbes for destruction of contaminants that will be desorbed from the porous medium. 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.

Two approaches are being taken to simulate the site conditions and to predict the effectiveness of bioremediation at PORTS. Continuous flow column studies and anaerobic batch reactor (microcosm) studies are being performed. Two column studies, a simultaneous anaerobic and aerobic column and a sequential anaerobic and aerobic column, are in progress with plans to begin a second simultaneous column. Higher overall TCE destruction has been achieved in the simultaneous column with TCE removal as high as 98%. Moderate vinyl chloride (VC) concentrations remaining in the column effluent have continued to be a problem with the simultaneous column. Attempts of increasing aerobic degradation of VC via increased hydrogen peroxide addition has greatly improved VC destruction. The sequential column has been showing lower percentage of TCE destruction, 70-80%, but has shown greater daughter product destruction and lower effluent concentrations of VC. In an attempt to increase anaerobic activity, and TCE destruction, better control of pH through buffers and possible reinoculation of the anaerobic zone is being explored.

Preliminary microcosm studies have been performed to establish an experimental procedure for their use in this study. Factors such as head space volume, substrate addition, biomass concentrations, trace metal and nutrient concentrations, and possible agitation are being considered. Initially it appears that substrate addition and initial head space volume are critical to maintaining the integrity and the effectiveness of each microcosm. Utilizing mineral salts concentrations and reducing agent concentrations similar to those in the column study's synthetic ground water yield positive initial results. Ideally the microcosms planned for future study will yield information on the rate of TCE degradation, the ability of native organisms at PORTS to remove TCE and its daughter products, and the viability of using residual surfactant from the initial surfactant flood as an alternate substrate.

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1.0 INTRODUCTION

Chlorinated aliphatic hydrocarbons (CAHs) contamination in soils and groundwater is a wide-spread problem at Portsmouth Gaseous Diffusion Plant Site (PORTS) and many other DOE sites. These solvents often move downward through the soil profile and the groundwater accumulating as DNAPL over an aquitard. Reliable and cost effective field technologies are needed to cleanup the site. To date, when remedial measures are implemented to achieve source containment and/or plume containment at DNAPL sites, the measures nearly always include pump-and-treat. Approaches based on extracting contaminated groundwater with pumps and subsequently treating it above ground have proven ineffective for removing much of the immiscible DNAPL phase mass. To accomplish source mass reduction, another approach is to use surfactants to enhance the dissolution of DNAPLs followed by in situ bioremediation.

In situ bioremediation of CAHs will often involve amendments to enhance the degradation processes. These will include injection of substrate, nutrients, and electron acceptors into the plume after flushing of DNAPL zone to stimulate activity of natural microbes for destruction of contaminants that will be desorbed from the porous medium. 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.

2.0 PURPOSE

The purpose of the research is to evaluate biopolishing of contaminants at PORTS after surfactant flooding. The surfactant flood will probably utilize an anionic surfactant and an alcohol such as isopropanol. Due to all unknown factors involved in the surfactant flood, it is not possible at this time to develop a good estimate of the concentrations of contaminants and surfactant that will be left in the formation after the flood. Therefore a range of levels will be evaluated in both columns and microcosms. It is possible that the isopropanol or perhaps other contaminants already present in the formation may serve as primary substrate for methanogenic and methanotrphic organisms. This possibility will be evaluated by not adding a separate primary substrate (typically methanol) during the study. Both columns and microcosms will be used to evaluate biopolishing at PORTS and to evaluate the ability of methanotrophic, methanogenic, and other selected bacteria for cost-effective biotransformation of TCE and other volatile organic compounds (VOC's) found at PORTS.

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).

The test area at PORTS is designated X701B and is illustrated in Figure 1. This area originally contained a holding pond which received liquid wastes, including chlorinated solvents, from industrial operations elsewhere on

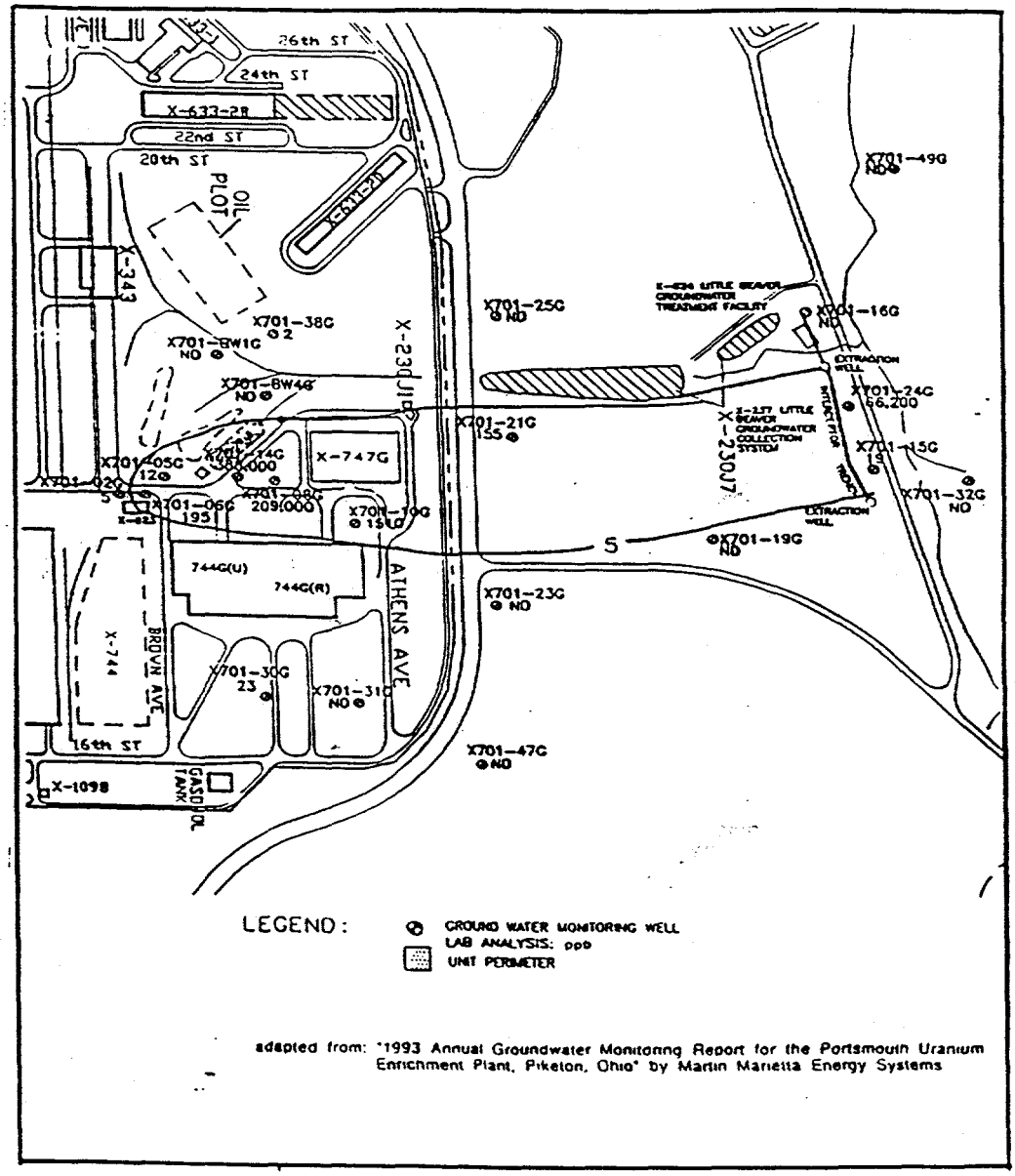


Figure 1. Site Map of the X701B Test Area (Source: Intera)

site. The X701B area is underlain by lacustrine silts and clays and by deeper alluvium. These Quaternary units lie on the Sunbury shale which, in turn, overlies the Berea sandstone. The geologic and hydrologic properties of the proposed test site is presented in Table 1 and the hydrostatigraphy of the proposed test site is presented in Figure 2. The Gallia alluvium was deposited by the ancient Portsmouth river, which left abandoned alluvial and fluvio-lacustrine deposits across the PORTS site. Hydraulic conductivities in the Gallia are of the order of 10^{-2} to 10^{-3} cm/s. The Gallia is underlain by the Sunbury shale, which is estimated to have a vertical hydraulic conductivity on the order of 10^{-8} cm/s.

Groundwater in the Gallia underlying X701B flows from the north and west across the X701B holding pond and continues east toward Little Beaver Creek. Groundwater flow is directly affected by the thickness of the Gallia which is generally two to six feet thick in the vicinity of X701B. A groundwater divide is present west of X701B. The groundwater flow direction is constant throughout the year with the gradient exhibiting very little seasonal change. The gradient is flattest in the vicinity of X701B and steepens east of X230J7 toward Little Beaver Creek. The steeper gradient is due to decreasing thickness of the Gallia.

The DNAPL within X701B has a specific gravity of approximately 1.4 and the viscosity is measure as 4 centipoises. The DNAPL is a multi-component liquid composed of TCE, PCE, and a number of minor components including PCB and 1,1-DCE. The approximate concentration of DNAPL from the X701B area is presented in Table 2. It should be noted that the chemical analysis only identified a small fraction of the DNAPL components and the listed quantities are probably significantly underestimated, in particular TCE. Recent measurements of TCE indicate that TCE concentrations at the perimeter fence have reached 800 mg/L.

4.0 METHODOLOGY

The principal focus of the investigation is to evaluate the performance of biopolishing of contaminants at PORTS after surfactant flooding. This research was organized into five phases, as follows:

Phase 1: Literature Review.

Phase 2: Procure/Synthesize Water And Soil Samples

Phase 3: Characterize Groundwater and Soil samples

Phase 4: Evaluation of Biopolishing Using Columns

Phase 5: Evaluation of Biopolishing Using Microcosms

5.0 WORK PERFORMED THIS PERIOD

In this quarter, the site data were obtained from Intera, Inc. and reviewed; the existing columns continued to operate in both sequential and simultaneous modes; and preliminary microcosm studies have been performed to determine the experimental parameters for future batch studies using actual groundwater and soil from PORTS. Parts for a second simultaneous column have been ordered, as well as a computer system capable of performing more accurate analysis of gas chromatograph data than current equipment. An Orion Model 96-17BN chloride probe was purchased to analyze the Cl^- concentration in the effluent. This will allow more accurate mass balance calculation and assurance that all contaminants are accounted for.

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

Table 1. Geologic and Hydrogeologic Properties of the X701B Area (Source: Intera)

FORMATION	LITHOLOGY	HYDRAULIC CONDUCTIVITY (cm/s)	APPROXIMATE AVERAGE THICKNESS (m)
Minford	Clay	8.1E-08	4.6
Minford	Silty clay	1.5E-06	3.0
Gallia	Sand	E-02 to E-03	1.5
Sunbury	Shale	K_v = E-08	3.0
Berea	Sandstone	5.6E-05	9.1
Bedford	Shale	2.1E-05	30

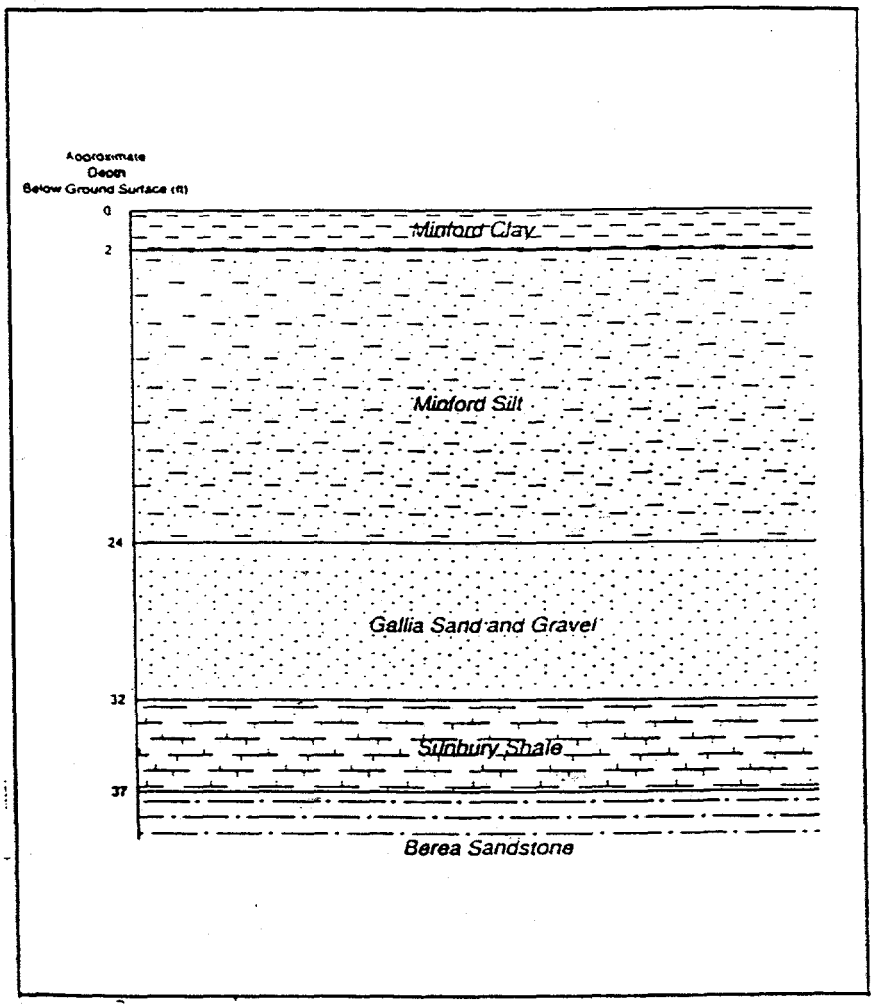


Figure 2. Hydrostatigraphy of the X701B Test Area (Source: Intera)

Compounds Identified in DNAPL Sample	Quantity (g/L)	Notes
Trichloroethene	12	
Tetrachloroethene	3.6	Exceeds initial calibration range
Perchloromethane	0.22	"Carbon tetrachloride"
1,1-dichloroethene	0.034	
1,1,2-trichloro-1,2,2-trifluoroethane	1.6	(CFC-113), tentatively identified
1,1,1-trichloroethane	2.3	Tentatively identified
1,1,2-trichloroethane	0.12	Tentatively identified
Toluene	0.028	Tentatively identified
Xylenes	0.060	Tentatively identified
1,2,4-trimethylbenzene	0.080	Tentatively identified
Polychlorinated biphenyls	820 ug/g (0.08%)	Identified as PCB-1254

Table 2. DNAPL Composition from Pumping Well BW2G (Source: Intera)

1. Literature Review— 50% complete

Numerous journal articles on microcosm preparation and studies have been consulted in fine-tuning the microcosm batch studies.

2. Procure/Synthesize Water and Soil Samples— 0% complete

Delays at the PORTS site have prevented the approval and shipment of groundwater and soil samples. Preparations are being made to instead synthesize groundwater in the lab.

3. Characterize Groundwater and Soil Samples— 50% complete

Data has been collected from Intera on groundwater and soil contents. More in-depth and up-to-date information is being sought from Intera.

4. Evaluation of Biopolishing Using Columns— 50% complete

Column studies are ongoing. Determination of column nutrient requirements to aid destruction of TCE and its daughter products has been completed. Further studies include optimization of electron donor concentration and pH to increase TCE/daughter product destruction even further.

5. Evaluation of Biopolishing Using Microcosms— 40% complete

Preliminary determination of experimental parameters which will provide effective and reliable results have been nearly completed. The next step will be to prepare microcosms using actual groundwater and soil samples from PORTS to determine the effectiveness of various parameters on TCE removal.

6. Preparation and Submission of Quarterly and Final Reports–25 % Complete

Assuming equal weight for each of the 6 project tasks noted above, it is estimated that the overall project is 35.8% complete.

6.0 RESULTS AND DISCUSSION

Experimental studies performed in this quarter include column operations and anaerobic microcosm testing. Results of these studies are presented in this section.

6.1 Sequential Columns.

A schematic diagram of the sequential column setup is presented in Figure 3. The anaerobic and aerobic columns have been operated in a sequential mode continuously in this quarter. Table 3 shows the substrate and inorganic concentrations entering the anaerobic column for various time periods in this quarter. Aerobic condition in the second column is achieved by injecting H_2O_2 to the column. CH_3OH is added to the aerobic column as the primary substrate. Doses of H_2O_2 and CH_3OH are presented in Table 4.

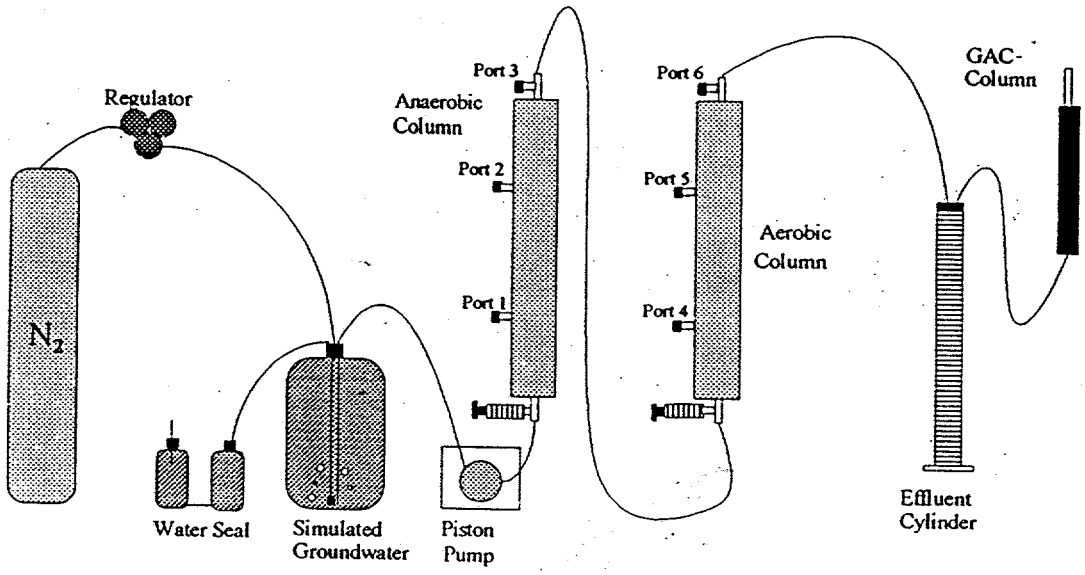


Figure 3 Schematic Diagram of the Sequential Column Setup

Table 4. Sequential Aerobic Column Operational Conditions

Chemical	5/1 -5/20	5/21 - 5/31	6/1 - 6/7	6/8 - 6/14	6/15-6/30
H_2O_2, mg/L	220	220	220	220	262
CH_3OH, mg/L	54	54	54	54	54
HRT, hours	12	24	24	24	24

During initial operation from May 1 to May 20 the total hydraulic retention time (HRT) in the anaerobic and aerobic columns was 24 hours. It was decided to raise the HRT to 48 hours and to establish inlet concentrations for TCE and Methanol of 20 mg/L and 800 mg/L respectively.

During the last week of May questions concerning why the sequential column was yield such low percent removal were raised. It was felt that perhaps high ORPs in the anaerobic column could be responsible. To alleviate this the Na_2S concentration in the ground water was raised to 40 mg/L. In following weeks performance improved marginally.

The increase in Na_2S concentration, however, caused a decrease in the redox potential (ORP) in both the anaerobic and aerobic sections of the column. As observed in Table 6, the ORP value in the aerobic bottom port decreased to -21.2 mV and the dissolved oxygen (DO) concentration fell to 0 mg/L. The DO had been holding about 1 to 2 mg/L in the aerobic portion of the column. To raise the DO concentration and keep methanotroph activity, the hydrogen peroxide (H_2O_2) concentration was increased by 20% (220 mg/L to 262 mg/L on July 15 as noted in Table 4. The additional H_2O_2 made only a slight improvement in the DO from 0 to 0.93 mg/L.

TCE removal rates in the aerobic and aerobic columns, and the overall TCE removal in the sequential column system are presented in Table 5. During its initial operation period in May, lower TCE removal was observed in the column effluents. This is believed to be a result of a leaking seal on the ground water pump allowing air to be pumped into the column. The detrimental results included fluctuating flow rates and elevated oxidation reduction potential (ORP) in the aerobic column, as shown in Table 6. The ground water pump was replaced in the week of May 12. After a transitional period, the performance of system stabilized providing an overall TCE removal rate between 66-76%.

Table 5. TCE Removal throughout the Sequential Columns (%)

	5/1 - 5/20	5/21 - 5/31	6/1 - 6/7	6/8 - 6/14	6/15 - 6/30
Anaerobic Top writ Influent	47	-17	76	75	66
Aerobic Top writ Anaerobic Top	0	20	24	3	26
Over all	46	7	82	76	75

Table 6. Average ORP Values in mV for the Sequential Columns

	5/1-5/12	5/13-5/20	5/21-6/6	6/7-6/12	6/13-6/18	6/19-6/30
Aerobic Top	72	-54	-27	19.2	-20	-48.1
Aerobic Bottom	28	-64	-33	2.6	-21.2	-40.2
Anaerobic top	30	-32	-126	-137	-214	-138.7
Anaerobic Bottom	-48	-154.6	-130	-171	-112	-125

Cis-, trans-, and 1,1-DCE, and VC may be produced from biological transformation of TCE. Concentrations of these daughter products have been measured during the column study and used to evaluate the performance of the anaerobic and aerobic columns. Table 7 shows the concentrations of these daughter products in the effluent of anaerobic and aerobic columns for various time periods in this quarter. Low concentrations of these daughter products in the effluents indicate that most of these compounds were degraded in the columns.

Table 7. Daughter Product Concentrations (ug/L) in the Sequential Columns (5/1-6/30)

Date	5/1-5/20		5/21-5/31		6/1-6/7		6/8-6/14		6/15-6/30	
Port	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top
cis-DCE	22	4	73	23	7	16	3	ND	1	9
trans-DCE	ND	ND	ND	35	ND	ND	ND	ND	9	ND
1,1-DCE	22	17	ND	ND	ND	ND	5	17	20	ND
VC	16	ND	ND	8	6	15	4	7	ND	ND

ND-- not detected

6.2 Simultaneous Column

A schematic diagram of the simultaneous setup is given Figure 4. The simultaneous column can be divided into three reaction zones, anaerobic, facultative and aerobic. Tables 8, 9 and 10 show the substrate and inorganic concentrations entering the anaerobic, facultative and aerobic zone, respectively, for various time periods in this quarter.

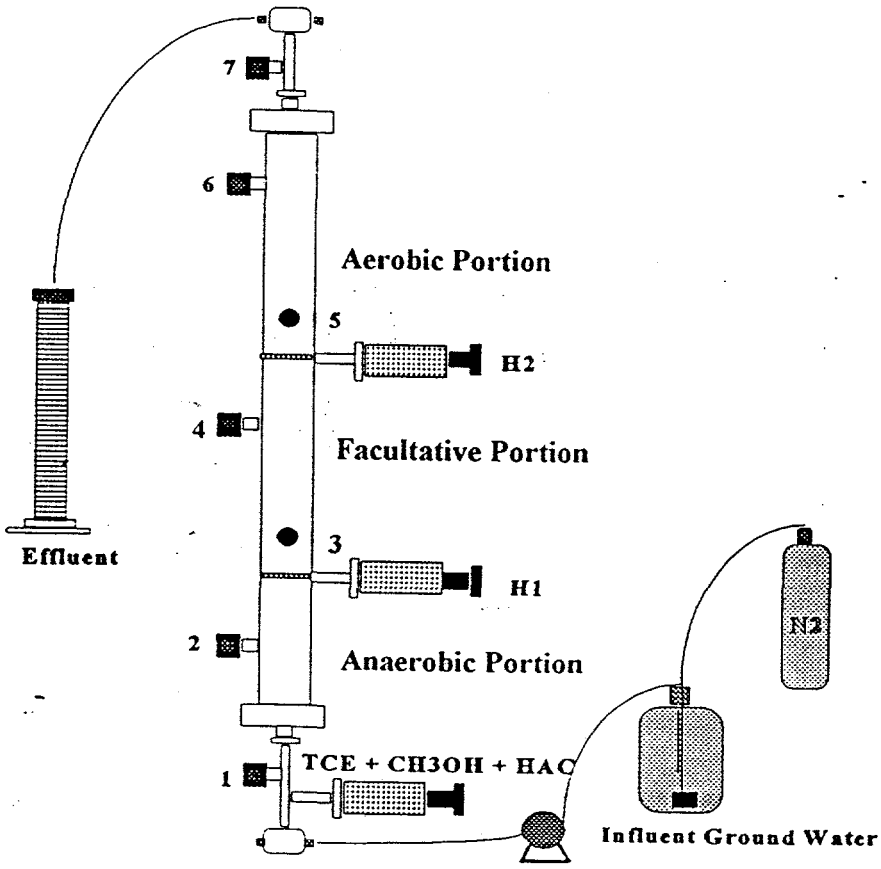


Figure 4. Schematic Diagram of the Simultaneous Column Setup

Table 8. Simultaneous Column Anaerobic Zone Operational Conditions (Concentrations, mg/L)

Chemical	5/1-5/20	5/21-5/31	6/1-6/7	6/8-6/14	6/15-6/30
NH_4Cl	28.35	28.35	28.35	28.35	28.35
K_2HPO_4	2.92	2.92	2.92	2.92	2.92
KH_2PO_4	2.11	2.11	2.11	2.11	2.11
$MgCl_2.6H_2O$	5.76	5.76	5.76	5.76	5.76
$MnCl_2.4H_2O$	1.92	1.92	1.92	1.92	1.92
$CoCl_2.6H_2O$	3.84	3.84	3.84	3.84	3.84
$ZnCl_2$	1.92	1.92	1.92	1.92	1.92
$CaCl_2.2H_2O$	6.34	6.34	6.34	6.34	6.34
H_3BO_3	0.58	0.58	0.58	0.58	0.58
$NiCl_2.6H_2O$	1.92	1.92	1.92	1.92	1.92
$Na_2MoO_4.2H_2O$	0.768	0.768	0.768	0.768	0.768
L-Cysteine	24.0	24.0	24.0	24.0	24.0
$Na_2S.9H_2O$	24.0	24.0	24.0	24.0	24.0
$NaHCO_3$	76.8	76.8	76.8	76.8	76.8
Yeast Extract	5.0	5.0	5.0	5.0	5.0
$FeCl_2 \cdot 4H_2O$	6.0	6.0	6.0	6.0	6.0
Vitamin B-12	4.81	4.81	4.81	4.81	4.81
Methanol	650	800[1]	800	800	800
Acetic Acid	0	0	0	0	0
TCE	20	20	20	20	20
HRT, hrs	8	16	16	16	16

[1] To establish same initial conditions as the sequential column.

Table 9. Simultaneous Column Facultative Zone Operational Conditions

Chemical	5/1 -5/20	5/21 - 5/31	6/1 - 6/7	6/8 - 6/14	6/15-6/30
H_2O_2, mg/L	110	110	110	110	110
CH_3OH, mg/L	57	57	57	57	57
HRT, hours	8	16	16	16	16

Table 10. Simultaneous Column Aerobic Zone Operational Conditions

Chemical	5/1 -5/20	5/21 - 5/31	6/1 - 6/7	6/8 - 6/14	6/15-6/30
H_2O_2, mg/L	332	332	332	332	396
CH_3OH, mg/L	60	60	60	60	60
HRT, hours	8	16	16	16	16

The simultaneous column has continued its excellent performance with high TCE destruction rates. Changes in the operation of the simultaneous column have been limited to changing the ground water flow to provide a 48 hr HRT, and a 10% increase in the peroxide concentration in the aerobic zone. The following tables summarize the column concentrations. After adjusting HRT from 24 hours to 48 hours, the performance of the simultaneous column has been stable with overall TCE removal rate ranging from 89-98%, as shown in Table 11.

Table 11. Percent Removal throughout the Simultaneous Column.

	5/1 - 5/20	5/21 - 5/31	6/1 - 6/7	6/8 - 6/14	6/15 - 6/30
Anaerobic Top wrt Influent	35	na	97	92	94
Aerobic Top wrt Anaerobic Top	57	na	31	53	-88
Over all	71	92	98	96	89

High VC concentration in the column effluent continues to be a problem. It is believed that this problem can be solved by increasing dissolved oxygen concentration in the aerobic zone to promote aerobic activities. The increase of hydrogen peroxide dose in the aerobic is believed to have improved the daughter product destruction during the last time period of this quarter.

Table 12. Daughter Product Concentrations (ug/L) in the Simultaneous Column (5/1-6/30)

Date	5/1-5/20		5/21-5/31		6/1-6/7		6/8-6/14		6/15-6/30	
Port	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top	Aer. Top	Anaer. Top
cis-DCE	615	141	74	ND	225	779	82	136	329	340
trans-DCE	ND	ND	49	ND	48	68	12	12	13	19
1,1-DCE	63	45	ND	ND	ND	ND	ND	ND	32	9
VC	234	186	3505	ND	6045	4772	1914	2838	1876	2327

ND -- not detected

Table 13. Average ORP Values in mV for the Simultaneous Column

	5/1-5/17	5/18-6/12	6/13-6/18	6/19-6/26	6/28-6/30
Aerobic Top	-15	-51	9.4	26.6	66
Facultative Zone	9.8	-121	-24	-25.7	15
Anaerobic Bottom	-188	-202	-201	-143	-114

6.3 Anaerobic Microcosm Studies

Three anaerobic microcosm batches have been prepared for the purpose of determining the experimental parameters of future microcosms. The goals were 1) to find the environmental conditions which caused the bacteria to most effectively degrade TCE; and 2) to provide quality analysis/ quality control within the limits of available laboratory equipment.

Batch 1 was utilized to determine if the microcosms should be provided substrate (in the form of methanol) 1) only upon initial creation of the microcosm; or 2) periodically when methane production halts. It has been decided that substrate should be provided periodically to allow for most effective removal of TCE.

Batch 2 was utilized to determine the basal salt requirements for a batch microcosm. A basal salt concentration higher than that being provided to the columns was used in the microcosms. Minimal degradation of TCE indicated a concentration identical to that of the columns was necessary.

Batch 3 was a larger batch, utilized to determine several parameters. It was necessary to decide if the microcosms required constant agitation to increase TCE degradation, or if one manual agitation per day would suffice. A new culture of anaerobic bacteria from a wastewater treatment plant was also compared with the old culture from the maintenance reactor. Finally, a decision was to be made on the addition of reducing agents, based upon their usefulness in aiding the reduction of TCE. A matrix of this microcosm appears in Table 14. The experiments are not complete, so no reliable results can be provided. However, it has been learned from these microcosms that a headspace of greater than 10 mL will be needed in future microcosms. This will prevent a buildup of pressure within the microcosm which can disrupt its integrity, invalidating the results.

Table 14. Matrix for Microcosm Batch #3

	Constant Agitation	Once/day Agitation
RA	O1, O2 N1, N2 CA	
No RA		O1, O2 N1, N2 CB
RA		O1, O2 N1, N2 CC

Key:

RA = With reducing agents
No RA = Without reducing agents

N= New culture (from wastewater treatment plant)
O= Old culture (from maintenance reactor)
C= Control (no biomass)

N.B. -- Each row in the table defines a particular set. The numbers indicate duplicates for QA/QC (e.g. O2 indicates Old culture, microcosms #2). The letters following the control designate sets. (e.g. CA indicates the control for set A).

7.0 CONCLUSIONS

Two approaches are being taken to simulate and predict the effectiveness of bioremediation at PORTS. Continual flow column studies and anaerobic batch reactor (microcosm) studies are being performed. Two column studies, a simultaneous anaerobic and aerobic column and a sequential anaerobic and aerobic column, are in progress with plans to begin a second simultaneous column. Overall TCE removal has been highest in the simultaneous column with percent removals for one pass as high as 98%. Moderate vinyl chloride (VC) concentrations remaining in the column effluent have continued to be a problem with the simultaneous column but attempts to increased aerobic degradation via increased hydrogen peroxide addition has greatly improved VC destruction. The sequential column has been showing lower percent destruction, 70-80%, but has shown greater daughter product destruction and lower effluent concentrations of VC. In an attempt to increase anaerobic activity, and TCE destruction, better control of pH through buffers and possible reinoculation of the anaerobic zone is being explored.

Preliminary microcosms have been performed to establish an experimental procedure for their use in this study. Factors such as head space volume, substrate addition, biomass concentrations, trace metal and nutrient concentrations, and possible agitation are being considered. Initially it appears that substrate addition and initial head space volume are critical to maintaining the integrity and the effectiveness of each microcosm. Utilizing mineral salts concentrations and reducing agent concentrations similar to those in the column study's synthetic ground water yield positive initial results. Ideally the microcosms planned for future study will yield information on the rate of TCE degradation, the ability of native organisms at PORTS to remove TCE and its daughter products, and the viability of using residual surfactant from the initial surfactant flood as an alternate substrate.

8.0 WORK PLANNED FOR NEXT QUARTER

Further site characterization data is required. Specifically pertaining to ground water composition, including phosphorous and nitrogen content, in the event that ground water from the site can not be obtained. Additional

information must be gathered on the native microorganisms and other contaminants present. If permitted ground water and soil samples will be obtained from the PORTS site. Otherwise the ground water will be synthesized in the lab.

Continued operation of the existing simultaneous and sequential column is planned. Parts for a second simultaneous column have been ordered and will be constructed and begin operation next quarter. The second simultaneous column will allow for greater flexibility and the evaluation of more data in a shorter time period.

Microcosm tests will be performed to establish the effectiveness of the surfactant used in the surfactant flood for a primary substrate. The ability of organisms native to the PORTS site to degrade TCE will be determined in these test as well. These test will be performed with three different contaminant concentrations.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

Technical problems were encountered when the ground water pump for the sequential column malfunctioned allowing air to be pumped through the column. The pump was repaired but the sequential column continues to operate at levels below those obtained in the past. It is hoped that with continued operation the column's performance will improve.

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

Administrative problems have caused delays in the reception of ground water and soil samples from PORTS. Additionally, it is unclear at this time if any samples will be permitted off site.

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DEVELOPMENT AND IMPLEMENTATION OF A DECISION SUPPORT SYSTEM FOR MANAGEMENT OF THE EM50 TECHNOLOGY DEVELOPMENT PROGRAM
METC SUBTASK 1.7A

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Morgantown, West Virginia

By:
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ABSTRACT

It has become apparent that there is a need for a means to organize and catalog various activities in the Office of Science and Technology Program in such a way that decision makers can take full advantage of the portfolio of R&D projects to meet the needs of the DOE Weapons Complex cleanup. An effort has begun to provide such a means and has proceeded to the point where a database system has been designed, but not fully implemented. The purpose of the present effort is to take a relational database system (implemented in Microsoft Access) that has an application front end written in Visual Basic and provide a useable product to the Department of Energy by October 15, 1996. The final product will include the database system with its front end application fully populated with data from one of the focus areas (Subsurface Contaminants). A decision tool process will be provided to assist in analysis and prioritization of the technology development portfolio being sponsored by the DOE EM-50 program.

To that end, the current effort involves three major tasks: 1. examine the data set that exists for the Subsurface Contaminants Focus Area and correct and complete information pertaining to all projects; 2. make a critical assessment of the coding for the application front end to the database; and 3. assess, recommend, and implement decision tools that provide the rigorous analyses needed to build justifiable, documented group decisions about the R&D portfolio.

Follow-on activity will include the further population of the database with the other 4 focus areas' data sets.

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1.0 INTRODUCTION

The Waste Policy Institute is developing a means to organize and catalog the activities in the Office of Science and Technology program, and to assist decision makers in optimizing the portfolio of R&D projects to meet the needs of the DOE Weapons Complex cleanup. This effort has proceeded to a point where a database system has been designed, but not fully implemented.

2.0 PURPOSE

The objective of this effort is to take a relational database system (implemented in Microsoft Access) that has an application front end written in Visual Basic and provide a useable product to the Department of Energy by October 15, 1996. The final product will include the database system with its front end application fully populated with data from one of the focus areas (Subsurface Contaminants). A decision tool process will be provided to assist in analysis and prioritization of the technology development portfolio being sponsored by the DOE EM-50 program. Follow-on activity will include the further population of the database with the other 4 focus areas' data sets. A facilitated decision process will be provided to DOE to help analyze their funding decisions and justify their programs. At the point where the system is operational, it may be desirable to discuss its further extension to other agencies such as the Air Force Human Systems Center where the original concept for such a tool originated.

3.0 BACKGROUND

The status of the development at this time is:

1. The database system has been defined with 5 database files that can be inter-related. The relationships have not been established at this time.
2. A partial data set from the Plumes focus area has been entered into the databases. The data need to be validated, updated, and missing information entered.
3. Decision criteria have not been defined in the databases; these need to be defined to include, for example, "gate" criteria for advancing to next development phase, risk analysis, stakeholder input, system performance and cost/benefit criteria. These additional criteria need to be defined, fields created, and information developed to characterize the new technologies.
4. The front end application needs to be debugged and made operational. Additional selection and sorting criteria will need to be programmed to display the outputs of the new criteria. There are some fundamental "bugs" in the application front end that preclude extraction of the database into accurate reports. Data entry through the application front end is not error-free.
5. A decision process needs to be defined and implemented that will query the databases and allow a facilitated weighting and prioritization of the technology portfolio. This process needs to be software based and coupled to the relational databases. Minimal software development is desirable in the decision tool application.

4.0 METHODOLOGY

There are three inter-related activities that need to be accomplished to provide a useable decision support methodology. These activities will proceed in parallel.

1. Validate and complete the data collection and data entry for the Subsurface Contaminants focus area. This task involves the collection of current program information, validation of the commercially available technologies, site needs validation, and problem definitions.
2. Finalize the code development for the front end application to query and display the database information.
3. Analyze decision support tools that will be most applicable and useful in the portfolio analysis and optimization, select tools, and implement them to use the database information.

These tasks are inter-related and must be executed in concert with each other to assure that the final product is functional and usable.

The first major activity is to examine the data set that exists for the Subsurface Contaminants focus area. The data set is incomplete (for example, the current projects are not documented in the database). Additional data may be needed to fully reflect the consolidation of Plumes and Landfills focus areas into the Subsurface Contaminants focus area. The data need to be linked in a relational sense among the data tables to preserve the linkages between needs, technologies, problems, etc. The resources to do this work are located in the Aiken field office of WPI that is providing support to the focus area. This office will have the necessary data and the expertise to provide the quality control checks needed to validate the data.

The second major activity is to make a critical assessment of the coding for the application front end to the database. This application is the interface with the user that processes queries, provides structured data entry capability and prepares reports from the queries for screen or hard copy display. The Visual Basic application that exists contains serious "bugs" that need to be fixed. It may be desirable, after fully analyzing the application, to do major rewriting of the code. This activity can be carried out using resources from Virginia Tech in Blacksburg under the guidance of WPI's corporate Information Technology group. This group will also restructure the data tables to incorporate the missing data fields needed to implement the decision support.

The third major activity is to assess, recommend, and implement decision tools that provide the rigorous analyses needed to build justifiable, documented group decisions about the R&D portfolio. The implementation of the tools will be through software links between the databases and the tools, and will provide reporting capability of the results of the decision analyses. The approach recommended for this activity is to use university management school faculty from Virginia Tech and West Virginia University who are

involved in decision process modeling. To that end Waste Policy Institute and Virginia Tech are working in collaboration with West Virginia University staff.

5.0 WORK PERFORMED THIS PERIOD

The WPI Team has been working with Virginia Tech and West Virginia University (WVU) personnel to develop a prototype system to support decision-making efforts for the Subsurface Contaminant Focus Area. The three groups met on May 28 & 29 in Blacksburg, VA to discuss the existing system and the steps necessary to complete system development. Key issues which were addressed included: (1) database design, (2) data availability, and (3) decision analysis requirements beyond what the database program can provide. On June 3 the team met with DOE personnel in Aiken, SC. The objective of this meeting was to outline to DOE the plan for completing the prototype system and to learn first hand what the desired user outputs "or capabilities" of the system should be. A third meeting was held June 12 in Aiken to further discuss and refine the database design and data requirements. Specific work performed by task for the reporting period is described below.

Task 1 - Subsurface Contaminant Data Validation

Current program information for the Subsurface Contaminants Focus Area (SCFA) have been validated and provided to the Virginia Tech personnel responsible for database design. This information included data from recent efforts to prioritize problems and technological needs within the two DOE/EM program areas recently combined to form the SCFA (Contaminated Plumes and Landfills focus areas), as well as the "Plumes Focus Area Logic Diagram: A Tool for Matching Technologies and Plumes-Focused Needs."

Task 2 - Data Assembly

The WPI Team located in Aiken, SC initiated efforts to assemble missing data required to fully populate a prototype system capable of assessing site-specific problems and technological needs for the SCFA.

Task 3 - Data Entry

To the extent that available validated data can be incorporated into the new database structure, data entry has commenced.

Task 4 Existing Database Application

Virginia Tech personnel devoted a significant portion of time toward understanding the current TechInvest system in terms of the program itself and in terms of the data in the database tables. This effort is documented in a report entitled "Documentation of TechInvest Prototype 1.0b (Beta)."

Task 5 - Database Development

Virginia Tech personnel have been working closely with WPI Team members in Aiken, SC to develop a database design and a structure of the decision process which will allow the application of decision analysis tools capable of meeting customer needs.

6.0 RESULTS AND DISCUSSION

The review of the TechInvest prototype revealed that it exhibits only part of the functionality outlined in both the project proposal and by the DOE customer at the June 3 meeting in Aiken, SC. Specifically, the data in the prototype is not structured based on an integrated model that is driven by decision support needs, and therefore relationships in the data are difficult to discern. Furthermore, the TechInvest prototype contains five separate databases each containing at least 25 data tables. Thus, there are over 125 tables. However, the tables and associated fields are almost identical for each of the databases resulting in a large amount of redundancy, as well as a cumbersome and slow system. Based on these findings, Virginia Tech has recommended that the database be restructured in order to meet the following objectives:

- Capture customer needs (system capabilities) not previously considered
- Remove redundancies
- Provide for effective linkages between databases
- Allow for more dynamic application of decision analysis tools

The WPI Team has concurred with this recommendation and database redesign efforts aimed at the stated objectives have commenced. The data in the 125 plus tables has been extracted and entered into one consolidated database with four tables. The field names were also updated to make them more descriptive and to mirror the field names in data acquired from the SCFA.

7.0 CONCLUSIONS

Database development is proceeding in line with the planned schedule and is estimated to be fifty percent complete. The WPI Team (Aiken) has provided a comprehensive data structure and associated data fields which must be incorporated into the system to meet customer needs. Due to the expanded capabilities that the system must address, the WPI Team is addressing additional data gaps. This effort includes reviewing data existing within the TechInvest System and data previously provided to Virginia Tech to determine where additional data is required. See "Technical/Administrative Difficulties" below.

8.0 WORK PLANNED FOR NEXT PERIOD

As stated, Virginia Tech personnel are working toward a schedule demonstration of the redesigned prototype system on July 9 in Blacksburg, VA. Efforts in support of this demonstration include developing descriptions of the data fields and identifying standard data entry pull-down menus. WPI Morgantown and WVU are collaborating on this effort. In addition, Virginia Tech will began efforts toward developing the back-end decision analysis tools including the development of the criteria necessary for reaching critical decisions. WPI Aiken will continue efforts to assemble, validate and input the SCFA data necessary to populate the system.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

Efforts related to task 1 through 3 have been slow to get off the ground. The reasons for this are as follows:

1. Expanded customer identified needs relative the initial TechInvest prototype requirements.
2. Outdated data currently housed in the TechInvest prototype.
3. Recent merger of two EM programs into one Focus Area (SCFA) resulting in a two-fold increase in data requirements.

WPI Team members in Aiken are currently addressing these issues and anticipate data collection, validation, and entry efforts will be completed in late July. Data validation will, however, require a greater percentage of the time originally allocated for the combined data-related tasks (e.g., tasks 1 - 3).

DEVELOPMENT OF A PROTOTYPE DATABASE AND DECISION SUPPORT SYSTEM FOR MANAGEMENT OF THE EM-50 TECHNOLOGY DEVELOPMENT PROGRAM METC TASK 1.7B

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ABSTRACT

The prototype system to be developed in this project will provide a database and a decision support system to assist decision makers in optimizing the portfolio of R&D projects relating to the clean-up of subsurface contaminants at DOE sites. The database will provide a means of organizing and cataloging pertinent information on specific clean-up problems, as well as information on existing and potential technologies that may be utilized to solve those problems.

The decision support system will consist of a collection of quantitative tools to be used to suggest and evaluate possible solutions, subject to the decision maker's assessment of such factors as the importance of relevant information, the magnitude of associated risks, and the probabilities of rewards to be realized. The work of this project will build on previous work to build an initial database and existing software to provide access to the database. A team of professors and graduate students from Virginia Tech and one professor from West Virginia University will carry out the work of this project.

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EXECUTIVE SUMMARY

Worked performed this period includes an analysis of available decision support tools, analysis of the data requirements and work to be accomplished, and the plans for the design of an on-line help system for documentation of the subsurface contaminants focus area domain.

The TechInvest project combines an existing database, which is under the process of revision and validation, with decision support tools to aid in matching remediation technologies to environmental management problems. Decision support systems help decision-makers to make sound decisions by integrating data with various decision-making models. Included in this report are brief summaries of several decision-making tools and an assessment of their applicability to the TechInvest problem. The analysis indicates that the analytic hierarchy process would be the best selection for use in this project, along with a decision analysis tool to assess the affect of risk.

Data analysis has revealed that much of the data in the existing database is redundant, and the structure of the database is not optimal. The interface performs slowly and is not well documented. In spite of these problems, the functionality of the existing TechInvest program will be maintained in order to provide a consistent transition for users who may be familiar with the old system as the problems in database design and the functionality of the user interface are addressed.

Future work will primarily involve building an on-line help system for the TechInvest project. This will aid model builders in understanding the terminology of the environmental management domain, and it will help users to understand how decision support systems work.

1.0 INTRODUCTION

The Department of Energy has initiated a project, under the name of TechInvest, to analyze, prioritize and select technologies to be funded and applied to waste clean-up problems at various DOE sites. Some initial work on the TechInvest project has been completed, and this project has been initiated to complete that work, providing a working prototype decision support system by September 30, 1996 for the Subsurface Contamination Focus Area. Work will be carried out by personnel at Virginia Tech (Professors Laurence Moore, Saifur Rahman, and Tarun Sen with graduate student assistance, as well as Professor James Denton at West Virginia University.

The work will begin with a review of the existing database, and revision of its design as required. The user interface program will also be reviewed and redesigned as required. The following work will consist of designing and implementing a decision support system to allow users to select the best combination of technologies for investment in the environmental management program.

2.0 PURPOSE

This project will complete the work on the initial TechInvest project by validating and entering data to the database where required. In addition, decision support tools will be added to aid in the process of prioritizing and selecting technologies to be applied to surface contamination problems. The criteria used for decision making should be consistent with the "gate" criteria used to evaluate projects for advancement to succeeding development phases, and consider costs, benefits, and risks from the standpoint of the stakeholder.

The finished product will provide DOE with the capability to analyze funding decisions and justify their programs using sound analytical reasoning, minimizing decisions that may appear to be arbitrary or made on an ad-hoc basis.

3.0 BACKGROUND

DOE has identified the need for a means of assuring that investment made in research and development in the Environmental Management program will result in the optimal benefit toward cleaning-up the department's sites. The key to achieving this goal is through the development of a decision-making process for technology management that is customer-oriented, and can link the most appropriate technology development activities with site clean-up operations. The Technology Investment Decision Model has been designed to assure that funding decisions are made at all stages of technology development in a manner consistent with technical and nontechnical criteria for performance and acceptance by the customer.

A relational database has been designed using Microsoft Access and partially populated with data on surface contamination problems and applicable technologies. A user interface, written in Visual Basic, has also been designed to allow decision makers to enter, edit, and add data, as required, to the existing database. There are currently 5 separate databases in TechInvest, with partial data from the Subsurface Contaminants focus area. The data require validation, with updating required in certain cases, and missing data provided in other cases. There are some operational difficulties (bugs) with the Visual Basic interface which require fixing so that accurate reports may be generated and new data may be entered.

This project will validate the database, fix the user interface, and add decision support tools to the database for selecting a technology portfolio in the most intelligent manner.

4.0 METHODOLOGY

Preliminary activities will consist of examining the existing data set, revising data where applicable, and adding data to incomplete sections. Appropriate relational links are needed to complete the logic structure of the database. The user interface, which allows the database to be queried, provides access to enter and revise data, and generates reports, needs to be checked for coding errors and debugged. The result of this preliminary effort will be a database system populated with a significant subset of site-specific data and technology data from the Subsurface Contaminants Focus Area.

The database will be used in conjunction with decision support tools to allow a decision-maker to select the most appropriate technology development portfolio to deal with subsurface

contamination problems in the DOE EM-50 program. The decision support tools will allow decision makers to analyze alternate technologies, prioritize alternatives, and provide justification for funding decisions.

Research will be undertaken to select appropriate decision support tools for this task. First, there must be an understanding of the current decision-making process, as well as perceived needs and desires for improvements in the current decision-making process. The most appropriate methodology or methodologies will be selected from available decision support techniques. Eventually, all focus areas will be represented in the database.

The performance of the DSS will be assessed at two intermediate prototype stages prior to project completion. The initial prototype will demonstrate the interface between the database and the user, but will not utilize the full database. Based on client input, specific functions and features will be added to the DSS to produce an intermediate prototype. The intermediate prototype will then be demonstrated to and evaluated by the client. Based on client feedback, the prototype will be further refined and modified. In addition to the suggested modifications, the final product will include linkage to the full database. The client will therefore be intimately involved during the development process to assure that the resulting DSS provides the required functionality.

5.0 WORK PERFORMED THIS PERIOD

Worked performed this period includes an analysis of available decision support tools, analysis of the data requirements and work to be accomplished, and beginning work on the design of an on-line help system for documentation of the problem domain.

5.1 REVIEW OF DECISION SUPPORT TOOLS

The TechInvest project utilizes a database for problems and potential technological solutions and decision support tools to aid in matching the problem to the solution. A decision

support system (DSS) help decision-makers to make sound decisions by integrating data with various decision-making models. A DSS enables the decision-maker to process large volumes of data quickly, and create useful information for making tactical and strategic decisions.

A DSS is useful for making unstructured decisions and semi-structured decisions. Unstructured decisions are made in situations that are nonrepetitive. Intuition, judgment, and experience play a critical part in this type of decision-making. For this reason, different individuals often arrive at significantly different decisions using the same data. Semi-structured decisions are similar, except some of the elements of the problem are routine and can be approached with standard mathematical procedures such as calculus or linear programming.

A DSS is a collection of integrated tools that allow a user to easily access relevant data and apply various qualitative and quantitative analysis tools. They usually allow the user to change assumptions and enter queries. It provides a user-friendly means for bringing together data, analytical models, and human judgment.

The major functions of a DSS include model building, "what if" analysis, goal seeking, risk analysis, and graphical analysis. Model building helps the decision-maker identify and develop decision-making models by taking into account input variables and their interrelationships, assumptions, and constraints. "What if" analysis is the process of assessing the impact of changes made to model variables. Goal Seeking allows decision-makers to identify the optimal means of achieving a stated goal. Risk analysis allows the decision-maker to evaluate uncertainties associated with different decisions. Graphical analysis is the display of data in a format that is easy to understand, allowing the decision-maker to quickly digest large volumes of data.

Various tools can be used as part of a DSS or in combination with a DSS to enhance decision-making. The following paragraphs will discuss expert systems, neural networks, fuzzy logic, mathematical programming, the analytic hierarchy process, and decision analysis.

An expert system is a computer program that has captured human knowledge to solve problems that require the know-how of an expert. Expert systems are designed to emulate the reasoning processes that experts use to solve specific problems. Such a system can be used by a non-expert to improve his or her problem solving capabilities, or they can be used by experts to provide knowledge assistance. They are particularly useful to propagate scarce knowledge, improve decision-making, and provide consistent results.

Expert systems are composed of two major parts: the development environment, used by the builder of the expert system, and the consultation environment, used by the nonexpert to obtain expert knowledge and advice. Major components of expert systems include a knowledge base, an inference engine, and a user interface.

The knowledge base includes facts concerning the problem situation and rules concerning how to utilize knowledge to reach a conclusion. The inference engine is a control mechanism that provides a methodology for reasoning about information in the knowledge base to formulate

conclusions. It provides directions about how to use the system's knowledge by developing the agenda that organizes and controls the steps taken to solve problems. This is accomplished by interpreting which rules apply to a situation, and scheduling the application of those rules to obtain a consistent path of reasoning. The user interface provides a friendly means of communication with the user, usually via natural language supplemented with menus and dialog boxes. Capability to trace the reasoning path of conclusions is important to provide justification for conclusions, and to transfer knowledge to the user.

Expert systems operate by conducting a bi-directional dialog with the user, asking him or her to provide facts about a specific situation. After accepting the user's answers, the inference engine will be used to reach a conclusion. In the course of reasoning, the expert system may ask the user for more information. Upon conclusion, the expert system will provide the user with the result and an explanation of how that result was reached.

Neural networks are a branch of artificial intelligence which is based on the structure of the brain. The human brain is a complex biological network of billions of highly interconnected cells called neurons. These cells receive information from thousands of similar cells, and send their signals out to other cells based on the pattern of the incoming signals. The neurons are connected to each other at synapses, which attach weights to incoming signals so that each of the signals has a different effect on the neuron. The net incoming signal determines the strength of the outgoing signal sent from the neuron. Learning occurs in the brain in the form of changes to the synapses. Through learning, the response to stimuli can change.

Artificial neural networks are similar to the brain in that they contain neurons interconnected by weighted paths. Learning is achieved by adjusting the weights until a desired response is obtained. Artificial neural networks are much smaller in the number of neurons and the number of interconnections than biological brains, and their capabilities do not yet approach those of the brain.

The most popular neural network model is back propagation, which is an algorithm for training layered feed-forward neural networks. In these networks, the neurons are arranged in layers, and signals are propagated in one direction only, from the input layer, through the hidden layer(s) to the output layer. Patterns presented to the input layer are associated, via learning, to desired patterns in the output layer.

The first step in designing a neural network is to determine exactly what the inputs and outputs represent. There needs to be some historical data to provide a set of correct responses for training. The neural network will learn the required associations without the application of rules or formulas concerning the data. This is very different from the expert system, which requires that explicit rules and formulas be provided.

Fuzzy logic is a relatively new field which allows vague information to be processed in a logical fashion. It uses set theory with some additional capabilities to allow inexact data to be

processed. Fuzzy logic is usually used in conjunction with other decision-making techniques, such as neural networks or expert systems to solve problems.

Neural networks offer an ideal means of processing fuzzy data since they, by there nature, do not produce exact results. Often, input data provided to a neural network is inexact or vague, and may be expressed in degrees such as high, medium, or low. Fuzzy outputs in neural networks are often interpreted as probabilities or degrees of uncertainty. A fuzzy expert system may use fuzzy data as input or output and may also apply probabilistic rules. Since probability measures require exact arguments, the fuzzy data must undergo a process called defuzzification prior to the application of a rule. Then the result is returned to the fuzzy state through the process of fuzzification.

Mathematical programming techniques are methods used to solve structured problems, but they can be applied in a semi-structured decision support system to provide solutions to parts of the problem under consideration. All mathematical programming applications require modeling a problem by formulating an objective junction to be maximized or minimized, and a set of constraints which describe the limitations of the model variables or relationships between model variables that must be maintained. Linear programming is used when the objective function and the constraints are linear in the variables. Variations on linear programming include integer programming, mixed-integer programming, quadratic programming, and nonlinear programming. In cases where there are multiple criteria for optimization, goal programming can be used.

The analytical hierarchy process (AHP) is designed to solve complex problems involving multiple criteria. The process requires the decision maker to provide judgments about the relative importance of each criterion and then specify a preference on each criterion for each decision alternative. The output of AHP is a prioritized ranking indicating the overall preference for each of the decision alternatives.

The first step in AHP is to develop a representation of the problem in terms of an overall goal. A set of criteria then must be put forth to show how the degree of achievement of the goal will be measured. Finally, decision alternatives are evaluated as to their performance in satisfying each criterion of the overall goal.

AHP requires that the decision-maker specify his or her judgments about the relative importance of each criterion in terms of its contribution to the achievement of the overall goal. Then, AHP asks the decision maker to indicate a preference or priority for each decision alternative in terms of how it contributes to each criterion. Given the information on relative importance and preferences, a mathematical process is used to synthesize the information and provide a priority ranking in terms of the overall preference.

The method of pairwise comparison is used to establish priority measures for both the criteria and the decision alternatives. In a pairwise comparison, the decision-maker must indicate the relative preference of alternatives and the relative importance of criteria, considering two alternatives or criteria at a time. He or she may indicate an equal preference, a moderate

preference, a strong preference, a very strong preference or an extreme preference. During this process, the consistency of the decision-maker's judgments is monitored through the computation of a consistency ratio. In cases of drastic inconsistency, the decision-maker may wish to revise some judgments. At the end of the exercise, the most preferable alternative is indicated, and all alternates are ranked with a numerical representation of their preference. Analysis can be done to examine the effects of changes in the preferences of the decision-maker.

Decision analysis can be used to determine optimal strategies when a decision maker is faced with several decision alternatives and an uncertain or risk-filled pattern of future events. Decision problems can be structured in the form of decision trees when a sequence of interrelated decisions must be made, and the sensitivity of the decision to changes in assumptions can be determined. It is also possible to determine the value of obtaining more information about a problem.

5.2 DATA REQUIREMENTS AND WORK PLANS

A meeting was held at Virginia Tech, Blacksburg, Virginia on May 28 and 29 to discuss the status of the existing data and how that data should be best utilized in the decision support system to be built. Present at the meeting were the following WPI personnel: Ray Malinovsky (Dayton), Rob Vagnetti (Morgantown), John Dancz (Aiken), and Jack Davis (Blacksburg). From Virginia Tech, represented were Brian Gehrt (CSTI), Tarun Sen (Accounting), Mark Kubik (Accounting), Saifur Rahman (Electrical Engineering), Arnie DeCastro (Electrical Engineering), and Larry Moore (Management Science). James Denton was present from West Virginia University.

Discussions on the first day concerned the status of the existing database and the Visual Basic user interface that had been provided for the original TechInvest software. Much of the data in the database has been found to be redundant, and the structure of the database is not optimal. Most of the data fields consist of descriptive text, which is not suitable for decision making. The interface performs slowly and is not compatible with windows. The coding has not been well documented, and is inefficient.

Despite these problems, the original TechInvest data and program will be used as much as possible, since there may have been significant buy-in to the system from the user community. The data contained in TechInvest, despite its shortcomings, is valuable to decision-makers because it can be easily accessed via the program.

The concept of TechInvest is to provide a vehicle for matching environmental management problems with technologies that can provide solutions for those problems. Such a match should be made based on customer needs. Those needs are, in part, technical in nature, but they also have a high public relations component. Decisions about funding technology development need to be capable of being justified rather than appearing arbitrary. TechInvest will provide this capability.

There is not always agreement as to the importance of various factors involved in the problem-technology match. An ideal decision support system will allow for differing opinions among decision-makers as to the relative importance of various factors. For example, one individual may feel that in situ treatment is a requirement, whereas another may not. Obviously, the assessment of risks and benefits associated with various technologies can differ among individuals. The decision support system to be used in TechInvest should allow for a meaningful range of possibilities.

The final product will be a decision aid rather than a decision maker. It will allow individual decision makers to adjust their own inputs concerning the importance of technological and non-technological factors, risks, costs, and benefits. Based on these inputs, the best decision will be suggested. Different decision-makers may, therefore, arrive at different decisions using TechInvest. What is valuable about the process is that discussions about the best decision can be directed by the inputs used to arrive at that decision.

TechInvest will contain data concerning problems and data concerning technologies. The decision support tools will propose technological solutions to the problems by matching the technologies to the problems. In this way, the logic and reasoning behind funding decisions will be documented. The portability of the Windows-based software will allow customers, stakeholder, and technology developers to view the current decisions and the rationale for those decisions.

Considerations for technologies include: advantages, deficiencies, cost, side-effects, public acceptability, risk, permanence, and commercial viability.

5.3 CAPTURING DOMAIN EXPERTISE

There is a need for a document, written in language that is understandable to non-DOE personnel, that describes the domain of the problem being worked on. Most importantly, the document would include definitions of the many specialized words, phrases, and acronyms used

be DOE and WPI personnel in the environmental management program. Involvement of James Denton will be valuable because of Morgantown Location, with access to the WPI office there, which contains much of the documentation required. There is a need to know what terms such as "site", "problem", "need", "performance criteria", "technology", and "requirements" mean in the context of the project. Sometimes these terms take on specific connotations that different people in different situations may not grasp.

There is also a need for the users of TechInvest to learn the language of the decision support methods being used. Terms such as "alternative" and "criteria" have special meanings in AHP. Given these needs, a useful vehicle for communicating information might be an on-line help system. Such a system would provide domain expertise for model builders by defining terms used by DOE and WPI personnel, overcome the barriers to understanding imposed by the use of specialized language or jargon, and provide a list of commonly-used acronyms to aid in clarifying the problem domain.

The use of an on-line help program as the documentation vehicle has several advantages. First, it has an easy-to-use interface that is familiar to all users of Windows software. Second, it can be distributed cheaply and quickly via electronic mail. Third, it has several useful features including hypertext jumps, the ability to include graphics with hot spots, the ability for individual users to add annotations, searching by keyword, browsing through defined sequences, and navigation through history lists. Finally, it may be possible to add the context-sensitive help system to the final TechInvest product.

6.0 RESULTS AND DISCUSSION

Expert systems offer the benefit of increasing the output and productivity of personnel by giving access to the knowledge and experience of experts to anyone in the organization. Scarce expertise can be captured and stored. Expert systems can also work faster than their human counterparts, and the quality of their decisions is increased due to better consistency and fewer errors. Expert systems can also be made flexible enough to fit an individual decision-maker's preferences. They are easy to operate since natural language queries are used to communicate between the computer program and the user. Reliability is high since expert systems do not get "burned-out" as humans do.

Expert systems can also be designed to integrate the opinions of several experts, and provide decisions and analysis superior to that of any one individual. Incomplete and uncertain information can easily be handled, with "I don't know" recognized as a valid user response. Users

of expert systems find them useful in training novices. The novice can gain experience from interacting, with the expert system, which provides explanations for its reasoning. In this way, expert systems provide a useful vehicle for knowledge transfer to remote locations.

On the negative side, the act of building an effective expert system is a difficult and time-consuming endeavor. Knowledge must be accessible, meaning that the experts must be willing and able to spend many hours being interviewed to extract their specialized knowledge. The process of extracting that expertise is not trivial, but rather requires an experienced knowledge engineer. The services of experienced knowledge engineers are difficult to find and are very expensive. Much time is required for the extraction of knowledge, meaning that completion of an expert system usually requires years rather than months. The applicability of expert systems is limited to a narrow domain; extending the expert system to similar but different problems requires significant effort. Finally, in building the knowledge base, care must be taken to avoid reacting to judgmental biases.

Neural networks offer the advantage of eliminating the knowledge engineering phase, since they can learn from experience. However, they require that some historical data, or "the right answer" be available for training. They reacts well to missing or uncertain information, and have been shown to be effecting in pattern recognition applications. Unlike expert systems, when confronted with new and unexpected information, neural networks can often extrapolate a meaningful response. Operation is very fast once training has been accomplished, but training large systems can be prohibitive in terms of computational time.

Neural networks provide no justification for their answers. There is no reasoning path, as is provided with expert systems. It is difficult to perform sensitivity analysis, or examine the effect of changing assumptions on the problem solution. An despite some successful applications reported in the literature, neural networks are not yet a proven technology. They are bad at serial logic, precise computations, deduction and logical thinking. In some circles, they may be regarded as a "black art".

The analytic hierarchy process offers the advantage of dealing effectively with multiple criteria. Operation of the system, using pairwise comparisons, is extremely simple, with safeguards provided to reduce the possibility of inconsistencies in user evaluations. Since preferences and the relative importance of criteria are determined from the user, the system will be adaptable to different individuals or groups. The system highlights differences among individuals in their assessment of risks and preferences and in this way encourages consensus building. Discussions are focused on potential disagreements concerning the relative importance of criteria, or the relative merits of alternatives. The user interface can make AHP appear to be a very intuitive approach that is aiding a decision-maker to make a decision, rather than making a decision for the decision maker.

The other methods discussed above are probably not useful by themselves, but may be combined with other techniques to enhance problem solving capability. Fuzzy logic, for example, can be combined with expert systems or neural networks to better handle imprecise data.

Mathematical programming can provide very precise optimal solutions, but is sensitive to changes in a dynamic environment. Decision analysis provides a useful method of handling uncertainty when coupled with the analytic hierarchy process.

7.0 CONCLUSIONS

In order to conform with previous expectations, the TechInvest database will maintain much of its existing functionality, but will be redesigned to enhance efficiency. It will then be populated with date from the subsurface contamination focus area. This work will be done by the team at Virginia Tech with cooperation from WPI personnel.

Modeling of the decision support package will be done using the analytic hierarchy process in combination with a decision analysis package for dealing with uncertainty. The analytic hierarchy process will provide the best fit of tool capabilities for this type of portfolio selection problem. Differing opinions among users with respect to the importance of decision criteria as well as the effectiveness of various technology alternatives fit in well with the AHP technique. There also is a wealth of expertise among the Virginia Tech personnel in this area.

The use of expert systems is precluded mainly due to time restrictions. Development time for expert systems is typically longer than the time available for this project. Neural networks are not being used primarily because of the risk involved with their adoption. While they have been successful in many applications, there is no history of their performance in an application similar to this project. User confidence in the answers provided by neural networks cannot be assumed since the network provides no reasons for its answer.

Domain expertise will be developed and provided by James Denton at West Virginia University with the cooperation of the WPI Morgantown office. The main activity to be completed in this area will be the design and implementation of an on-line help system. This system will be used by the model builders during model construction to aid in their understanding of the technical terminology and issues of the environmental management domain. It will also be used by the ultimate users of the TechInvest software to provide explanatory capability for the workings of the decision support system. Ultimately, the help system can be included with the TechInvest software to provide context-sensitive help.

8.0 WORK PLANNED FOR NEXT PERIOD

The first task for next period is to build the on-line help system. Since the model builders (at Virginia Tech) require domain information more immediately than users require modeling information, initial efforts will be made in this area. Working with personnel at WPI, primarily in the Morgantown Office, definitions will be obtained from existing documents and personnel. The initial element of the help system will be a glossary, including acronyms, since this will be most useful immediately to the model builders. Upon completion of the glossary, and executable Windows-based help file can be distributed to the model builders.

Proceeding concurrently with work on the glossary will be design work on the general layout of help entire help system. The design will identify primary topics, sub-topics, and navigation links between them. This will allow for the planning of jumps, pop-ups, and secondary windows in the help system. Browse sequences will be planned to allow the user to navigate through the system in a logical manner. Graphic elements will be included with hot spots to link to text explanations. Finally, a list of keywords will be developed to allow searching capability.

Data entry will follow the design phase. The ForeHelp help authoring system by ForeFront, Incorporated will be used to create the system.

It will also be necessary to provide assistance to the Virginia Tech team as the decision support system is being build. It will be important in this phase to capture the decision-making methodologies of the potential users of the system. The criteria for decision making and the alternatives available to decision makers must be well documented at this stage. Interviews will be carried out with WPI personnel to determine the appropriate decision and valuation procedures.

A GIS-BASED INFRASTRUCTURE

FOR SITE CHARACTERIZATION AND REMEDIATION

METC Task No. 2.1

Quarterly Technical Progress Report
Reporting Period:
April 1,1996 - June 30, 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:
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ABSTRACT

The overall goal of this effort is to determine an effective geographic information system (GIS)-based infrastructure for describing, characterizing, and remediating contaminated sites. The work is being carried out with the remediation needs of the U.S. Army Corps of Engineers Huntington, WV district office as a basis, providing the benefit of real needs of on-going remediation projects. Working closely with METC and the Corps of Engineers, during 1996 we will (a) achieve actual on-site application of the system to a Corps project in Mason County, WV, (b) assess and augment the infrastructure for use in decontamination and decommissioning (D&D) efforts, and (c) develop a prototype interactive tutorial system to effectively transfer infrastructure concepts and skills to prospective users and managers.

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EXECUTIVE SUMMARY

This document constitutes the required Quarterly Report for the second quarter of 1996, for Task No. 2.1 under the DOE/METC/WVU Cooperative Agreement, contract no. DE-FC21-92MC29467. It documents technical accomplishments and provides cost status as of June 30, 1996.

Of the three primary tasks (2, 3 and 4), we are progressing on schedule for tasks 2 and 4. For Task 2, we are in the process of working with Huntington District Corps personnel to map and possibly model using GIS, the effect of pump and treat of an underground aquifer on the plant life around the wetlands of a section of the contaminated area at the WV Ordnance site.

Task 3 is scheduled to begin in August 1996.

For Task 4, we have begun building the prototype interactive tutorial system using Director 4.0. We have built a framework for the chapters and lessons, and have built one lesson based on the framework. We have included a few screen shots from the lesson with this report.

In summary, we are in an excellent position to successfully complete all tasks during the calendar year.

1.0 INTRODUCTION

Under the 1995 METC contract, the Marshall University (MU) Environmental Center determined and set up an effective geographic information system (GIS) based infrastructure for describing, characterizing and remediating contaminated sites. The 1995 effort resulted in (1) a detailed description of hardware and software comprising a system proven effective through experimentation and evaluation. (2) operating procedures for effective system use, (3) educational/training materials for technology transfer, and (4) recommendations for follow-on system implementation. In carrying out this effort, we worked with the U.S. Army Corps of Engineers, Huntington, WV District, using their needs for characterization and remediation of contaminated sites as a realistic basis for determining system requirements. In this multi-year effort, we are strongly emphasizing the need to integrate this resulting technology into activities of interest and benefit to DOE. The working relationship with the Corps of Engineers has been closely coordinated with METC.

2.0 PURPOSE

This follow-on work for calendar year 1996 continues to address the DOE focus area Cross Cutting Innovative Technologies, Characterization sub-area. The results of this year's effort will be (1) actual on-site application of the GIS-Based Infrastructure in an ongoing project of the Corps of Engineers in Mason County, West Virginia, (2) assessment and augmentation of the Infrastructure for use in decontamination and decommissioning (D&D) efforts, and (3) development and evaluation of a prototype interactive tutorial system to effectively transfer the Infrastructure technology and underlying GIS concepts and skills to prospective users and managers.

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 an earlier METC task (1994), Marshall University evaluated ICASE/GRACE for use by the Huntington USACE District.

4.0 METHODOLOGY

Following are descriptions of the 1996 tasks to be conducted, and associated schedules.

Task 1: *Information Required for the National Environmental Policy Act.*

Schedule: Within 60 days of contract award.

Task 2: *Application of the GIS-Based Infrastructure at the West Virginia Ordnance Site.*

Personnel from Marshall University will work as a team with Corps of Engineers personnel to transfer the GIS-Based Infrastructure technology to actual use on a project managed by the HTRW Section of the Huntington District office. The project will include obtaining/ developing digitized maps of the WV Ordnance area, and associating on-line with the maps data characterizing contaminated sites (actual data when available, or modeled) in various forms from many sources. We will work with Corps personnel in all aspects of the project, including translating data for compatibility, entering data into the GIS database, and associating it with corresponding map elements.

Since the area of this site is very large (about 3000 acres), it will present many challenging issues such as organization of database tables, interaction of multiple contaminants from various locations on the site, handling of incomplete and/or inconsistent data, and extraction of the effect of individual contaminants.

Once the database is established, it will be possible to model various contamination scenarios. Based on such scenarios, we will model and assess remediation strategies for some of the contaminants, in collaboration with the Corps of Engineers. The Environmental Resource Management Application (ERMA) package, which is an Intergraph product, will be used for this purpose.

Schedule: January 1 through September 30, 1996.

Task 3: *Assessment and Augmentation of the Infrastructure for D&D Use.*

In concert with METC personnel, we will make use of available characterization of contaminated sites within WV Ordnance to assess strategies for D&D. The GIS-Based Infrastructure, with its open software architecture, accommodates incorporation of additional models. The WV Ordnance site data resulting from Task 2 will provide a diversity of contaminants and geological characteristics for evaluating D&D remedial technologies and operational strategies. We will coordinate the selection of specific sites and technologies with METC, prior to undertaking. We will support METC in evaluating remediation approaches relative to specific D&D contaminated sites, by means of models operating on site data. The Intergraph ERMA remediation software will be considered for applicability in this effort, as well as models available to METC and the Corps of Engineers.

Schedule: August 1 through December 31, 1996.

Task 4: *Prototype Development and Evaluation of an Interactive Tutorial System.*

By use of commercially available courseware authoring tools, we will develop a prototype interactive tutorial system to transfer the GIS-based technology concepts and skills to users and managers. The tutorial sessions will provide step by step lessons incorporating real data. The approach will be based on sound pedagogical principles, and will be practically oriented to maximize use on the job. The tutorials will mimic the interface (menus, buttons and windows) of the actual system. We will incorporate selectable modes by degree of user sophistication, so that more or less guidance is provided based on need. We will also develop tutorial materials of varying abstraction/detail based on the needs of various personnel--ranging from managers to the every-day user of GIS technology. In these lessons we will cover representative facets of the Intergraph MGE system, and additional models and features incorporated into our GIS-Based Infrastructure. A significant benefit of the resulting approach will be the availability of the tutorials for use and reuse after an employee begins to use the skills on the job.

We will conduct a limited field test of the prototype using a representative range of personnel in order to ensure its effectiveness and make any needed adjustments. The result of this effort will be a working prototype incorporating proven concepts which can later serve as the basis for developing an operational tutorial system.

Schedule: January 1 through December 31, 1996.

5.0 WORK PERFORMED THIS PERIOD

5.1 Activities

During this period, we met the requirements for Task 1 and continued our efforts on Task 2 (Application of the GIS-Based Infrastructure at the West Virginia Ordnance Site) and Task 4 (Prototype Development and Evaluation of an Interactive Tutorial System). The following paragraphs give more details on each task.

Task 1: *Information Required for the National Environmental Policy Act.*

A completed National Environmental Policy Act (NEPA) was submitted on April 17, 1996.

Task 2: *Application of the GIS-Based Infrastructure at the West Virginia Ordnance (WVO) Site.*

During the last quarter, we had begun working on the map and GIS data of WVO site provided by the Nashville District Corps office. Nashville District Corps is actually in charge of collecting and entering the data from the WVO site, whereas Huntington District Corps has the management responsibilities for the data. We have been unable to get data from Nashville on a continuing basis.

However, the Huntington Corps personnel are involved in a project to pump and treat an aquifer in an area under the WVO site which has been contaminated by surface contaminants. The pump and treat operation is scheduled to begin in August of 1996. It is envisioned that the pump and treat process may affect the water level, and hence the plant life in and around the wetlands on the site. Thus, the Corps is required to establish a monitoring plan to document the possible effects of the pump and treat process. We have had several discussions with the Corps personnel for using GIS technology for the monitoring process. The Corps is in the process of setting up a contract with the College of Science of Marshall University for before-and- after monitoring of the water level and plant life of the wetlands in the area. Under the auspices of this METC contract, we will provide mapping, GIS, and groundwater modeling (using MGE IRMA) support. The monitoring process plan has been presented to the WV Division of Environmental Protection (DEP), WV Division of Natural Resources (DNR) and the community.

We purchased the update of the RIS software for the new version of SQL Server database. This upgrade was necessary for reading and working with the WV Ordnance data.

Task 3: *Assessment and Augmentation of the Infrastructure for D&D Use.*

Scheduled to begin August 1, 1996.

Task 4: *Prototype Development and Evaluation of an Interactive Tutorial System.*

We have made progress on the prototype interactive tutorial system using Director 4.0. We have built a framework for the chapters and lessons, and have built one lesson based on the framework. We have included a few screens from the lesson (appendix B).

Since multimedia tutorial files are relatively large, they would have to be distributed on a CD. We purchased a CD-ROM writer and have successfully used it to create tutorial CD's. We also purchased a soundcard and additional memory for the machine used for creating the multimedia tutorial.

5.2 Costs

The following is an unofficial summary of costs incurred during this quarter; Marshall University Research Corporation is the agent for formal contract and financial transactions.

Please note that we actually purchased $1,359.00 in equipment this quarter. However, $964.77 for the Director Multimedia software bundle expended during the First quarter, was re-credited this quarter to the contract, and billed to a different Environmental Center contract, due to its greater need for that effort.

Salaries	$ 16,163.65
Benefits	$ 3,220.37
Students	$ 2,955.93
Supplies	$ 385.34
Travel	$ 0.00
Equipment	
< $1000	$ 394.23
> $ 1000	$ 0.00
Total Direct Costs	$ 23,119.52
Indirect Cost (less Equipment)	$ 8,785.43
Total	$ 31,904.95

6.0 RESULTS AND DISCUSSION (CURRENT PERIOD)

We are progressing on schedule with Task 2 and Task 4. We are working with the Huntington District Corps personnel to set up a mechanism of providing support for the monitoring and modeling project which will use GIS technology for documenting the effect of the pump and treat process of a contaminated aquifer under the WV Ordnance Site. We are also making good progress with development of the tutorial system.

7.0 CONCLUSIONS (CURRENT PERIOD)

We are on schedule with the 1996 tasks, have an excellent working relationship with the Corps of Engineers, and are well positioned to achieve successful completion of all tasks during this year.

8.0 WORK PLANNED FOR NEXT PERIOD

8.1 Activities

We will continue our efforts on Task 2 and Task 4. We will seek through discussions with the Director of the Co-operative agreement, Dr. Bud Cook, identification of appropriate focus for Task 3, and begin work on Task 3 accordingly. The Huntington Corps is also involved with another project at Dolly Sods, WV which is also an unexploded ordnance site. Corps personnel have approached us with regards to use of GIS technology, and conversion of data of the site maintained in MGE format to ARC/Info format. Based on further discussions, we may provide the necessary support to the Corps for this project, which may also be of interest to the U.S. Forestry Service.

8.2 Costs

The following table summarizes anticipated costs for the next quarter.

Salaries	$ 18,317.96
Benefits	$ 3,758.51
Students	$ 4,673.76
Supplies	$ 901.80
Travel	$ 839.40
Equipment	
< $1000	$ 647.32
> $1000	$ 1,126.71
Total Direct Costs	$ 30,265.46
39 % Indirect Cost (less Hardware)	$ 11,364.11
Total	$ 41,629.57

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

Even though we have been unable to get data on WV Ordnance Site on a continuing basis, we have identified a project with the Huntington Corps at the WV Ordnance site for which GIS technology can be used effectively for monitoring and modeling purposes.

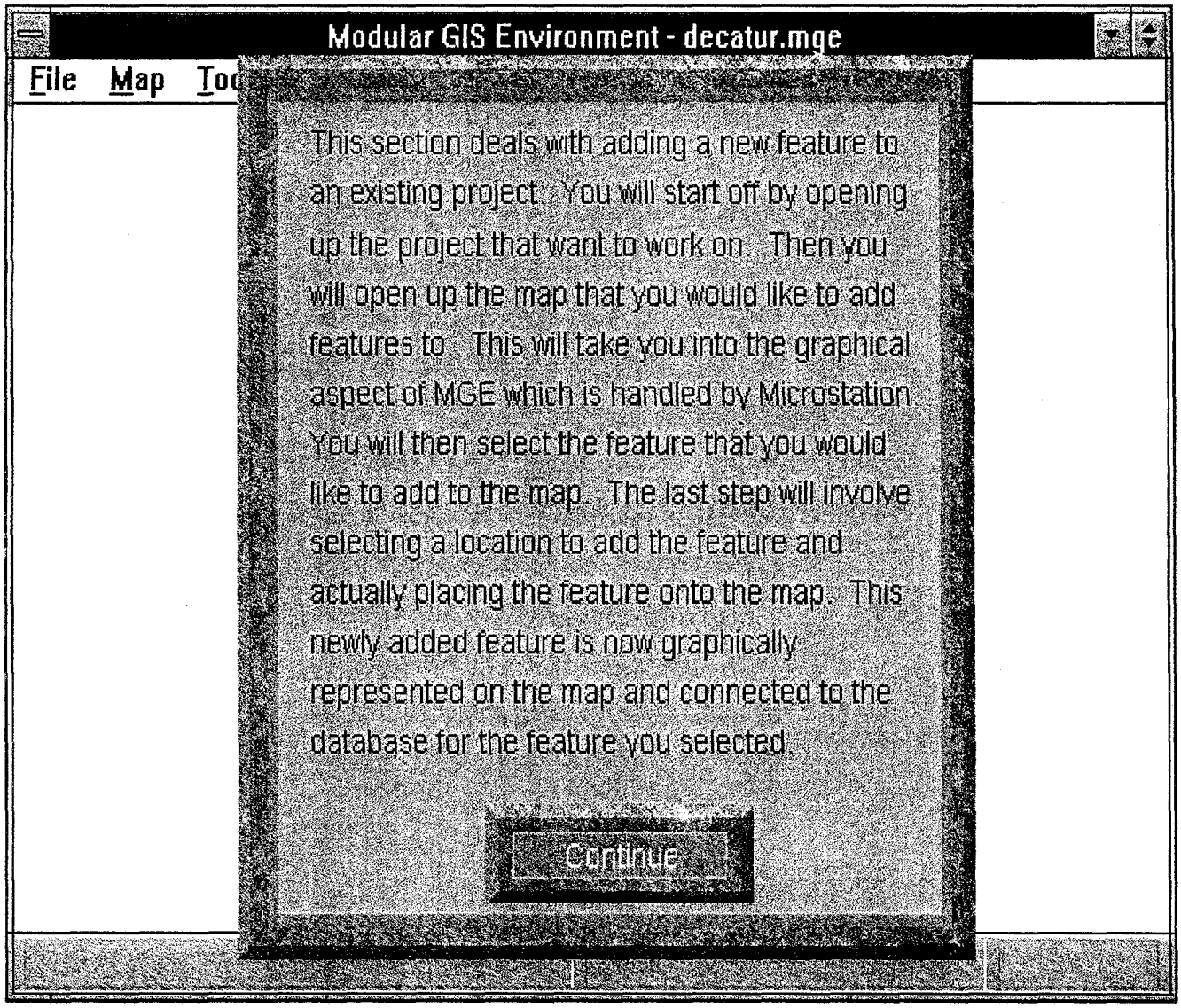
APPENDICES

A. LIST OF ACRONYMS AND ABBREVIATIONS

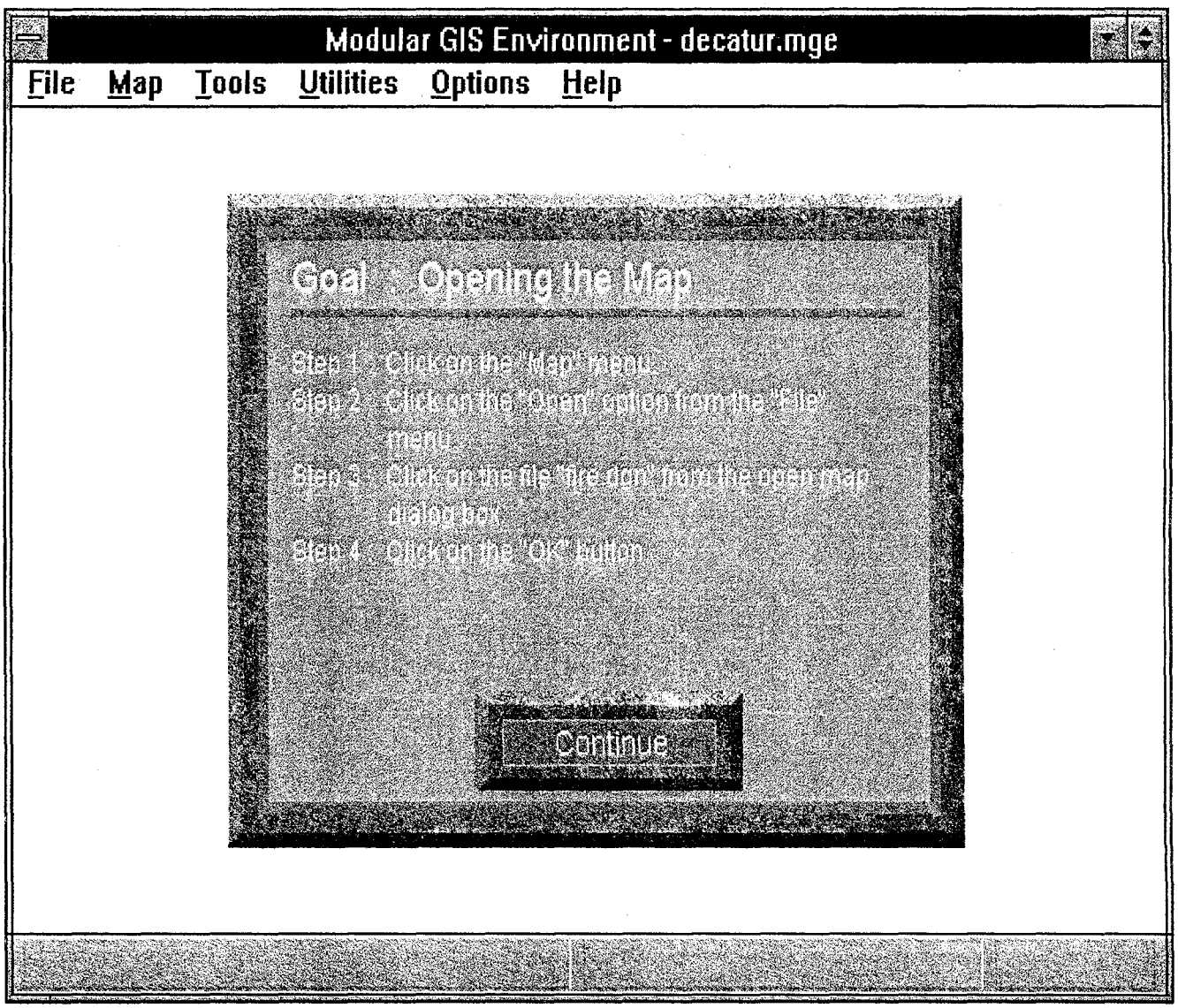
ASCII	American Standard Code for Information Interchange
CD-ROM	compact disk read only memory
COTS	commercial off-the-shelf
D&D	decontamination and decommissioning
DOS	disk operating system
ERMA	Environmental Resource Management Application (an Intergraph product)
GB	gigabyte; approximately 1,000 MB
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
MU	Marshall University
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

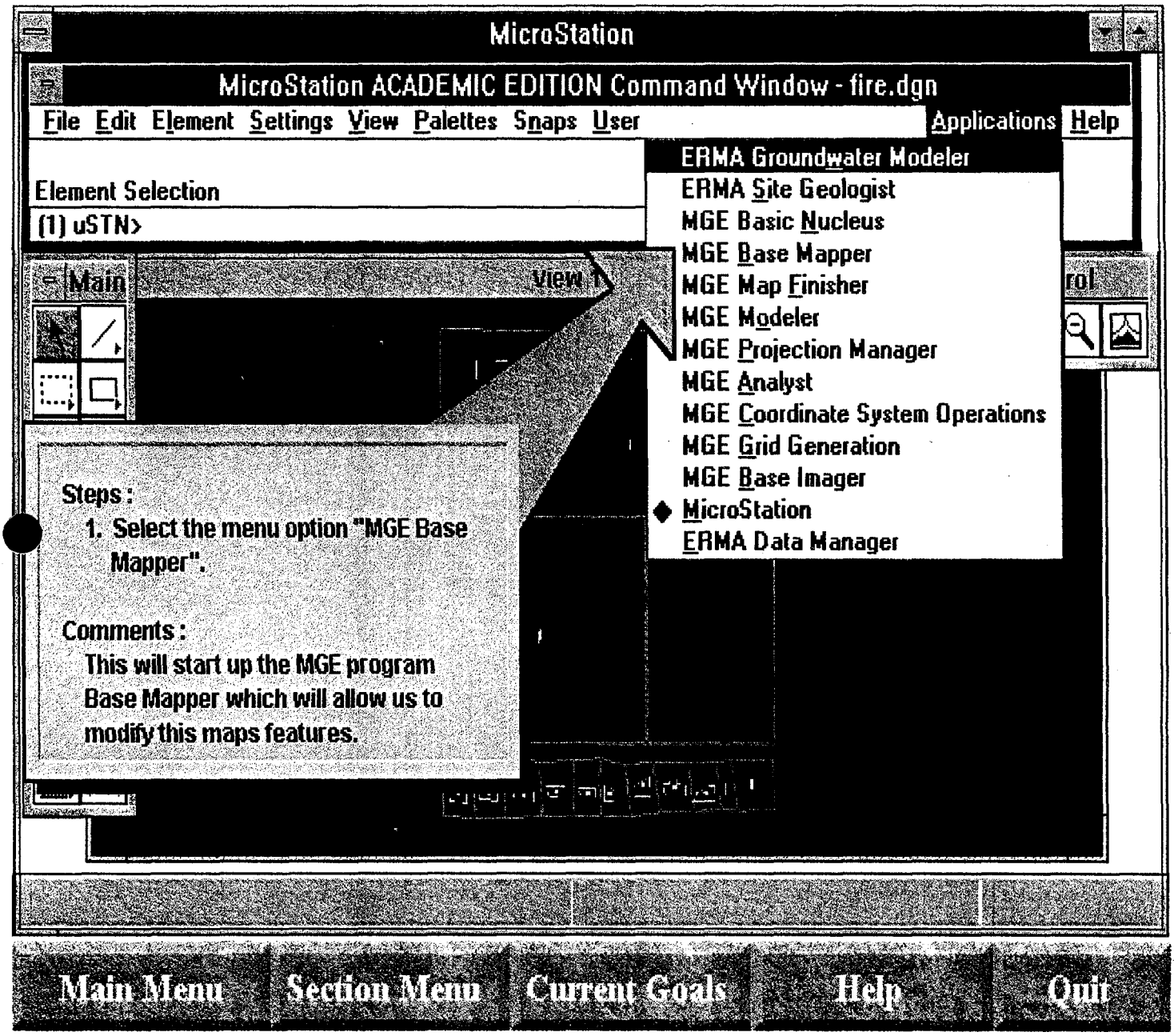
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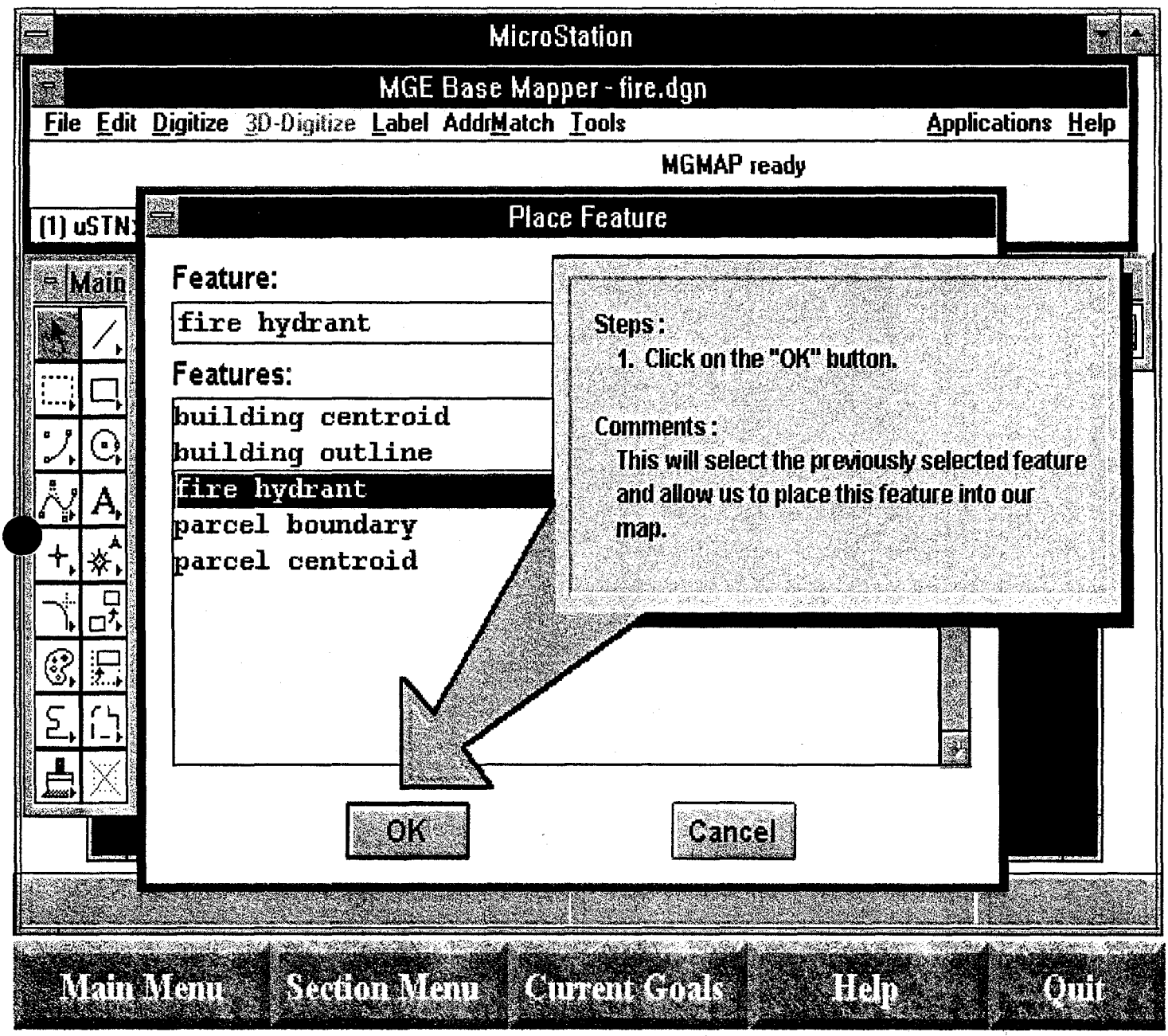




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Modular GIS Environment - decatur.mge
File Map Tools Utilities Options Help
Goal : Opening the Map
Step 1 : Click on the "Map" menu.
Step 2 : Click on the "Open" option from the "File" menu.
Step 3 : Click on the file "nge.dgn" from the open map dialog box.
Step 4 : Click on the "OK" button.
Continue


MicroStation
MicroStation ACADEMIC EDITION Command Window - fire.dgn
File Edit Element Settings View Palettes Snaps User
Applications
Help
Element Selection
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Main
View 1
ERMA Groundwater Modeler
ERMA Site Geologist
MGE Basic Nucleus
MGE Base Mapper
MGE Map Finisher
MGE Modeler
MGE Projection Manager
MGE Analyst
MGE Coordinate System Operations
MGE Grid Generation
MGE Base Imager
MicroStation
ERMA Data Manager
Steps :
1. Select the menu option "MGE Base Mapper".
Comments :
This will start up the MGE program Base Mapper which will allow us to modify this maps features.


MicroStation
MGE Base Mapper - fire.dgn
File Edit Digitize 3D-Digitize Label AddrMatch Tools Applications Help
MGMAP ready
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Main
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fire hydrant
parcel boundary
parcel centroid
Steps:
1. Click on the "OK" button.
Comments:
This will select the previously selected feature and allow us to place this feature into our map.
OK
Cancel
Main Menu
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Treatment of Mixed Wastes via Steam Reforming

METC Task No.2.2

Quarterly Technical Progress Report
Reporting Period: April 1 - June 30, 1996

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

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

This work addresses the evaluation of the destruction efficiency of RCRA organic components and surrogates in a steam reforming atmosphere. The benefit of using a steam atmosphere to destroy RCRA organics, e.g. dichlorobenzene, lies in the virtual elimination of dioxins and furans in the product gases. This technology has been proven by ThermoChem Inc., Columbia, MD, which currently is developing a two-stage fluidized bed unit to dispose of mixed wastes. The work outlined in this proposal addresses the quantification of the destruction efficiency of key RCRA organics and surrogates in the second stage of the ThermoChem process. A series of experimental runs will be performed in a 6.5 cm internal diameter reactor. The purpose of these runs is to evaluate the efficiency of destruction of organic materials as a function of residence time, gas composition and reaction temperature. In addition, the efficacy of using catalysts to improve the destruction efficiency will be determined.

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Executive Summary (Current Work)

During the current reporting period the gas chromatograph was upgraded with a FID (flame ionization detector) and sucessfully calibrated for toluene and dichlorobenzene (DCB). The calibration curves for these two compounds are presented in the report and show a linear relationship between the mass of the sample injected and the area count from the chromatograms. In addition, the temperature profile in the reactor was measured using 3 type-K thermocouples at different axial locations. The radial temperature profile was essentially flat with the axial profile being flat, i.e., constant temperature, in the region between the furnace heating elements and showing a rapid cooldown zone outside the heated region. The temperature profile is shown in a figure in the report. Finally, the experimental program was initiated and a run was performed in which toluene was reformed in a steam environment. At a temperature of 700°C the toluene was seen to react to give two primary products. Initial work suggests that one of the products is methanol, which leads us to believe that the toluene reacts to form methanol and benzene.

The experimental part of the program had to be temporarily halted, due to a failure in a high temperature gasket and the gas distributor plate which caused a leak of reactants and made mass balance closure impossible. The reactor is currently being repaired and the experimental program will be restarted and continued through the next reporting period.

1.0 Introduction

The treatment and destruction of mixed wastes is becoming an increasingly important problem in the environmental arena. Many of the problems associated with mixed wastes are due to the wide variety in the type, content and form of the waste itself. For example, clothing contaminated with small quantities of radioactive elements and sludges from fuel storage tanks would both be considered mixed wastes. The challenge, therefore, in dealing with this type of waste is to create processes which are flexible enough to handle a wide variety of feeds and to render them harmless to the environment. This research is aimed at determining the destruction efficiencies of RCRA organics in a variety of reforming atmospheres and at different temperatures. The work is essentially supporting an on going effort by ThermoChem Inc., Columbia, MD to develop a two stage process for the treatment of mixed wastes.

2.0 Purpose

There have been several reports regarding the destruction of organic materials at elevated temperatures in a variety of non-oxidative environments (1,2,3). However, the results are generally applicable to specific equipment and cannot be easily extrapolated to different operating conditions. The purpose, therefore, of this work is to systematically evaluate the destruction efficiencies of a variety of organic materials at different conditions and to establish correlations to support the design of new equipment.

This work relates directly to an existing process developed by ThermoChem Inc., Columbia, MD, and will be performed in close association with ThermoChem Inc.

3.0 Background

The ThermoChem Process utilizes a two stage fluidized bed system to volatilize and subsequently destroy organic materials. The process uses the first stage fluid bed to vaporize organic material from shredded mixed wastes and to concentrate the inorganic material in the remaining solids. The inorganic portion of the waste, containing heavy metal compounds etc., is eventually vitrified with glass frit in a separate unit. The gas from the first stage is sent to a second stage, operating at elevated temperatures (1600 - 1800°F), where the organics are reformed in a steam environment. In addition to steam, the ThermoChem process may have some hydrogen and carbon monoxide in the gas entering the second stage. The use of hydrogen and carbon monoxide as additional reforming gases and the possibility of using a catalyst to promote the reforming reaction are of interest in this process and will be investigated in this research.

It is envisioned that the results of this work will help to define the optimum conditions for the steam reforming process and to determine the efficacy of using a catalyst to promote

destruction efficiency of RCRA organics and surrogates in such a process.

4.0 Methodology

The work proposed is a continuation of a current project under the WVU/METC cooperative agreement. The scope of the current project was modified to enable a closer working relationship with ThermoChem Inc. which currently is developing a process to destroy mixed wastes via steam reforming. At present, the test equipment consists of a 6.5 cm inside diameter stainless steel reactor which is expected to operate in the temperature range of 850 - 930°C (approx. 1600 - 1800°F). The bed is mounted in a vertical, 3-zone tube-furnace. The feed gas, mixtures of hydrogen, carbon monoxide and dioxide and steam, are fed from gas bottles and are metered through valves and flowmeters to the reactor. Organic liquid material is fed from a pressurized tank via a flowmeter and vaporized prior to being sent into the reactor.

The object of the current work is to quantify the destruction efficiency of RCRA organics and surrogates in a steam reforming atmosphere for a variety of operating conditions. A gas chromatograph, fitted with a flame ionization detector, will be used to evaluate the destruction efficiency of the organic material down to the 99.99% level of destruction or better. The need for a catalyst to improve the destruction efficiency will be addressed if the homogeneous reaction rates are too low. The tasks for this project are outlined below.

Task 1: Information Required for the National Environmental Policy Act.

Task 2: Upgrading and Calibration of Gas Chromatograph.

The gas chromatograph currently in use in Dr. Turton's laboratory will be upgraded with a Flame Ionization Detector (FID) to enable destruction efficiencies of up to and greater than 99.99% to be measured accurately. Once the GC has been upgraded a series of tests will be performed to calibrate the unit for measuring the organic components used in this work. Calibrations will consist of running the test bed at low temperatures (<200°C) using an inert or non-inert carrier gas and injecting (spraying) the organic material at different flowrates into the bed. Samples will be taken after the gas cooler and used to calibrate the peaks obtained from the GC. A minimum of three concentrations points, for each organic material, will be used to calibrate the gas chromatograph. Due to the widely differing characteristics of the organic materials used in this study it may be difficult to identify all the components in a reasonable time using a single column in the GC. Since the destruction efficiency of the RCRA organics and aromatic surrogates (in this case ethylene glycol, di-chlorobenzene, toluene and naphthalene) are the most important measures of the process's effectiveness, these will be evaluated and used as the measure of the destruction efficiency.

Task3: Experimental determination of Destruction Efficiency of Organic Material without the use of Catalyst.

The experimental program to be used in this part of the work will consist of an experimental test matrix in which the following independent variables will be varied:

	Number of Levels
Temperature	3 (1800, 1700 and 1600°F)
Residence Time	2 (1 and 2 s)
Hydrogen Content of Gas	3 (0, 5% and 10% on a volume basis)
Carbon Monoxide Content of Gas	2 (0 and 5% on a volume basis)

This test matrix is consistent with the needs of ThermoChem Inc. and was discussed with Mr. G.Voelker and Dr. R.Chandran of ThermoChem Inc. The organic materials to be tested were also discussed with ThermoChem Personnel and the materials given in Task 2 above will be used in the preliminary tests.

The dependent variables will be the destruction efficiencies of the organic components fed to the bed. Currently the organic feed material of interest consists of the following components: Toluene, DiChlorobenzene, Ethylene Glycol, Naphthalene. These components may be substituted with other RCRA components or surrogates, if the destruction efficiencies of other organics are desired.

Task 4: Correlation of Experimental Results

Using the results from Task 3 the conversion (destruction) of the different organic species will be correlated with the independent variables listed above in Task 3. The experimental results and correlation will be compared to existing homogeneous kinetics data in the literature. Any limitations, due to equilibrium considerations, will be investigated.

Task 5: Experimental determination of Destruction Efficiency of Organic Material using Catalyst.

The investigation into the use of catalysts to promote the destruction of the organic materials will be investigated if the results of Task 3 indicate that this is necessary. This phase of the work will involve input from ThermoChem Inc. The test matrix for part of the work will include operating temperature, gas composition, and gas-solid contact time in the reactor using a fixed organic feed. The mode of operation of the reactor will be a packed or fluidized bed and the particle size will be chosen to obtain the required gas residence time with a bed height of 24-30" of catalyst.

Task 6: Preparation of Quarterly and Annual Reports

Three quarterly and one annual report will be prepared for this project.

5.0 Worked Performed in this Period

The major portion of the work performed in this period centered around testing and calibrating the Gas Chromatograph. The temperature profile in the reactor was also established by heating the bed and taking three radial temperature measurements at several axial positions in the reactor. Finally, the experimental test program was initiated using toluene as the test organic material and steam as the reactant gas. The results of each of these tasks is presented separately below.

5.1 Upgrading and Testing of Gas Chromatograph

The SRI 8500 gas chromatograph was upgraded with an FID (flame ionization detector) in order to quantitfy the organic content of the reactor effluent gas. The chromatograph column was also changed from a packed 1/8" column to a 30 m long, 0.53mm bore capillary column coated with a 1.2 μm film of carbowax (Altech No. 19659). This column is suitable for detecting the organics used in this study, e.g., toluene, dichlorobenzene etc.

In order to calibrate the gas chromatograph for the organic compounds of interest in this study, a series of standard solutions were made using carbon disulfide as the solvent. Both toluene and dichlorobenzene (DCB) were used in the calibration and the results are sumarized in Tables 1 and 2 below. These results are also plotted in Figures 1 and 2. From these figures it is clear that the GC shows good linearity for both these compounds over a wide range of sample sizes. Further calibration has been done (not shown here) to establish the lower level of reliable detection and this corresponds to destruction efficiencies around 99.99%.

Table 1: Results for the Calibration of the Gas Chromatograph using Toluene

Toluene in Sample Injected into GC (μg)	Area Count from GC
138.5	38,718
105.6	27,750
53.6	16,548
12.2	6,231
0.0122	690

Table 2: Results for the Calibration of the Gas Chromatograph using Dichlorobenzene

DCB in Sample Injected into GC (μg)	Area Count from GC
193.4	28,524
139.7	23,082
51.7	7,463
.0517	88

Each area count value shown in the above tables is the average of two independent tests. The corresponding retention times for toluene and DCB were 4.2 and 7.7 minutes. respectively, using helium as the carrier gas at a flowrate of approximately 9 ml/min. The chromatograms for each of the calibration runs are not included in this report but are available on request. The sucessful calibration of the GC signifies the completion of Task 2 of this project.

5.2 Temperature Profiles in the Reactor

In order to establish the temperature uniformity of the reactor furnace and indeed the temperature profile within the reactor it was decided to probe the reactor using three 36" long type-K thermocouples. The reactor was filled with 3mm ceramic balls (1/8" catalyst support), supplied by Jaeger Products, Inc., Houston, TX. This packing serves two purposes. First, it acts as a resistance to gas flow and hence provides for the uniform flow of gas through the bed. Second, due to the large thermal mass of the packing, it provides a very stable and uniform temperature environment in which the reactions can take place.

The uniformity of the reactor temperature was checked by placing three thermocouple probes at the same height and spaced at 120° from eachother, as illustrated in Figure 3. The experimental procedure consisted of allowing the bed to come to equilibrium (for a time of 2 hrs after start-up) and then the temperatures registered by the three thermocouples were recorded. The thermocouples were then moved up in the reactor, allowed to reach equilibrium and again the temperatures were recorded. This procedure was repeated at several vertical locations and the results are illustrated in Figure 4. From this figure it can be seen that the thermocouples show very good agreement between eachother, at the same axial location, indicating a flat radial temperature profile. Moreover, the axial temperature profile is very uniform except at the top of the bed where a rapid cool-down zone is seen to occur, as expected, above the top of the highest heater.

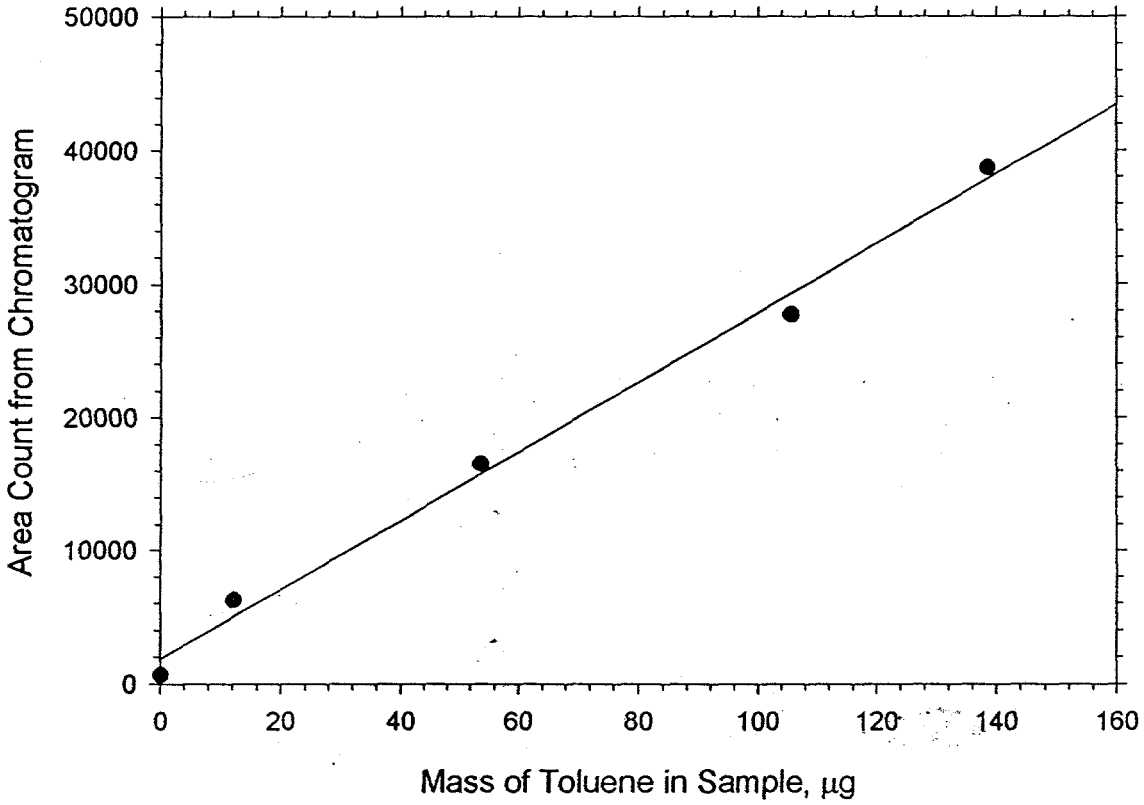


Figure 1: Calibration of Gas Chromatograph for Toluene

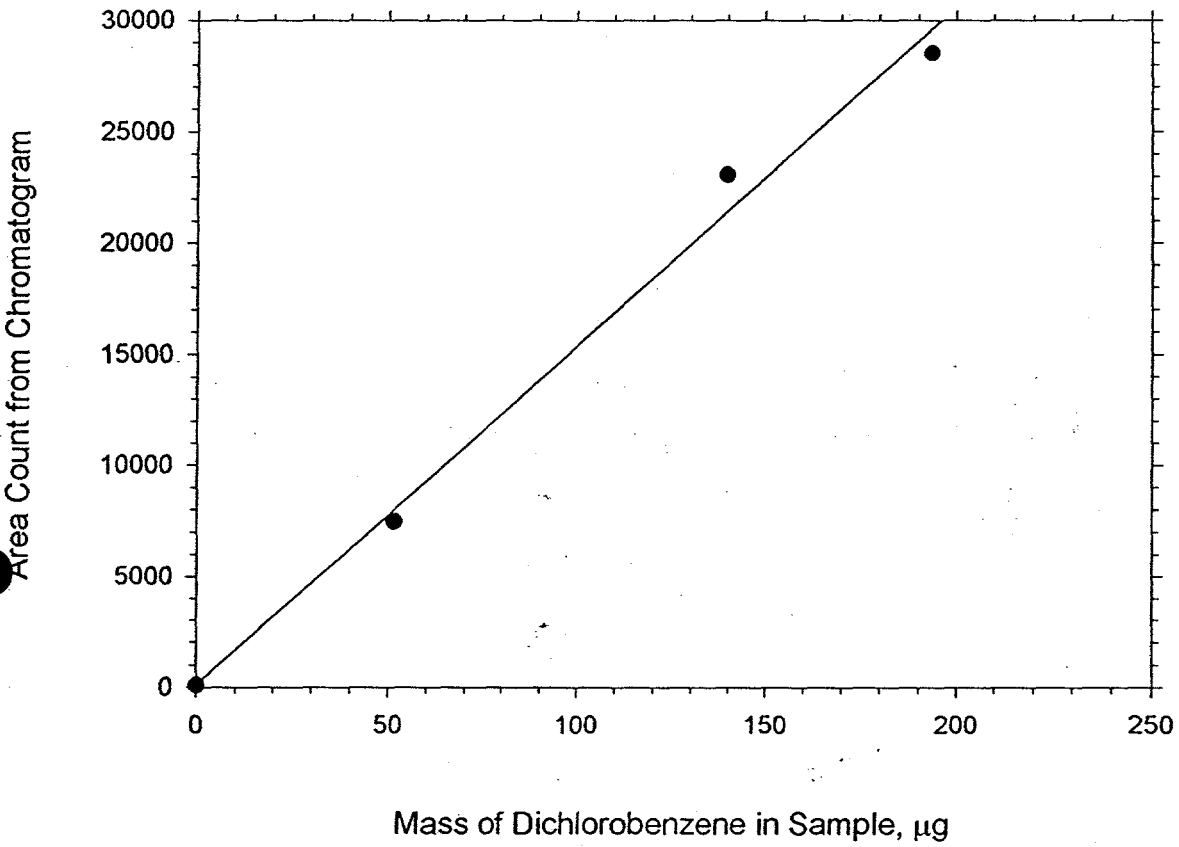


Figure 2: Calibration of Gas Chromatograph for Dichlorobenzene

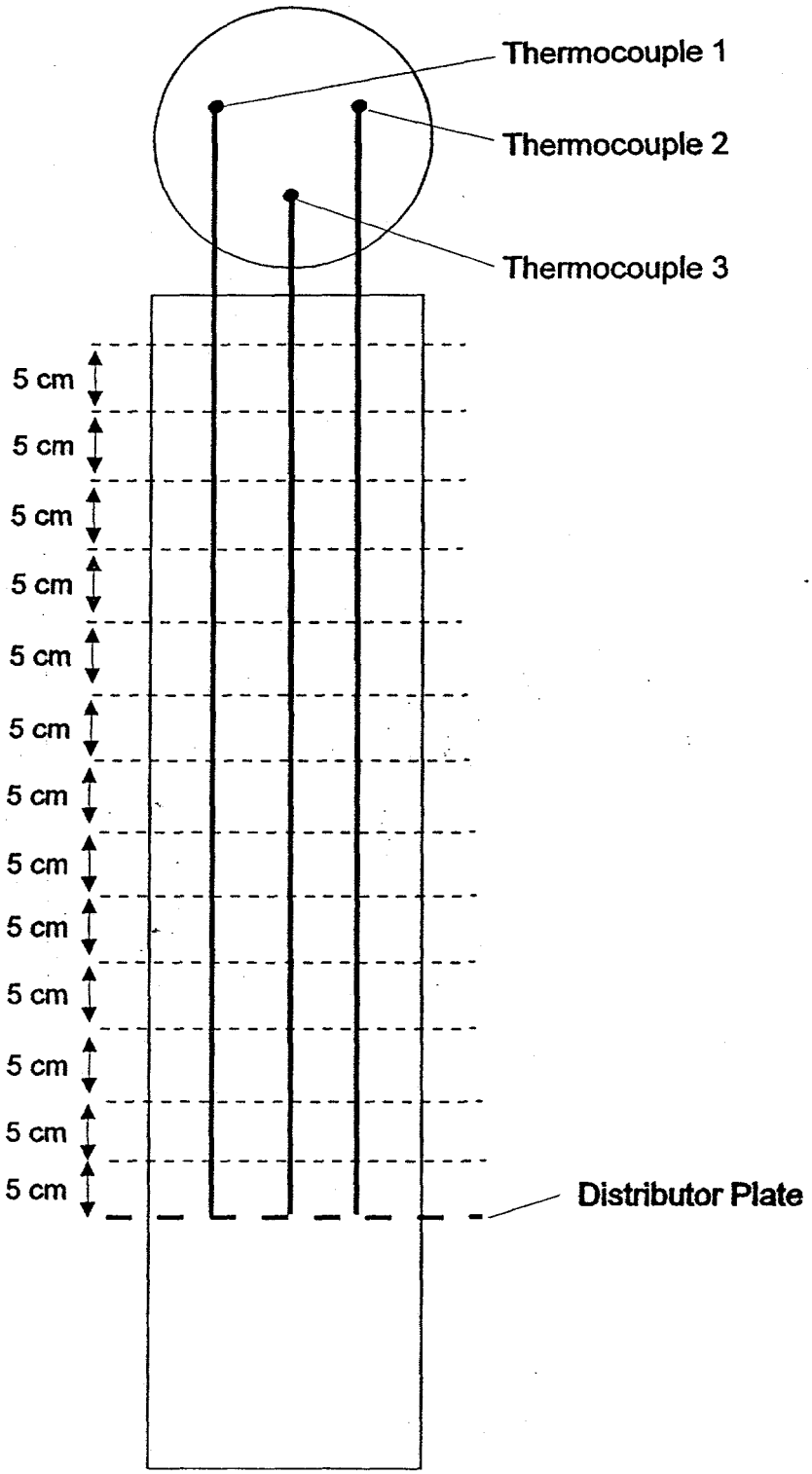


Figure 3: Location of Thermocouples used to Measure Temperature Profile in Reactor

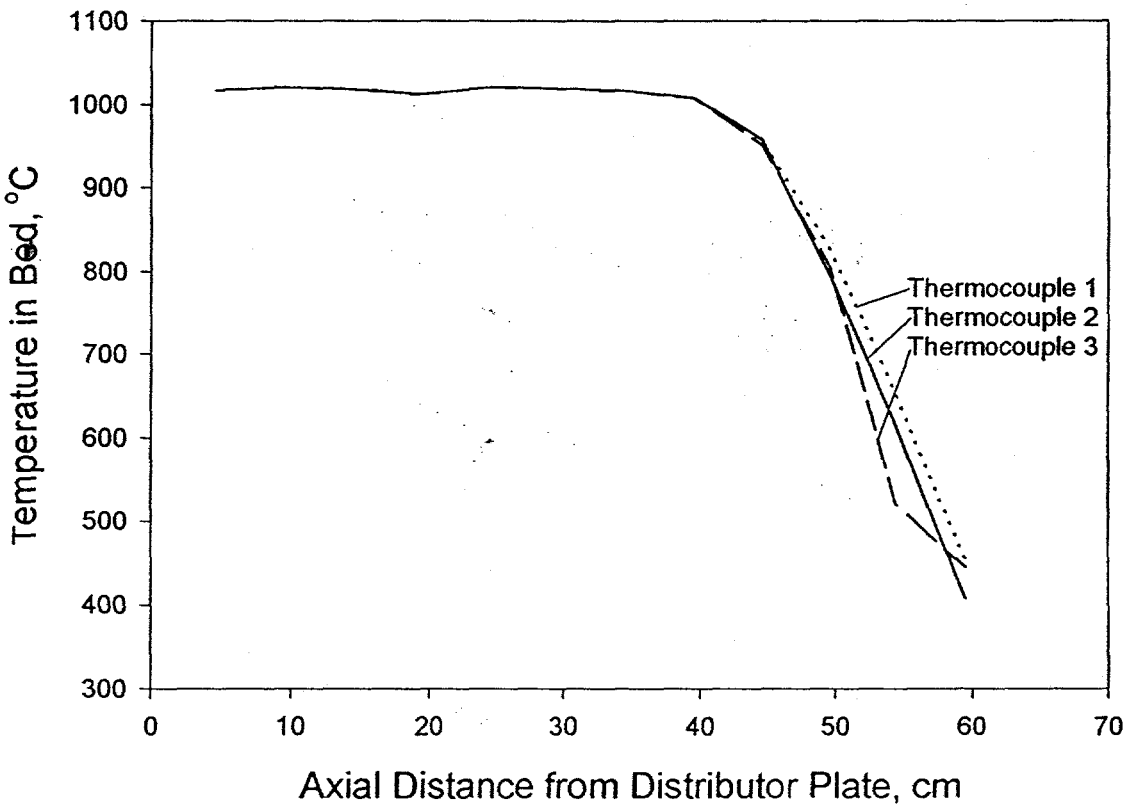


Figure 4: Temperature Profile in Packed Bed Reactor

5.3 Destruction of Toluene in a Steam Environment

The destruction of toluene using steam was examined as the first step of implementing Task 3 of this research. The first set of experiments was carried out at a temperature of 700°C (1292°F) in order to investigate the low temperature end of the test matrix. Further tests at higher temperatures were planned for this reporting period, however, several problems arose which curtailed the experimental program and these are explained in Sections 6.0 and 9.0 below.

6.0 Results and Discussion for Current Reporting Period

The calibration of the GC was sucessfully completed using two of the model organic compounds to be used in this work (toluene and DCB). In order to check the temperature uniformity within the reactor a series of tests were performed by probing the reactor, packed with inert ceramic balls, with three type-K thermocouples. The temperature distribution in the radial direction was essentially flat. The axial distribution was also uniform, except at the reactor exit where the temperature fell drastically above the third heating zone.

The experimental program, to investigate the destruction efficiency (conversion) of organics in a steam reforming atmosphere, was initiated this period. The experimental procedure consisted of heating the reactor to the desired temperature and then injecting steam and the organic compounds to be tested into the bed, via a single heated tube which delivered the reactants to just below the distributor plate. The system was allowed to attain steady state and then the reactor effluent was tested for unreacted organic by taking a sample of gas, using a heated syringe, and injecting the sample into the GC. During the course of the run it was discovered that the gasket at the distributor. and the distributor itself, had failed causing the majority of the reactants to bypass the reactor and flow upwards between the reactor outer wall and the inside of the furnace. Clearly this failure negated the run and has delayed significantly the progress of the experimental program.

However, it is worth mentioning that prior to the gasket failure, two samples of the reactor effluent gas were measured and that significant peaks were detected at retention times of 0.55 and 2.58 minutes, as well as the expected peak for toluene at around 4.20 minutes. Subsequntly, the peak at 2.58 minutes has been identified as methanol. It is believed that at the relatively low temperatures occuring in the reactor a portion of the toluene may be reacting with water to yield methanol and benzene. At present this conclusion is somewhat speculative and must be verified when the bed is repaired and the run repeated. However, this may be an important step in understanding the mechanism by which the steam first breaks down the toluene.

7.0 Conclusions for Current Period

The GC has been successfully calibrated and gives repeatable results for toluene and DCB. The temperature profile within the reactor is very uniform as verified by thermocouple probe readings at various locations within the reactor.

The experimental program is still underway. There are no quantifiable results at present due to the gasket and distributor failure mentioned in Section 6.0. However, one interesting result is that there appears to be a significant quantity of methanol produced at low temperatures (700°C) and this may provide some insight into the reaction mechanism by which the destruction of the organics by steam is initiated.

8.0 Work Planned for Next Period

The work planned for the next period consists of making the necessary repairs to the reactor, i.e., fabricate a new distributor plate and gaskets, and continuing with the experimental program (Task 3).

9.0 Technical and Administrative Difficulties for Current Period

As specified in Section 6.0 during the start of the experimental runs a gasket and distributor plate failure were observed. This failure caused reactants to bypass the reactor and made material balance closure impossible.

Appendix

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2. Durai-Swamy, K., D.W. Warren, and M.N.Mansour, "Indirect Steam Gasification of Paper Mill Sludge Waste," *Tappi J.*, Vol 74, 137-143, 1991

3. Galloway, T.R., and J.L.Sprung, "Destruction of UST Organics and Nitrates, Polymeric Organic Wastes, and Chlorocarbon Solvents by Steam Reforming," *Proceedings of the Information Exchange Meeting on Waste Retrieval, Treatment and Processing*, Houston, TX, March 15-17, 1993.

Acronyms and Abbreviations

FID - Flame Ionization Detector
GC - Gas Chromatograph
RCRA - Resource Conservation and Recovery Act (1976)
SRI - Scientific Research Instruments, Inc.
DCB - Dichlorobenzene

USE OF CENTRIFUGAL MEMBRANE TECHNOLOGY WITH NOVEL MEMBRANES TO TREAT HAZARDOUS/RADIOACTIVE WASTES

METC Task No. 2.3

Quarterly Technical Progress Report
Reporting Period: 4/1/96 - 6/31/96

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

For:
U.S. Department of Energy
Office of Fossil Energy
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ABSTRACT

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and is discharged. The concentrate exits at the edge of the membrane packs.

The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance and increasing the volume of waste treated per area of membrane. Because of the reactive nature of most DOE wastewaters, the use of conventional membrane materials may not be viable. Thus, specialty membranes that can separate hazardous contaminants from the permeate stream and are chemically and radiologically stable will also be tested.

The objective of this research is to investigate the feasibility of using centrifugal membrane technology combined with innovative membranes for the of treatment hazardous/radiological wastes. The following tasks will be completed during this research: 1) perform extensive literature review on membrane technology, 2) identify and acquire waste and membranes, 3) modify, acquire, and be trained in the use of SpinTek technology, and 4) test and evaluate SpinTek technology and specialty membranes.

The following variables will be monitored as a function of run time: 1) contaminant concentration in concentrate and permeate, 2) membrane flux, 3) temperature and pressure, 4) conductivity and pH of all liquids. The following parameters will be used to judge the effectiveness of the process: 1) contaminant concentration in the permeate, 2) physical and chemical resistance of membranes, 3) volume and waste reduction factors, 4) quantity and quality of residuals, 5) energy and requirements, 6) ease of operation and likelihood of process upsets.

The result of this work will be a technology that can treat a variety of wastes such as contaminated groundwater, mixed-waste process water, and existing waste residual (*e.g.*, low-level waste). The process can be used for both inorganic (*e.g.* radionuclides and heavy metals) and organic contaminants. It is envisioned that the volume reduction factors for this technology will be high and a relatively a low amount of residual requiring additional treatment will be produced.

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EXECUTIVE SUMMARY

In the second quarter the SpinTek technology was used to treat two O/G wastes having an oil content of about 0.2 % ("pond effluent") and 5% ("mill coolant"). Two runs were conducted for each waste type. System pressures and rotational speeds were 32-34 psi and 1750 rpm, respectively. The membrane, PV-100K, had a molecular weight cut-off of 100,000. Permeate flux, turbidity, O/G, TSS, COD, and TOC were measured.

For pond effluent - Run 1, 44 gallons of waste were treated. Influent wastewater characteristics were as follows: O/G = 1,080 mg/L, TSS = 900 mg/L, COD = 4,660 mg/L, TOC = 2,540 mg/L and pH = 5.2. The system was operated in semi-batch mode for 7.3 hr, and in the batch mode for 3.9 hr. The mean flux was 175 gal/ft^2-d in semi-batch mode and 120 gal/ft^2-d in batch mode operation. The flux in the batch mode was lower than the semi-batch mode because the O/G concentration was much higher. The final concentration factor was 20x and volume reduction was 95 percent. Permeate turbidity ranged from 2.2 to 60.3 NTU. Permeate O/G concentrations ranged from 9 to 12 mg/L in semi-batch mode and from 23 to 54 mg/L in the batch mode. As expected, the permeate O/G concentration increased with the concentration factor because of the large amount of O/G that was retained by the membrane. The average O/G removal efficiency was 98 percent. Permeate TSS concentrations were less than the detection limit (5 mg/L) in both the semi-batch and batch mode operation. COD and TOC removal efficiencies were about 71 and 80 percent, respectively.

For pond effluent - Run 2, 220 gallons of waste were treated. Influent wastewater characteristics were as follows: O/G = 1,850 mg/L, TSS = 300 mg/L, COD = 9,640 mg/L, TOC = 2,050 mg/L and pH = 6.5. The system was operated in the semi-batch mode for 65 hr and in the batch mode for 6.5 hr. The mean flux during semi-batch operation was 156 gal/ft^2-d and was 86 gal/ft^2-d in the batch mode. The final concentration factor was 100x and the volume reduction was 99 percent. During semi-batch operation the permeate turbidity levels were generally below 5 NTU. After operation was switched from semi-batch to batch mode, the turbidity level increased dramatically due to the large concentration of O/G and high temperatures (approaching 150°F). Permeate O/G concentration ranged from 7 to 17 mg/L in semi-batch mode and from 16 to 78 mg/L in batch mode. At the higher temperatures observed during batch operation the membrane pores enlarged allowing more oil droplets into the permeate. Permeate TSS ranged from 14 to 28 mg/L in semi-batch mode and from 18 to 25 in the batch mode. O/G and TSS removal efficiencies were 98 and 93 percent, respectively. Removal efficiencies for COD and TOC were 94 and 91 percent, respectively.

For mill coolant - Run 1, 76 gallons of waste were treated. Influent wastewater characteristics were as follows: O/G = 23,000-49,500 mg/L, TSS = 3,000-6,700 mg/L, COD = >15,000 mg/L, TOC = 6,000-6,900 mg/L and pH = 7.4. The system was operated in the semi-batch mode for 29 hr and in the batch mode for 4 hr. The initial flux was at 80 gal/ft^2-d, increased to 150 gal/ft^2-d as the temperature increased and then declined to 58 gal/ft^2-d. At this point the system was shut down and cleaned. Flux increased to 80 gal/ft^2-d and then decreased to about 38 gal/ft^2-d at the end of semi-batch operation. After a second cleaning, the flux increased to the 100 gal/ft^2-d, and then decreased to 22 gal/ft^2-d. The final concentration factor was 12.7x and volume reduction of

92 percent. Permeate turbidity varied between < 10 NTU and 1,500 over the course of the run. After cleaning, the turbidity was below 10 NTU but then increased with time. Permeate O/G, TSS, COD, and TOC concentrations were high due to the large O/G concentrations in the feed tank and the high temperatures. The high temperatures adversely affected the retentive characteristics of the membrane.

For mill coolant - Run 2, 63 gallons of waste were treated in Run 2. Influent wastewater characteristics were the same as in mill coolant - Run 1: The system was in the semi-batch mode for 35 hr but was not operated in the batch mode because of low fluxes. The system was cleaned three times with the flux improving after each cleaning. However, the maximum flux was lower than the maximum flux from before the previous cleaning indicating that the membrane had become permanently fouled. Because the membrane had fouled, batch down was not attempted. The final concentration factor was 5.2x and the volume reduction was 76 percent. Turbidities were below 10 NTU initially and after each cleaning but then increased with operational time. Removal efficiencies for O/G and TSS were 98.5 and 95.5 percent, respectively. COD and TOC removal efficiencies were 54 and 76 percent, respectively.

The average virgin membrane flux before wastewater treatment was 220 gal/ft^2-d. The clean water fluxes (CWFs) after pond effluent treatment were 287 and 257 gal/ft^2-d for Runs 1 and 2, respectively. The higher CWFs for the pond effluent compared with the virgin membrane were due to the presence of cleaning solution in the system. The cleaning soaps decreased the viscosity of the water resulting in a higher permeate flow rate. The CWFs after treatment of mill coolant were 162 and 62 gal/ft^2-d for Run 1 and 2, respectively. It is apparent that fouling of the membranes occurred when the hot mill coolant was treated. Fouling can be reduced by running the system at a lower temperature (lowering the temperature of the system will protect the integrity of the membrane as well as reduce the amount of oil that is able to slip into the membrane and clog the pores) and using a more durable membrane (*e.g.*, ceramic) Both of these topics will be investigated in the third quarter.

The primary technical difficulty during the second quarter was the inability to control temperature of the feed tank. A commercial heat exchanger was acquired but was not effective thus, a heat exchanger was designed, constructed and successfully tested by WVU researchers. For future experiments, strict temperature control will be practiced.

1.0 INTRODUCTION

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and is discharged. The concentrate exits at the edge of the membrane packs. The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance, increasing the volume of waste treated per area of membrane, and increasing the contaminant/solids concentration in the residual (*i.e.* increases volume reduction factor). SpinTek's centrifugal membrane technology represents an improvement over conventional ultrafiltration technology and increases the number of waste streams that can be treated using membrane treatment.

2.0 PURPOSE

The purpose of this research is to investigate the feasibility of using centrifugal membrane technology combined with innovative membranes for the treatment hazardous/radiological wastes. The result of this work will be a technology that can treat a variety of wastes such as waste from DOE decontamination/decommissioning efforts, biological wastes, and waste with a high solids content (*e.g.*, low level tank waste), contaminated groundwater, mixed-waste process water, and existing waste residual. The process can be used for both inorganic (*e.g.* radionuclides and heavy metals) and organic contaminants. It is envisioned that the volume reduction factors for this technology will be high and a relatively a low amount of residual requiring additional treatment will be produced.

3.0 BACKGROUND

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The fluid stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate ("clean" liquid) is forced through the membrane and is collected in the hollow shaft and is discharged. The concentrate (liquid containing the contaminants) exits at the edge of the membrane packs.

With time, the membrane surface will become fouled resulting in a decrease in the permeate flow rate. To reduce fouling in conventional membrane systems, a large portion of the concentrate is recycled back to the membrane unit producing large liquid velocities near the membrane surface. The large velocities increase turbulence which reduces the thickness of the fouling layer. In centrifugal membrane systems, the rotation of the membrane disk induces the turbulence required to minimize the thickness of the fouling layer. In conventional membrane systems, maximum surface velocities of about 15 ft/s are possible while with centrifugal systems surface velocities of 60 ft/s are typical. As the concentrate thickens with treatment time, conventional systems are not able to maintain the high velocities because of the difficulty in pumping viscous material at large flow rates. Because the centrifugal membrane system does not rely on pumping to produce the required surface velocities, extremely concentrated wastes can be treated.

Membrane systems are typically operated in either the semi-batch mode or the batch mode. In the semi-batch mode, fresh waste is added to the system at a rate equal to the permeate production rate. In the batch-mode, which normally occurs at the end of semi-batch operation, no fresh waste is added to the system and the concentrate remaining from semi-batch operation is concentrated further ("batch down"). During batch-down, large concentration factors are achieved (permeate is still being produced reducing the concentrate volume).

All membrane technologies are volume reduction technologies because contaminants are not degraded or destroyed. Thus, an important measure of the efficiency of membrane technology is the concentration factor (CF). The CF during semi-batch and batch-down operation are calculated using the following two equations:

Semi-Batch Operation

$$CF_{SB} = 1 + V_{perm}/V_{feed\ tank}$$

Batch-Down Operation

$$CF_{BD} = CF_{SB} \times [V_{feed\ tank}/(V_{feed\ tank} - V_{perm})]$$

where,
CF_{SB} = concentration factor during semi-batch operation.
V_{perm} = volume of permeate produced, gal.
$V_{feed\ tank}$ = volume of the feed tank (15 gal), gal.
CF_{DB} = concentration factor during batch-down operation.

Concentration factors are expressed as 1X, 2X, *etc.*, and increase with treatment time. CFs in excess of 100X are obtainable with the membrane technology. Another measure of treatment efficiency is the permeate flux (volume of permeate/membrane area per time). The permeate flux for a given membrane is dependent on the waste's viscosity, solids content, and temperature. These waste characteristics can also change during treatment.

Membrane's that are used for ultrafiltration are characterized by the molecular weight of a molecule that is not allowed to pass through the membrane. For example, the membrane used in this quarter's research had a molecular weight cut-off (MWCO) of 100,000. In theory, compounds having a molecular weight greater than the MWCO would be retained by the membrane and compounds with molecular weights less than the MWCO would pass through the membrane and be contained in the permeate. It should be noted that the MWCO designation is somewhat misleading because a molecule having a molecular weight less than the membrane's MWCO may still be retained by the membrane because its unique geometry.

4.0 METHODOLOGY

Centrifugal membrane technology will be tested using several combinations of wastes and membranes. For each membrane type, the clean water flux (CWF) will be determined for the virgin membrane. The CWF serves as a baseline indicator to determine if the membrane is 1) permanently fouled and 2) sufficiently cleaned. For each waste-membrane combination, the SpinTek system will be operated first in the semi-batch mode and then at the end of the treatment run in the batch mode. The following variables will be monitored during technology testing:

1. Contaminant concentration in concentrate and permeate.
2. Membrane flux.
3. Temperature and pressure.
4. Conductivity and pH of all liquids.

Permeate flux, contaminant(s) concentration in the permeate, concentration factor, operational ease, and the membrane's physical/chemical resistance and cleanability will be used to judge the effectiveness of the process. Several runs will be conducted for each membrane-waste combination. Special attention will be placed on identifying the quantity and quality of any residuals produced. Quality assurance/quality control practices, as outlined in US EPA's Test Methods for Evaluating Solids Wastes, will be followed. The use of standard analytical methods (*i.e.*, ASTM, Standard Methods for the Measurement of Water and Wastewater, etc.) will also be followed.

5.0 WORK PERFORMED DURING THIS PERIOD

The following work was conducted during the period 4/1/96 to 6/31/96: 1) continuation of literature search, 2) waste and membrane identification and acquisition, and 3) technology testing.

1.1 Literature Search

A comprehensive literature search on membrane technology was conducted in the first quarter of this research and over 75 articles and reports have been acquired. As new relevant documents come to light the material will be requested through West Virginia University's Interlibrary Loan program.

1.2 Waste and Membrane Identification and Acquisition

The identification of wastes and membranes that warrant further study will be on ongoing task for this research project. In this quarter two actual oil/grease (O/G) wastewaters were acquired from a local industry. The first waste, designated as "pond effluent", had an (O/G) content of about 0.2%. The second waste was an industrial coolant having an (O/G) content of about 5%. The use of actual waste as opposed to synthetic is more economical and provides a better opportunity to judge system performance. In addition, numerous researchers have investigated the treatment of (O/G) wastes using conventional ultrafiltration systems thus, a comparison between the SpinTek and conventional systems can be made. Also, because an O/G waste is one of the more difficult wastes to treat, the limits of the SpinTek system can be established.

Several polymeric membranes having molecular weight cut-offs (MWCO) that range from 3,000 to 100,000 and a ceramic membrane having a pore size of 0.1 μm have been acquired from SpinTek. These membranes will be tested in the third quarter.

1.3 Technology Evaluation

In the second quarter the SpinTek technology was used to treat two O/G wastes having an oil content of about 0.2 % ("pond effluent") and 5% ("coolant"). Results and discussion are presented in Section 6.0.

6.0 RESULTS AND DISCUSSION

In this chapter results from the treatment of two O/G wastewaters will be presented and discussed. The first waste, designated as "pond effluent", had an (O/G) content of about 0.2%. The second waste was an industrial coolant having an (O/G) content of about 5%. A schematic of the experimental apparatus is provided in Figure 1. Figures are included at the end of the text portion of Section 6.0.

POND EFFLUENT

Two treatment runs were performed on the pond effluent and the results will be discussed separately in the next two sections.

Run 1

Forty-four gallons of O/G pond effluent were treated in Run 1. Influent wastewater characteristics were as follows: O/G = 1,080 mg/L, TSS = 900 mg/L, COD = 4,660 mg/L, TOC = 2,540 mg/L and pH = 5.2. The system was operated under the following conditions: pressure = 34 psi, rotational speed = 1,750 rpm, semi-batch mode = 7.3 hr, and batch mode = 3.9 hr. Flux and concentration factors, temperature and permeate quality results are presented in subsequent sections.

Flux and Concentration Factor: The flux and concentration factor verses operational time are presented in Figure 2. The flux ranged from 126 to 208 gal/ft^2-d (mean ± standard deviation: 175 ±24 gal/ft^2-d) in semi-batch mode. When the wastewater volume was reduced from 44 to 15 gallons, the operational mode was switched from semi-batch to batch. During batch operation the volume of wastewater was reduced from 15 gal to 2.2 gal. The two sharp decreases in flux (at 7.3 and 10.1 hr) occurred because the system was shut down for an extended period of time and the waste temperature dropped (flux decreases with decreasing temperature). In the batch mode the permeate flux ranged from 57 to 176 gal/ft^2-d (120 ± 30 gal/ft^2-d). The flux in the batch mode was lower than the semi-batch mode because the O/G concentration was much higher. The overall concentration factor was 20x and volume reduction was 95 percent.

Temperature: The feed and permeate temperature changes during the operation are presented in Figure 3. During semi-batch operation the temperature increased rapidly within the first two hours and then slowly increased during the remainder of semi-batch operation. At the end of semi-batch operation (7.3 hr) the system was stopped for 40 minutes and at hour 10.2, the system was stopped for 20 hr (overnight). After both shutdowns the temperature decreased but increased when the system was restarted. Feed tank temperature correlated directly with permeate flux - flux increased with increasing temperature. Feed tank temperature during batch mode was higher than in semi-batch mode because no raw wastewater (which was at room temperature) was introduced to the feed tank during batch operation and heat from rotation and pumping built up in the system. The high flux in the batch mode despite the high O/G concentrations was due to the higher temperatures. Temperatures in excess of 130°F were observed during batch operation. The membrane used in these experiments is rated to 120°F thus, a heat exchanger will be installed for third quarter research.

Permeate Quality: Permeate turbidity verses operational time is presented in Figure 4. Turbidity ranged from 2.2 to 60.3 NTU (27 ± 11.7 NTU). Permeate O/G and TSS concentrations verses the concentration factor are presented in Figure 5. O/G concentrations ranged from 9 to 12 mg/L (11 ± 2.6) in semi-batch mode and from 23 to 54 mg/L (39 ± 22) in batch mode. As expected, the permeate O/G concentration increased with the concentration factor because of the large amount of O/G that was retained by the membrane (especially during batch down). The average O/G removal efficiency was 98 percent. Permeate TSS concentrations were less than the detection limit (5 mg/L) in both the semi-batch and batch mode operation. Permeate COD and TOC verses the concentration factors are presented in Figure 6. COD ranged from 1,170 to 1,590 (1,350 ± 128) and TOC ranged from 405 to 880 (511 ± 133). COD and TOC removal efficiencies were about 71 and 80 percent, respectively. Both COD and TOC removals were not a function of concentration factor because the COD/TOC in the permeate was largely made up of compounds having molecular weights below 100,000 (*i.e.*, these compounds are not retained by the membrane under any circumstances).

Run-2

Two hundred and twenty gallons of O/G pond effluent were treated in Run 2. Influent wastewater characteristics were as follows: O/G = 1,850 mg/L, TSS = 300 mg/L, COD = 9,640 mg/L, TOC = 2,050 mg/L and pH = 6.5. The system was operated under the following conditions: pressure = 32 psi, rotational speed = 1,750 rpm, semi-batch mode = 65 hr, and batch mode = 6.5 hr. Flux and concentration factors, temperature and permeate quality results are presented in subsequent sections.

Flux and Concentration Factor: Permeate flux and concentration factors verses operational time are presented in Figure 7. At about 3 hours, air pressure to the system was interrupted and the flux decreased to 65 gal/ft^2-d. The system was restarted and ran for several hours to determine if the flux would increase back to initial levels. After 1.5 hr it was apparent that the membrane had become fouled and cleaning was required. Waste was removed from the system and stored. Five gallons of cleaning solution were prepared using the following recipe (recommended by SpinTek): 180 g of laundry detergent and 2 teaspoons of dishwashing soap. After cleaning, the stored waste was placed back in the feed tank and the system was restarted. The flux immediately after cleaning was 330 gal/ft^2-d and decreased to 200 gal/ft^2-d within two hours and then slowly declined to 100 gal/ft^2-d during the 55 hour operation. The mean flux was 156 gal/ft^2-d. The larger flux after cleaning can be attributed in part to the residual soap that was in the system following cleaning (the soap decreased the viscosity of the waste).

After the waste was concentrated from 220 to 15 gallons, the operational mode was switched from semi-batch to batch. Waste was further concentrated from 15 to 2.2 gallons. The flux ranged from 79 to 97 gal/ft^2-d (86 ± 6) in the batch mode. The final concentration factor was 100x and the volume reduction was 99 percent.

Temperature: Feed tank and permeate temperature versus operation time are presented in Figure 8. The feed tank temperature increased rapidly during the first six hours of operation and then gradually increased to 125°F over the course of semi-batch operation. During batch operation the feed tank temperature increased to 160°F because room temperature wastewater was not being

added to the feed tank. As mentioned previously, the membrane used in these experiments is rated to 120°F thus, a heat exchanger will be installed for third quarter research.

Permeate Quality: Permeate turbidity verses operational time is presented in Figure 9. During semi-batch operation the majority of samples had turbidity levels below 5 NTU. After operation was switched from semi-batch to batch mode, the turbidity level increased dramatically due to the large concentration of O/G and high temperatures. Permeate O/G and TSS concentration verses the concentration factor are presented in Figure 10. O/G concentration ranged from 7 to 17 mg/L (11 ± 4) in semi-batch mode and from 16 to 78 mg/L (44 ± 31) in batch mode. At the higher temperatures observed during batch operation the membrane pores enlarged allowing more oil droplets into the permeate. Permeate TSS ranged from 14 to 28 mg/L (20 ± 4) in semi-batch mode and from 18 to 25 in batch mode. O/G and TSS removal efficiencies were 98 and 93 percent, respectively. Permeate COD and TOC concentrations verses the concentration factor are presented in Figure 11. COD ranged from 372 to 890 mg/L (537 ± 146), and TOC ranged from 142 to 276 mg/L (193 ± 43). The higher COD concentrations observed at larger concentration factors are related to the higher O/G concentrations. Removal efficiencies for COD and TOC were 94 and 91 percent, respectively.

Mill Coolant

Two treatment runs were performed on the mill coolant and the results will be discussed separately in the next two sections.

Run 1

Seventy-six gallons of hot mill coolant were treated in Run 1. Influent wastewater characteristics were as follows: O/G = 23,000-49,500 mg/L, TSS = 3,000-6,700 mg/L, COD = >15,000 mg/L, TOC = 6,000-6,900 mg/L and pH = 7.4. The system was operated under the following conditions: pressure = 32 psi, rotational speed = 1,750 rpm, semi-batch mode = 29 hr, and batch mode = 4 hr. Flux and concentration factors, temperature and permeate quality results are presented in subsequent sections.

Flux and Concentration Factor: Permeate flux and concentration factors verses operational time is presented in Figure 12. The initial flux was 80 gal/ft^2-d, increased to 150 gal/ft^2-d as the temperature increased and then declined to 58 gal/ft^2-d at an operational time of 21 hr. At this point the system was shut down and cleaned as described earlier. The system was restarted and flux increased to 80 gal/ft^2-d and then decreased to about 38 gal/ft^2-d at the end of semi-batch operation (29 hr). At this point the waste had been concentrated from 76 to 15 gallons. The flux continued to decline during batch operation and the system was shutdown and cleaned at 30.5 hr. After cleaning, the flux increased to 100 gal/ft^2-d, and then decreased to 22 gal/ft^2-d. At the end of batch down there were six gallons of concentrated wastewater left in the feed tank resulting in a concentration factor of 12.7x and a volume reduction of 92 percent.

Temperature: Feed tank and permeate temperatures versus operational time are presented in Figure 13. The temperature of the feed tank increased from 95°F to 124°F within the first five hours, and then gradually increased to 137°F at the end of semi-batch operation. The feed tank temperature increased to 155°F during batch operation. The two dramatic temperature drops (21

and 30.5 hr) were due to system cleaning. In third quarter research, provisions will be made to heat the waste to the desired temperature prior to starting/restarting the SpinTek system.

Permeate Quality: Permeate turbidity verses operational time is presented in Figure 14. Turbidity was below 10 NTU for the first 13 hours of operation but increased to 760 NTU at 21 hr. After cleaning, the turbidity was below 10 NTU but then increased dramatically. After the system was cleaned a second time, turbidity decreased to below 10 NTU and remained low for about 3 hours but then increased to about 1,500 NTU. At this point the run was ended.

Permeate O/G and TSS concentrations verses the concentration factor are presented in Figure 15. O/G concentration ranged from 120 to 740 mg/L (443 ± 310) in semi-batch mode and from 17,000 to 19,500 mg/L (18,250 ± 1,770) in batch mode. Permeate TSS ranged from 8 to 1,252 mg/L (237 ± 498) in semi-batch mode and ranged from 2,000 to 2,922 mg/L (2,460 ± 650) in batch mode. The high concentrations of O/G and TSS during batch mode were due to the large O/G concentration and the high temperatures. The high temperatures adversely affected the retentive characteristics of the membrane. Permeate COD and TOC concentrations verses the concentration factor are presented in Figure 16. Permeate COD and TOC concentrations ranged from 5, 490 to >15,000 mg/L (upper detection limit) and from 1,310 to 2,660 mg/L (1,910 ± 630), respectively The high COD and TOC concentrations correlate well with the O/G concentration (*i.e.*, in this case, O/G contributed significantly to both COD and TOC).

Run 2

Sixty-three gallons of hot mill coolant were treated in Run 2. Influent wastewater characteristics were the same as in Run 1: O/G = 23,000-49,500 mg/L, TSS = 3,000-6,700 mg/L, COD = >15,000 mg/L, TOC = 6,000-6,900 mg/L and pH = 7.4. The system was operated under the following conditions: pressure = 32 psi, rotational speed = 1,750 rpm and semi-batch mode = 35 hr. The system was not operated in the batch mode. Flux and concentration factors, temperature and permeate quality results are presented in subsequent sections.

Flux and Concentration Factor: Permeate flux and concentration factors verses operational time are presented in Figure 17. Initially the flux was 95 gal/ft^2-d but increased to 148 gal/ft^2-d after two hours of operation because of the increase in feed tank temperature. The system was cleaned three times (15, 21.5, and 28.5 hr). Flux improved after each cleaning, but the maximum flux was lower (148, 100, 80, and 50 gal/ ft^2-d) than the maximum flux from before the previous cleaning indicating that the membrane had become permanently fouled. Because the membrane had fouled, batch down was not attempted. The final concentration factor was 5.2x and the volume reduction was 76 percent. The final concentration factor and volume reduction were lower because no batch down was performed.

Temperature: Feed tank and permeate temperature versus operation are presented in Figure 18. When the system was cleaned, the feed temperature dropped sharply, but increased as the experiment carried on. Temperatures approaching 150°F were common. In future research feed tank temperature will be controlled.

Permeate Quality: Turbidity verses operational time is presented in Figure 19. Turbidity levels were below 10 NTU during the first 11 hours of operation and then increased to 350 NTU within the next 4 hours. After the first cleaning, low permeate turbidity levels lasted for about 4 hours, but then increased to 550 NTU. The second cleaning was conducted at 21 hours. The turbidity decreased to about 20 NTU and remained low for about 3 hours. Turbidity again increased to 900 NTU, and the third cleaning was conducted, after which turbidity dropped, but after 3 hours again increased dramatically. At this point the run was ended.

Permeate O/G and TSS concentrations verses the concentration factor are presented in Figure 20. O/G concentration ranged from 96 to 972 mg/L (433 ± 365). Permeate TSS ranged from 30 to 334 mg/L (168± 124). Removal efficiencies for O/G and TSS were 98.5 and 95.5 percent, respectively. Permeate COD and TOC concentrations verses the concentration factor are presented in Figure 21. COD ranged from 5,890 to 7,800 mg/L (6890 ± 680) and TOC ranged from 712 to 2,520 mg/L (1,550 ± 660). COD and TOC removal efficiencies were 54 and 76 percent, respectively.

System Cleaning Testing

The clean water flux (CWF) for a virgin membrane and for membranes after each cleaning during waste treatment are presented in Figure 22 (Note: for each treatment run a new membrane was used).. The average virgin membrane flux before wastewater treatment was 220 gal/ft^2-d. The CWFs after pond effluent treatment were 287 and 257 gal/ft^2-d for Runs 1 and 2, respectively. The higher CWFs for the pond effluent compared with the virgin membrane were due to the presence of cleaning solution in the system. The cleaning soaps decreased the viscosity of the water resulting in a higher permeate flow rate. The CWFs after treatment of mill coolant were 162 and 62 gal/ft^2-d for Run 1 and 2, respectively. It is apparent that fouling of the membranes occurred when the hot mill coolant was treated. Fouling can be reduced by running the system at a lower temperature (lowering the temperature of the system will protect the integrity of the membrane as well as reduce the amount of oil that is able to slip into the membrane and clog the pores) and using a more durable membrane (*e.g.*, ceramic) Both of these topics will be investigated in the third quarter.

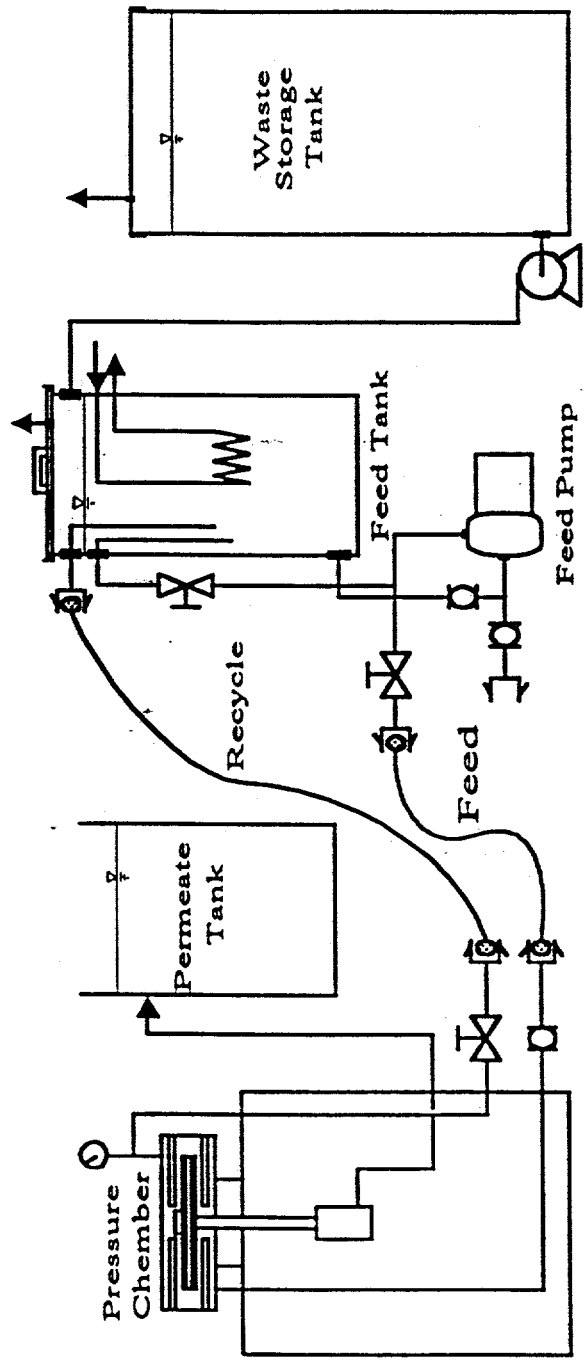
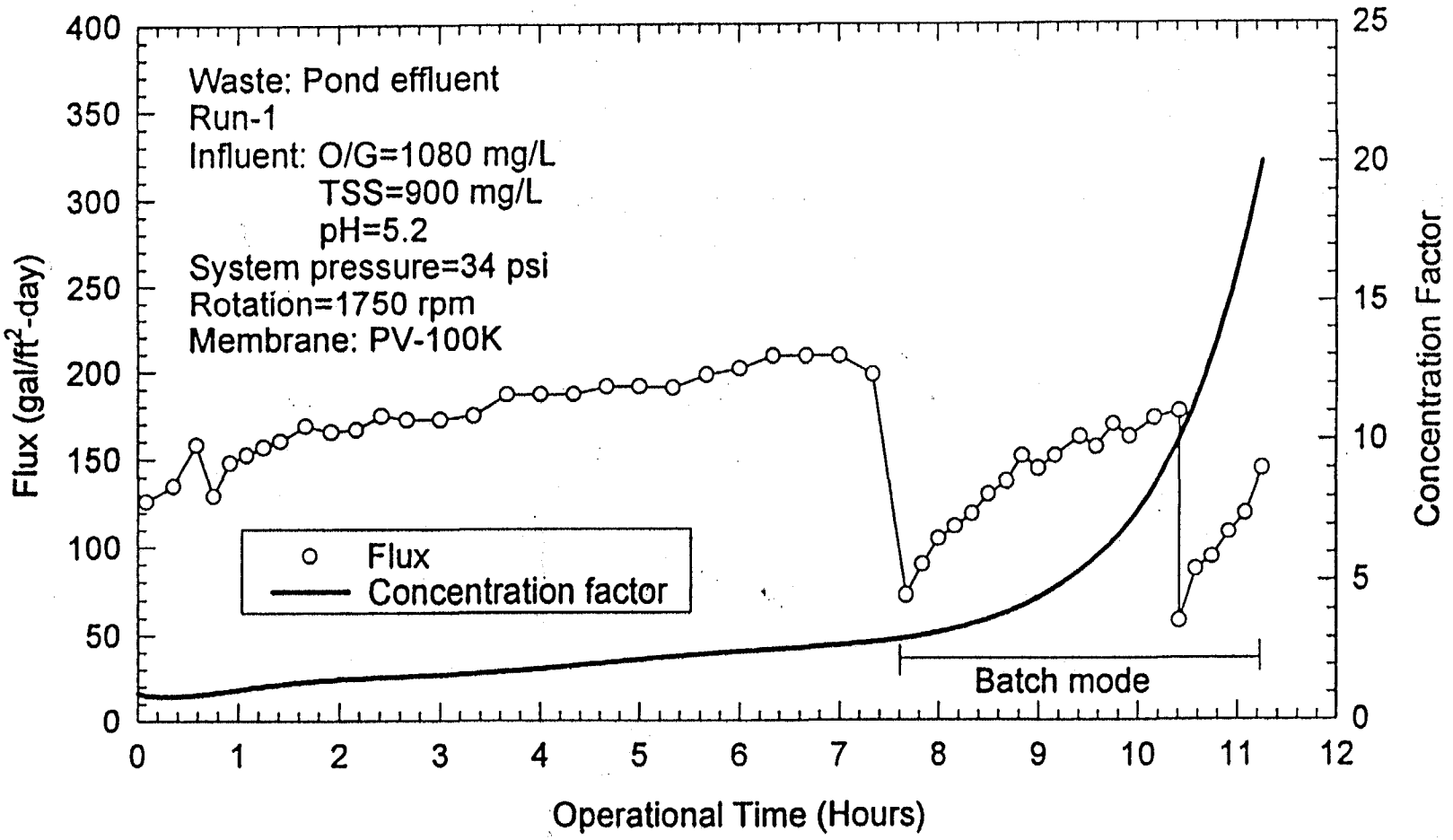


Figure 1. Schematic of Experimental Apparatus.



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Figure 2. Permeate Flux and Concentration Factors Versus Operational Time for Pond Effluent - Run 1.

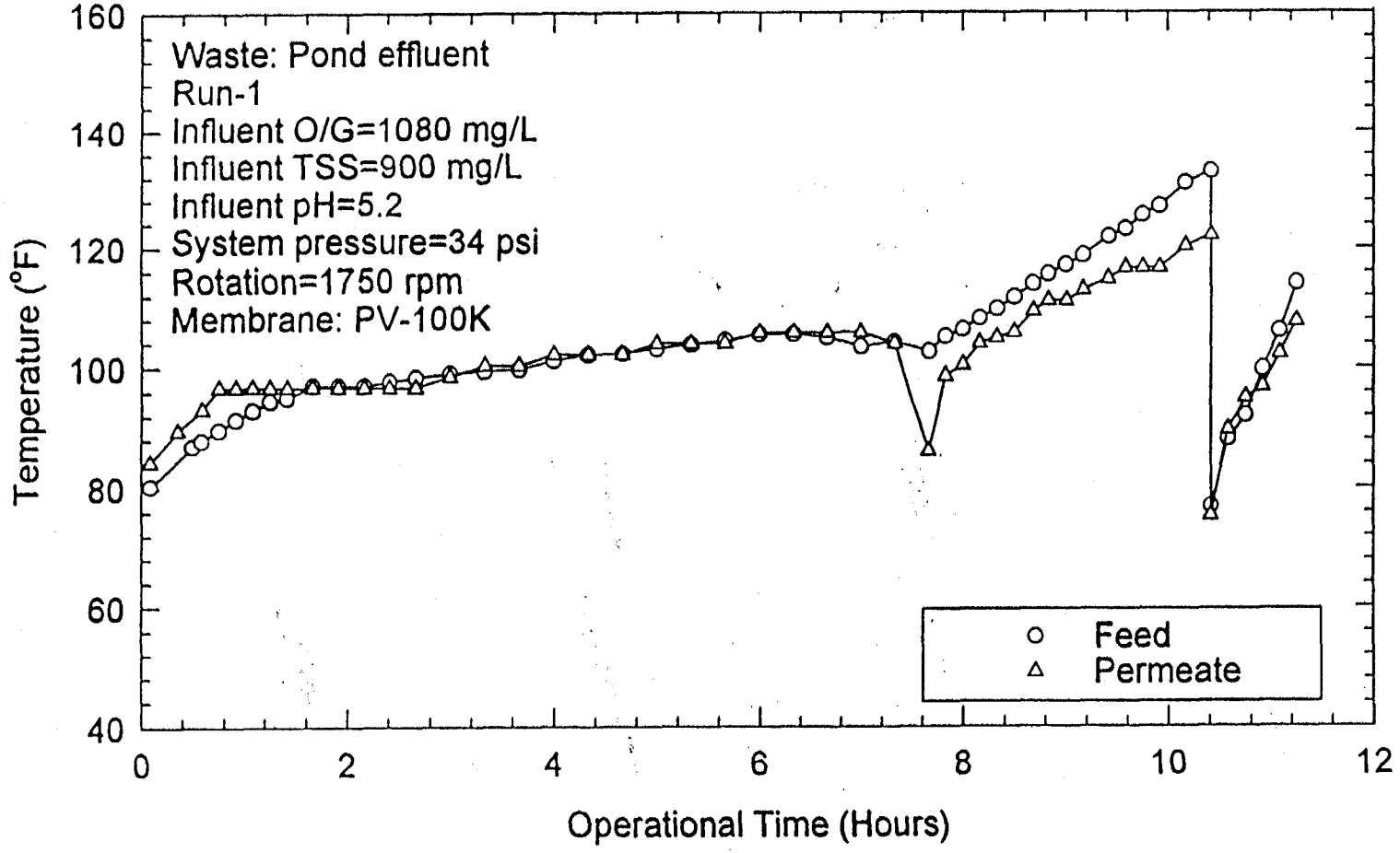


Figure 3. Feed Tank and Permeate Temperature Versus Operational Time for Pond Effluent - Run 1.

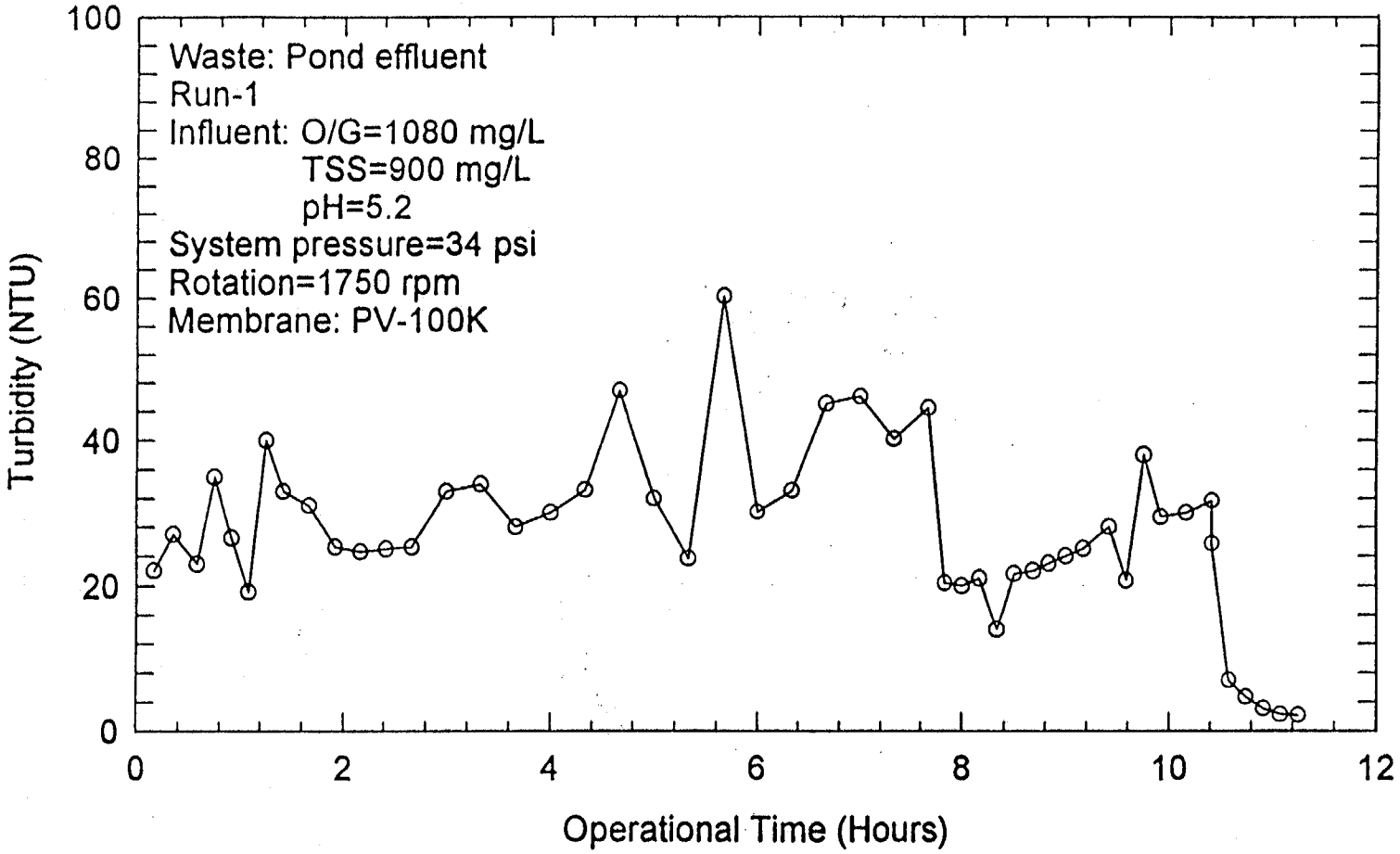


Figure 4. Permeate Turbidity Versus Operational Time for Pond Effluent - Run 1.

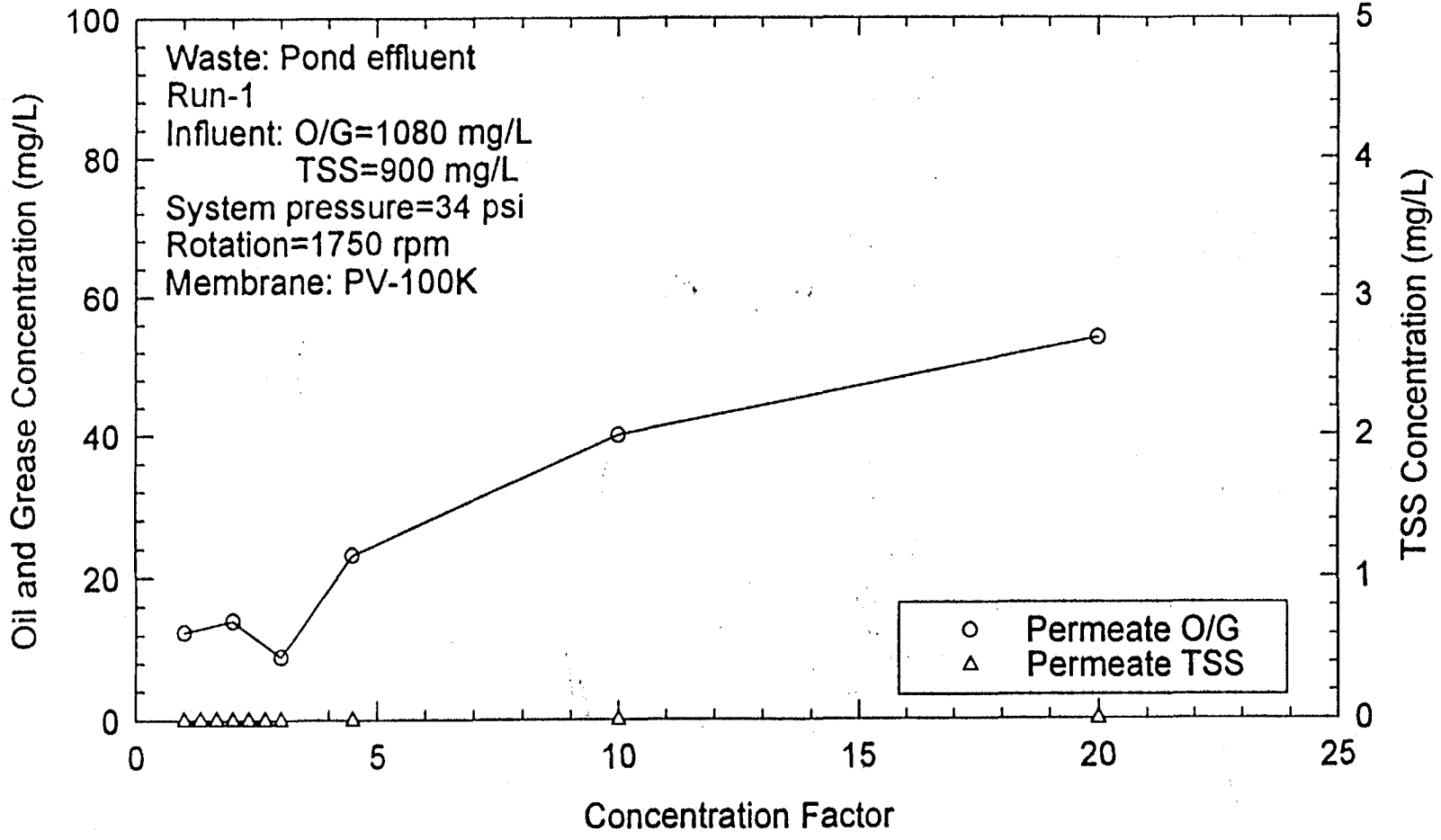


Figure 5. Permeate Oil/Grease and TSS Concentrations Versus Concentration Factor for Pond Effluent - Run 1.

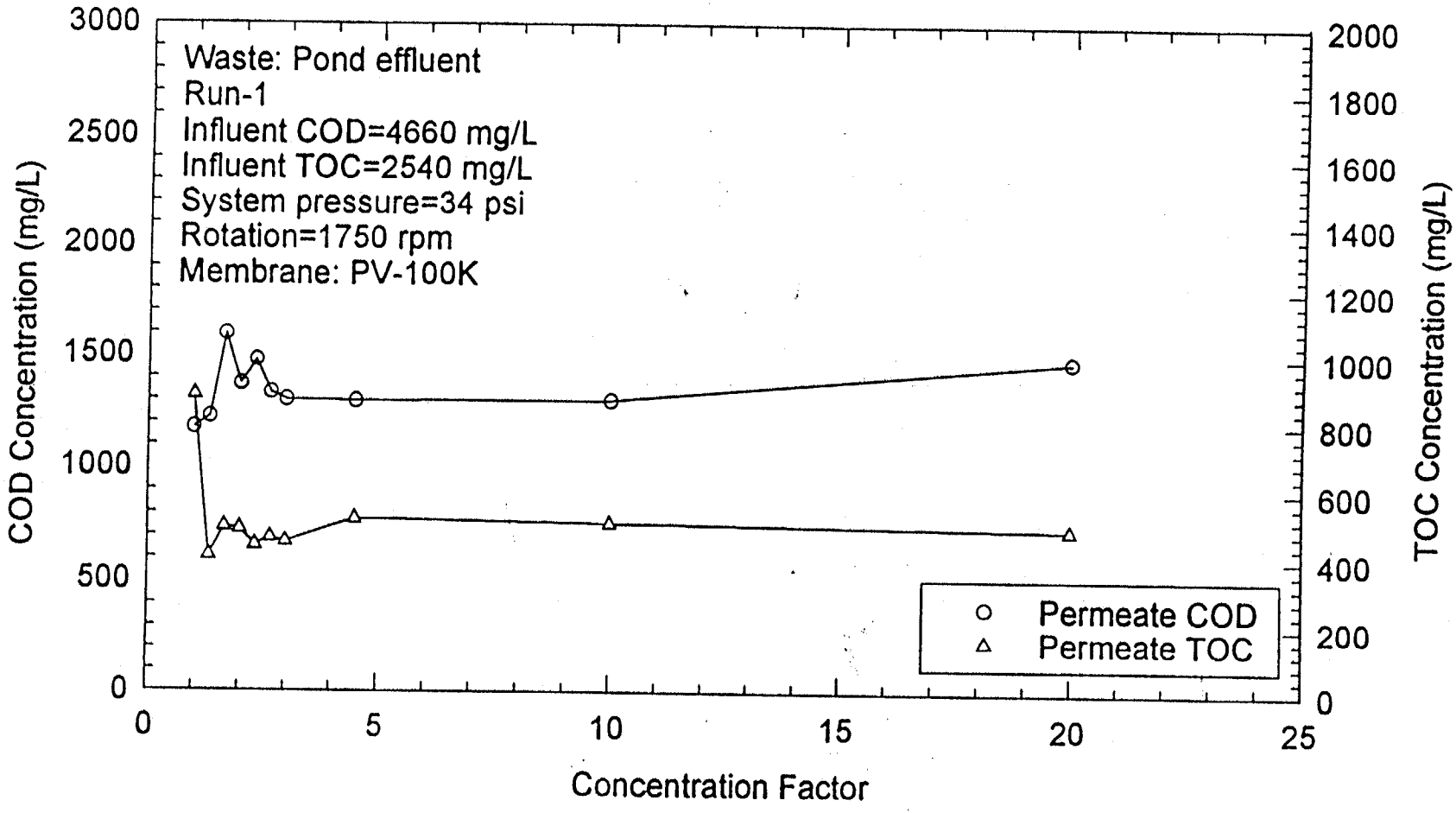


Figure 6. Permeate COD and TOC Concentrations Versus Concentration Factor for Pond Effluent - Run 1.

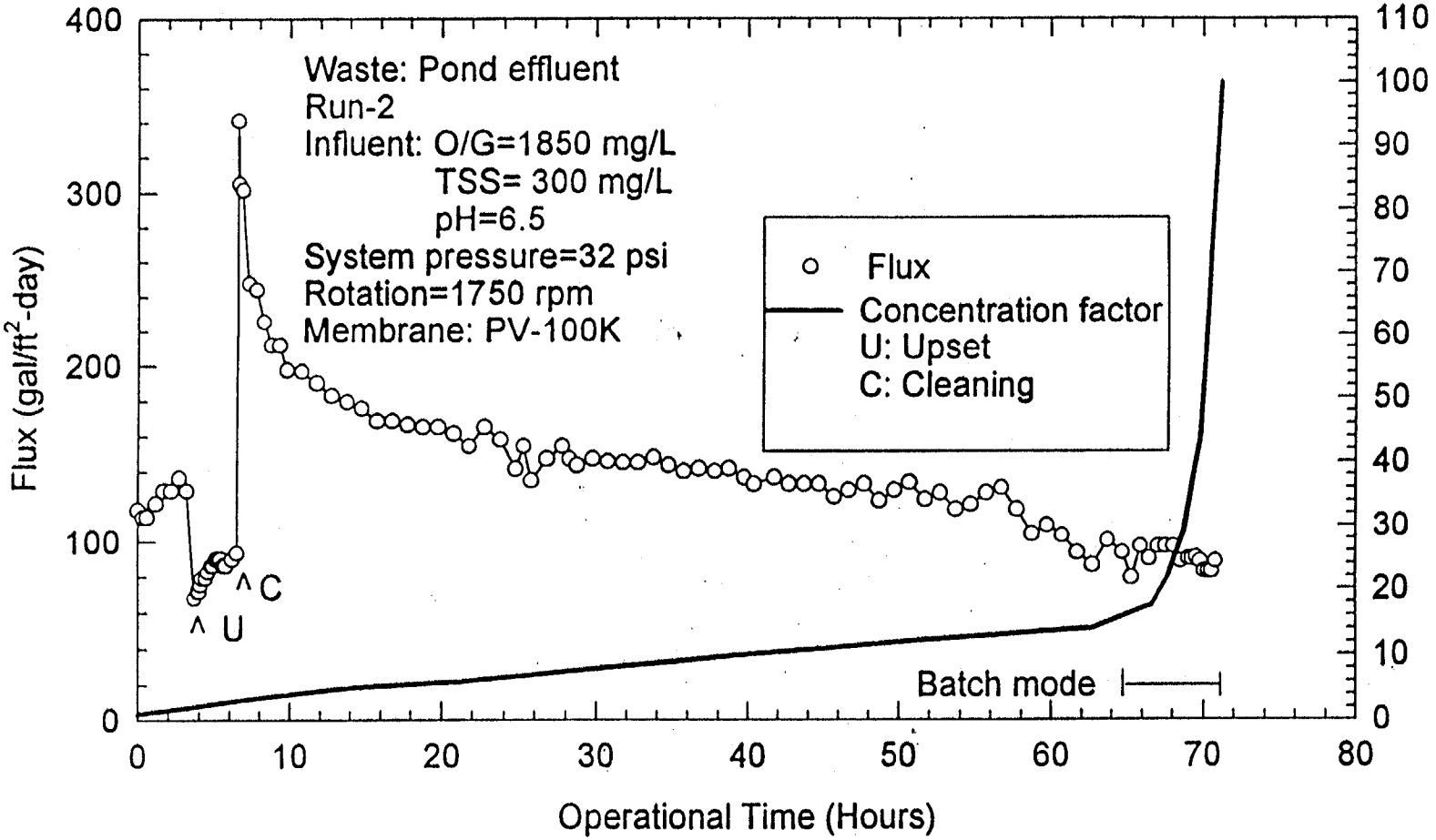


Figure 7. Permeate Flux and Concentration Factors Versus Operational Time for Pond Effluent - Run 2.

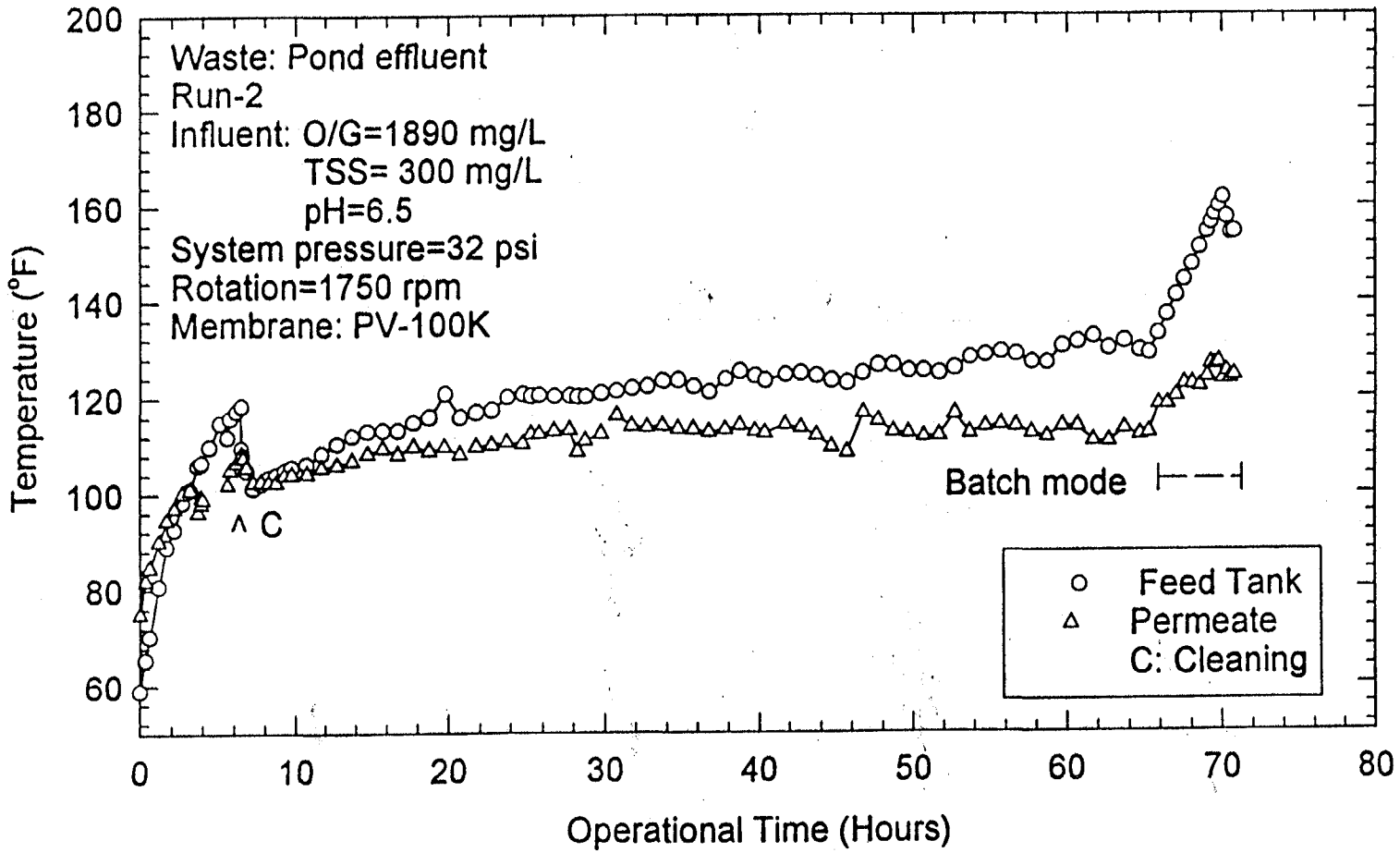


Figure 8. Feed Tank and Permeate Temperature Versus Operational Time for Pond Effluent - Run 2.

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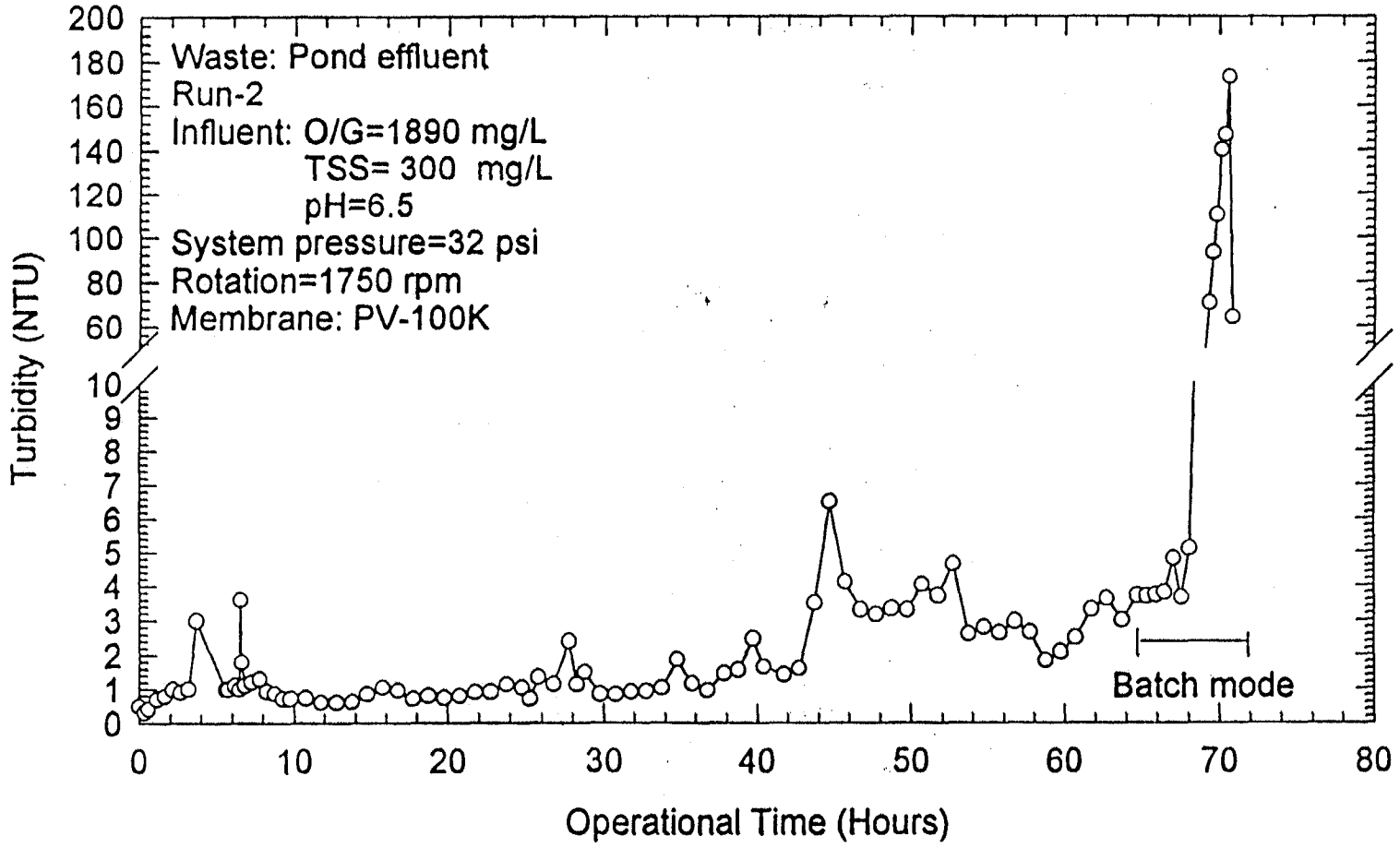


Figure 9. Permeate Turbidity Versus Operational Time for Pond Effluent - Run 2.

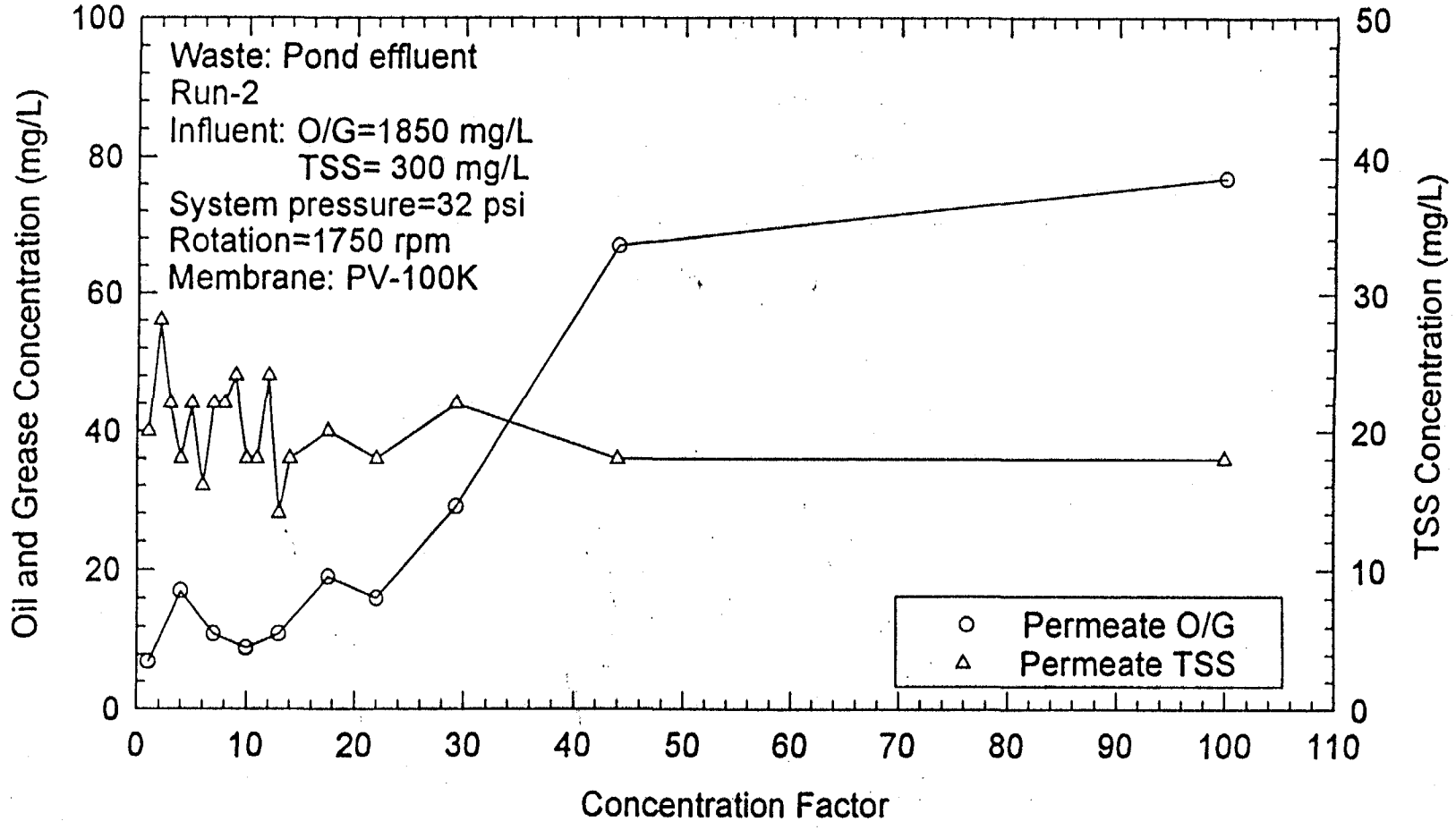


Figure 10. Permeate Oil/Grease and TSS Concentrations Versus Concentration Factor for Pond Effluent - Run 2.

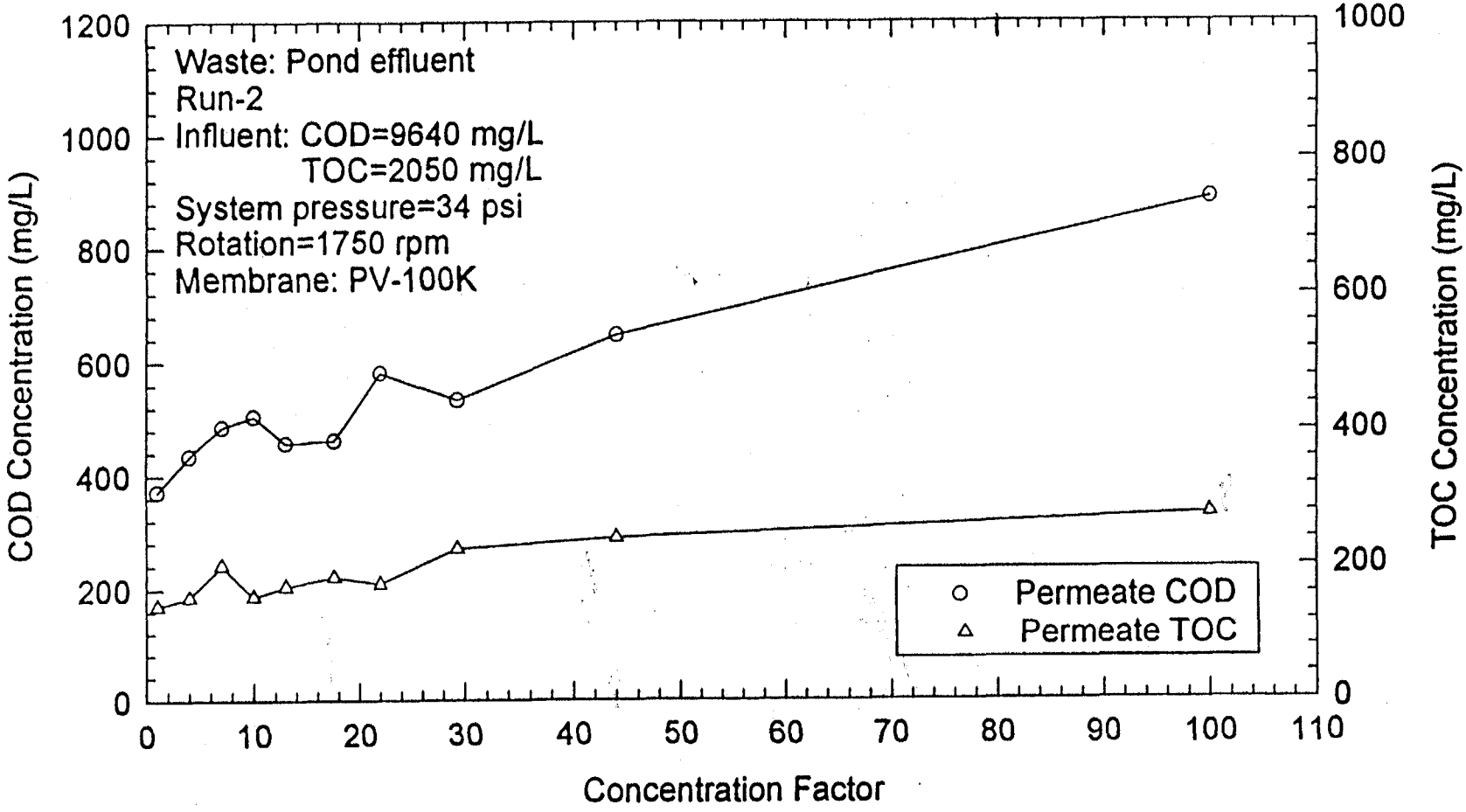


Figure 11. Permeate COD and TOC Concentrations Versus Concentration Factor for Pond Effluent - Run 2.

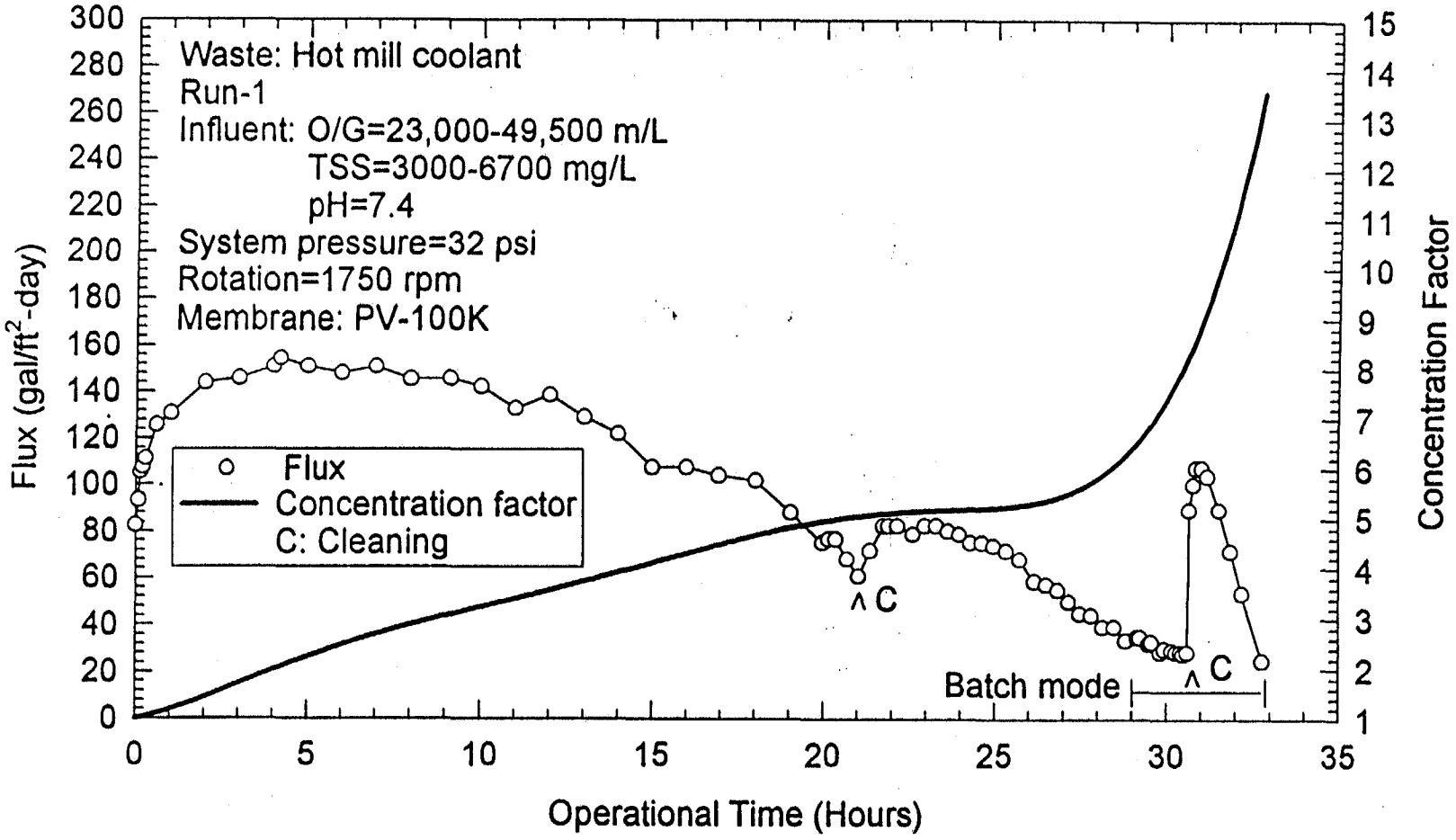


Figure 12. Permeate Flux and Concentration Factors Versus Operational Time for Mill Coolant - Run 1.

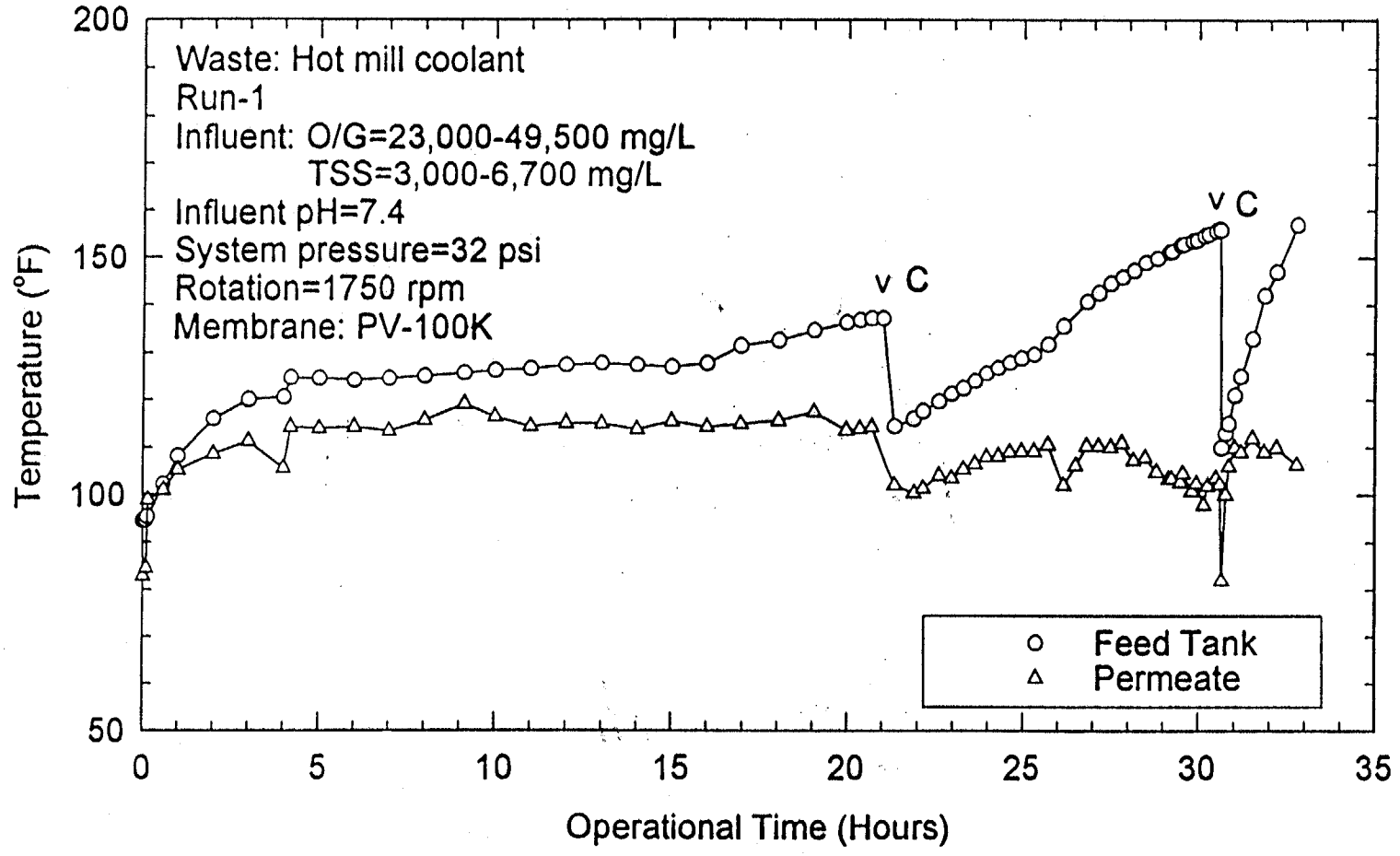


Figure 13. Feed Tank and Permeate Temperature Versus Operational Time for Mill Coolant - Run 1.

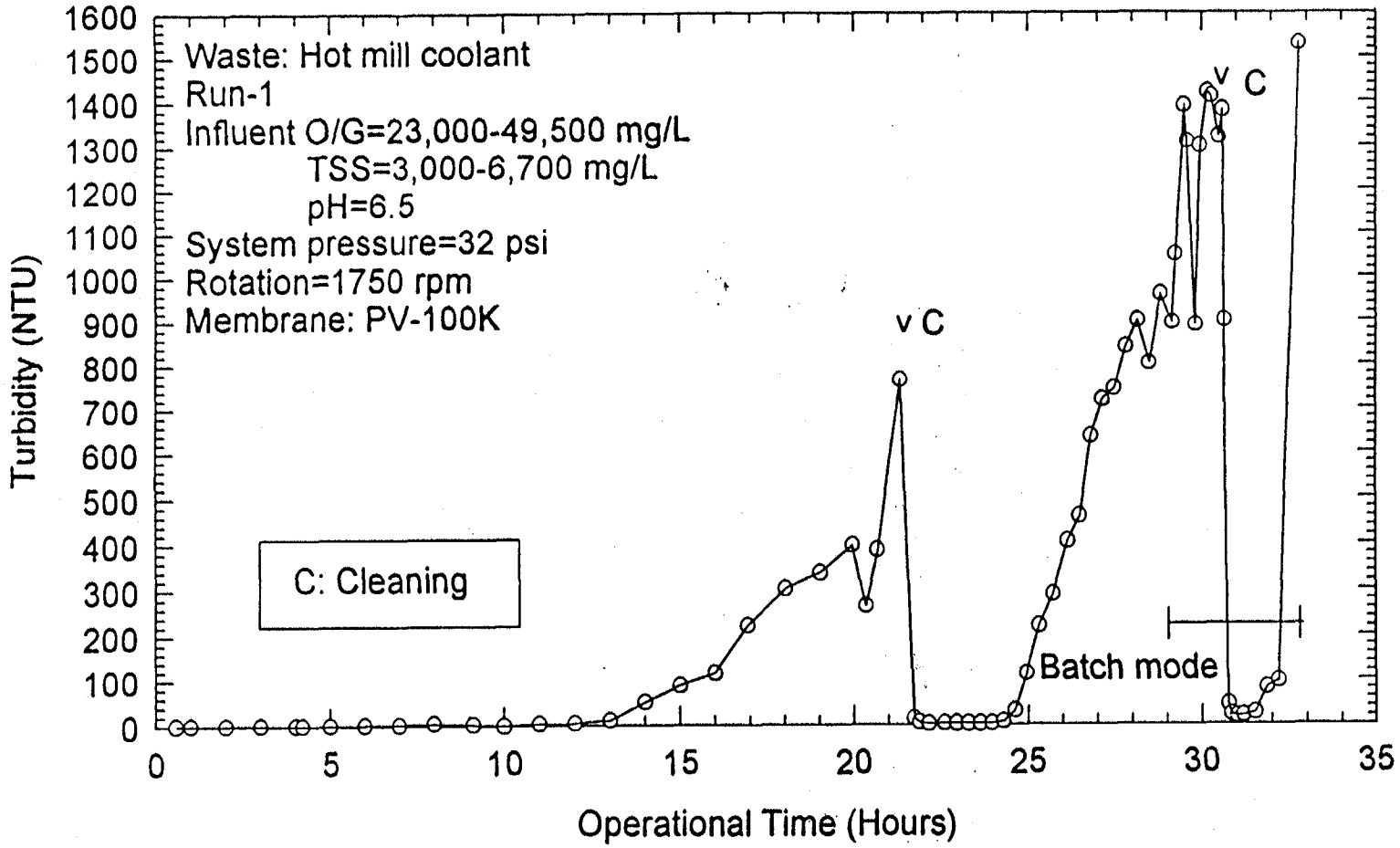


Figure 14. Permeate Turbidity Versus Operational Time for Mill Coolant - Run 1.

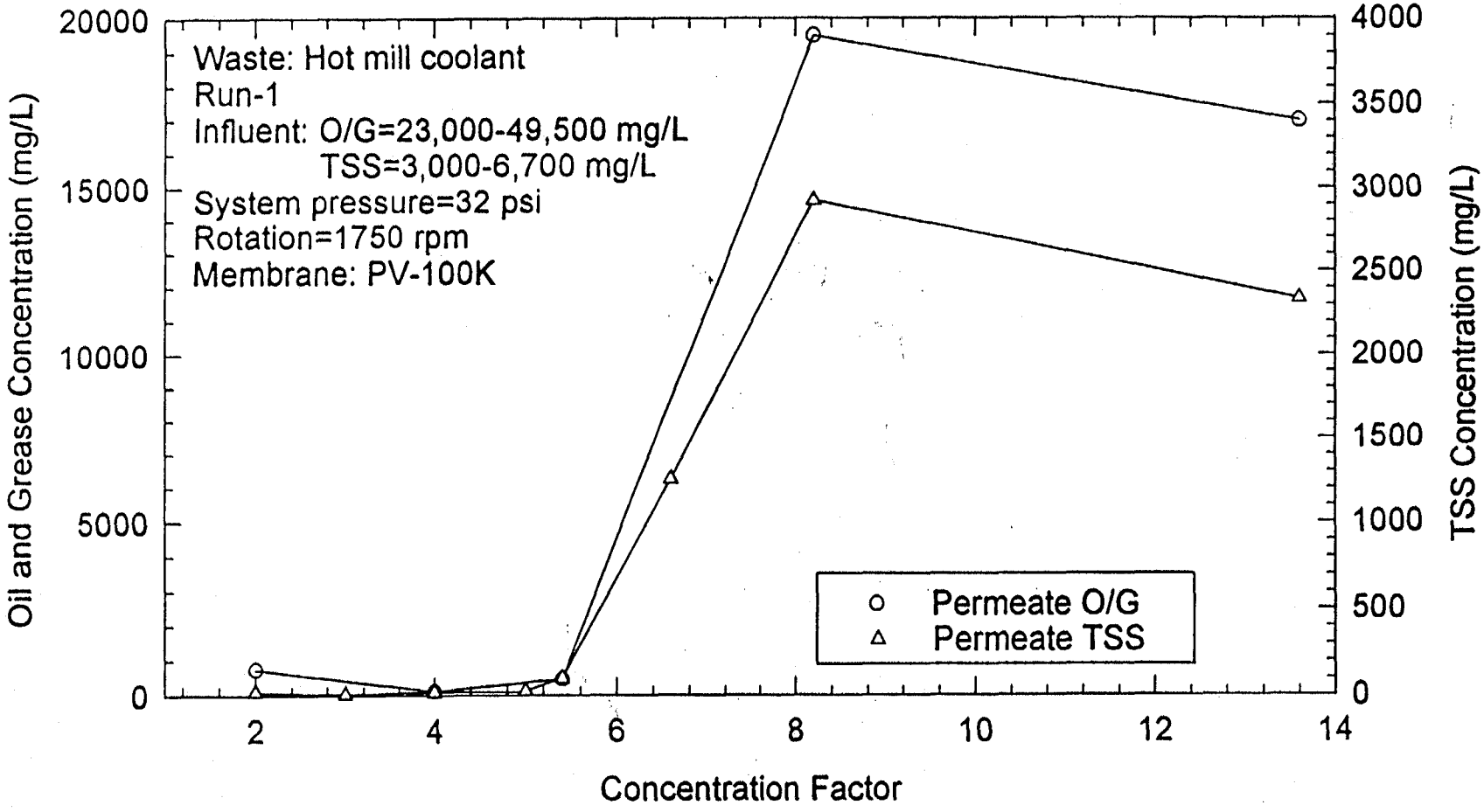


Figure 15. Permeate Oil/Grease and TSS Concentrations Versus Concentration Factor for Mill Coolant - Run 1.

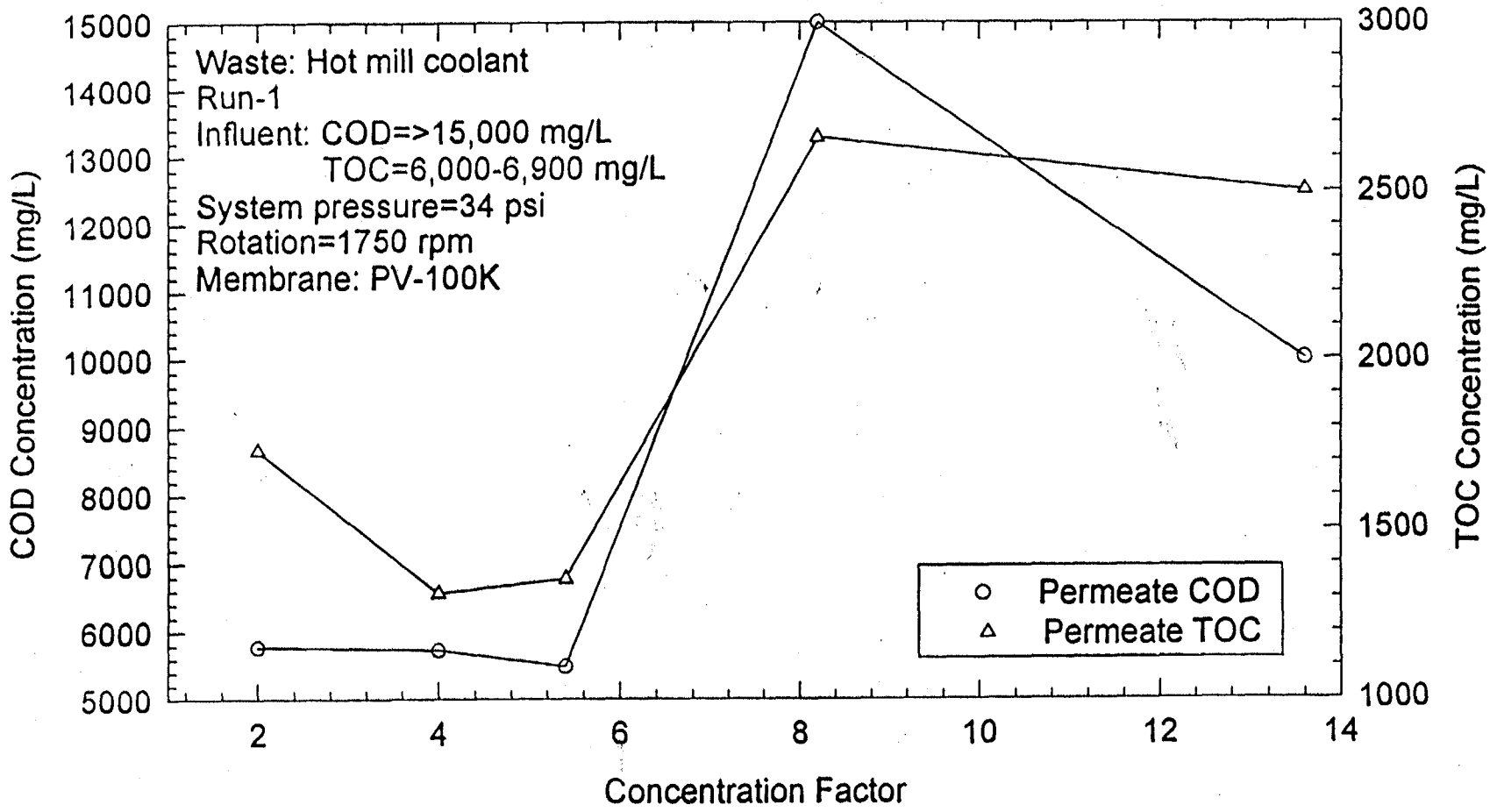


Figure 16. Permeate COD and TOC Concentrations Versus Concentration Factor for Mill Coolant - Run 1.

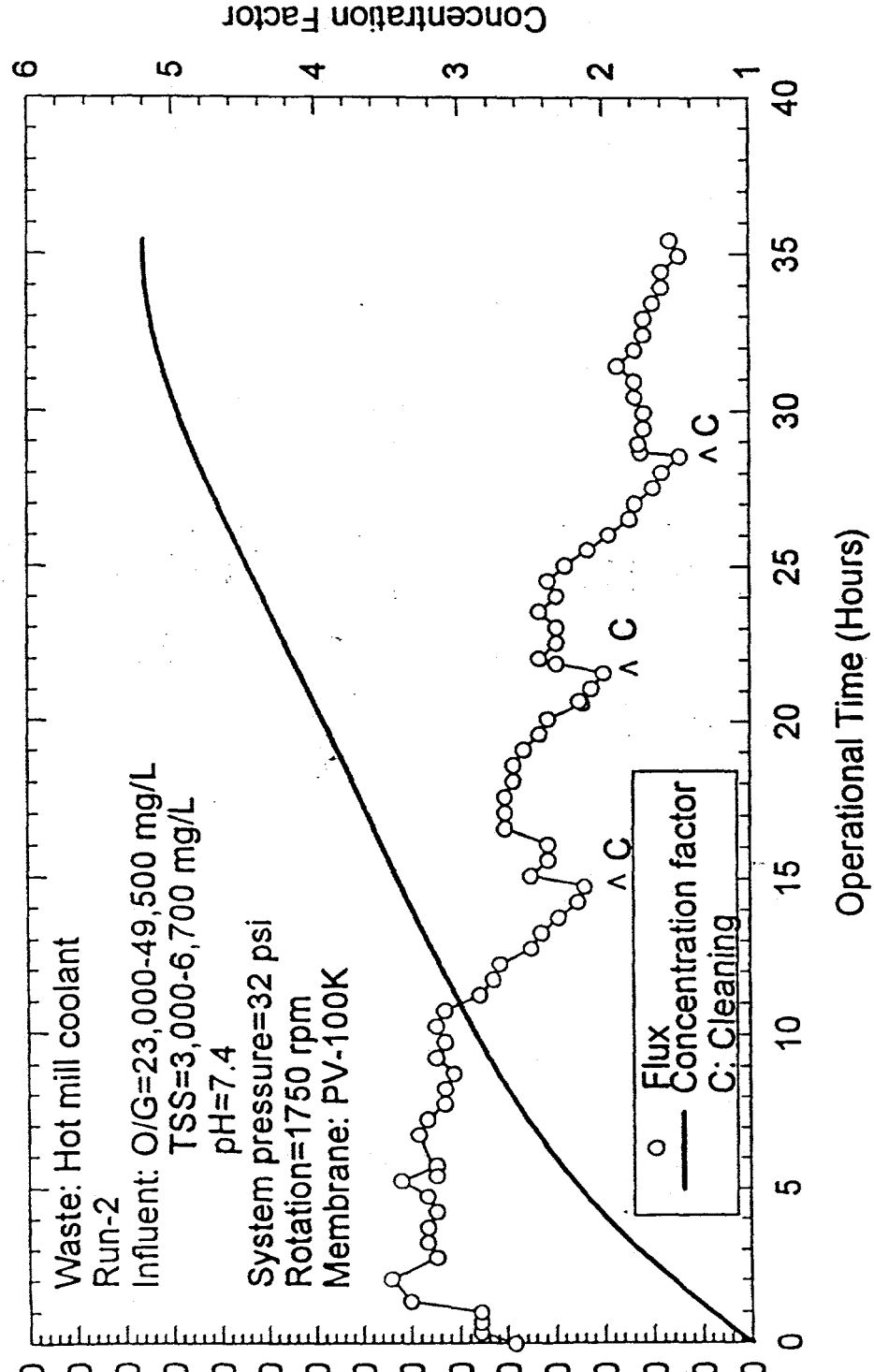


Figure 17. Permeate Flux and Concentration Factors Versus Operational Time for Mill Coolant - Run 2.

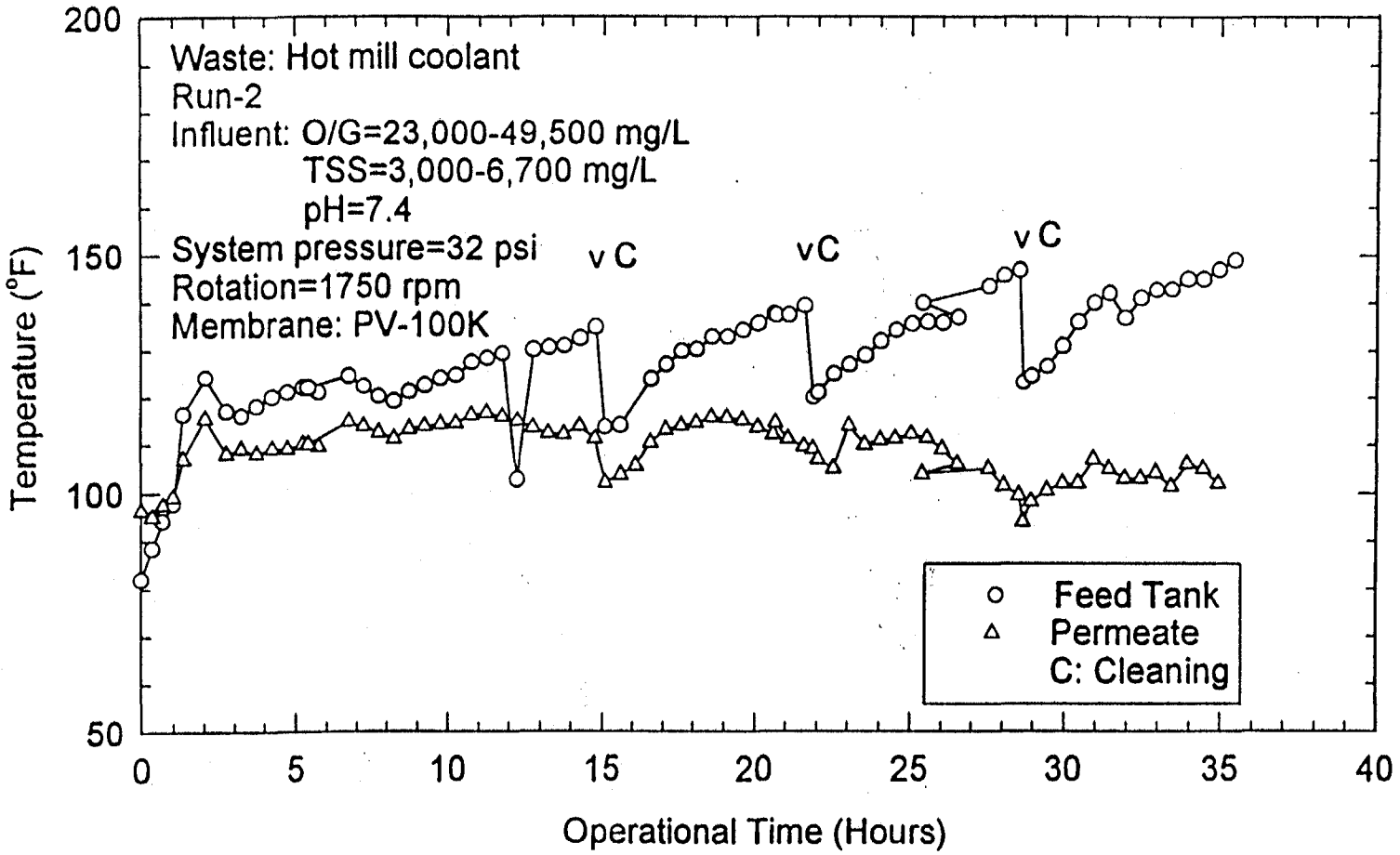


Figure 18. Feed Tank and Permeate Temperature Versus Operational Time for Mill Coolant - Run 2.

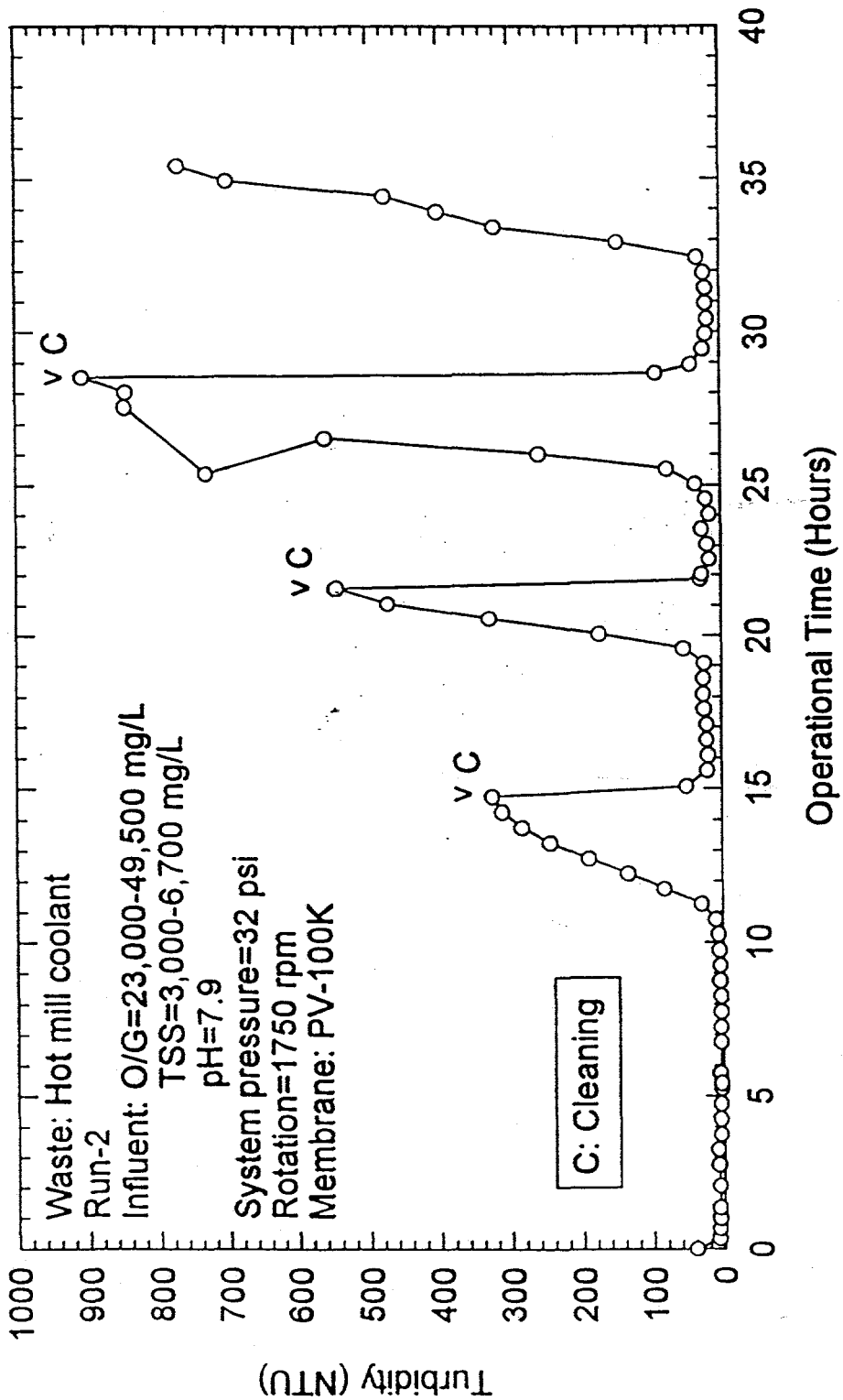


Figure 19. Permeate Turbidity Versus Operational Time for Mill Coolant - Run 1.

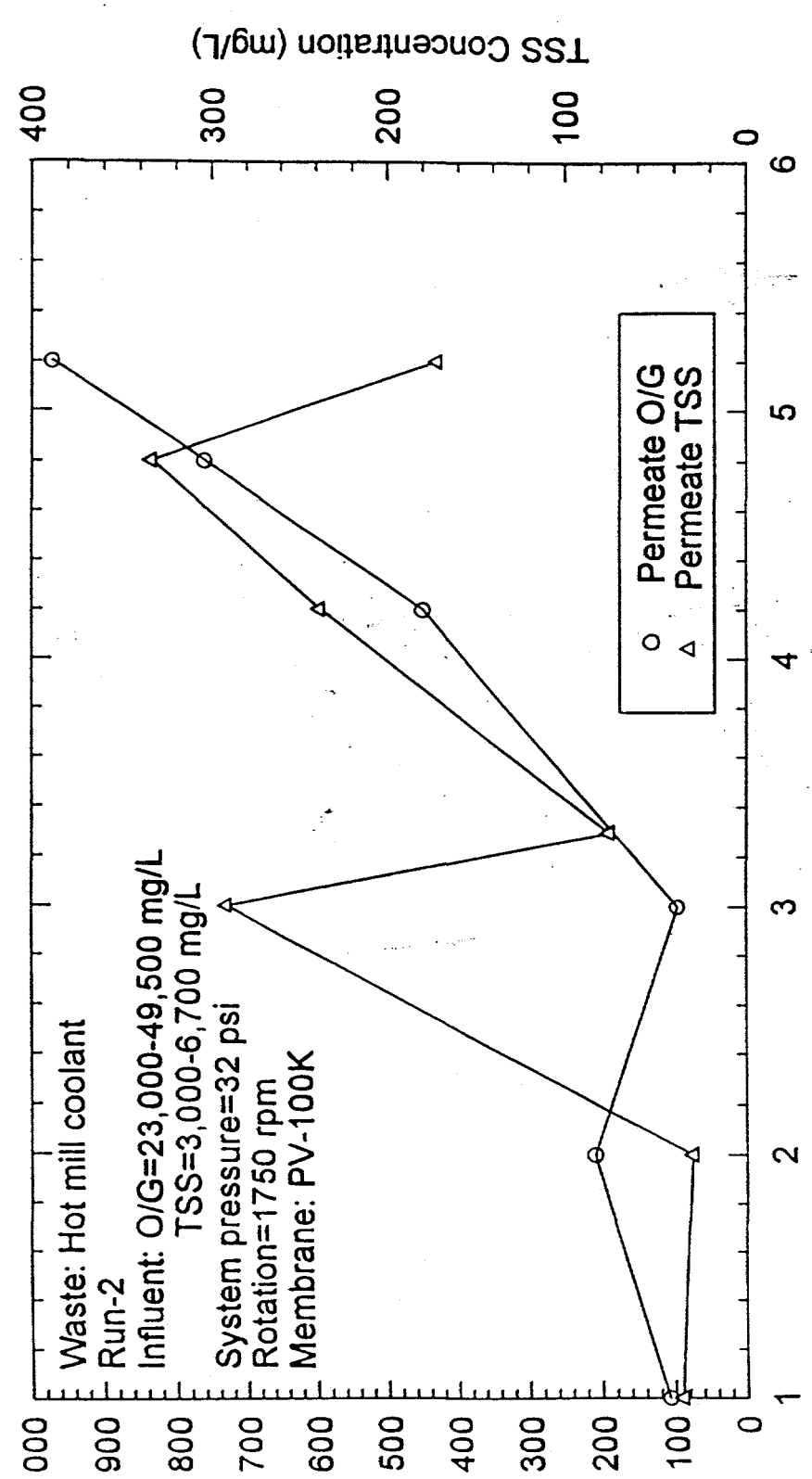


Figure 20. Permeate Oil/Grease and TSS Concentrations Versus Concentration Factor for Mill Coolant - Run 2.

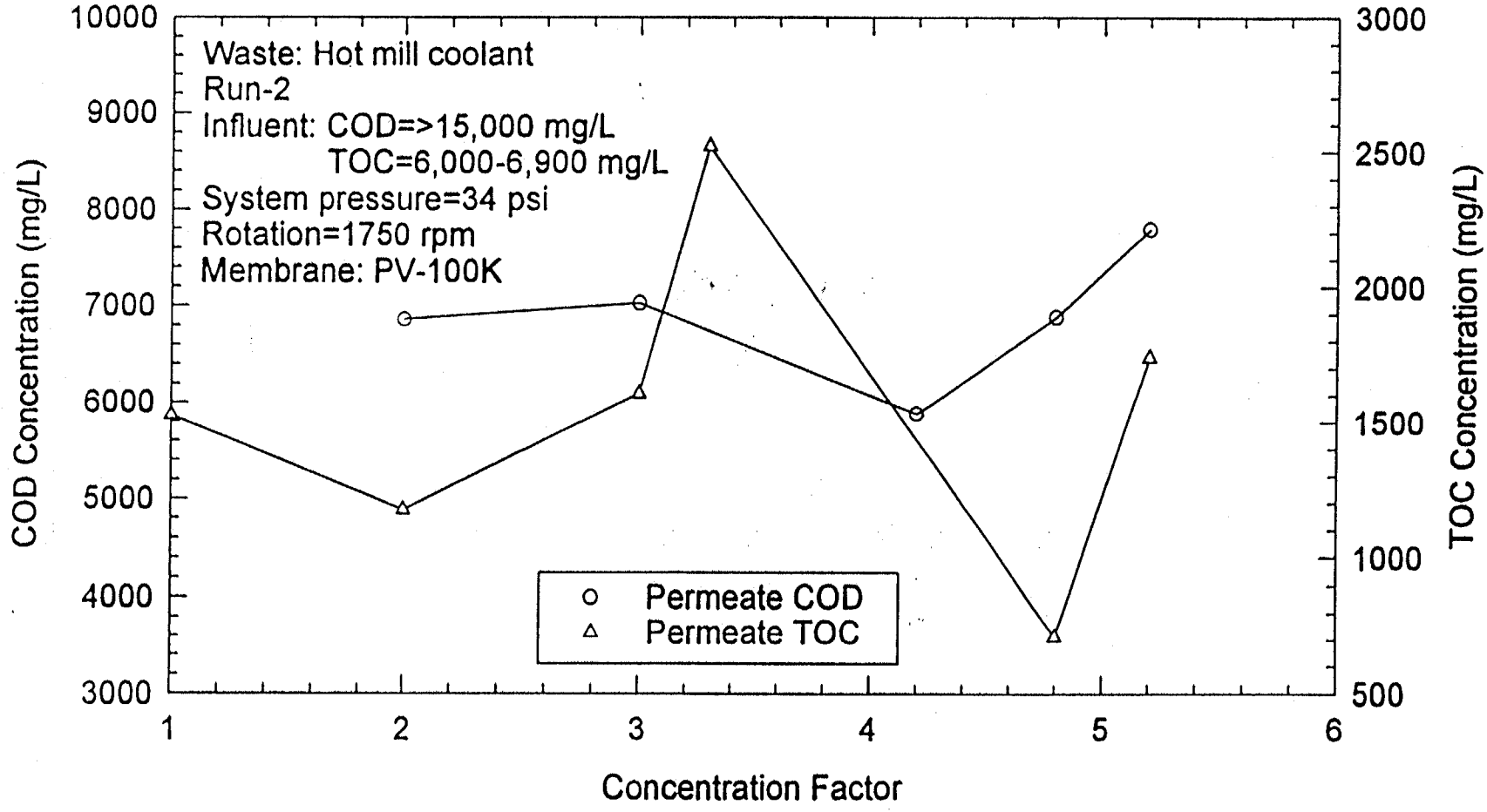


Figure 21. Permeate COD and TOC Concentrations Versus Concentration Factor for Mill Coolant - Run 2.

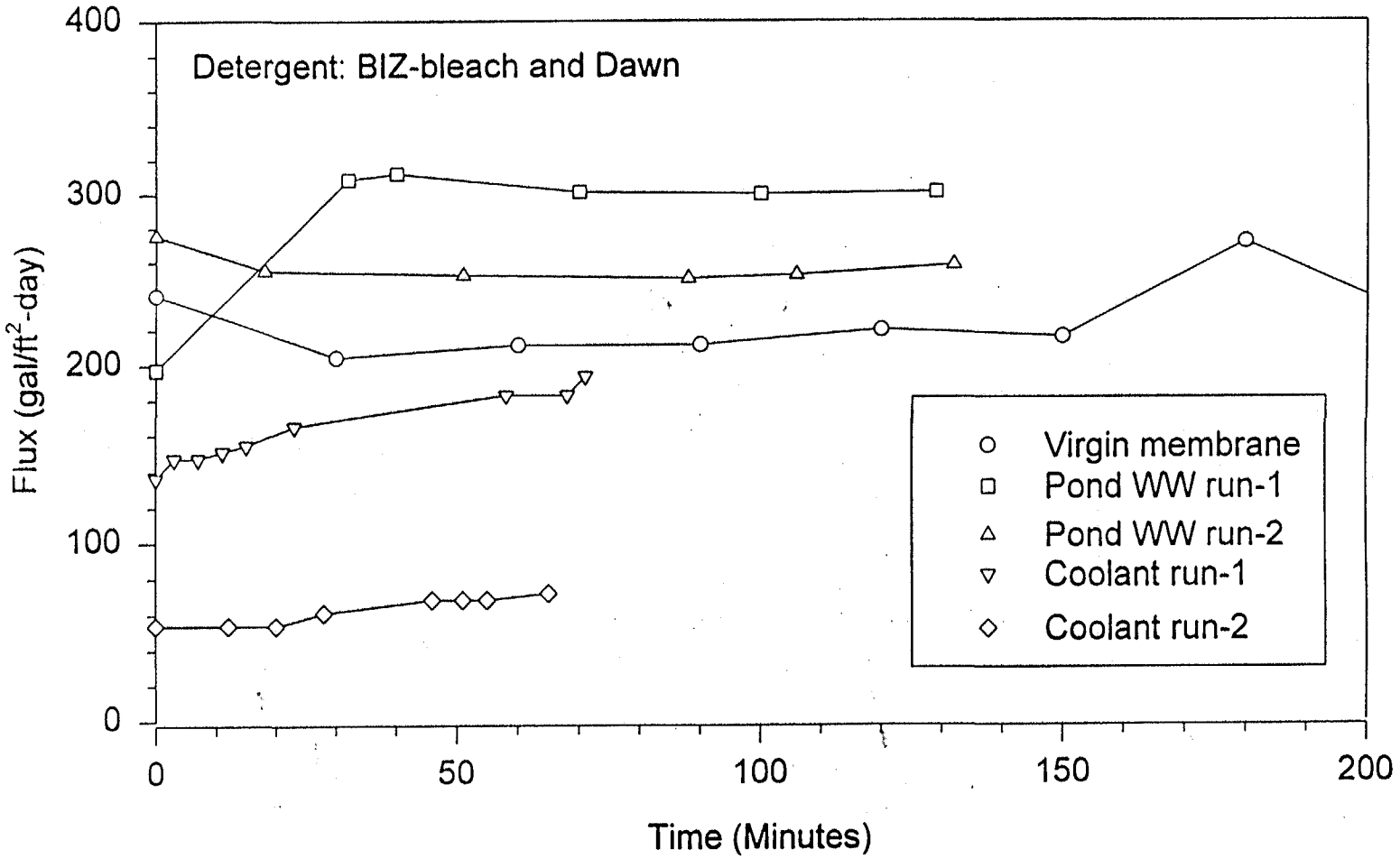


Figure 22. Clean Water Fluxes for Virgin Membrane and After Each Membrane Cleaning.

7.0 CONCLUSIONS

Based on extensive testing of the technology, it is apparent that the SpinTek centrifugal membrane technology is effective in treating oil/grease wastes. Concentration factors and volume reductions as large as 100x and 99 percent, respectively were observed. O/G and TSS removal efficiencies were generally greater than 98 percent. Membrane fouling is a concern for wastes with very high O/G content as is system temperature.

8.0 WORK PLANNED FOR NEXT QUARTER

The following work will be conducted during the third quarter: 1) testing of the technology under strict temperature control using the polymeric membrane employed in second quarter work and 2) treatment of the same O/G wastes using a ceramic membrane.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

The primary technical difficulty was the inability to control temperature of the feed tank contents. A commercial heat exchanger was acquired but was not effective thus, a heat exchanger was designed, constructed and successfully tested by WVU researchers. For future experiments, strict temperature control will be practiced.

ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

Report for Period
ending June 30, 1996

Work Performed Under METC Task 2.4
as Part of the WVU-DOE Cooperative Agreement.
Contract No.: DE-FC21-92MC29467

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

By:
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June 1996

ABSTRACT

The use of electrochemistry is an effective means to remove heavy metal contaminants from aqueous effluent streams. This project deals with the development and testing of novel carbon materials for the electrochemical removal of radionuclides and heavy metal ions from aqueous wastes. Both electroplating and electrosorption are employed for this task. The purpose of this work was to develop and test carbonaceous materials for their ability to perform this task. This is accomplished by using a "packed-bed" of the carbon material in a "flow-through" electrochemical remediation cell.

The concentration of heavy metal ions and radionuclides in waste streams is usually very low: typically 1 to 1000 ppm. These low concentrations lead to relatively low current densities and low conversion of electroactive species at electrodes with a small surface area. Therefore, the electrolytic cell must be designed to increase the degree of conversion of the electroactive species (metal ion) as it passes through the remediation cell. This increase in conversion can be obtained by two means: (1) the use of a 3-dimensional electrode (increase surface area and residence time) and (2) turbulence (rotated electrode or flowing stream). The desire is to create a very high ratio of electrode surface area to electrolyte volume within the cell, coupled with turbulent mass transport within the electrode material. In this type of electrode, it is possible to control conversion efficiency using the length of electrode material through which the contaminated waste must pass.

This purpose of this work is to develop and test a cathodic material with an extremely large ratio of surface area to volume. This will be accomplished by using a packed-bed of conductive carbon, either as carbon fibers or carbon foams. Activation of these materials can lead to even greater surface areas. The increased surface area can help minimize the length of electrode through which the solution must pass. This decreased distance leads to reduced resistance to solution flow.

The removal of cadmium, lead, copper, nickel, strontium and uranium from aqueous samples using a small-scale model of the electrolytic cell has already been demonstrated in our laboratory. Removal efficiencies above 90% have been observed for continuous removal over a 72 hour period. This corresponds to an effluent concentration below 10 ppm for a inlet solution feed of 100 ppm. This work shall examine the use of this electrolytic remediation cell on waste streams containing radionuclides and "real" samples (obtained from industrial partners) and for the selective removal and recovery of precious metals. The final objective is to transfer this technology for "on-site" use in industrial applications.

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EXECUTIVE SUMMARY

Novel types of carbon materials have been tested for their ability to remove radionuclides and heavy metal ions from aqueous samples via electroplating and electrosorption. Removal efficiencies above 90% have been obtained for the reductive removal of cadmium, lead and copper. Long-term removal of lead over using electroplating on carbon nanofibers, vapor grown carbon fibers and carbon foam decreased the concentration of a 100 ppm lead feed to less than 10 ppm. Even after 72 hours, the carbon nanofibers showed no sign of saturation. For the 72 hour period, a capacity of 1.025 $g_{Pb}/g_{carbon\ fibers}$ is realized. An even greater capacity is expected at saturation.

Removal via electrosorption using carbon nanofibers produced similar results, but with an early drop-off of efficiency and a much smaller capacity (7.1×10^{-4} $g_{Pb}/g_{carbon\ fibers}$ for a 57 hour period). This is due to the neutralization of the charge on the carbon surface caused by the electrosorption of the positively charged metal ions. It is envisioned that for aqueous streams, electrosorption will be applied to remove radionuclides and other metal ions that have reduction potentials more negative than that of water. The removal of radionuclides would decrease the volume of radioactive waste produced from the clean-up of decommissioned nuclear sites.

The recovery of metals was demonstrated using lead ions. The recovered effluent resulted in a 7-fold concentration of lead after reversal of the potential applied to the carbon material. This resulted in a decrease in the volume of lead waste by one-seventh.

The removal of nickel ions from solution directly onto the bare carbon materials was inefficient. By plating a small amount of copper onto the carbon surface prior to use, enhanced removal efficiencies were obtained. At pH 7.0, a removal efficiencies of 89% was achieved.

The electrosorption of strontium was also examined. A removal efficiency of 34.4% was achieved using "pelletized" carbon nanofibers. At pH 10.0 and using a coating of MnO_2, removal efficiencies were improved to 68%.

The electrolytic removal of uranium was exceptional. For a inlet feed concentration of 100 ppm uranium, an effluent stream was obtained with uranium concentrations near or below 1 ppm. Long-term removal of uranium was accomplished using the smaller remediation cell. For a 42 hour period, excellent removal of uranium was achieved (99%). Drop-off in removal efficiency was observed beyond 42 hours due to clogging of the carbon material. Recovery and concentration of the uranium waste decreased the volume from 2 liters down to 95 mL and concentrated the uranium to 1543 ppm. This is equivalent to a capacity of 0.15 $g_{uranium}/g_{carbon}$.

ELECTROCHEMICAL REMEDIATION OF RADIONUCLIDES AND HEAVY METAL IONS

INTRODUCTION

PURPOSE

The purpose of this research was to assess the feasibility of using novel carbonaceous devices to remove radionuclides and heavy metal contaminants from aqueous streams. This work addresses the fabrication, behavior and analytical utility of these novel carbonaceous materials. Electrochemical techniques were employed to meet this objective.

BACKGROUND

Currently, there exists a rather serious problem associated with several nuclear production and processing facilities in the US. Over the years, large quantities of low-level radioactive waste, some in aqueous solution, have been accumulating at these sites in storage. Moreover, at some sites, this material has already leaked out and contaminated the soil over wide surface areas. In order to attack this problem, the DOE has expressed its desire to investigate new remediation techniques by promoting extremely applied and focused research programs. The work centers on the development of new procedures to remove and concentrate heavy metals and radionuclides from these low-level wastes. Most of the waste is in the form of aqueous solution and the new technique must be capable of reducing the concentration of contaminants down to parts per million (ppm) and in some cases parts per billion (ppb). Since the quantity of these wastes is large, the remediation procedure must be efficient and capable of being scaled-up in a predictable manner.

Industrial contacts have voiced a desire to remove several heavy metals from various aqueous streams. Heavy metal contaminants discussed include nickel, cadmium, copper, lead and chromium. Based on the standard reduction potentials, all of these metals should be excellent candidates for the technique developed in this program.

A technique which can be used to remove metal ions from solution is the electrochemical reduction or adsorption of the metal ions. In this procedure, a conductive surface acts as a electrode. A negative potential is applied to the electrode surface. The metal ions in solution are transported to the electrode surface via convection. Upon reaching the electrode surface, the metal ions are

adsorbed. If the potential is sufficiently negative the ions will be reduced and plated onto the electrode surface. In either case the metal ions are removed from the aqueous waste. While such a procedure is effective at lowering the concentration of the metallic species on the small scale, application at the large scale has been hindered due to the relatively small surface area of the metallic electrodes. This work assesses the performance of novel carbonaceous materials with large surface areas to remove radionuclides and heavy metal ions and their ability to be scaled up to applicable size.

Electrochemical techniques pertain to measurements involving the flow of electrons during a reduction-oxidation (redox) reaction. These measurements involve current, potential, charge and/or time as the primary variables. Electrochemical studies typically incorporate the use of a three-electrode system. This system includes a working, reference and auxiliary electrode. The redox reaction occurs at the surface of the working electrode as a result of the applied potential. Therefore it is critical to chose a suitable material for the working electrode. To be effective, the material must meet certain requirements. The electrode material should exhibit good electrical conductivity, be chemically inert over the potential region of interest, show favorable electrochemical behavior with the analyte(s), have a low background current and have an easily reproducible surface (1). Carbon materials are well suited for use as working electrodes. Graphite (2,3), carbon paste (4), glassy carbon (5) and reticulated vitreous carbon (RVC) (6) are a few examples of carbonaceous materials that have been used as working electrodes. A detailed discussion of carbon electrodes has been compiled by Dryhurst and McAllister (7).

Carbonaceous materials have been used to produce flow-through porous electrodes. Electrode materials have included graphite chips (8) or granules (9), glassy carbon grains (10), crushed graphite (11), screens of graphite (12) or carbon (13) and RVC (14). These porous flow-through electrodes have been used to remove metal ions from aqueous solutions. This is of major importance to industrial processes and environmental applications. The large surface area of porous flow-through electrodes makes them excellent candidates for the removal of metal ions from solution. Removal efficiencies approaching 100% can be achieved (14).

Discussions with METC personnel have ascertained the identity of several transuranics and radionuclides of concern. These metals include uranium, plutonium, cesium and strontium. Due to their large negative standard reduction potentials and the instability of the solid metals in water, electrosorption will be assessed for their removal. Due to the hazards of working with radioactive species, non-radioactive isotopes or surrogates will be employed. Strontium and uranium can readily be measured using polarography.

Once the metals have been removed from solution and accumulated onto the electrode surface, they can be recovered by reversing the applied potential. To recover selectively the metals, careful control of the applied potential is crucial. By applying a potential sufficiently negative to electroplate only one metal, it can be removed from the stream. Subsequent remediation cells with increasingly more negative potentials can be used in series to remove other metals. Each metal can thus be removed and recovered selectively.

The present work addressed the use of various carbon materials, including carbon fibers and porous carbon foams, to produce porous flow-through electrodes for the removal of metal ions from aqueous media. The resulting effluent was monitored downstream to assess the decrease in analyte concentration and hence the electrode efficiency.

EXPERIMENTAL METHODOLOGY

A schematic diagram of the apparatus used to carry out these experiments is shown in Figure 1. It was designed in the WVU lab and was produced by the WVU machinist. The carbonaceous material to be tested is placed between a platinum mesh screen and a filter. The platinum mesh is used to establish electrical contact to the carbon material. The purpose of the filter is two-fold. The filter prevents the carbon from flowing out of the cell and acts to distribute the solution evenly throughout the carbon bed. A predetermined potential is applied to the carbon material using a potentiostat. The sample solution is pumped through the carbon material and the unwanted metal contaminants are removed.

For the cathodic removal of metal ions, a potential more negative than the standard reduction potential of the metal ions of interest is applied to the working electrode (see Table I). This applied potential forces the plating of the metals onto the electrode surface thus removing the contaminant metal ions from solution.

Many metals can not be reduced at the electrode surface due to their large negative standard reduction potentials. The problem with these species is that their reduction potentials are more negative than that required to electrolyze water to hydrogen gas (H_2) and hydroxide ions (OH^-). Hence for aqueous solutions, water will be electrolyzed before these metals are electroplated onto the carbon surface. In these cases, electrosorption is utilized. Electrosorption incorporates a negative potential which is more positive than the potential to reduce the metal ion. The positive charge of the metal ion is attracted to the negative charge on the electrode surface. The metal ions are loosely bound to the electrode surface due to electrostatic forces and are removed from the aqueous stream. Due to the neutralization of charge on the electrode surface,

lower removal efficiencies are expected. It is anticipated that most radionuclides will be removed by electrosorption since they generally have large negative standard reduction potentials (see Table I, for examples of Sr^{+2} and U^{+2}).

Experimental parameters require optimization to maximize the removal of these metal ions. These parameters include pH, electrolyte concentration, solution flow rate, applied potential and carbon bed thickness. Conversion efficiency, long-term stability and loading capacity must be assessed as well. Finally, the pressure drop and flow rate characteristics of the solution flowing through the carbon bed need to be evaluated.

CARBON SAMPLES

Several carbonaceous electrode materials have been obtained from a variety of sources for comparison. To date, the following samples have been obtained.

- Reticulated Vitreous Carbon (RVC) Foam (Duocel®, 3% density) from Energy Research & Generation, Inc. (ERG, Oakland, CA). 10, 20, 30, 45, 80 and 100 pores per inch (ppi).
- Vapor Grown Carbon Fibers (VGCF) (Pyrograf III, Lot ADNH, 104-107) from Applied Sciences, Inc. (ASI, Cedarville, OH).
- Vapor Grown Carbon Fibers (Pyrograf III, Lot AN-201, "as grown") from Applied Sciences, Inc.
- Vapor Grown Carbon Fibers (Pyrograf III, Lot AN-201, "oxidized") from Applied Sciences, Inc.
- Vapor Grown Carbon Fibers (Pyrograf III, Lot P-2, "pelletized", regular "AN" fiber) from Applied Sciences, Inc.
- "Coal-Derived" Carbon Foam (23 NMP, Sample # 001) from WVU (Morgantown, WV).
- "Coal-Derived" Carbon Foam (23 NMP, Sample # 001, crushed foam, 420-707 μm) from WVU.
- Carbon Nanofibers (#1094-A) from PSU (University Park, PA).
- Carbon Nanofibers (#1094-B) from PSU.
- Carbon Nanofibers (NF46, unsupported) from PSU.

- Graphite Fiber Mats from PSU.
- Carbon Nanofibers grown on Graphite Fiber Mats (#0295) from PSU.
- Graphite Felt (#0695-A) from PSU.
- Carbon Nanofibers grown on Graphite Felt (NF46, F100, CN37 and CF37 from PSU.

RETICULATED VITREOUS CARBON (15)

Reticulated Vitreous Carbon (RVC) is an open-pore material with a honeycomb (foam) structure (14). RVC is a form of carbon that combines some of the properties of glass with normal industrial carbon. RVC has a large void volume (97%) and a small surface area (0.09 m^2/gram). It has a self-supporting rigid structure, a low resistance to solution flow and is resistant to temperatures up to 600 °F in air (16). A more thorough discussion of vitreous carbon is available in the literature (17-21). The samples obtained had various pore sizes. Sizes included 10, 20, 30, 45, 80 and 100 ppi (pores per inch). The 100 ppi RVC foam was tested in our study.

VAPOR GROWN CARBON FIBER (22)

The VGCF manufactured by Applied Sciences, Inc. (ASI) is produced by a combination of catalytic and chemical vapor deposition processes which allow for control of the fiber dimensions, such as filament length and diameter. Lengths are available from 1 mm to tens of centimeters and diameters can vary from under 0.2 μm to over 100 mm. The resulting fiber has a lamellar morphology and is highly graphitic. Cross section and overall views of these samples were provided in the first year's quarterly reports.

"COAL-DERIVED" CARBON FOAM

These particular samples of carbon foam are made from coal-derived pitches produced at WVU by a novel solvent extraction process. By careful control of experimental parameters, an ultra-low ash foam precursor (pitch) is produced which upon careful heat treatment results in a low-density carbon foam structure. This "green" foam is then calcined at temperatures around 1000 °C and a highly conductive material results. The foam has an open-cell structure, enabling it to be used as an efficient carbon electrode.

CARBON NANOFIBERS

The carbon nanofibers were produced by our first year collaborators at The Pennsylvania State University (PSU). The nanofiber material is a microscopic version of a carbon fiber. It is produced by the metal catalyzed decomposition of certain hydrocarbons (23-24). Various degrees of graphitization are possible.

GRAPHITE FIBER MATS and GRAPHITE FELTS

Obtained commercially and supplied to WVU by Dr. Baker at The Pennsylvania State University.

All materials were treated with a dilute solution (10%) of nitric acid prior to use as the electrode material. If necessary to help activate and clean the surface, mild electrochemical of chemical methods were employed.

WORK PERFORMED THIS PERIOD

EXPERIMENTAL

Reagents:

Stock solutions of cadmium, lead, copper, uranium, strontium and nickel were prepared using atomic absorption standard solutions (Fisher Scientific, Fair Lawn, NJ) and deionized water. The deionized water used was further purified using a NANOpure™ ultrapure water purification system (Barnstead-Thermolyne, Dubuque, IA). These solutions were stored in polyethylene containers to avoid contamination. The 1.0×10^{-4} M mercury ion solution used for anodic stripping voltammetry was prepared from $Hg(NO_3)_2$ as needed. The mercury ion and sample solutions were prepared in 0.1 M KNO_3 (potassium nitrate) supporting electrolyte. The pH was adjusted using nitric acid. (All chemicals were certified ACS grade purchased from Fisher Scientific unless otherwise noted).

Surface Area Measurements:

The surface area of the samples has been determined and the data are shown in Table II. The surface areas were obtained at WVU using a Gemini III 2375 Surface Area Analyzer (Micrometrics Instrument Corporation, Norcross, GA). Standard operating procedures have been followed as outlined in the operator's manual.

A pre-weighed sample of the carbonaceous material was placed into a clean, dry sample tube. The sample was thoroughly de-gassed using nitrogen. The dewar was filled with liquid nitrogen and the system prepared for analysis.

The sample tube was connected to the analysis port and the balance tube was connected to the balance port. Care was taken to minimize exposure of the sample to air. The doors to the sample station were closed and the analysis initiated. Saturation pressure was set to 740.53 mm Hg and the evacuation rate to 599 mm Hg/min. The Gemini III 2375 performs automated analysis. It is capable of performing simultaneously BET multipoint and single point surface area, Langmuir surface area, t-method micropore and BJH adsorption/desorption distribution. The resulting data were recorded on an Epson plotter (Model P84FA).

Construction of the Remediation Cell:

The remediation cell (see Figure 1) was produced using a Lexan™ rod (5.0 cm diameter and 6.0 cm long). The flow channel (1.6 cm i.d.) was drilled through the Lexan™ body. A threaded Lexan™ plug was used to press the carbonaceous material between a platinum mesh and a piece of filter paper. The pressure on the carbon material can be easily adjusted by turning the threaded plug. The Ag/AgCl reference electrode (3M NaCl, Model RE-4, BioAnalytical Systems, Inc. (BAS) West Lafayette, IN) was introduced through a Lexan™ sleeve positioned 90 degrees to the flow channel. Leakage was prevented using an o-ring and compression fitting. A piece of coiled platinum wire inserted at the outlet of the cell was used as the auxiliary electrode. Contact to the working electrode was established via a platinum mesh.

Evaluation of Carbonaceous Materials:

The carbonaceous material to be studied was pretreated to clean, oxidize and assist in the wetting of the carbon surface. This was accomplished by placing the carbon material in a dilute solution (10%) of nitric acid overnight in a covered beaker. The material was then thoroughly washed using deionized water. The carbonaceous material was weighed and then positioned into the metal remediation cell using a clean glass rod.

The threaded plug is used to press the carbonaceous material between a platinum mesh and a piece of filter paper. The pressure on the carbon bed can be easily adjusted by turning the threaded plug. Rigid samples, such as RVC, were positioned using a snug fit. Electrical contact to the working electrode was established using the platinum mesh. The reference electrode was inserted into the sleeve and all three electrodes were connected to the potentiostat. The cell was connected to the pump using Tygon tubing and a 0.1 M KNO_3 electrolyte

solution was pumped through the flow cell. In order to help remove air bubbles and wet the electrode surface, a mild electrochemical pretreatment was used. The remediation cell was held at +1.00 V for 10 minutes followed by -1.00 V for 10 minutes.

The performance of the carbonaceous material under study was tested by placing a solution containing a known concentration of metal ions into the sample reservoir. The solution was then allowed to pass through the remediation cell at a known flow rate and applied potential. The potential of the remediation cell was controlled using a Power Module (Model PWR-3, BAS). The performance was assessed by measuring the metal ion concentration in the effluent and comparing it to the initial ion concentration. The percentage efficiency of the remediation cell is equal to the percentage of metal ions removed from the solution by the remediation cell. (For these studies, the effluent was collected in Nalgene bottles for subsequent analysis via voltammetry and/or atomic absorption).

Anodic Stripping Voltammetry:

The thin-layer flow cell was purchased from BAS (Model LC-44-01000). The working electrode was glassy carbon disk (0.3 cm diameter) over which the solution flows. Two 50 μm spacers were used to produce the flow channel and direct the sample solution across the carbon disk. Prior to use, the glassy carbon disk was polished using successive slurries of 1.0, 0.3 and 0.05 μm alumina until a mirror-like surface was obtained. The glassy carbon disk was then rinsed thoroughly with deionized water and assembled. All potentials were measured relative to the Ag/AgCl reference electrode (BAS, Model RE-4). Stripping voltammograms at the thin-layer flow cell were obtained using the BAS Model CV-27 Voltammograph in conjunction with a Hewlett Packard Model 7044B X-Y Recorder.

Polarography:

Polarographic data was obtained using a Static Mercury Drop Electrode (SMDE) (Model 303A, EG&G Instruments, Princeton Applied Research, Princeton, NJ) in conjunction with a potentiostat (Model 263A, EG&G) and interface (Model 507, EG&G). This system has been received and has been assembled. Upon assembly and calibration, this instrument was utilized to measure the uranium ion concentrations in the effluent stream. (The 100 ppm solution being tested is below the detectable limits of Atomic Absorption. Polarography can be used to measure uranium concentrations down to 20 ppb). The SMDE can be used to measure many other metals in the ppb to ppm range.

Atomic Absorption:

Spectroscopic data were obtained using an Atomic Absorption Spectrophotometer (Model 2380, Perkin-Elmer, Norwalk, CT). Procedure and experimental conditions were outlined in the Pekin-Elmer "Analytical Methods of Atomic Absorption Spectrophotometry" Cookbook. All standards and samples were matrix-matched prior to analysis.

RESULTS and DISCUSSIONS

Several carbonaceous materials were examined for their performance as the cathode material. Each sample was tested to determine the effect of adsorption (no applied potential) and electroplating. Their performance was evaluated on their ability to remove the metal ions from solution.

To confirm minimal contribution from the platinum mesh to the metal removal, the system was first tested in the absence of any carbonaceous material. The response of the original feed solution was compared to the response of the effluent collected at -1.00 V. It was shown that the platinum mesh does not contribute significantly (<2%) to the removal of the metal ions. Therefore, the removal of the metal ions is due to their interaction with the carbonaceous material and is not significantly influenced by the platinum mesh.

In order to assess electrosorption, the carbon electrodes were tested for their ability to remove cadmium and lead at potentials more positive than that required to reduce the metal ions. The removal of cadmium was examined at various potentials above and below its theoretical reduction potential. Figure 2 shows the ASV response for a cadmium solution passed through the remediation cell at these potentials. Based on the initial cadmium feed concentration (100 ppb), the potential at which cadmium should be reduced is -0.58 V. Electrosorption removed 46% of the cadmium from the solution at -0.20 V and 78% at 0.40 V. At potentials more negative, electroplating removes 89% at 0.60 V, 91% at 0.80 V and nearly all (99%) at -1.00 V. The percentage of cadmium removed versus applied potential is also shown (inset).

Figure 3 shows the response for lead under the same conditions. The theoretical reduction potential for lead is -0.54 V. Removal of lead via electrosorption is shown also to occur at potentials more positive than the reduction potential. The removal efficiencies were 88% at -0.20 V and 92% at -0.04 V.

Continuous removal of lead from an aqueous stream using electroplating and electrosorption was used to demonstrate the long-term effectiveness of carbon nanofibers. The lead solution was passed through the remediation cell and the ions were removed by applying the desired potential to the carbon nanofibers. A potential of -1.00 V was applied to the remediation cell to remove lead ions via electroplating. Over a 72 hour period, removal efficiencies of 89% or greater were achieved for an inlet concentration of 100 ppm lead. Calculation of the lead removed over this period demonstrates a capacity of 1.025 $g_{Pb}/g_{carbon\ fibers}$, but it should be stressed that even at 72 hours, the carbon showed no signs of saturation (see Figure 4).

Removal of lead ions via electrosorption was carried out using a potential of -0.40 V. For an inlet lead ion concentration of 100 ppb, good removal efficiencies (90%) were obtained for the first 12 hours (see Figure 5). After that time a noticeable decrease in efficiency is evident. The removal efficiency drops to less than 50% after 57 hours. This decrease in removal efficiency is expected due to the neutralization of charge on the electrode surface. Regeneration of the carbon nanofibers would be required to maintain high removal efficiencies. For the first 12 hours of removal a capacity of 1.9×10^{-4} $g_{Pb}/g_{carbon\ fibers}$ is obtained. At 57 hours this capacity increases to 7.1×10^{-4} $g_{Pb}/g_{carbon\ fibers}$. Electrosorption of lead using a 100 ppm lead feed was attempted. Due to the smaller capacity of the carbon nanofibers when using electrosorption, the efficiency should drop off very quickly. As expected, within the first two hours the removal efficiency dropped to less than 20%.

The final desire is to recover the metals once they have been removed from the aqueous stream. It is possible to recover the metal ions plated on the electrode simply by reversing the potential. The metal ion concentration in the resulting effluent is more greater than that of the feed. Electrodeposition and the subsequent recovery from carbon nanofibers was demonstrated with a 100 ppm lead ion feed. The lead ions were removed from the aqueous stream using an applied potential of -1.00 V. Subsequent recovery of the lead at an applied potential of +1.00 V, produced an effluent stream more concentrated in lead. The lead concentration in the recovered effluent was 730 ppm, demonstrating a 7:1 concentration of the waste stream. Individual metal ions can be removed and recovered selectively by these means.

A summary of the electrodeposition removal efficiencies for the carbon samples tested to date are shown in Table III. These results demonstrate that carbonaceous materials are extremely effective for the removal of heavy metal ions from solution.

Industrial Application:

Contact has been established with Dr. Paul Brezovec at Concurrent Technologies Center (CTC), Johnstown, PA. It has been proposed that the electrochemical method developed in this research be applied to their nickel-plating line for the removal and recovery of nickel. The final rinse stage produces an aqueous waste contaminated with nickel. The objective is to purify the rinse water for reuse and to recover the nickel for recycling back into the plating process.

Contact has been made with Dr. Dave Szlag of the Environmental Protection Agency (EPA) in Cincinnati. The desire is to remove lead from aqueous solution obtained by washing lead from the contaminated soil on military firing ranges.

A local plating industry, Swanson Plating Company (Morgantown, WV) has been identified as a source of "real" samples for testing the remediation cell. Identification of the metals and acquisition of samples is ongoing.

Removal of nickel at the experimental conditions used for lead and cadmium resulted in low removal efficiencies. Due to the unique chemistry of nickel, careful attention must be given to increase the removal. Table IV demonstrates the need for tailoring the removal process of nickel. By applying a more negative potential (i.e. -1.60 V) enhanced removal efficiencies are obtained (97.9%). But at this potential the water is reduced and current is wasted due to the production of hydrogen gas. By simply pre-plating a small layer of copper or mercury, enhanced removal efficiencies are obtained. The removal efficiency is also dependent upon the pH of the contaminant solution. For a 100 ppm nickel solution at pH 7.0, a small layer of pre-plated copper and a remediation cell potential of -1.20 V, 89.1% of the nickel is removed.

Radionuclides:

Two metals have been identified that need to be removed from aqueous wastes generated at several nuclear production and processing facilities: strontium and uranium. Both of these metals are available in non-radioactive forms. Strontium can be easily measured by atomic absorption at all levels under study. Atomic absorption can not be used to determine uranium concentrations below 100 ppm. Therefore, polarography will be used to facilitate the measurement of uranium. Polarography can determine uranium concentrations between 20 ppb and 500 ppm. The "static mercury drop electrode" used for polarography was received this quarter and has been assemble and tested.

No removal of strontium was observed using the untreated WVU foam. This was expected due to the relatively low surface area (0.5 m^2/g) of the "non-activated" carbon foam. Activation of the foam surface could increase the surface area to values necessary for the electrosorption of strontium and such an activation apparatus is in preparation.

The improvement in removal efficiencies using the higher surface area carbon fibers is shown in Table V. Removal of strontium using carbon nanofibers resulted in 5.90 % of the strontium to be removed. Usage of the ASI carbon fibers improved this removal to 34.4%. This improvement is most likely due to differences in the surface properties of the two carbon fibers. Alternative removal schemes, similar to those used for nickel have been examined to improve the removal of strontium from the aqueous waste. The use of a coating of MnO_2 improved the removal efficiency in a pH 11.0 solution to 68%.

The removal of uranium was examined using ASI carbon nanofibers. No removal was observed for adsorption (no applied potential). Upon applying a potential of -1.00 V, almost immediate removal of uranium is seen. Long-term removal of uranium was examined over a 48 hour period. Within the first hour the uranium concentration drops well below 5 ppm and it was not until the carbon material began to clog that any appreciable amount of uranium passed through. Even at 47 hours, when the solution flow has noticeably slowed, the effluent concentration only rose to 16.3 ppm. This large removal is believed to be caused by electrochemically-induced precipitation of the uranium oxide. Results for the long-term removal of uranium are shown in Figure 6.

3-inch Prototype Remediation Cell:

Construction of the 3-inch prototype remediation cell has been completed. A schematic of the apparatus is shown in Figure 7. The assembled system includes a flowmeter to measure flow rates and a manometer to measure the pressure drop across the remediation cell. The remediation cell was produced by machining a 4-inch Lexan™ rod. The 3-inch diameter flow channel was drilled through the Lexan™ body. Via the threaded plug, the depth of the carbon electrode bed can be varied between 0.5 and 4.0 inches. Electrical contact is established in the same manner used in the smaller cell. The prototype has been assembled and parametric studies have begun.

Meetings and Presentations:

During the last quarter, three presentations of this research were made:

The first was on June 12, 1996 at Concurrent Technologies Corporation. The application discussed was the removal and recovery of nickel from the wash baths used in their nickel plating process.

The second was on June 18, 1996 at Applied Sciences Inc. in Cedarville, OH. Discussions are ongoing into how their carbon nanofibers can be altered to improve removal efficiencies. Large amounts of carbon samples are being prepared for use in the 3-inch prototype cell.

The third was on June 19, 1996 at the Environmental Protection Agency in Cincinnati, OH. Application of the electrochemical remediation for the removal of lead from soil washing was the primary application.

CONCLUSION

All proposed objectives have been met to date (see Table VI). An extensive search of the literature has been conducted in the areas of heavy

metal removal, waste water treatment and water remediation. More than 150 papers have been amassed in these areas with special interest in the areas of electrochemistry and electrowinning using carbonaceous material. Further effort has been exerted in order to find applications of this technology to radionuclides.

The thin layer flow cell to be used as the detector for anodic stripping voltammetry has been assembled and has been thoroughly tested. This testing included characterization, calibration and verification. The flow cell will be connected "on-line" and used to monitor continuously the concentration of metal ions in the effluent stream.

The Static Mercury Drop Electrode (SMDE) to be used as the detector for polarography has been assembled and has been thoroughly tested. This testing included characterization, calibration and verification. Polarographic analysis was performed "off-line" and used in particular for uranium.

The Atomic Absorption Spectrophotometer has been similarly tested. The testing has been performed using specific hollow cathode lamps specific for the individual metals under analysis. Spectrophotometric analysis was performed "off-line" for strontium, cadmium, lead and nickel.

The performance of the commercially available RVC as a cathode was satisfactory. Improved removal efficiencies were obtain with the novel carbon materials utilized in this study. Loose carbon nanofibers with a relatively large surface area (200 m^2/g) effectively removed over 90% of cadmium and lead from an aqueous sample. Vapor Grown Carbon Fibers supplied by ASI also worked well for the removal of cadmium and lead by electroplating. The "coal-derived" foam produced in the WVU laboratory was an excellent cathode material. The concentration of lead in the effluent dropped below detectable amounts after only 4 hours. This demonstrated removal efficiencies approaching 100%.

The current industrial application of this technology was for the removal of nickel from a rinse solution used in the plating industry. Upon selection of the proper experimental conditions, a removal efficiency of 89.1% was obtained. This was accomplished by adjusting the pH of the waste stream and by pre-planning a small amount of copper onto the carbon surface to help catalyze the reduction of nickel.

The removal of strontium was demonstrated using carbon nanofibers. Removal efficiencies up to 34.4% were obtained, but removal capacity was soon reached. Other removal schemes with similar metal reaction mechanisms to those used for nickel are being examined. The use of a coating of MnO_2, resulted in a removal efficiency of 68%.

The removal of uranium was examined using ASI "oxidized" nanofibers. Preliminary work demonstrated high removal efficiencies due to the production of a precipitate on the electrode surface. Such large removal efficiencies are due to electrically-induced precipitation. The 48-hour-long study of uranium removal demonstrated excellent results until the remediation cell clogged. Prior to clogging, maximum removal efficiencies were obtained (99%). Reduction of the volume of uranium waste was demonstrated by decreasing the waste volume from 2000 mL to 95 mL, and concentrating the uranium from 100 ppm to 1543 ppm. This demonstrates a large capacity of 0.15 $g_{uranium}/g_{carbon}$. The use of the 3-inch remediation cell and larger quantities of carbon will allow for the treatment of larger volumes of low level radioactive wastes.

WORK PLANNED for NEXT PERIOD

In the next quarter, the following work will be conducted,

- Continue parametric studies on the 3" remediation cell.
- The removal of strontium will be maximized via tailoring the electrosorption process.
- The removal of uranium will be further studied to determine the mechanism of removal.
- Test the remediation cell's ability to remove nickel from "REAL" industrial samples.

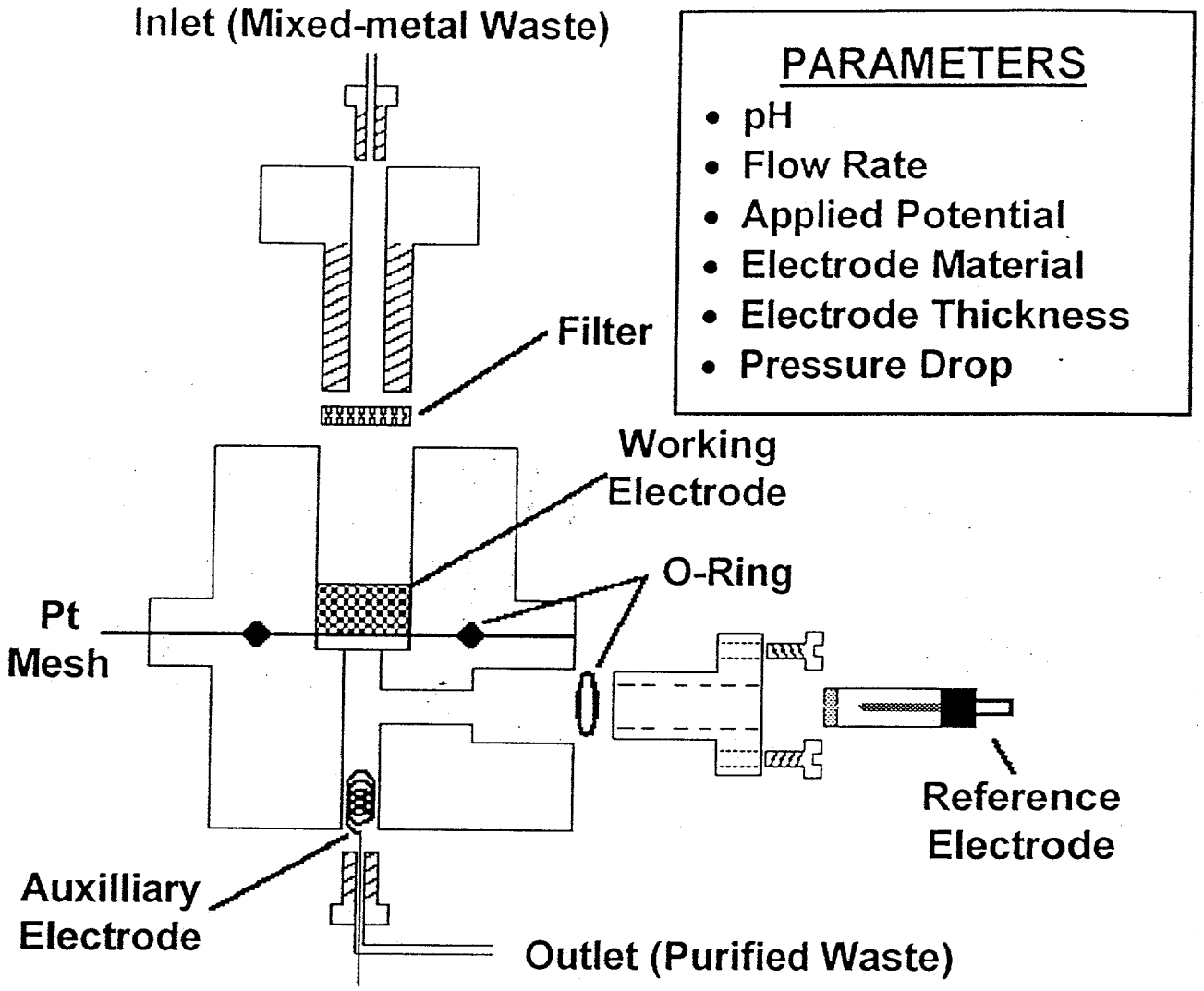


Figure 1. Schematic of Electrochemical Remediation Cell.

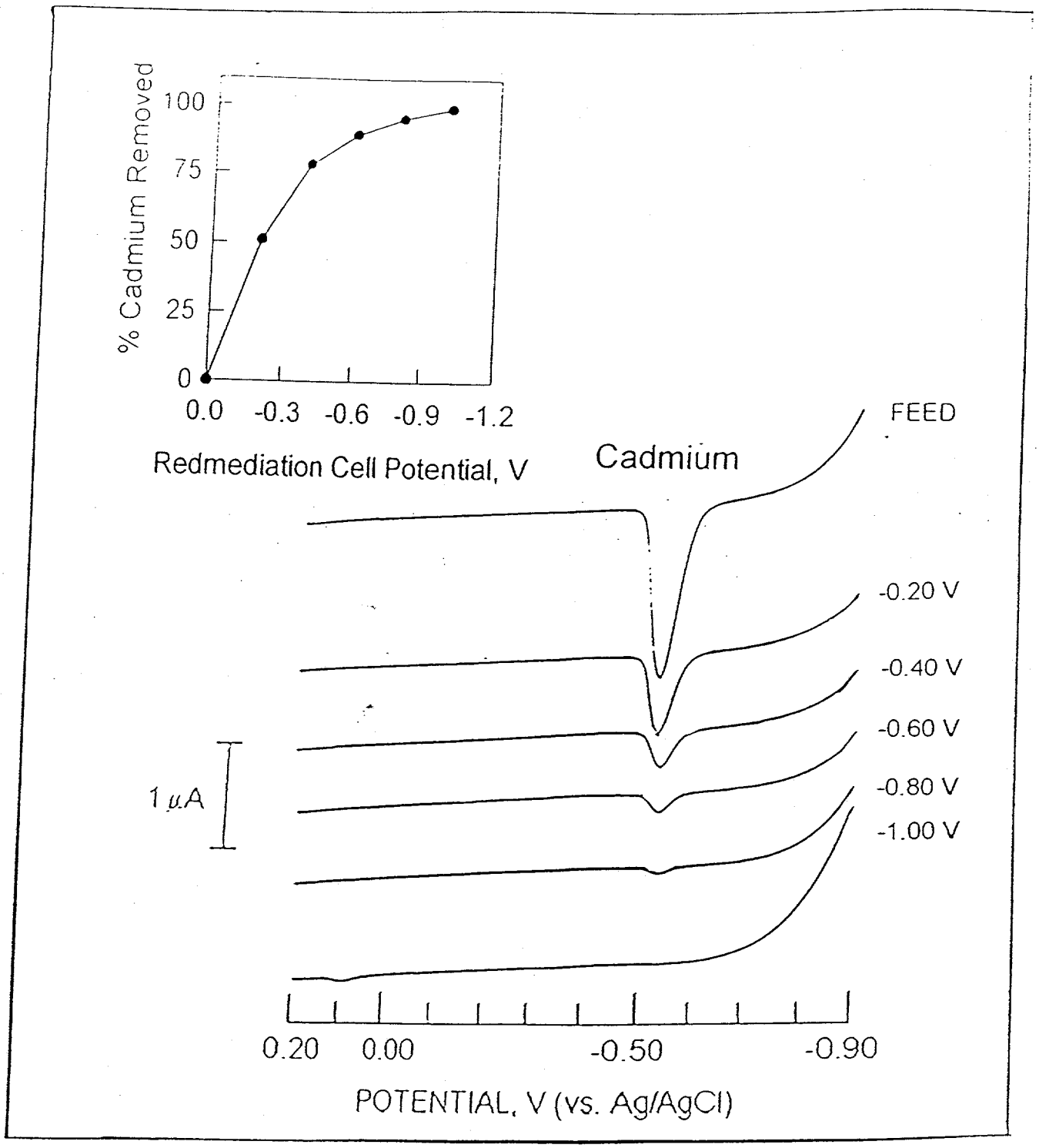


Figure 2. Effect of Remediation Cell Potential on Cadmium Removal.

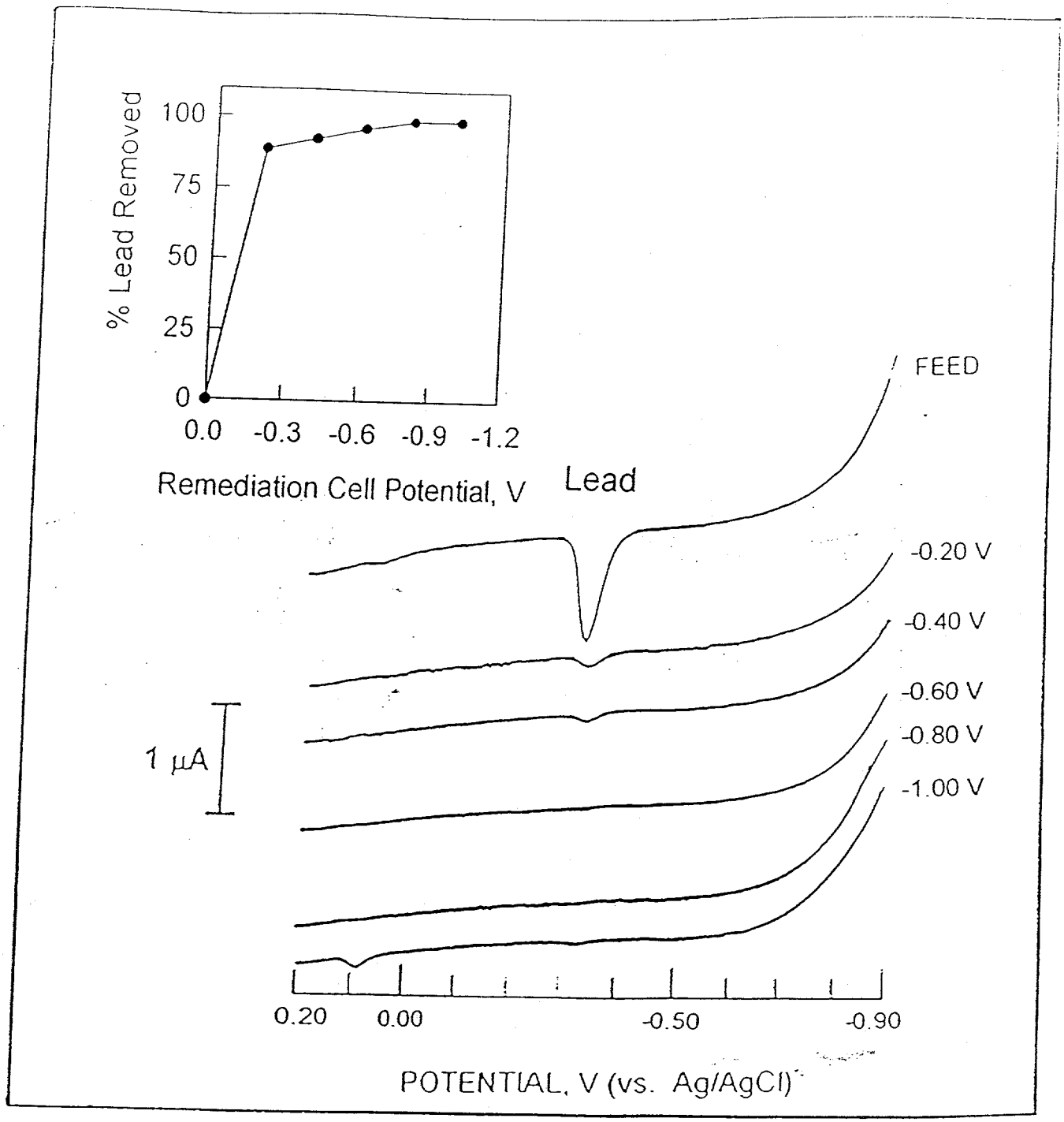


Figure 3. Effect of Remediation Cell Potential on Lead Removal.

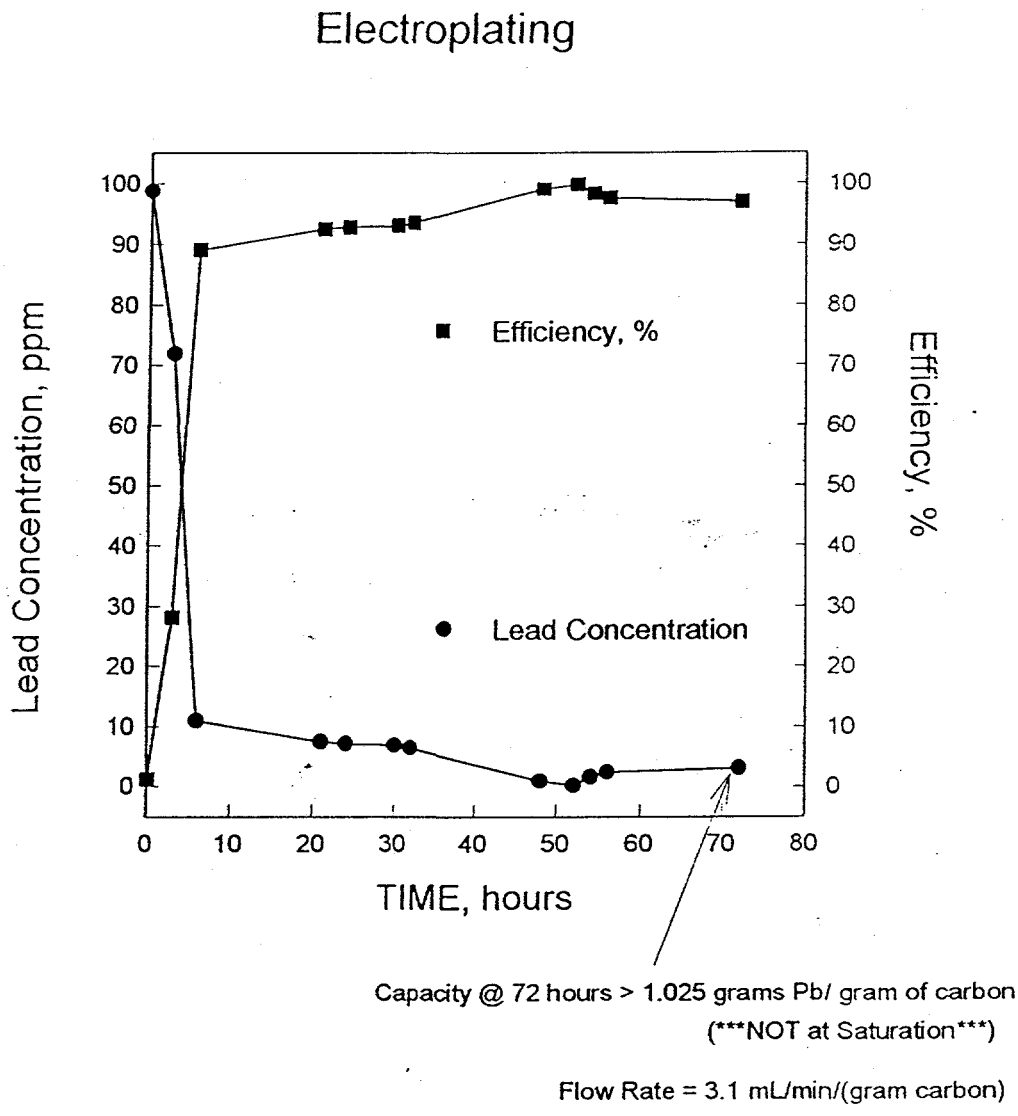


Figure 4. Long-Term (72 hr) Removal of Lead Using Carbon Nanofibers. (E_{CELL} = -1.0 V)

REMOVAL of Pb USING CARBON NANOFIBERS

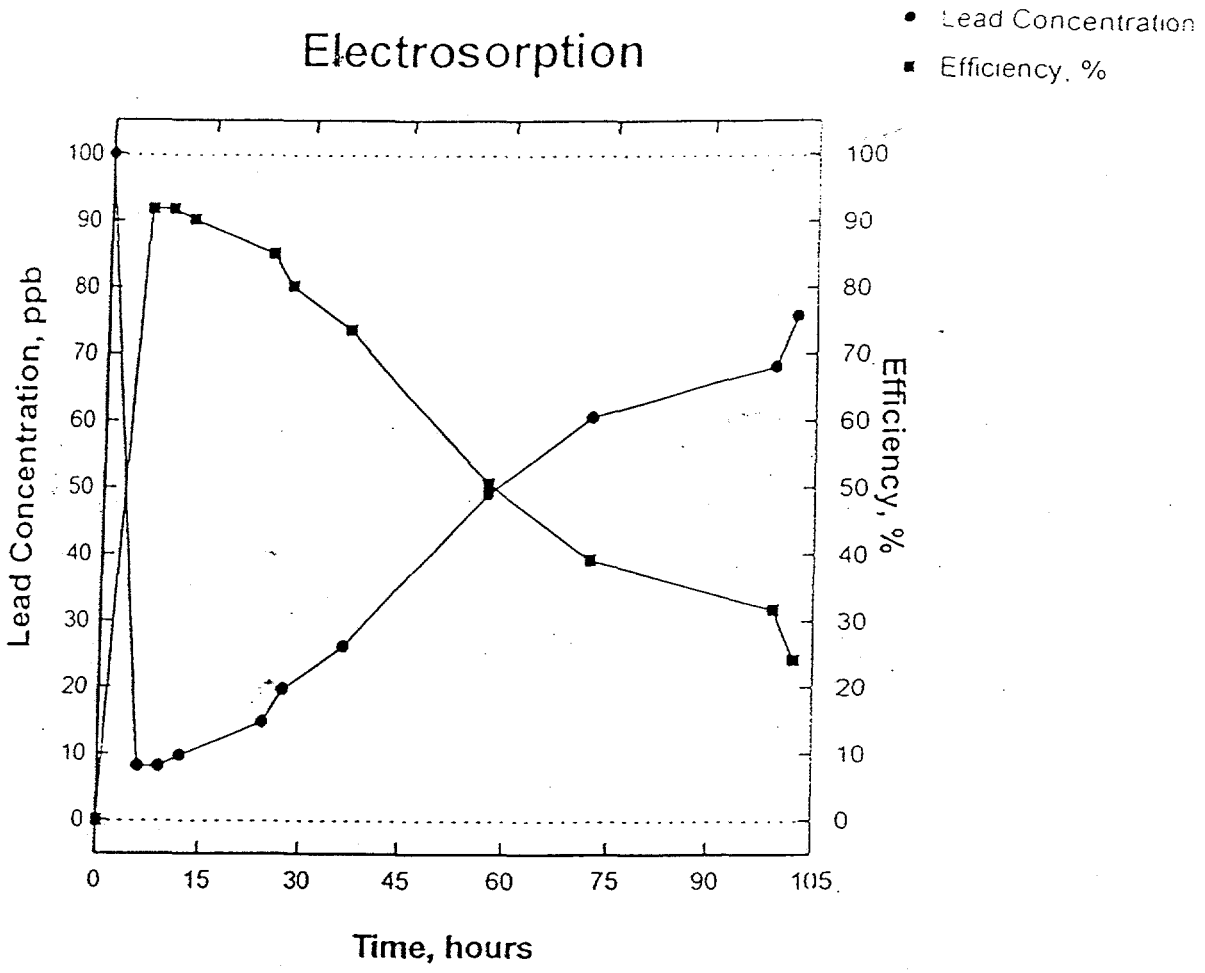


Figure 5. Long-Term (102 hr) Removal of Lead via Electrosorption.
(Conditions: E_{CELL} = -0.40 V)

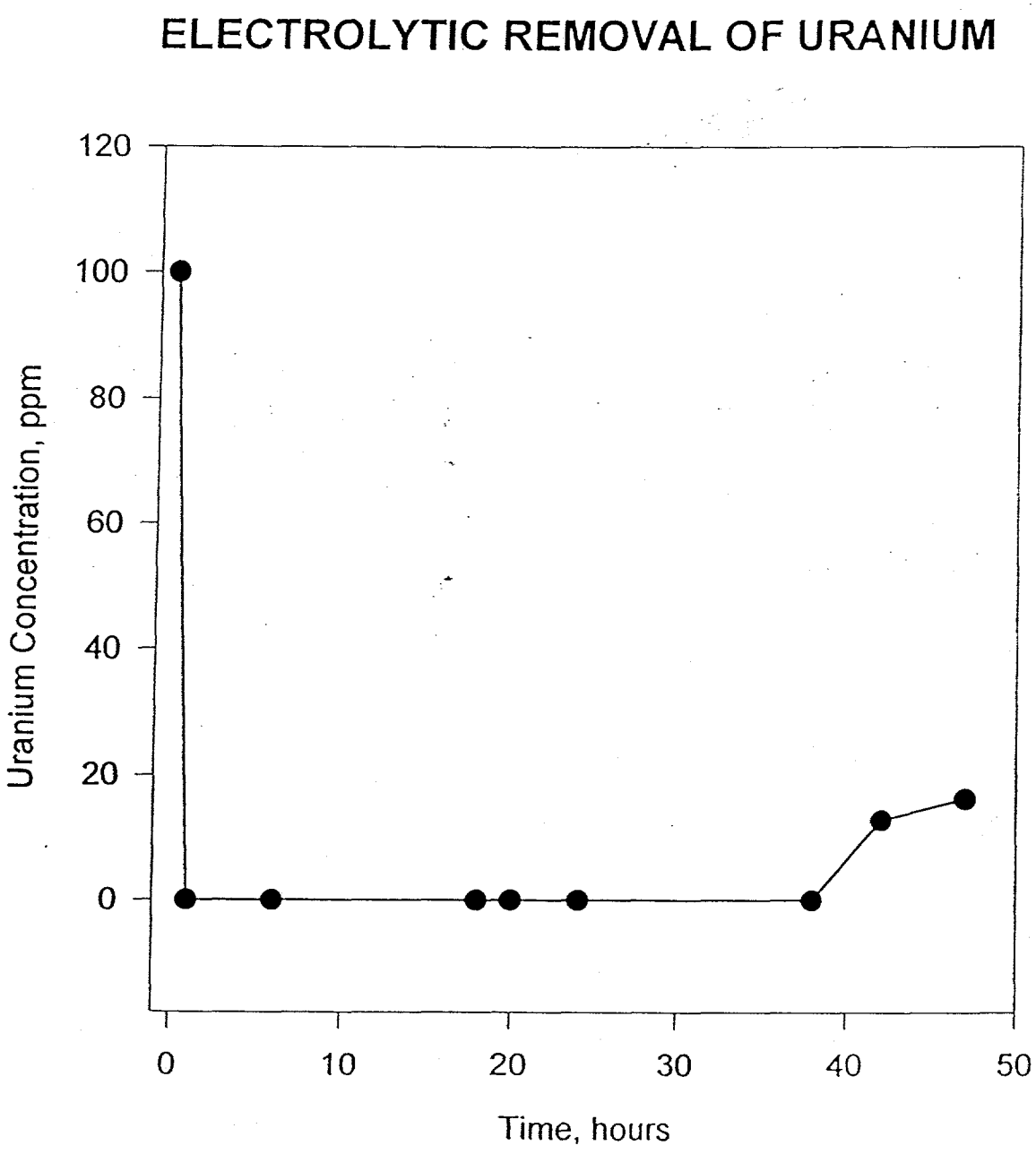


Figure 6. Long-Term 48 hr) Removal of Uranium.
(Conditions: same, E_{CELL} = -1.00 V)

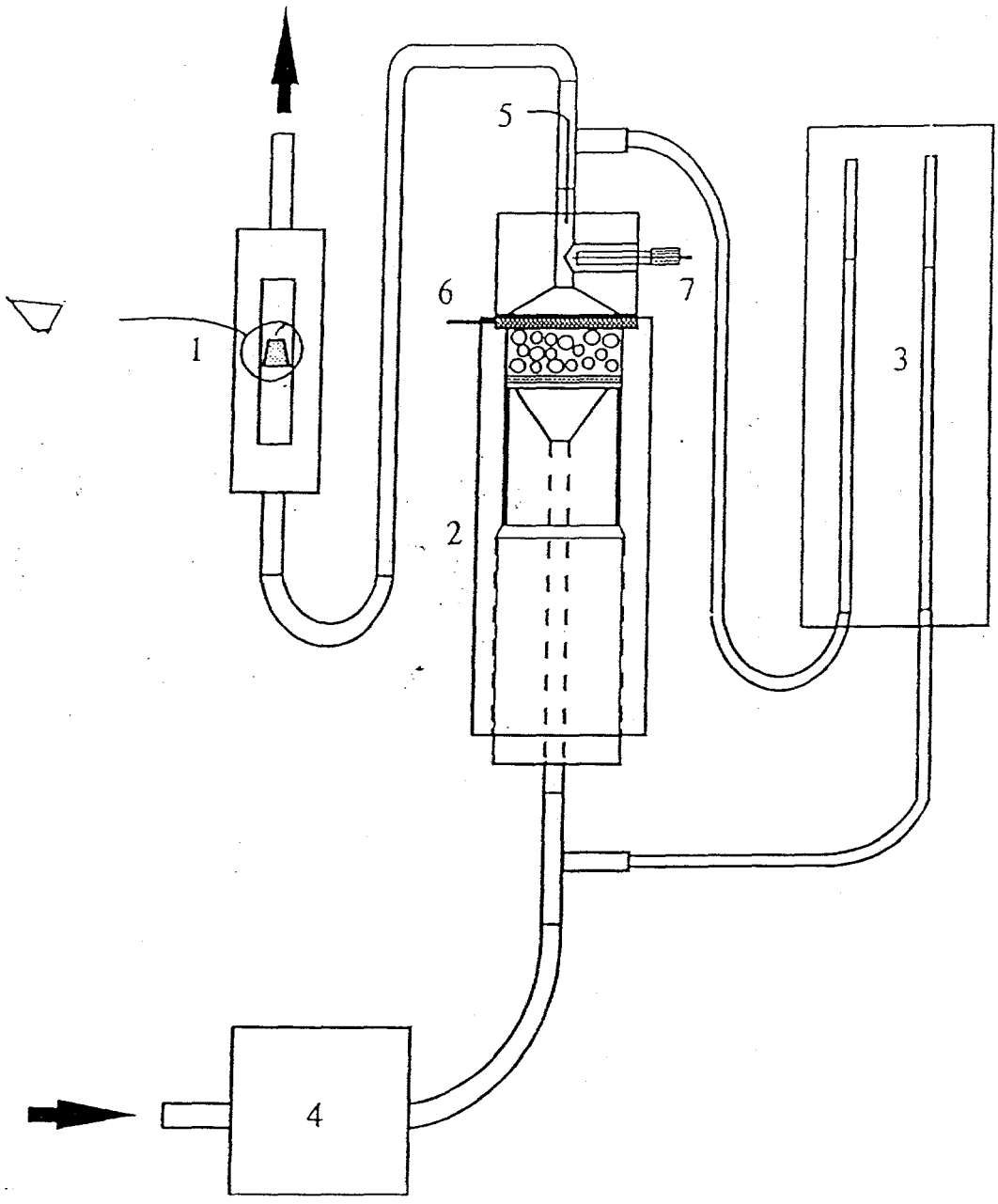


Figure 7. Schematic Diagram of the 3-inch Remediation Cell.
(1-Flowmeter; 2-Cell; 3-Manometer; 4-Pump; 5- Auxiliary Electrode; 6-Pt Contact to Working Electrode; 7-Reference Electrode.)

TABLE I: STANDARD REDUCTION POTENTIALS OF THE METAL IONS OF INTEREST

Reduction Reaction	E, V (vs. Ag/AgCl)
ELECTROSORPTION	
Sr^{+2} (aq) + $2e^-$ → Sr (s)	-3.108
U^{+2} (aq) + $2e^-$ → U (s)	-2.022
$2H_2O$ (l) + $2e^-$ → H_2(g)+ $2OH^-$ (aq)	-1.050
ELECTROPLATING	
Zn^{+2} (aq) + $2e^-$ → Zn (s)	-0.986
Cd^{+2} (aq) + $2e^-$ → Cd (s)	-0.624
Ni^{+2} (aq) + $2e^-$ → Ni (s)	-0.453
Pb^{+2} (aq) + $2e^-$ → Pb (s)	-0.348
Cu^{+2} (aq) + 2e- → Cu(s)	+0.115

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TABLE II: PROPERTIES of CARBON MATERIALS

Surface Areas

Material	Surface Area (m^2/gram)	
	BET	Langmuir
Vapor Grown Carbon Fibers (ASI)		
Regular "AN" Fiber	76.78 (73.6)*	122.66
Oxidized "AN" Fiber	25.78	-
Pelletized "AN" Fiber	20.25 (20.77)*	-
WVU "coal-derived" Foam (23 NMP)	0.52	-
Carbon Nanofibers		
1094-A	115.13 (227.8)*	186.78
1094-B	182.77 (192.3)*	286.03
NF-46	43.28	-
Graphite Fiber Mats	0.59	-
Graphite Mat with Fibers	99.92 (112.8)*	-
Graphite Felt	0.17	-
Graphite Felt with Fibers		
NF46	55.41	-
F100	54.54	-
CF37	13.96	-
CN37	35.31	-
VGCF	76.78 (73.6)*	122.66
RVC		
100 ppi	0.092	-
80 ppi	44.80	-
Activated Carbon	784.32	-

TABLE III: Removal Efficiencies for Cd and Pb

Cathode Material	Cathode Potentia V	Metal Removed	
		Cd	Pb
Platinum Mesh	0.00	0%	0%
	-1.00	0%	9%
RVC	0.00	16%	0%
	-1.00	50%	8%
Nanofibers (1094-A)	0.00	0%	0%
	-1.00	91%	95%
Nanofibers on Graphite Mats	0.00	0%	0%
	-1.00	90%	92%
Graphite Felt	0.00	13%	7%
	-1.00	22%	97%
Nanofibers on Graphite Felt	0.00	0%	0%
	-1.00	46%	99%
ASI Carbon Fibers			
"pelletized"	0.00	-	0%
	-1.00	-	98%
"oxidized"	0.00	-	0%
	-1.00	-	99%
WVU "*Coal-Derived*" Foam			
"crushed"	0.00	-	0%
	-1.00	-	99%

TABLE IV: IMMEDIATE INDUSTRIAL APPLICATION

(REMOVAL OF NICKEL VIA ELECTROPLATING)

$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$ $E° = -1.050$ V

$Ni^{+2}\ (aq) + 2e^- \rightarrow Ni\ (s)$ $E° = -0.453$ V

MATERIAL	SURFACE CONDITION	pH	E_{CELL}, Volts	TIME, hours	% REMOVED
WVU Foams	bare-crushed	3.5	-1.2	2	0.00
		7.0	-1.2	2	0.00
			-1.4	2	68.7
			-1.6	2	**97.9**
	w/ Cu	3.5	-1.2	2	49.0
				4	57.3
		7.0	-1.2	2	**82.4**
				4	**89.1**
	w/ Hg	3.5	-1.2	2	44.3
				4	47.6
				6	50.6

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TABLE V: DOE APPLICATION

REMOVAL OF STRONTIUM VIA ELECTROSORPTION

Sr^{+2} (aq) + $2e^-$ → Sr (s) E° = -3. 108V

$2H_2O$ (l) + $2e^-$ → H_2 (g) + 2 OH^- (aq) E° = -1.050 V

MATERIAL	CONDITION	pH	E_{CELL}, Volts	TIME, hours	% REMOVED
Nanofibers	bare	3.5	-1.00	2	5.90
				4	5.60
			-1.20	2	5.70
				4	3.20
WVU Foams	bare	3.5	-1.20	2	0.00
		7.0	-1.20	2	0.00
ASI	bare	7.0	-1.20	0.5	**34.4**
Nanofibers					
"pelletized"		11	-1.20	0.5	**52.8**
	MnO_2	11	-1.20	0.5	**68.0%**

TABLE VI: PROJECT COMPLETION

ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS of CARBON

Task #	WSB Code	Task Name	Duration	% Complete
1	1.0	Identify Surrogates for Radionuclides.	JAN	100%
2	1.1	Provide List of Surrogates.	FEB	100%
3	2.0	Characterize Carbonaceous Materials.	JAN-OCT	50%
4	3.0	Use Small Remediation Cell to Test Other Carbonaceous Materials.	JAN-OCT	50%
5	3.1	Assess Carbon Material's Ability to Remove Heavy Metals and Radionuclides	JAN-DEC	50%
6	4.0	Construct 3-inch Remediation Cell	JAN-APR	95%
7	4.1	3-inch Remediation Cell Constructed	APR	95%
8	4.2	Engineering Parametric Studies on 3-inch Cell	APR-DEC	10%
9	4.3	Derive Correlations	JUN-DEC	0%
10	5.0	Test Metal Removal and Recovery Schemes	JAN-DEC	40%
11	6.0	Obtain "REAL" Samples from Industry.	FEB-DEC	50%
12	6.1	Test Removal Schemes Using Small Cell on "REAL" Samples.	JAN-DEC	20%
13	6.2	Apply 3-inch Prototype to "REAL" Samples	AUG-DEC	0%
14	7.0	Analysis and Reporting		
15	7.1	Analysis and Data Reduction	JAN-DEC	40%
16	7.2	Reports and Manuscripts	JAN-DEC	50%
17	8.0	Closure	DEC	
18	9.0	Overall Work Complete	DEC	

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DEVELOPMENT OF INSTRUMENTAL METHODS FOR CHARACTERIZATION AND ANALYSIS OF NUCLEAR WASTES AND ENVIRONMENTAL CONTAMINANTS

METC Task No. 2.5

Quarterly Technical Progress Report
Reporting Period: 30 March 1996 - 28 June 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:
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ABSTRACT

Technetium 99 (^{99}Tc) and Iodine 129 (^{129}I), common constituents of nuclear wastes at Hanford, Washington, and other DoE sites, are important target analytes in both the tank wastes themselves and in site aquifers. Characterization and chemical speciation of both of these radionuclides in tank wastes and aquifers therefore represents an important DoE research goal. The work described herein focuses on the development of new analytical strategies for the chemical speciation and quantitation of ^{99}Tc and ^{129}I in simulated nuclear waste tank and aquifer matrices. These tasks are being accomplished through the development of new methodologies in the area of capillary electrokinetic separations. Capillary zone electrophoresis (CZE) and ion exchange capillary electrokinetic chromatography (CEC) methods are being developed for each of the target ions. The CZE studies center on the determination of optimum separation parameters including: selection of operating buffer composition and ionic strength, optimization of buffer pH, selection of operating potential and injection conditions, and development of detection strategies (including UV, indirect fluorescence, and radiometric detection). The CEC studies focus on the development of packed capillary columns for ion exchange separations. This approach should provide a higher analyte loading capacity and therefore improve detection limits. Here, the novel detection strategies employed will include indirect fluorescence detection for the determination of small quantities of ^{99}Tc and ^{129}I, and radiometric detection for the analysis of ^{99}Tc. It is expected that these developments will lead to rugged, reproducible, cost-effective means for determining ^{99}Tc and ^{129}I forms and levels in various matrices.

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EXECUTIVE SUMMARY

The focus of this research effort is the analysis of technetium 99 (^{99}Tc) and iodine 129 (^{129}I), common constituents of nuclear wastes at Hanford, Washington, and other DoE sites. These species are important target analytes in both the tank wastes themselves and in site aquifers. Characterization and chemical speciation of both of these radionuclides in tank wastes and aquifers therefore represents an important DoE research goal.

This work focuses on the development of new analytical strategies for the chemical speciation and quantitation of ^{99}Tc and ^{129}I in simulated nuclear waste tank and aquifer matrices. Capillary zone electrophoresis (CZE) and capillary electrokinetic chromatography (CEC) methods are being developed for each of the target ions. The CZE studies center on the determination of optimum separation parameters including: selection of operating buffer composition and ionic strength, optimization of buffer pH, selection of operating potential and injection conditions, and development of detection strategies (including UV, indirect fluorescence, and radiometric detection). In the first quarter, a reliable CZE method for separation of iodide (I^-) and iodate (IO_3^-) was developed. In this the second quarter, a detector was developed for the indirect fluorescence measurement of iodide, iodate, and perrhenate (ReO_4^-) [a surrogate for pertechnetate (TcO_4^-)], and the CZE method previously developed was extended to include perrhenate.

Later in the project (in the third and fourth quarters of this first project year), the CEC studies will focus on the development of novel packed capillaries (rather than open tubular, self-assembled monolayer modified capillaries) for anion exchange separations. This approach should provide even higher loading capacities and therefore vastly improved detection limits. Here, the novel detection strategies employed will include indirect fluorescence detection for the determination of small quantities of ^{99}Tc and ^{129}I, and radiometric detection for the analysis of ^{99}Tc.

It is expected that these developments in the field of microelectrokinetic separations will lead to rugged, reproducible, cost-effective means for determining ^{99}Tc and ^{129}I forms and levels in various matrices. Ultimately, these newly developed tools will be applied in the analysis of other target analytes.

1.0 INTRODUCTION

The development of several new tools for chemical analysis is proposed for the qualitative and quantitative determination of two important target analytes in Hanford site tank wastes and in site aquifers. Innovations in capillary zone electrophoresis and open tubular capillary electrokinetic chromatography will yield powerful methods for the separation of ^{99}Tc and ^{129}I from other components of simulated tank wastes and aquifer matrices. The use of novel detection strategies, including indirect fluorescence detection and radiometric detection, with the two separation methods will provide for the determination of trace quantities of ^{99}Tc and ^{129}I in small (pL to nL) volume samples, thus limiting human exposure to hazardous wastes. These advanced technology tools are expected to have commercial value, as evidenced by the interest and support of two firms which are active in the environmental analysis and remediation . industry: Selective Environmental Technologies, Inc. (Selentec), a small business headquartered in Atlanta, GA; and Battelle Northwest, a research institute and US Department of Energy Contractor with offices in Richland, WA. The interest of Selentec in the project is indicated by the attached letter of endorsement. Battelle's interest is indicated by the provision of laboratory facilities, equipment, and personnel in several stages of the project. The support of these two entities bodes well for the success of the project and for the possibility of transfer of the technology to the marketplace after sufficient development.

2.0 PURPOSE

Technetium 99 (^{99}Tc) and Iodine 129 (^{129}I), common constituents of nuclear wastes at Hanford, Washington, and other DoE sites, are important target analytes in both the tank wastes themselves and in site aquifers. [1] Characterization and chemical speciation of both of these radionuclides in tank wastes and aquifers therefore represents an important DoE research goal. The work proposed herein has as its purpose the development of new analytical strategies for the chemical speciation and quantitation of ^{99}Tc and ^{129}I in simulated nuclear waste tank and aquifer matrices. These tasks will be accomplished through the development of new methodologies in the area of capillary electrokinetic separations (both capillary zone electrophoresis (CZE) and capillary electrokinetic chromatography (CEC)) and the use of novel detection strategies for the determination of small quantities of ^{99}Tc and ^{129}I. It is expected that these developments will lead to a rugged, reproducible, cost-effective means for determining ^{99}Tc and ^{129}I forms and levels in various matrices.

The proposed studies address DoE needs in the focus area of *Crosscutting Technologies and Supporting Programs*, specifically in the sub areas of both *Innovative Technologies/Supporting Programs* and *Industry Programs*.

This project will foster the development of a strong research partnership between the US Department of Energy's Pacific Northwest Laboratory and the Department of Chemistry at West Virginia University. Prof. Remcho's research program in microscale separations will make a unique contribution to the US DoE effort to measure, remediate, contain, and monitor wastes produced at the Hanford Reservation over the past half-century. This contribution will be facilitated and augmented through Dr. Ballou's research program at Battelle-Northwest. Dr. Ballou has directed environmentally relevant research projects for the US DoE for over 20 years, and his unique expertise and laboratory facilities will both support the project and ensure a consistent focus on Hanford needs. This collaborative approach offers the following benefits:

1. the infusion of new ideas and technology into the Hanford waste cleanup effort;
2. an enhancement of West Virginia University's research effort in environmental analysis and remediation;
3. reduced research and development costs for DoE; and
4. the development of a strong and mutually beneficial bond between the US DoE's Pacific Northwest Laboratory and West Virginia University.

The high efficiency and high peak capacity typical of capillary electrokinetic separation techniques [2], coupled with the high selectivity of radiometric detection and high sensitivity of indirect fluorescence detection, will provide a powerful set of tools for characterization and chemical speciation of Hanford waste tank constituents. The technology developed in this initial research effort will be extended and applied to other analytes and matrices in follow-on studies.

3.0 BACKGROUND

Instrumental methods are being developed for the determination of ^{99}Tc and ^{129}I in simulated nuclear waste tank and aquifer matrices. The use of simulated matrices in method development provides a wide margin of safety by minimizing/eliminating exposure to radioisotopes and by eliminating the need to transport radioactive species. The use of simulants also allows for rapid method development because of the increased simplicity of working with a non-radioactive, well-defined matrix. These combined benefits result in savings in both time and expense.

The target analytes, iodine and technetium, are primarily present in solution as iodide, iodate, and pertechnetate anions. These anions are the focus of the initial research. In the

interest of safety and practicality, a surrogate stable isotope of iodine(^{127}I) is being employed in developing both CZE and CEC methods for iodine determination. ^{127}I, end product of the mass 127 decay chain, is also a component of tank waste and is present in a concentration similar to that of ^{129}I. ^{99}Tc will be handled in trace quantities using the unique facilities and expertise available at Battelle-Northwest.

4.0 METHODOLOGY

The separation technologies to be employed in conducting the work include both CZE and CEC. CZE is conducted by introducing a small (~10 nL) sample into the open end of a 50 to 100 μm ID fused silica capillary, about 50 cm in length, whose ends are immersed in buffer-filled reservoirs. The sample is introduced either electrokinetically, by applying ca. 50 V/cm for 2-10 seconds; or hydrodynamically, by applying 3-10 psi for 2-10 seconds, while the inlet buffer reservoir is replaced with the sample reservoir. A potential gradient of 100-500 V/cm is then applied along the axis of the capillary, resulting in the separation of analytes according to differences in their charge and size. In addition to the electrophoretic movement of analytes induced by their charge, species are swept along the capillary via electroosmosis: bulk transport of solution in the capillary. Electroosmosis arises from the electrochemical double layer at the charged surface of the capillary when shear forces are generated by application of the high potential. Detection of the separated analyte zones is usually achieved using a UV detector, with a segment of the capillary itself serving as the optical flow cell. Here, the polymeric coating of the fused silica capillary is abraded or burned to produce a clear fused silica surface with excellent UV and visible optical transmission characteristics.

CEC is a promising new technique for achieving microscale separations. [3] Essentially, CEC represents the intersection of capillary electrophoresis and open tubular liquid chromatography. As such, it provides the unique benefits of each of these two techniques while overcoming some of the limitations of each. CEC is conducted in either packed or open fused silica capillaries (~10 to ~ 150 μm ID). The stationary phase may be either covalently attached to the fused silica capillary or formed as a self-assembled monolayer of small molecules (for open tubular CEC) or immobilized on a solid support particle which is then packed into the capillary (conventional CEC). In all other respects, the instrumentation employed in CEC is identical to that used in CZE.

The detection strategies employed will include: 1) UV detection for development of a CZE method for the determination of iodine; 2) indirect fluorescence detection for sensitivity optimization in the determination of iodine and technetium by both CZE and CEC; and 3) radiometric detection for the determination of ^{99}Tc by both CZE and CEC.

5.0 WORK PERFORMED THIS PERIOD

5.1 Development of CZE Methods for Analysis and Speciation.

0.01 M stock solutions of NaI, $NaIO_3$, and $NaReO_4$ (Sigma Chemical Co., St. Louis, MO, USA)were prepared in distilled, deionized water for use in method development. Serial dilutions of these were made in the appropriate buffer solutions as necessary for each stage of the experimental work. Unless otherwise noted, 50 μm ID fused silica capillary tubing (Polymicro Technologies, Phoenix, AZ, USA), 365 μm in OD, was used in all of the work described herein. Total capillary length (L_{tot}) was 65 cm, the effective length (length to detector, L_{det}) was 50 cm. All work was carried out using an ATI-Unicam (Boston, MA, USA) Crystal 310 CE system. Separations were conducted with the anode at the outlet reservoir due to the fact that $\mu_{ep} > \mu_{eof}$ for all of the analytes studied.

5.1.1 Analysis and Speciation of Ionic Iodine Species.

Work continued on the separation of the iodine target species. ^{129}I and ^{127}I are most often present in solution as iodide (I^-) and/or iodate (IO_3^-). The charge/volume ratio for these two species in solution was found to be sufficiently different to allow for facile separation by capillary zone electrophoresis in standard operating buffer solutions. This technique entailed the axial application of a 100 to 500 V/cm potential gradient to the separation capillary using a high voltage power supply. The platinum electrodes used in this method were immersed into two small reservoirs filled with aqueous buffer solutions, one at each end of the fused silica capillary in which the separation is conducted. A window for optical detection was burned near an end of the capillary using a fiber optic fusion splicer (Alcoa-Fujikura, Atlanta, GA, USA). UV detection was employed in initial studies. Both I^- and IO_3^- absorb in the low UV (~200 nm), allowing for non-radioactive (^{127}I) iodide and iodate to be determined by CZE-UV when working at moderately high analyte concentrations. Initial experiments were conducted using a 25 mM β-alanine operating buffer at pH 3.5, and employed direct UV-Vis detection at 220 nm. Poor results prompted a shift to a 100 mM acetate buffer system, pH 4.5, which allowed for analysis of iodide with a limit of detection of approximately 10^{-3} M. Excessive analysis times led to the addition of 1 mM CTAB (cetyltrimethylammonium bromide) in an effort to increase the speed of the separation. Later work indicated that phosphate buffers would allow for optimal separation and detection conditions. These results are discussed briefly in section 6.0, below, and were described in detail in the previous report deliverable.

5.1.2 Analysis and Speciation of Ionic Rhenium and Technetium Species.

Technetium is most often present in solution as pertechnetate (TcO_4^-) ion. Since no stable isotope of technetium exists, the close and non-radioactive chemical homolog of technetium, rhenium, is being used initially to significantly simplify the experimentation. Perrhenate (ReO_4^-) ion is being used to determine appropriate operating and detection conditions. These conditions will then be validated first with standard solutions of ^{99}Tc and then with simulated tank waste solutions containing ^{99}Tc. ^{99}Tc is a beta emitter, and thus should be detectable at relatively low levels using a commercially available Raytest Steffi™ radiometric detector (Raytest Inc., Wilmington, DE). [4] This detector has been delivered, and will be used in the third quarter of the project period at the Pacific Northwest National Laboratory. Use of this sensitive, highly selective detector will minimize exposure to radioactive sources and should provide the trace level detection capability necessary for determination of ^{99}Tc in tank waste simulant and aquifer samples.

Initial work on perrhenate analysis has begun. Detection is by UV-Vis at 190 nm and buffer solutions are as described in section 5.1.1, above. This should allow for analysis of iodide, iodate, and perrhenate in a single step.

5.2 Construction & Characterization of a Fluorescence Detector for CZE and CEC.

Work also continued on the construction of a fluorescence detector designed in-house. The necessary components were obtained and assembly of the system has been completed. The detector is designed to operate in concert with an existing ATI-Unicam (Boston, MA, USA) CE instrument. A schematic of the completed instrument is shown in Figure 1. The figure indicates the system as it is currently configured with a continuum source (Hg-arc lamp), though it is capable of operating with a laser light source as well. In the third quarter of the research period, work with the laser (an argon-ion unit) will commence.

By locating the detector directly in the instrument, detection takes place in a thermostatted compartment so that Joule heating effects can be minimized. Excitation of a fluorophore additive (on column) is accomplished, after selecting the excitation wavelength with an interference filter, from the broadband continuum source. The design allows for the facile incorporation of a laser, to attain even lower detection limits. Detection of emission is accomplished using a photomultiplier tube after filtering the collected light.

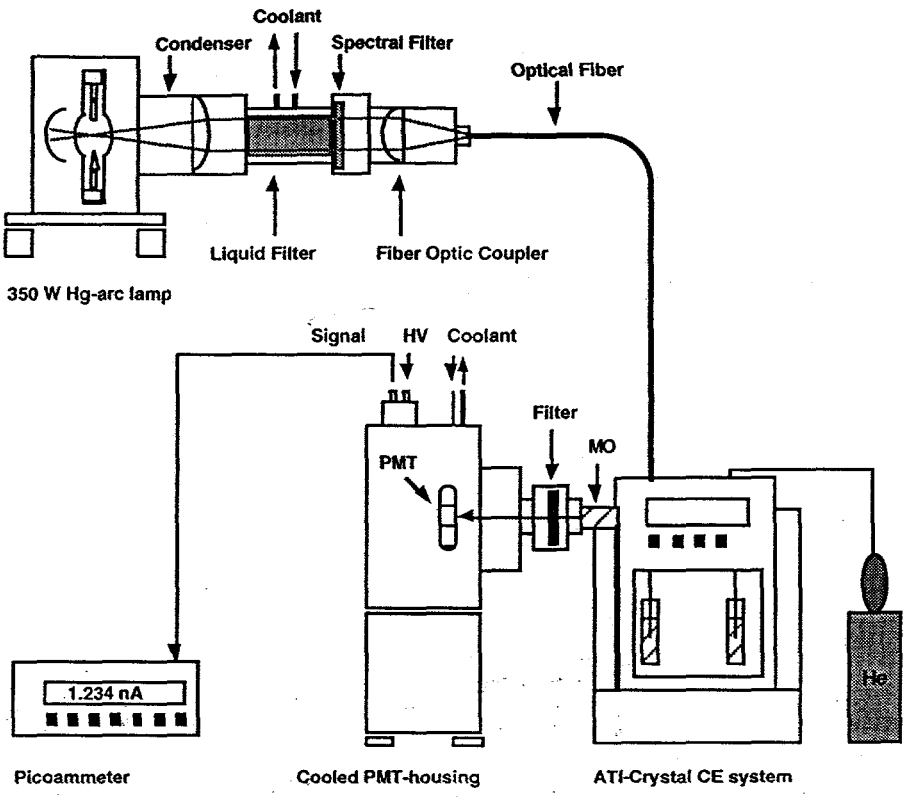


Figure 1: Schematic diagram of CZE-fluorescence detection system.

6.0 RESULTS AND DISCUSSION (Current Period)

6.1 Development of CZE Methods for Analysis and Speciation: Analysis and Speciation of Ionic Iodine Species & Ionic Rhenium and Technetium Species.

Work continued with the various operating buffer compositions (described in the first quarterly report as the *Operating Buffer Composition Study*) in an effort to further refine the CZE method. The four systems studied included:

1. β-alanine (25 mM, pH 3.50)
2. acetate (100 mM, pH 4.5)
3. acetate/CTAB (100 mM /1 mM, pH 4.5)
4. phosphate (25 mM, pH 2.9)

Work also continued on the, *Operating Buffer pH Study*, the, *Separation Step Field Strength Study*, and the *Generation of Calibration Curves for Quantitative Analysis*, as described in the previous report deliverable.

6.2 Construction & Characterization of a Fluorescence Detector for CZE and CEC.

6.2.1 Detector Design.

The following design specifications were established for the fluorescence detector:

- Simplicity (construction and operation)
- Low cost
- Flexibility (multiple wavelength and/or easy exchange of light source)
- Coupling to instrument (CE-system)

In order to meet these specifications, the setup illustrated in figure 1 was employed. A mercury arc-lamp, which has a large output from the UV to the IR (especially on certain wavelengths, e.g. 254 nm, 543.1 nm), was employed as a continuum light source. To protect the spectral filters from damaging IR radiation a water-cooled heat filter containing distilled water was used.

Selection of the excitation wavelength was achieved by using mercury line band pass filters, bandwidth 10 nm. The light was then coupled into a multimode optical fiber with a fiber optic coupler. The fiber was led into the back of the ATI Crystal CE system and coupled with a fiber optic beam probe to refocus the output of the fiber on the capillary (spot size ~ 400 mm). The fiber optic beam probe was mounted on a x-y-z micropositioner to facilitate alignment. The capillary was held by the detector block which contained a V-groove to retain the capillary. A lever was used to engage the capillary holding clamp, so that the capillary could be easily replaced without realigning the optical system.

Emission was collected using a high numerical aperture microscope objective. This objective was connected to a 1 inch filter holder, were the fluorescence was separated from the background using wide band fluorescence filters or long pass filters. Detection was accomplished using a photomultiplier tube (sensitive from the UV to the near IR), placed in a cooled housing for maximum sensitivity. The output of the PMT was led to a picoammeter, from which the analog output signal was digitized using an A/D converter (Rainin Instrument Company, Woburn, MA, USA) and recorded on a Power Macintosh 6100/60. The hardware necessary for construction of the detector is detailed in Table I.

6.2.2 Detector Block Design.

For excitation and detection of the emission an orthogonal arrangement was used, in which excitation and emission take place in an 90° angle. A detector block was designed (figures 2 and 3) and connected to the inside of the ATI-Crystal CE system, to facilitate installation and removal of the capillary without disturbing the optical alignment. The detector block also served to minimize stray light.

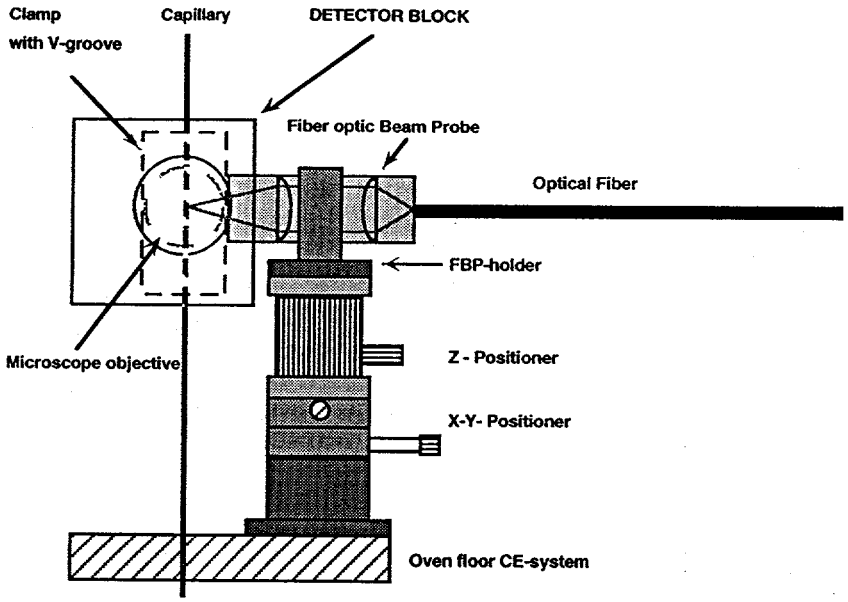


Figure 2: Front view of capillary detection system/clamping block.

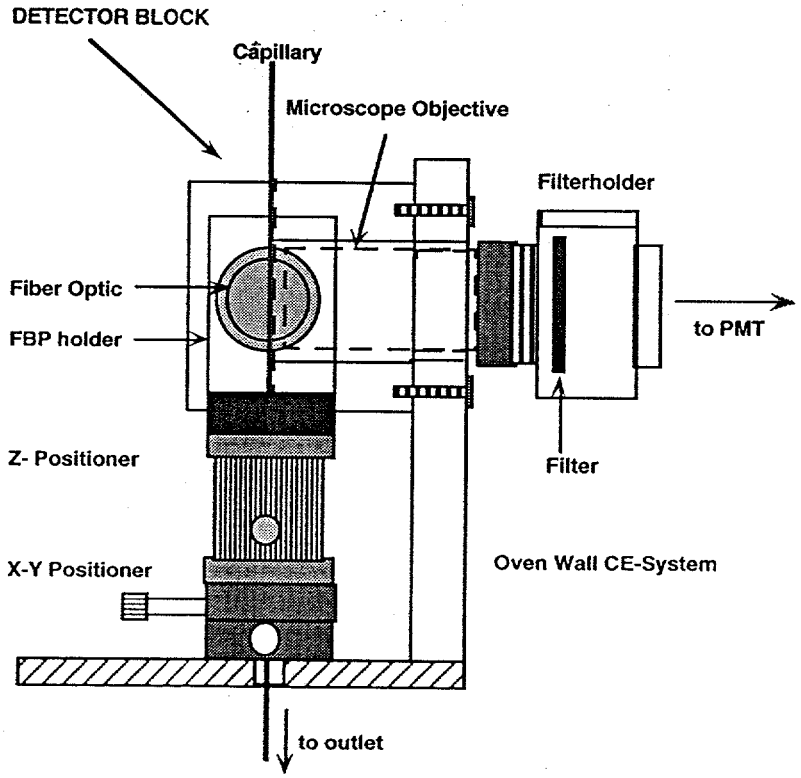


Figure 3: Side view of capillary detection system/clamping block.

Table I. Materials used in construction of the CZE-fluorescence detection system.

Component	Specification	Part No.	Manufacturer
Lamp Housing	Research housing for 200-500 W Hg lamps	6186	Oriel
Lamp	350 W Hg-arc	6286	Oriel
Power Supply	200 - 500 W	8530	Oriel
Lens	Fused Silica, f #/1.0		Oriel
Liquid Filter	H_2O filled for protection of spectral filter	61945	Oriel
Filter holder	2 inch filters	71260	Oriel
Filter	Bandpass, 546-10 nm	56561	Oriel
Fiber Coupler	F#/2 Fused Silica Lens	77800	Oriel
	11 mm ferrule for SMA term. fibers	77670	
Fiber optic cable	Fused silica, 400 μm	77511	Oriel
	SMA terminated	77571	
Fiber Beam Probe	Focusing Beam Probe	77646	Oriel
	Fused Silica Lenses	41210	
X-Y-Z positioners	X-Y- positioner	07TMC511	Melles Griot
	Z- positioner	07TMZ501	
Microscope Objective	63x, NA=0.85	040AS018	Melles Griot
Filter Holder	Holder for 1" filters		homemade
Filter	Broadband Fluorescence Filter 600-50 nm	57590	Oriel
Photomultiplier Tube	Multi-alkali PMT 180<λ<900 nm	R 928	Hammamatsu
HV supply for PMT	+/- 0-3000 V	230/03R	Hammamatsu (Bertan)
PMT Housing	Cooled 40 °C below ambient	TE-177RF	Products for Research
Picoammeter	100 fA < I < 2 mA	model 485	Keithley

6.2.3 Performance Evaluation of the Detector.

For evaluation of the performance of the fluorescence detector, a capillary zone electrophoretic experiment was performed. Rhodamin B was selected as a test solute for two reasons; it exhibits a high quantum yield and it absorbs maximally near one of the visible mercury lines (λ=543.1 nm)[5-7]. Experiments were carried out on an ATI-Crystal CE system. The capillary used had an inner diameter of 75 μm, a total length of 59.8 cm with the length to the detection window of 39.3 cm. Injection was performed electrokinetically at 10 kV for 0.10 minutes. Separation was carried out in a b-Alanine, 10 mM, pH 3.7 buffer system at 30 kV.

From this calibration graph, it is concluded that the response of the detector is linear over the range $7.5 \cdot 10^{-7}$ M to $5.0 \cdot 10^{-5}$ M . The concentration detection limit was determined to be $7.5 \cdot 10^{-7}$ M* for Rhodamin B giving a mass detection limit of $9.9 \cdot 10^{-15}$ mol with an injected volume of 13 nL. The detection limit was determined at $S = 3 * s_b$; with S = height of signal and s_b = standard deviation of baseline noise.

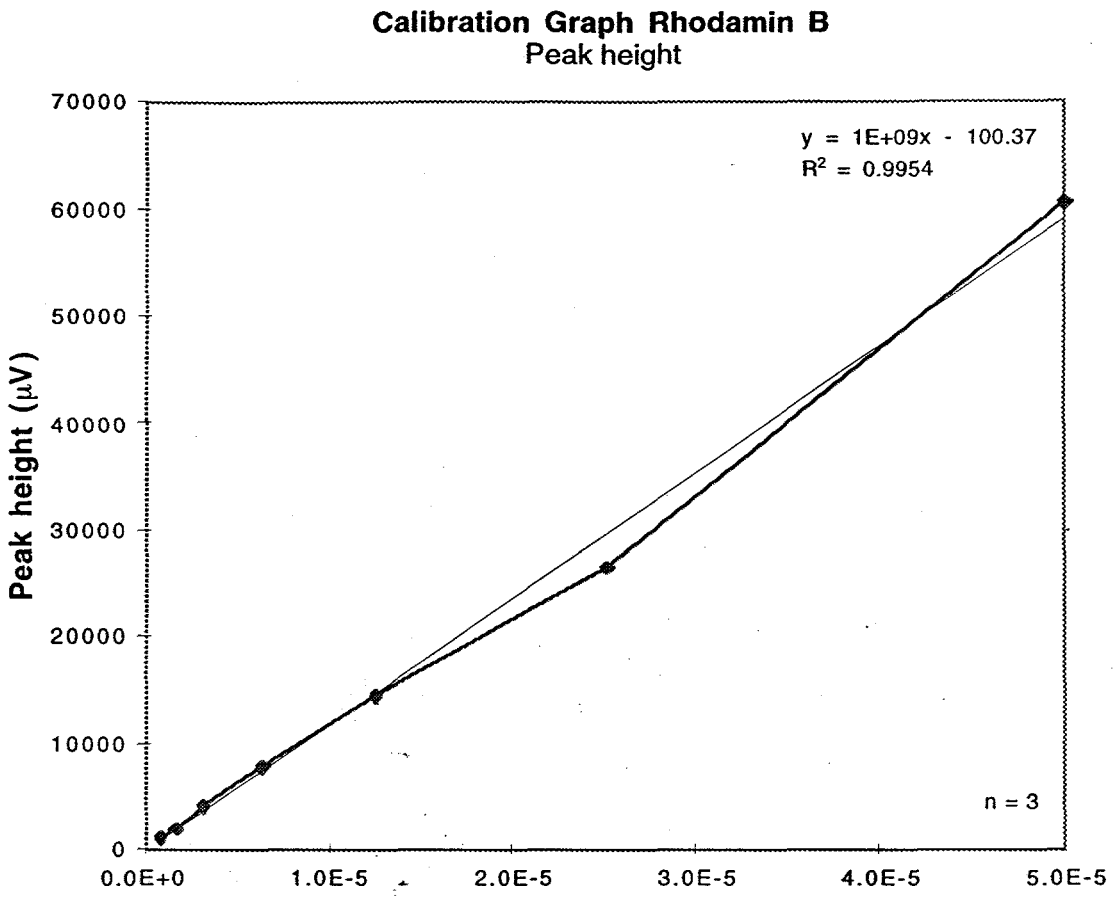


Figure 4: Determination of linearity and limit of detection for the CZE-fluorescence detection system employing a Hg-arc lamp continuum source. (Data is currently being collected using an Argon ion laser source.)

7.0 CONCLUSIONS (Current Period)

The newly constructed fluorescence detector was found to provide good detection limits for the test component used. Detection limits for the test solute (Rhodamin B) are on the order of $7.5 \cdot 10^{-7}$ M giving a mass detection limit of $9.9 \cdot 10^{-15}$ mol. The response of the detector proves to be linear over at least two orders of magnitude. Future work will be focused on further optimization, and use of a laser as an excitation source, lowering current detection limits by 2-3 orders of magnitude.

The project is on schedule and results continue to be encouraging. The CZE-UV method previously developed for the analysis of iodide, iodate, and perrhenate in standard solutions has been refined, though further refinement could be beneficial. In particular, the following problems should be and will be addressed in the coming months:

- variation of injection conditions to elucidate the effect of sample introduction on calibration curve linearity;
- elucidation of the effects of field-amplified sample injection on sensitivity, efficiency, and calibration curve linearity;
- careful study of the various fluorophore additives available and selection of an optimal specie for sensitive indirect fluorescence detection.

8.0 WORK PLANNED FOR NEXT PERIOD

Further refinement of the in-house constructed fluorescence detector will be undertaken. These refinements may consist of any of the following modifications:

- addition of a second microscope objective at the capillary-side terminus of the fiber optic light pipe to facilitate focusing of radiant power on the capillary lumen;
- addition of a slit in the optical path to improve spectral resolution;

The second stage of the iodine work will be conducted at the Battelle-Northwest facilities in Richland, WA. This portion of the project will require that Prof. Remcho travel to Richland to work directly with Dr. Ballou at Battelle's Atomic and Molecular Sciences laboratory. The investigators will continue to make use of Battelle's 3 mW 488 nm air-cooled Argon Ion laser for enhanced LIF detection sensitivity. This instrument will provide a detection sensitivity which is approximately one order of magnitude greater than that achieved at WVU.

Experimentation with radiometric detection of ^{99}Tc will commence. This work will also be conducted at Battelle, in the month of July. In addition, the applicability of indirect laser-induced fluorescence detection to perrhenate analysis will be studied. This technique will allow for the possibility of simultaneous analysis of ionic iodine and a technetium surrogate (Re) to be explored. Initial ^{99}Tc work will be conducted using the facilities and expertise of Battelle-Northwest, until such time that any necessary preparations and authorization are arranged for work to be conducted at WVU.

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PRODUCTION AND EVALUATION OF BIOSORBENTS AND CLEANING SOLUTIONS FOR USE IN DECONTAMINATION AND DECOMMISSIONING
METC Task No. 2-6A

Quarterly Technical Progress Report
Reporting Period:

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
Institute of Gas Technology
1700 South Mount Prospect Road
Des Plaines, Illinois 60018

ABSTRACT

The objectives of this project are to prepare and to evaluate biosorbents and cleaning solutions that may be useful in the decontamination and decommissioning (D&D) of U.S. Department of Energy facilities. In this collaborative project, the Institue of Gas Technology will make available to researchers at West Virginia University (WVU) biosorbents and cleaning solutions that are useful for D&D activities, but require filtration/liquid processing in order to be used in a practical process. Filtration tests will be performed by WVU.

During the past quarter biosorbent samples and decontamination solution samples were prepared and sent to the West Virginia University for filtration tests. Additionally, the composition of a wastewater stream typical of decontamination and decommissioning activities that will be used in biosorbent testing was identified.

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1.0 Introduction

The decontamination and decommissioning (D&D) of the Department of Energy facilities can result in the production of large volumes of wastewater containing metals, radionuclides, organic contaminants, and particulate material. Treatment of these wastewater streams is highly problematic because of their complexity and toxicity. Treatments appropriate for the removal of particulate material, such as filtration, are generally ineffective for the removal of soluble contaminants in D&D wastes such as metals and radionuclides. Techniques commonly used for the removal of metals and radionuclides from wastewater include the use of ion exchange resins; however, particulate material and organic contaminants present in D&D waste are incompatible with the use of ion exchange columns because of plugging/fouling. Biosorbents are biologically derived substances that can be used to sorb metals/radionuclides in a manner analogous to ion exchange resins, and biosorbents may be inexpensive in comparison with ion exchange resins.

The approach that is being tested in this project is the use of biosorbents, in a powdered form, added directly to D&D wastewater for the removal of metals and radionuclides. The use of biosorbents as powders rather than as ion exchange columns avoids the plugging/fouling problems associated with ion exchange columns. Also the powdered biosorbent should provide better contact and therefore more rapid metal/radionuclide binding than with ion exchange columns or immobilized biosorbent columns. D&D wastewaters require filtration in order to remove particulates and the same filtration step can be used to remove biosorbent particles and metals/radionuclides bound to them. It is expected that this approach will simplify and decrease the cost of treatment of D&D wastewater.

A related issue in D&D activities is the use of effective cleaning solutions, and the ultimate fate of used/spent cleaning solutions. The Institute of Gas Technology (IGT) has developed novel surfactant formulations that are highly efficient in the removal of organic and inorganic contaminants from solids. Ordinarily surfactants are discarded in spent D&D solutions. However, these surfactants can inhibit the subsequent treatment of these solutions and if not completely destroyed can contribute to the mobility of contaminants and thereby pose an environmental risk. This project will examine the possibility of using filtration to remove surfactants from D&D solutions, and possibly aid in the recovery/reuse of those surfactants, as well as aid in the treatment of D&D wastewater.

2.0 Purpose

The purpose of this project is to evaluate the use of biosorbents in conjunction with filtration to treat D&D wastewater. An additional purpose of the project is to evaluate the removal of surfactants from D&D solutions.

3.0 Background

IGT has experience in the production and use of biosorbents, and in the production and use of surfactants for removing contaminants from solids. The West Virginia University (WVU) has experience in filtration and possesses a bench-scale model of a novel centrifugal filtration device developed by SpinTek Corporation. IGT and WVU are collaborating on this project to

combine their areas of expertise to develop improved processes for the treatment of D&D wastewater.

4.0 Methodology

Bacterial Strains and Culture Media

Escherichia coli (ATCC 23724) was grown in nutrient broth (Difco) while *Zoogloea ramigera* 115 (ATCC 25935) was grown in nutrient broth supplemented with 25 g glucose per liter. Cultures were incubated at 30°C and the production of exopolysaccharide by *Z. ramigera* was monitored spectrophotometrically, and by measuring the viscosity of the medium. *Z. ramigera* cultures were harvested when viscosities exceeding 600 centipoise were achieved.

Immobilization of Dried Biomass

Biomass (cells plus exopolysaccharides if present) was harvested by centrifugation at 10,000 X g for 10 minutes and dried under vacuum in a rotary evaporator at 65°C. The dried biomass was ground to a uniform fine powder using a mortar and pestle. Dried, powdered biomass was used as is for metal-binding experiments.

Analytical Procedures

Atomic Absorption Spectrophotometry (AAS) (Model: 403, Perkin-Elmer Co.) Inductively Coupled Plasmic Emission Spectroscopy (ICPAES) (Model: Atom Scan 25, Thermo Jaorell Ash Co.) and ion exchange chromatography (Model DX-100, Dionex Corp.) were used for metal concentration analyses. Samples were diluted to 0.1-1.0 ppm to ensure accurate analysis. To remove the interference from suspended particles, samples were centrifuged (600 rpm, 5 min) and filtered by a 0.45-μm filter before injection into the AAS, ion exchange chromatography, or ICPAES apparatus.

Metal Adsorption Studies

Batch studies were performed using 100 mg of biomass in a 250-ml Erlenmeyer shaker flask containing 100 ml of 10 to 100 ppm metal solution (adjusted to pH 6.0 or 4.0 using HCl) and shaken for 15 minutes to 24 hours at a speed of 160 rpm at room temperature. Biomass was removed by centrifugation, the supernatant was decanted, filtered, and metal ions were then analyzed by AAS, ion exchange chromatography, or ICPAES.

Surfactant Solutions

Surfactants were prepared according to proprietary procedures.

5.0 Work Performed This Period

During the past quarter biosorbent samples and decontamination solution samples were prepared and sent to WVU for filtration tests. Additionally, the composition of a wastewater stream typical of D&D activities that will be used in biosorbent testing was identified. These

items fulfill three key milestones of the project and provide material needed by WVU to complete their portion of the project.

6.0 Results and Discussion

A biosorbent sample, some literature concerning biosorbents and metal treatment technologies, some information about the surfactant that we recommend for use in D&D, a surfactant sample and suggested compositions for D&D solutions was sent to WVU. I have recently prepared four biosorbent samples: hydrocarbon-degrading biomass (control biomass), Non-muciod *Zoogloea ramigera* biomass, muciod *Zoogloea ramigera* biomass, and exopolysaccharides obtained from muciod *Zoogloea ramigera.* Each biosorbent sample was dried and ground to a fine powder. It is intended that these biosorbent samples can be added directly to wastewater samples to bind metals followed by removal using the SpinTek filtration device. One of the enclosed articles describes the difference in metal binding performance between free and immobilized biomass (Gourdon 1990), and another publication describes the use of *Zoogloea ramigera* in metal removal using flocculation/centrifugation (Norberg 1984). The publication by Jellinek 1972, is included as a further example of the use of soluble agents for the removal of metals from wastewater. Our collaboration then will not be demonstrating anything novel as regards the removal of metals from wastewater using soluble polymers/biosorbents, but hopefully the data that WVU produces will demonstrate the advantage of the SpinTek filtration technology as regards performance and cost. The biosorbent and surfactant samples provided to WVU will enable them to perform their portion of this project.

As regards the composition of a D&D test solutions, there are no standard solutions used for this purpose that I could find. However, the Macaskie, 1991 (Crt. Rev. Biotechnol. 11: 41-112) article that I sent you earlier contains compositions of typical low level waste streams, fuel rod storage pond streams, and an Oak Ridge Labs' wastewater on pages 49, 50, and 63 respectively. Additionally, in Ayres, J. A., Decontamination of Nuclear Reactors and Equipment, Ronald Press, New York, 1970, one particularly relevant table is found on page 673 which describes a typical decontamination solution as containing

Compound	Concentration (% by weight)
surfactant	20%
sodium tripolyphosphate	40%
sodium carboxymethyl cellulose	3%
EDTA	1%
Filler	to 100%

This solution is used at full strength in cases of severe contamination, but is generally diluted with water by a factor of from 1 to 10. The final concentration of these components in D&D wastewater is diluted further because of rinsing, and possible mixing with other wastewater streams. Thus the final concentration of cleansing agents in D&D wastewater is variable but it might be

reasonable to assume that the concentrations listed above are diluted at least ten-fold in typical wastewater.

The D&D solution that IGT is developing for use in the removal of hydrophobic organic contaminants contains 3.5% tall oil amide (IGT-FF52 amide), 1% Standapol ES-2, 40% ethanol, and the rest water. This mixture is referred to as IGT-FF52. For decontamination of surfaces that contain metals and/or radionuclides the IGT-FF52 would be modified to also contain 1% EDTA. Thus the chemical composition of the D&D solution that we are recommending is simpler and contains less chemical than the typical D&D solution. The molecular weight of the IGT-FF52 amide will vary from 350 to 1000, and the size of micelles is not known precisely but should be 10,000 or greater. This surfactant is currently synthesized at IGT and we are looking for commercial products that can be used satisfactorily in this application. If we find one then we will send you a sample for filtration testing. Using a commercially available surfactant will make it easier to scale up our work and to more accurately predict costs of a process.

It is important to note that there are two fundamentally different types of solutions/wastewaters relevant to D&D activities: those that contain chelated metals, and those that contain no chelating agents. Both types of wastewaters are assumed to contain metals/radionuclides, but biosorbents can't be used to bind/remove chelated metals and chelated metals probably can't be removed by filtration. Wastewater that does not contain chelating agents can be treated with biosorbents for the removal of metals/radionuclides and can be subsequently treated by filtration. Wastewater streams resulting from uranium recovery operations, fuel rod storage ponds, and surface/groundwaters are examples of wastewater streams that may not contain chelating agents (or surfactants) and could be treated with biosorbents followed by filtration. Wastewater streams resulting from the decontamination of buildings and equipment will contain chelating agents and surfactants. While these wastewater streams would probably not benefit from the addition of biosorbents, the use of filtration may still be appropriate to remove particulate matter and to allow the recovery of surfactants.

Accordingly our tests should include two types of solutions. The surfactant/EDTA solution for use in D&D activities could be expected to contain IGT-FF52 amide at concentrations of 0.35% to 1%, and EDTA concentrations of 0.1% to 0.3%. No biosorbents would be added to this solution. In actual use spent D&D solution would contain other things such as ethanol, ES2 surfactant, organic contaminants, metals and radionuclides (chelated), and particulate material. For our test purposes I don't think that we need to add all of these components. For most tests just the IGT-FF52 amide alone or in combination with EDTA should suffice. The goal of these filtration tests would be to recover the surfactant. Some tests could also include clay to demonstrate the removal of particulate matter.

For tests in which biosorbents are present (surfactants and EDTA will be absent) the composition of a test solution is less clear. A typical low level wastewater contains

Compound	Concentration (ppm)
NO^3	17,000
SO^4	500
tributyl phosphate	30
kerosene	30-150
Fe	150
Na	400
K	30
Ca	10
Mg	10
U	10
Tc/Sr/Pu	.05

In such a wastewater the entirety of the radioactivity is present in the U/Tc/Sr/Pu compounds which are present at 10 ppm or less along with high concentrations of other ionic species. To selectively sorb the radioactive elements out of a complex mixture in which the radioactive elements are less than 0.1% of the total ionic species is unlikely. Additionally Bud Cook has expressed aninterest in demonstrating the removal of metals such as As, Cd, Hg, Pb, and Zn that are more typical of industrial wastewaters. First I will test the ability of biosorbents to remove La (a good surrogate for some actinide radionuclides), Sr, U, As, Cd, Hg, Pb, and Zn at concentrations of 10 ppm to 1 ppb. These will be batch tests. Then I will perform additional batch tests using NO^3, SO^4, Fe, and Na at the concentrations listed above in conjunction with the metal ions of interest. High concentrations of iron could be reduced by oxidizing/aerating the solution to form insoluble iron precipitates then adding the biosorbents to remove the metal ions of interest, then filtration could be used to remove the whole lot. After trying some batch tests we can discuss a limited number of conditions to test at bench scale using the SpinTek device. Probably we will decide on compositions for two wastewater streams: a surrogate industrial wastewater containing As, Cd, Hg, Pb, and Zn, and a surrogate low level wastewater containing La, Sr, U, NO^3, SO^4, Fe, and Na. Both of these wastewater streams should be amenable to treatment using biosorbents, and the goal of your tests should be to produce data that demonstrates that the SpinTek unit can treat these wastewaters faster, more effectively, and/or less expensively than alternative filtration technologies.

7.0 Conclusions

The project is proceeding as scheduled. Filtration tests using biosorbents and surfactant solutions should proceed as planned as should the evaluation of biosorbents to bind metals in a simulated D&D wastewater.

8.0 Work Planned for Next Period

Metal binding experiments to test the ability of biosorbents to remove metals from simulated D&D wastewater are planned.

USE OF SPINTEK CENTRIFUGAL MEMBRANE TECHNOLOGY AND SORBENT/CLEANING SOLUTIONS IN THE DECONTAMINATION AND DECOMMISSIONING OF DOE FACILITIES

METC Task No. 2.6B

Quarterly Technical Progress Report
Reporting Period: 4/1/96 - 6/31/96

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

For:
U.S. Department of Energy
Office of Fossil Energy
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ABSTRACT

The use of sorbents (biosorbents, powdered activated carbon) and cleaning agents (surfactants, chelation agents) to decontaminate surfaces such as pipes, walls, *etc.* represents a unique and cost-effective method for remediating DOE facilities. As envisioned, the sorbent or cleaning agents would be added to a liquid (most likely water) and the solution would be contacted with the contaminated surface. For example, a pipe that is contaminated with inorganic and organic contaminants can be contacted with a solution containing a surfactant (for the organics) and a chelating agent (for inorganics). After removal of the surface-bound contamination by the cleaning agents, a solid sorbent can be added to the liquid to bind the cleaning agent-contaminant compound. A major problem associated with this approach is the efficient separation of the sorbent/cleaning agent from the liquid phase using conventional separation techniques.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and discharged. The concentrate exits at the edge of the membrane packs. The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance and increasing the volume of waste treated per area of membrane.

The objective of this Task 2.6B research is to investigate the feasibility of using centrifugal membrane technology to separate sorbents/cleaning agents used in the decontamination/decommissioning of DOE facilities. The result of this effort will be the development of an efficient cost effective method for the decontamination/decommissioning of DOE facilities. An additional benefit of this research is the application of the experimental results to the treatment of other DOE wastes such as contaminated groundwater, mixed-waste process water, and existing waste residual (*e.g.*, Hanford Tank Farm Waste). It is envisioned that the volume reduction factors for this technology will be high and a relatively low amount of residual requiring additional treatment will be produced.

Work on the project will be performed by West Virginia University's Department of Civil and Environmental Engineering (WVU-CEE) and the Institute of Gas Technology (IGT). The following tasks will be completed by WVU-CEE: 1) selection and procurement of membrane(s) and 2) bench-scale testing of centrifugal membrane process. The following tasks will be completed by IGT: 1) identification and formulation of synthetic wastes and 2) selection and evaluation of sorbents and cleaning solutions. WVU-CEE and IGT will submit separate quarterly reports. A joint proposal will be prepare to obtain funding for D&D research through existing DOE ROAs and PERDAs.

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EXECUTIVE SUMMARY

Work started on the project on May 10, 1996. Three SpinTek runs were completed using a return waste activated sludge from a domestic wastewater treatment plant. The return waste activated sludge ("biomass") mimicked a biosorbent that is being developed by the Institute of Gas Technology (IGT). The SpinTek centrifugal membrane system successfully concentrated a biological waste that mimicked a biosorbent waste from a decontamination/decommissioning effort. Hydraulic and mass based concentration factors were in good agreement.

Permeate flux increased with increasing temperature and rotation speed. The decrease in viscosity from 85° to 110°F is approximately 25% percent while the flux increased by about 30 percent (89 to 128 gal/ft^2-d) over the same temperature range. The majority of the increase in flux with increasing temperature can be attributed to the decrease in viscosity. Permeate flux increased from 101 to 128 gal/ft^2-d as the rotational speed increased from 1,000 to 1,750 rpm. Increasing the rotational speed decreased the thickness of the fouling layer resulting in a decrease in membrane resistance. Permeate turbidity increased with temperature from 0.17 NTU to 0.53 NTU when the temperature was increased from 85° to 110°F. Reasons for this phenomenon are hypothesized as: 1) at higher temperatures the membrane pores may enlarge allowing more colloidal material to pass through the membrane, 2) oil droplets are more deformable and can squeeze through the membrane pore more easily, and 3) advective transport forces that push the colloidal material through the membrane increase with increasing flux. Turbidity increased from 0.53 to 1.74 when the rotational speed was decreased from 1,7500 to 1,000 rpm. Decreasing the rotational speed allowed more material to build up on the membrane surface and pass through into the permeate. This was especially true at end of the run when the feed tank TSS concentration was highest.

1.0 INTRODUCTION

The use of sorbents (biosorbents, powdered activated carbon) and cleaning agents (surfactants, chelation agents) to decontaminate surfaces such as pipes, walls, *etc.* represents a unique and cost-effective method for remediating DOE facilities. As envisioned, the sorbent or cleaning agents would be added to a liquid (most likely water) and the solution would be contacted with the contaminated surface. For example, a pipe that is contaminated with inorganic and organic contaminants can be contacted with a solution containing a surfactant (for the organics) and a chelating agent (for inorganics). After removal of the surface-bound contamination by the cleaning agents, a solid sorbent can be added to liquid to bind the cleaning agent-contaminant compound. A major problem associated with this approach is the efficient separation of the sorbent/cleaning agent from the liquid phase using conventional separation techniques.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and discharged. The concentrate exits at the edge of the membrane packs. The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance, increasing the volume of waste treated per area of membrane, and increasing the contaminant/solids concentration in the residual (*i.e.* increases volume reduction factor). SpinTek's centrifugal membrane technology represents an improvement over conventional ultrafiltration technology and increases the number of waste streams that can be treated using membrane treatment.

2.0 PURPOSE

The purpose of this research is to investigate the feasibility of using sorbents (biosorbents, powdered activated carbon) and cleaning agents (surfactants, chelation agents) to decontaminate surfaces (*e.g.*, pipes) and then to separate the sorbents/cleaning solutions from the aqueous phase using the SpinTek centrifugal membrane technology. The result of this work will be an effective decontamination/decommissioning process that can be used for inorganic (*e.g.* radionuclides and heavy metals) and organic contaminants.

3.0 BACKGROUND

Background information contained in this report pertains only to membrane technology. The Institute of Gas Technology (IGT) will provide, in a separate report, the required background information on the development/use of sorbents/cleaning solutions.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The fluid stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate ("clean" liquid) is forced through the membrane and is collected in the hollow shaft and then discharged. The concentrate (liquid containing the contaminants) exits at the edge of the membrane packs.

With time, the membrane surface will become fouled resulting in a decrease in the permeate flow rate. To reduce fouling in conventional membrane systems, a large portion of the concentrate is recycled back to the membrane unit producing large liquid velocities near the membrane surface. The large velocities increase turbulence which reduces the thickness of the fouling layer. In centrifugal membrane systems, the rotation of the membrane disk induces the turbulence (*i.e.*, shear force near membrane surface) required to minimize the thickness of the fouling layer. In conventional membrane systems, maximum surface velocities of about 15 ft/s are possible while with centrifugal systems surface velocities of 60 ft/s are typical. As the concentrate thickens with treatment time, conventional systems are not able to maintain the high velocities because of the difficulty in pumping viscous material at large flow rates. Because the centrifugal membrane system does not rely on pumping to produce the required surface velocities, extremely concentrated wastes can be treated.

Membrane systems are typically operated in either the semi-batch mode or the batch mode. In the semi-batch mode, fresh waste is added to the system at a rate equal to the permeate production rate. In the batch-mode, which normally occurs at the end of semi-batch operation, no fresh waste is added to the system and the concentrate remaining from semi-batch operation is concentrated further ("batch down"). During batch-down, large concentration factors are achieved (permeate is still being produced reducing the concentrate volume).

All membrane technologies are volume reduction technologies because contaminants are not degraded or destroyed. Thus, an important measure of the efficiency of membrane technology is the concentration factor (CF). The hydraulic-based CF during semi-batch and batch-down operation are calculated using the following two equations:

Semi-Batch Operation

$$CF_{SB} = 1 + V_{perm}/V_{feed\ tank}$$

Batch-Down Operation

$$CF_{BD} = CF_{SB} \times [V_{feed\ tank}/(V_{feed\ tank} - V_{perm})]$$

where,

CF_{SB} = hydraulic-based concentration factor during semi-batch operation.
V_{perm} = volume of permeate produced, gal.
$V_{feed\ tank}$ = volume of the feed tank (15 gal), gal.
CF_{DB} = hydraulic-based concentration factor during batch-down operation.

Concentration factors are expressed as 1X, 2X, *etc.*, and increase with treatment time. CFs in excess of 100X are obtainable with the membrane technology. Another measure of treatment efficiency is the permeate flux (volume of permeate/membrane area per time). The permeate flux for a given membrane is dependent on the waste's viscosity, solids content, and temperature. These waste characteristics can also change during treatment.

Membranes that are used for ultrafiltration are characterized by the molecular weight of a molecule that is not allowed to pass through the membrane. For example, the membrane used in this quarter's research had a molecular weight cut-off (MWCO) of 100,000. In theory, compounds having a molecular weight greater than the MWCO would be retained by the membrane and compounds with molecular weights less than the MWCO would pass through the membrane and be contained in the permeate. It should be noted that the MWCO designation is somewhat misleading because a molecule having a molecular weight less than the membrane's MWCO may still be retained by the membrane because its unique geometry.

4.0 METHODOLOGY

Centrifugal membrane technology will be tested using several sorbents/cleaning solutions. Several membrane types will be investigated. For each membrane type, the clean water flux (CWF) will be determined for the virgin membrane. The CWF serves as a baseline indicator to determine if the membrane is 1) permanently fouled and 2) sufficiently cleaned. For each waste-membrane combination, the SpinTek system will be operated first in the semi-batch mode. Towards the end of the treatment run the system will be operated in the batch mode. The following variables will be monitored during technology testing:

1. Contaminant concentration in concentrate and permeate.
2. Membrane flux.
3. Temperature and pressure.
4. Conductivity and pH of all liquids.

Permeate flux, contaminant(s) concentration in the permeate, concentration factor, operational ease, and the membrane's physical/chemical resistance and cleanability will be used to judge the effectiveness of the process. Several runs will be conducted for each membrane-waste combination. Special attention will be placed on identifying the quantity and quality of any residuals produced. Quality assurance/quality control practices, as outlined in US EPA's Test Methods for Evaluating Solids Wastes, will be followed. The use standard analytical methods (*i.e.*, ASTM, Standard Methods for the Measurement of Water and Wastewater, etc.) will also be followed.

5.0 WORK PERFORMED DURING THIS PERIOD

During the period 5/10/96 to 6/31/96, researchers from West Virginia University's Department of Civil and Environmental Engineering conducted experiments on the separation of a return waste activated sludge ("biomass" - used to mimicked a biosorbent decontamination/decommissioning waste) using the SpinTek system. A polymeric membrane having a molecular weight cutoff of 100,000 was employed. Results and discussion are presented in Section 6.0.

6.0 RESULTS AND DISCUSSION

In this chapter results from the separation of a return waste activated sludge will be presented and discussed. Three biomass wastewater treatment were conducted under different operational conditions. A schematic of the experimental apparatus is provided in Figure 1 (Figures are included at the end of the text portion of Section 6.0).

Run-1

Fifteen gallons of the biomass waste was treated under the following operating conditions: transmembrane pressure = 40 psi, rotation speed = 1750 rpm, feed temperature = 85°F, operational mode = batch and initial TSS concentration = 3,300 mg/L. Wastewater volume was reduced from 15 to 3 gallons (hydraulic concentration factor of 5). Because of the location of the pump inlet, the lowest attainable volume was 3 gallons. In future work, larger concentration factors will be achieved by increasing the initial volume of the waste.

The permeate flux and hydraulic-based concentration factor verses operational time are presented in Figure 2. The feed tank temperature versus operation time are presented in Figure 3. The temperature was controlled, using a heat exchanger, at 85°F ± 3. The flux was relatively stable, ranging from 72 to 100 gal/ft^2-d and averaged 89 ± 8 gal/ft^2-d.

Permeate turbidity verses operational time is presented in Figure 4. Turbidity ranged from 0.02 to 0.46 with mean and standard deviation of 0.17 ± 0.14. As a point of reference the turbidity of drinking water is below 1 NTU. In Figure 5, the hydraulic-based and TSS-based concentration factors (CF) are presented versus operational time. Also presented in Figure 5 is feed tank TSS concentration. The permeate TSS was always less than 5 mg/L (detection limit) and is not included in Figure 5. The agreement between the hydraulic and TSS based CFs was good. The initial TSS concentration was 3,300 mg/L and final feed tank TSS concentration was 14,280 mg/L resulting in a final TSS-based CF of 4.3 compared to the final hydraulic-based CF of 5. Biological activity could have reduced the feed tank TSS concentration given the high temperature and aerobic conditions resulting in a lower TSS-based CF.

Run-2

In Run 2, 15 gallons of biomass waste was treated under the following operating conditions: transmembrane pressure = 40 psi, rotation speed = 1750 rpm, feed temperature = 110°F, operational mode = batch and initial TSS concentration = 2,680 mg/L. Wastewater volume was reduced from 15 to 3 gallons (hydraulic-based CF = 5).

The permeate flux and hydraulic-based concentration factor verses operational time are presented in Figure 6. The feed tank temperature versus operation time are presented in Figure 7. The temperature was controlled at 110°F ± 2. Permeate flux ranged from 108 to 144 gal/ft^2-d and averaged 128 ± 11 gal/ft^2-d. Over the course of the run, the flux declined by about 25 percent (140 to 108 gal/ft^2-d).

Permeate turbidity verses operational time is presented in Figure 8. Turbidity ranged from 0.19 to 1.29 with mean and standard deviation of 0.53 ± 0.4. The turbidity was highest at the end of the

run when the feed tank TSS concentration was highest. In Figure 9, the hydraulic and TSS based CF and the feed tank TSS concentration are presented versus operational time. The permeate TSS was always less than 5 mg/L (detection limit) and is not included in Figure 9. The agreement between the hydraulic and TSS based CFs was good. The initial TSS concentration was 2,680 mg/L and final feed tank TSS concentration was 12,200 mg/L resulting in a final TSS-based CF of 4.6 compared to the final hydraulic-based CF of 5.

Run-3

In Run 3, 15 gallons of biomass waste was treated under the following operating conditions: transmembrane pressure = 40 psi, rotation speed = 1000 rpm, feed temperature = 110°F, operational mode = batch and initial TSS concentration = 2,265 mg/L. Wastewater volume was reduced from 15 to 3 gallons (hydraulic-based CF = 5).

The permeate flux and hydraulic-based concentration factor verses operational time are presented in Figure 10. Permeate flux ranged from 86 to 111 gal/ft^2-d and averaged 101 ± 7 gal/ft^2-d. Over the course of the run, the flux declined by about 23 percent (111 to 86 gal/ft^2-d). The feed tank temperature versus operation are presented in Figure 11. The temperature was controlled at about 110°F but there was a period of time when the temperature was about 106 °F. When the rotational speed was decreased there was less energy imparted to the system and temperature control was more difficult.

Permeate turbidity verses operational time is presented in Figure 12. Turbidity ranged from 0.47 to 6.8 with mean and standard deviation of 1.74 ± 1.9. The turbidity was highest at the end of the run when the feed tank TSS concentration was highest. In Figure 13, the hydraulic and TSS based CF and the feed tank TSS concentration are presented versus operational time. The permeate TSS was always less than 5 mg/L (detection limit). The agreement between the hydraulic and TSS based CFs was good. The initial TSS concentration was 2,265 mg/L and final feed tank TSS concentration was 11,840 mg/L resulting in a final TSS-based CF of 5.2 compared to the final hydraulic-based CF of 5.

Permeate Flux and Turbidity Comparison

In Table 1, average values of permeate flux and turbidity are presented for the three runs. Flux increased with increasing temperature and rotation speed. The decrease in viscosity from 85° to 110°F is approximately 25% percent while the flux increased by about 30 percent over the same temperature range. The majority of the increase in flux with increasing temperature can be attributed to the decrease in viscosity. Permeate flux decreased with decreasing rotational speed (Runs 2 and 3) because the fouling layer was thicker at 1,000 rpm. Permeate turbidity increased with temperature and rotational speed. At higher temperatures the membrane pores may enlarge allowing more colloidal material to pass and the advective transport forces increase with increasing flux. Decreasing the rotational speed allowed more material to build up on the membrane surface and pass through into the permeate. This was especially true at end of the run when the feed tank TSS concentration was highest.

Table 1. Average Permeate Flux and Turbidity

Run #	Operating Conditions	Flux, gal/ft^2-d	Turbidity, NTU
1	85°F - 1,750 rpm	89	0.17
2	110°F - 1,750 rpm	128	0.53
3	110°F - 1,000 rpm	101	1.74

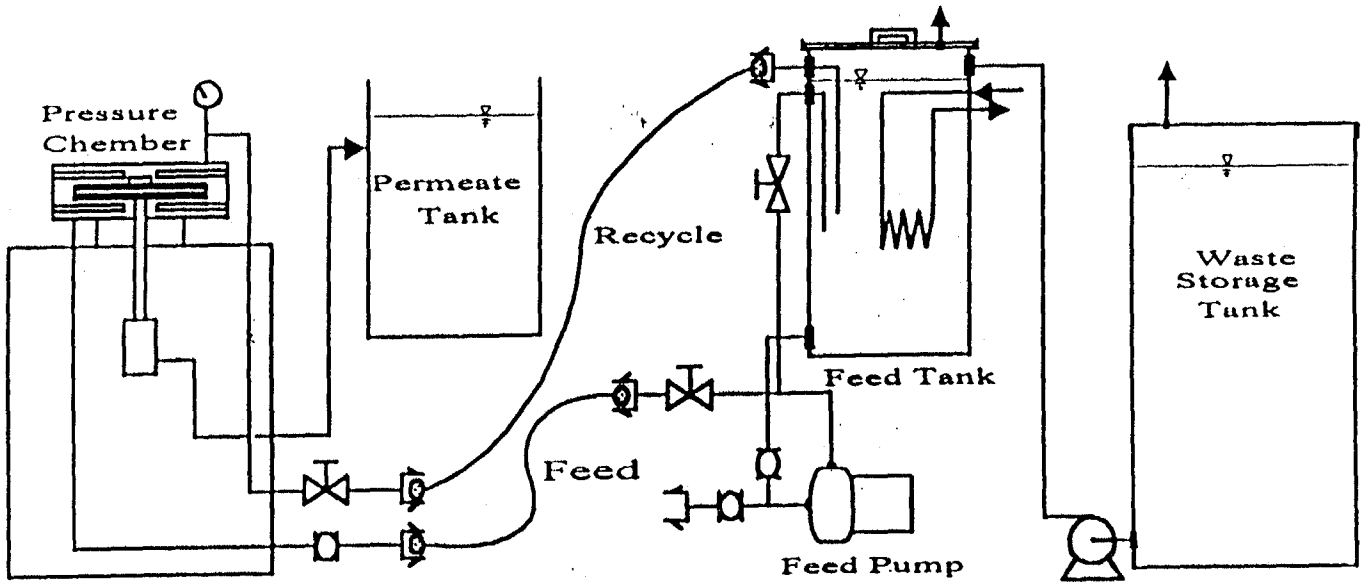


Figure 1. Schematic of Experimental Apparatus.

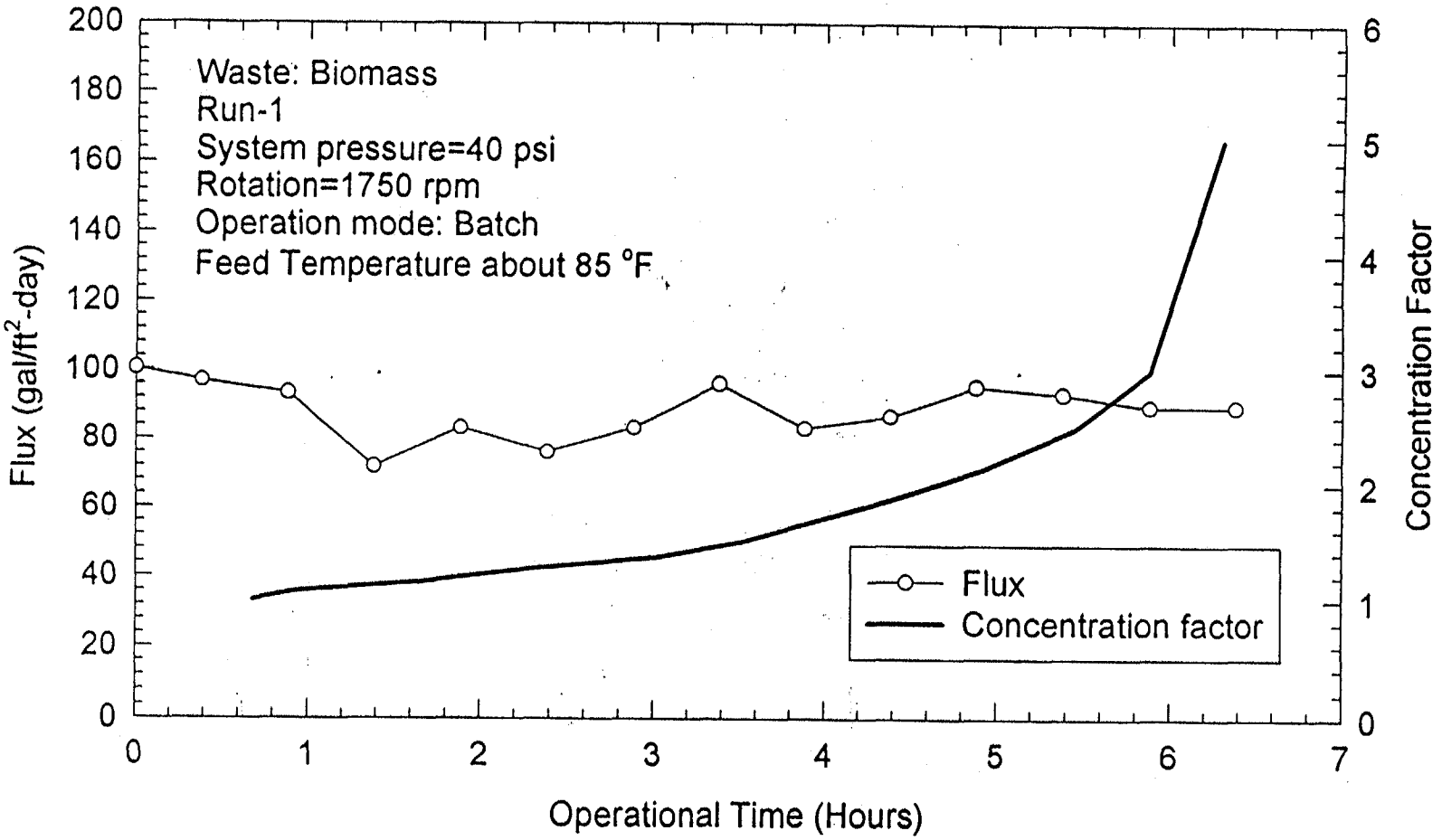


Figure 2. Permeate Flux and Hydraulic-Based Concentration Factor Verses Operational Time For Run 1.

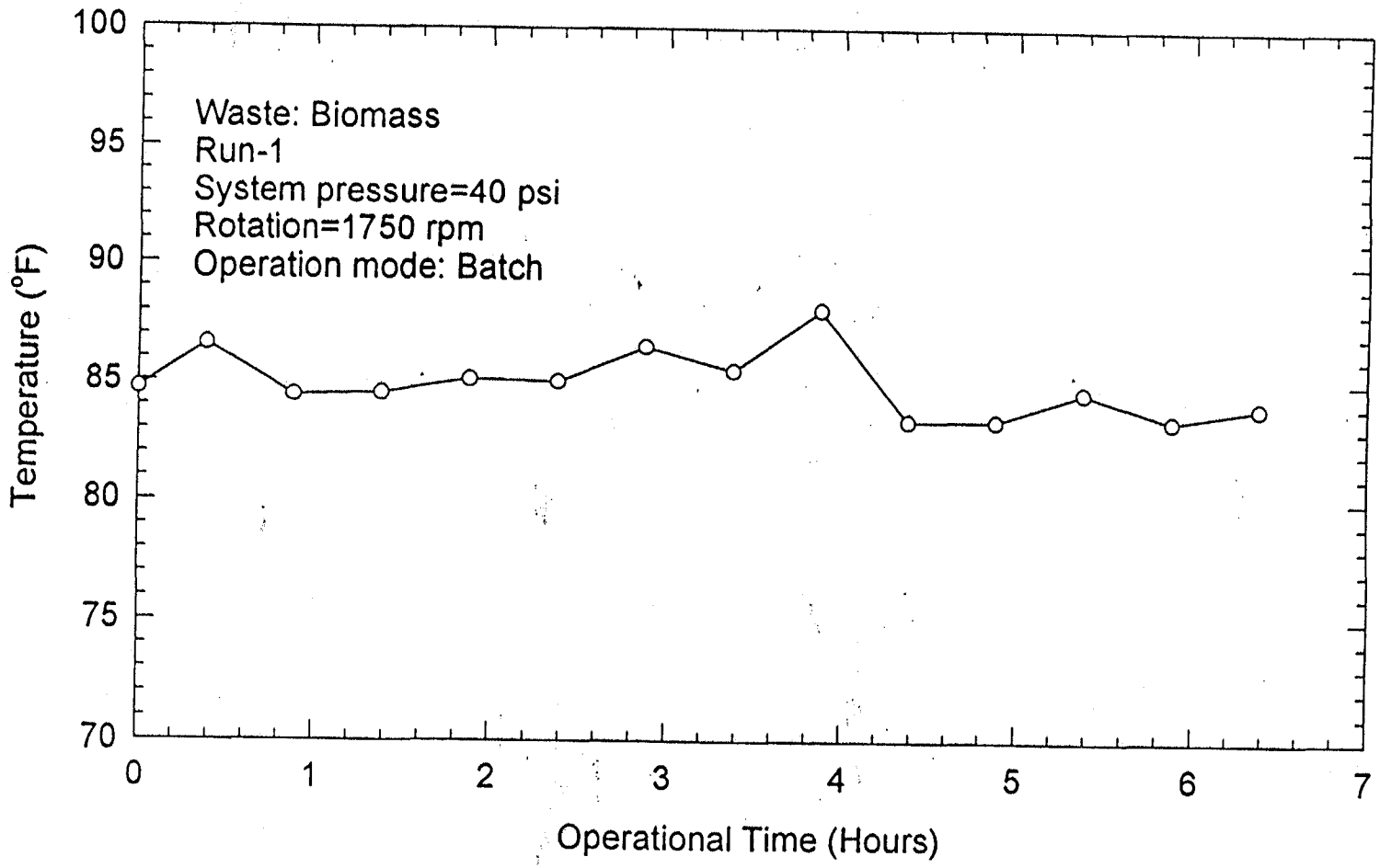


Figure 3. Feed Tank Temperature Versus Operational Time For Run 1.

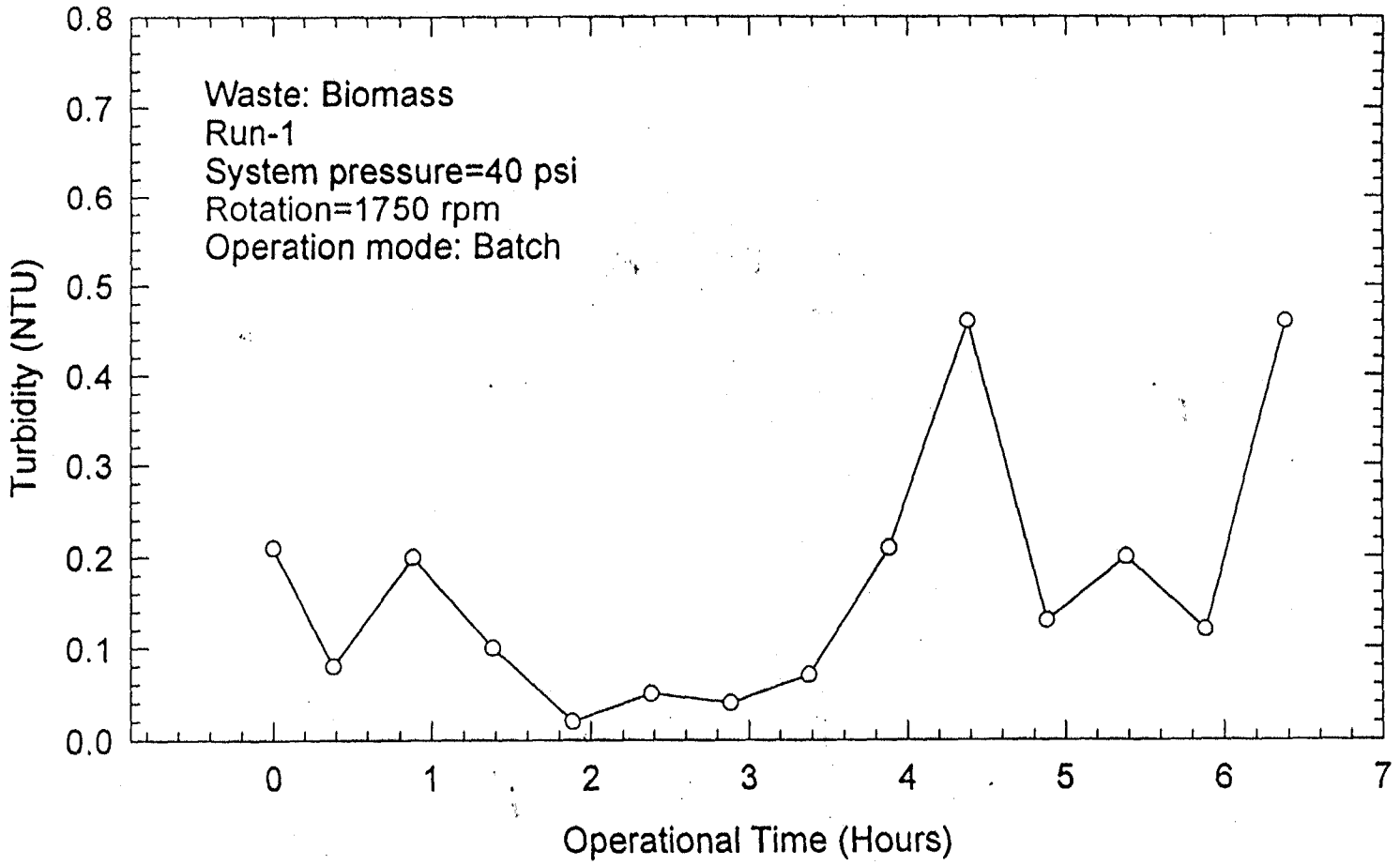


Figure 4. Permeate Turbidity Verses Operational Time For Run 1.

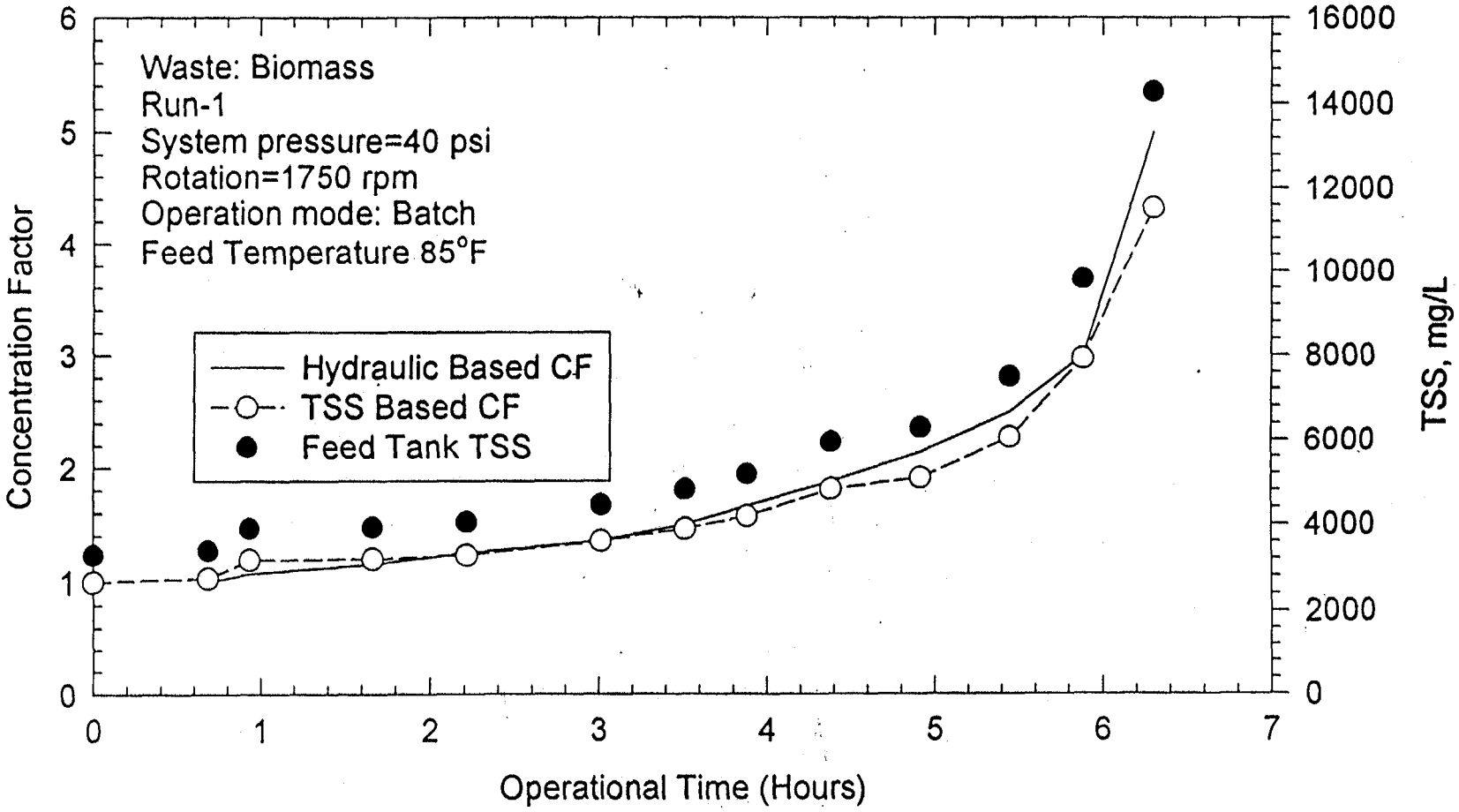


Figure 5. Hydraulic-Based and TSS-Based Concentration Factors, and Feed Tank TSS Concentration Versus Operational Time For Run 1.

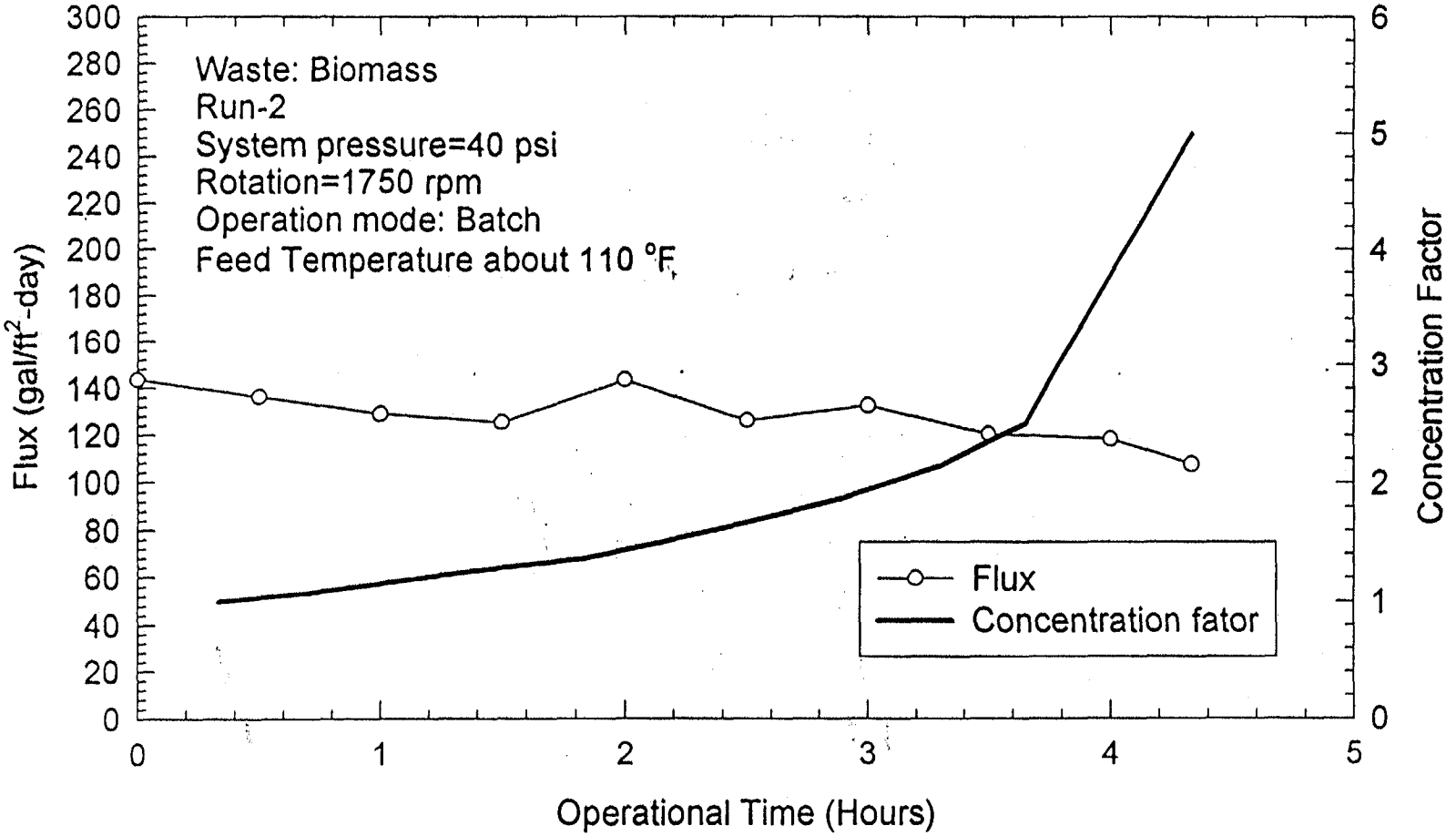


Figure 6. Permeate Flux and Hydraulic-Based Concentration Factor Verses Operational Time For Run 2.

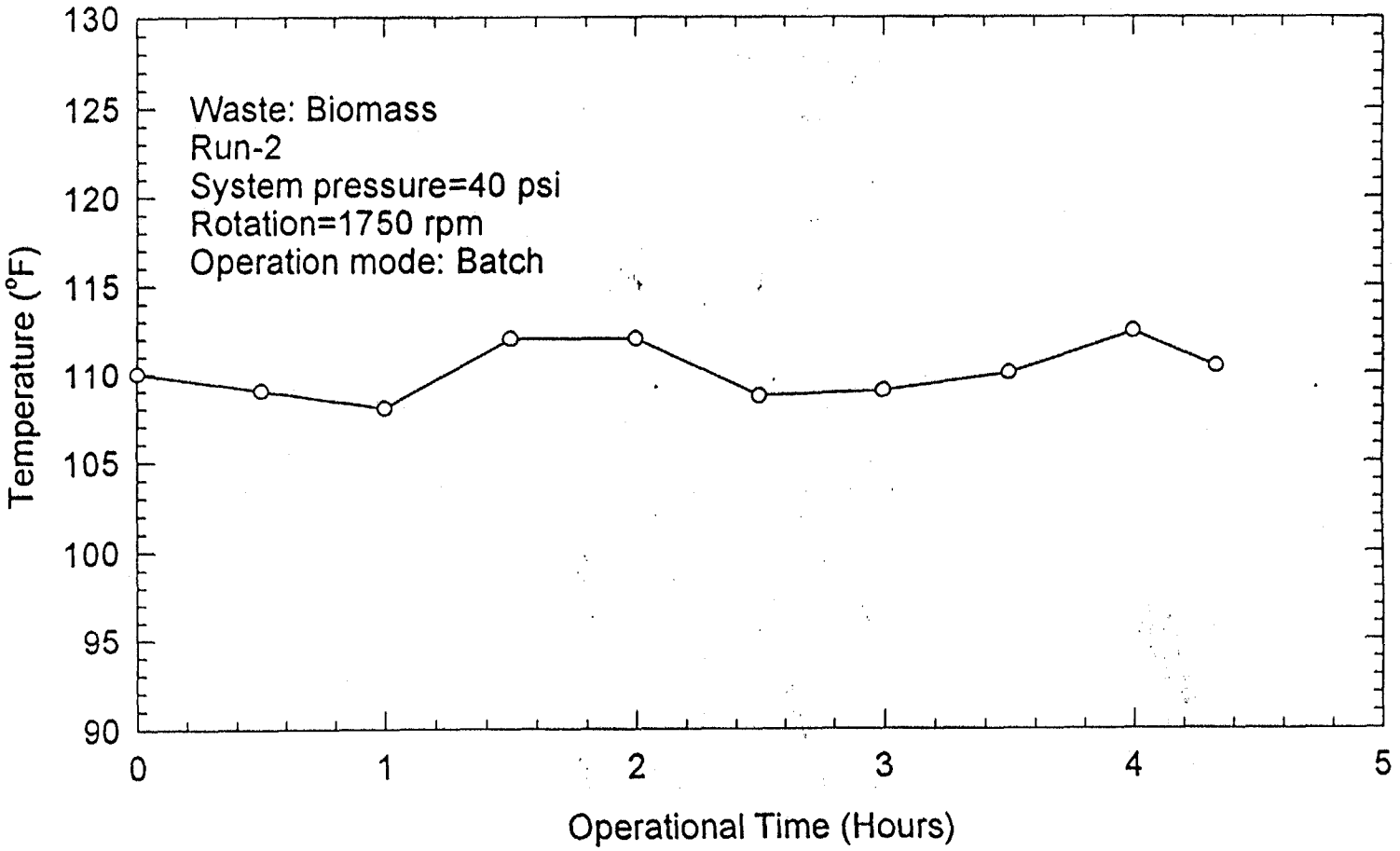


Figure 7. Feed Tank Temperature Versus Operational Time For Run 2.

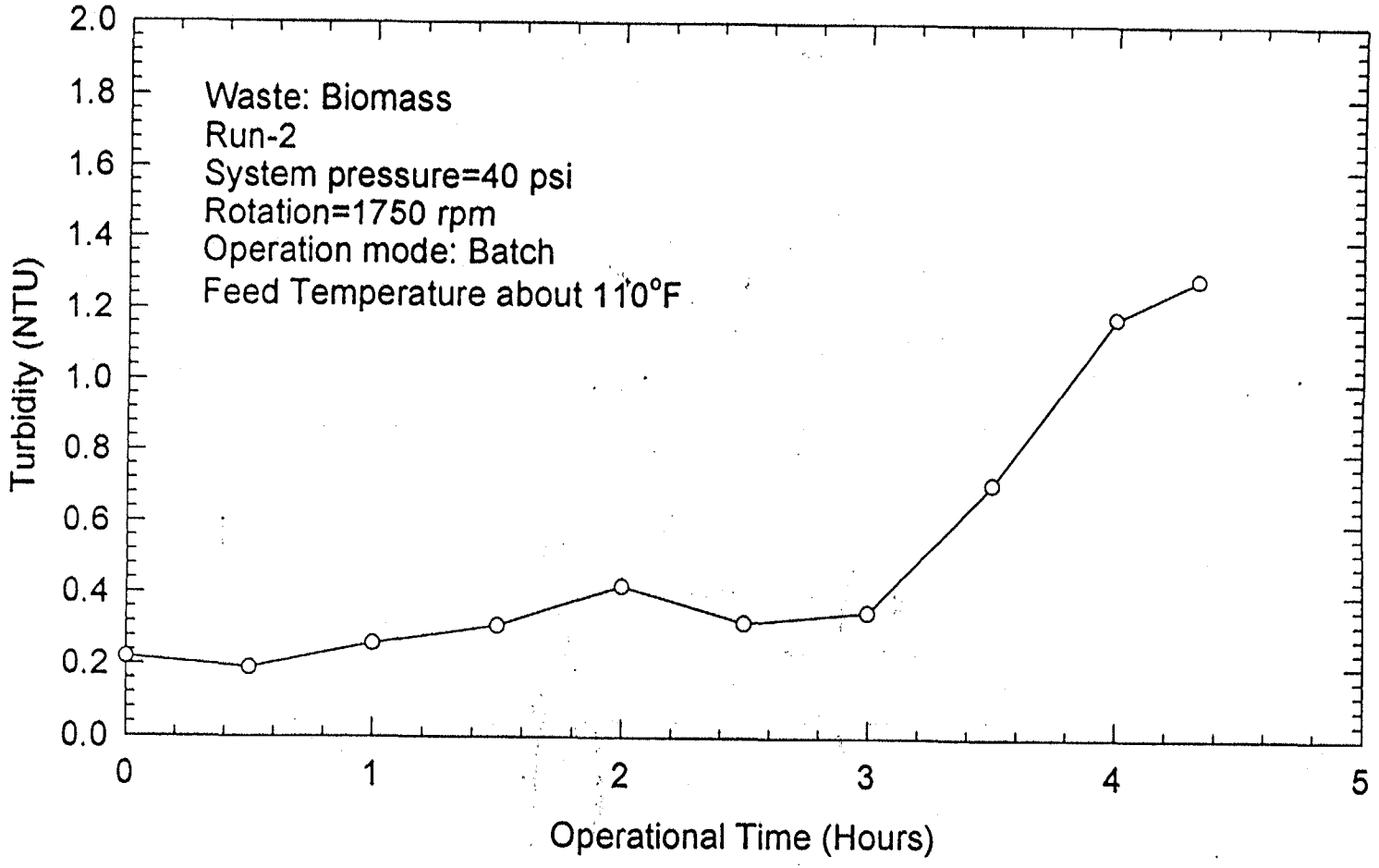


Figure 8. Permeate Turbidity Verses Operational Time For Run 2.

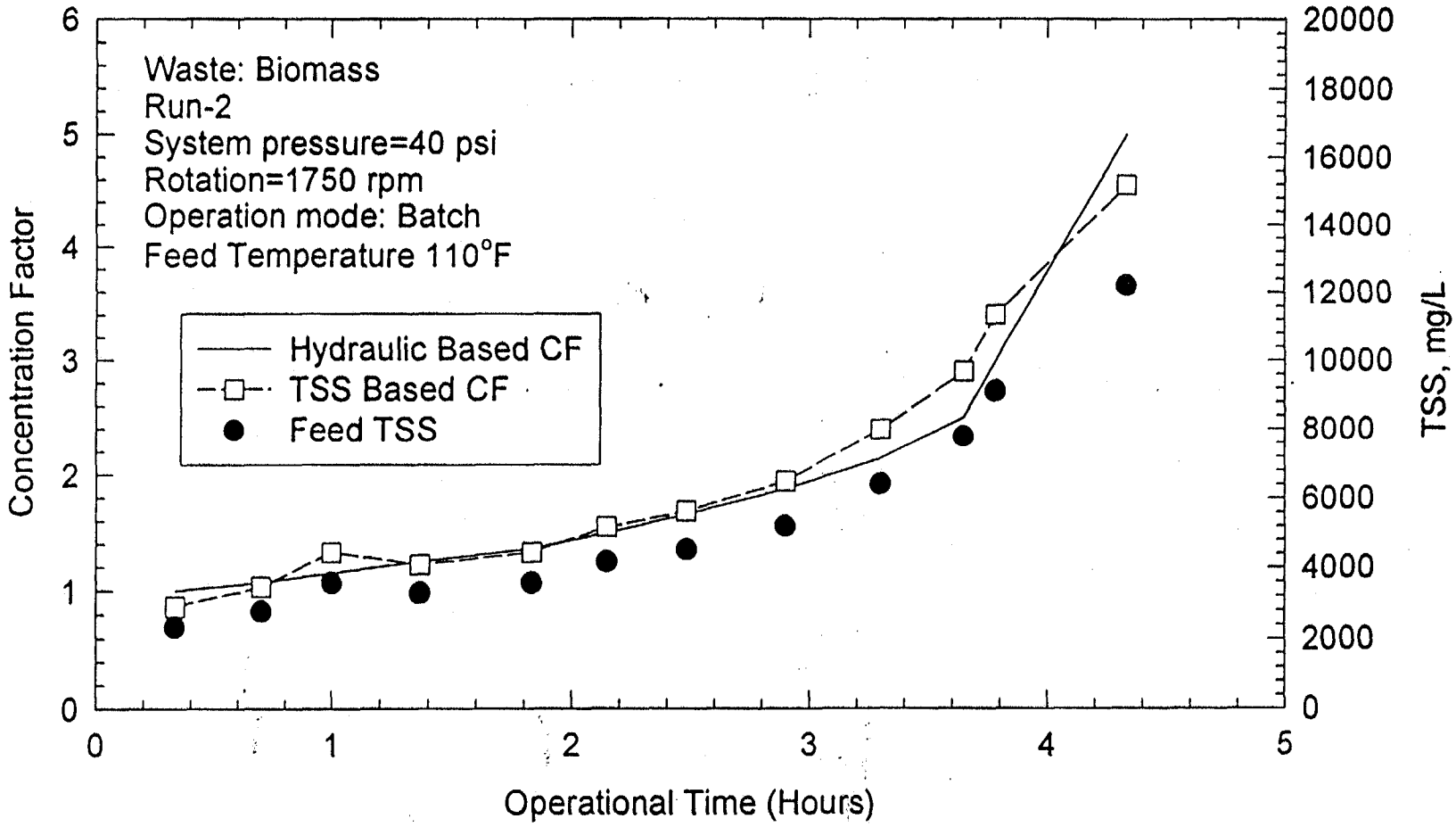


Figure 9. Hydraulic-Based and TSS-Based Concentration Factors, and Feed Tank TSS Concentration Versus Operational Time For Run 2.

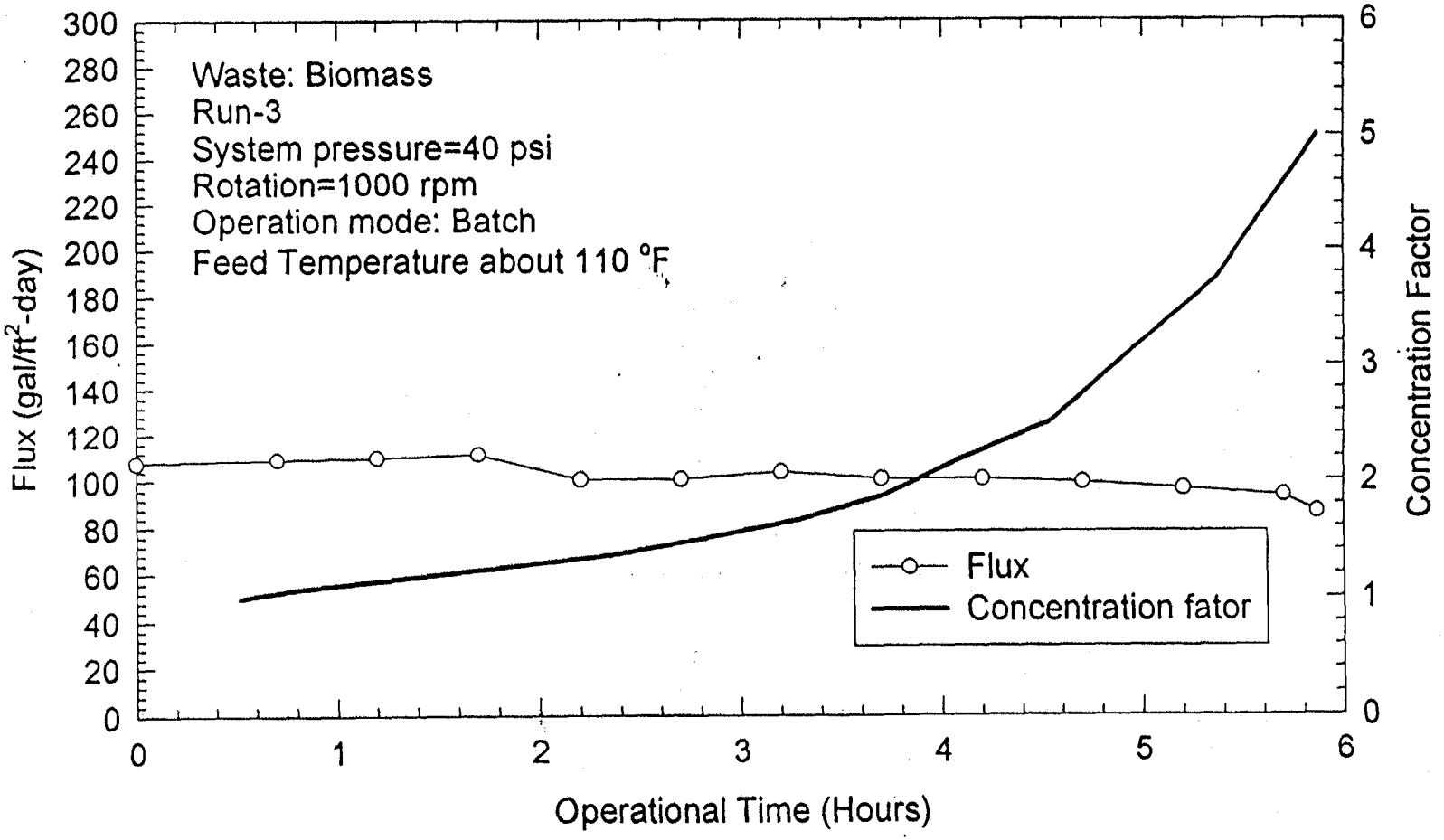


Figure 10. Permeate Flux and Hydraulic-Based Concentration Factor Verses Operational Time For Run 3.

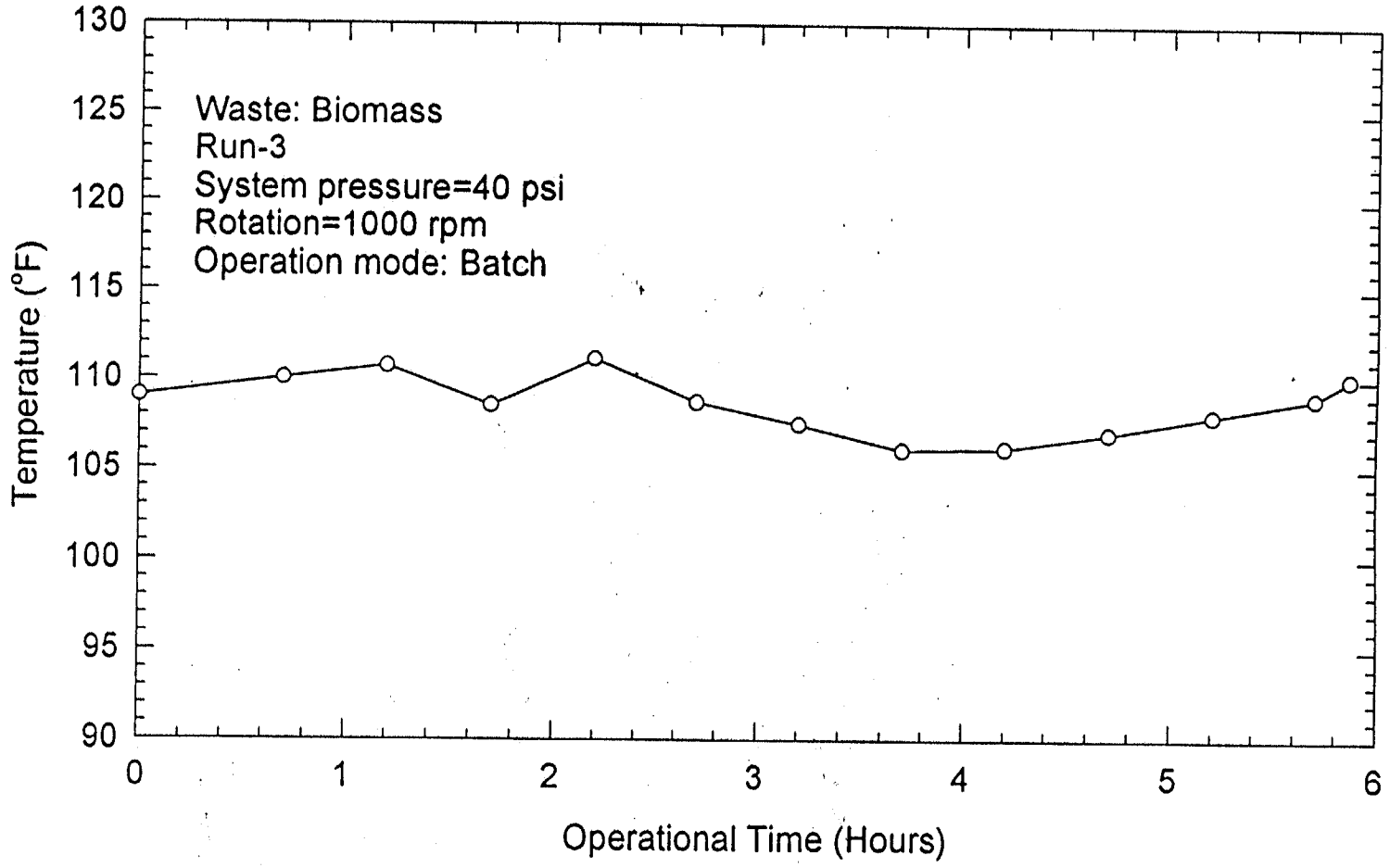


Figure 11. Feed Tank Temperature Versus Operational Time For Run 3.

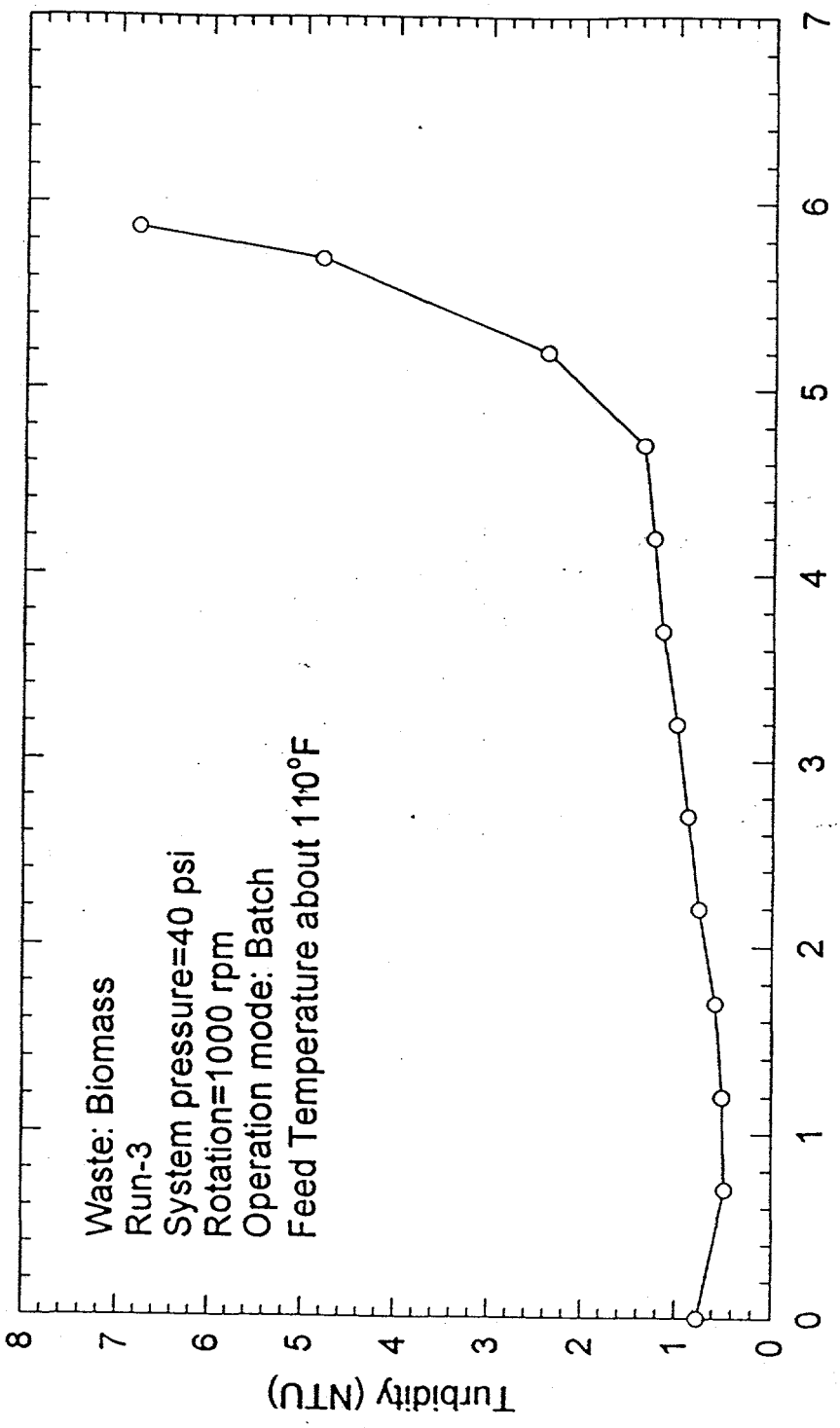


Figure 12. Permeate Turbidity Verses Operational Time For Run 3.

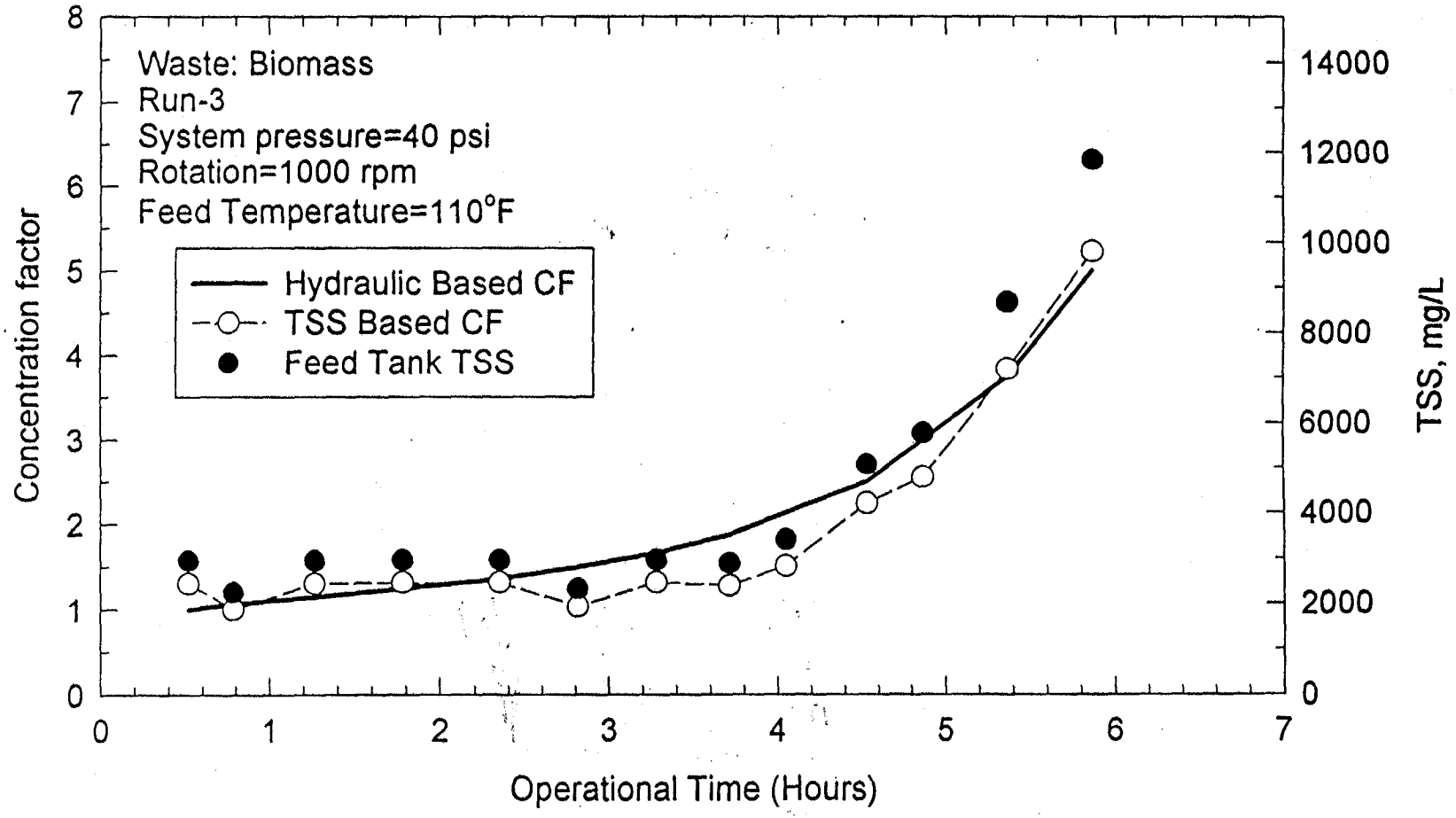


Figure 13. Hydraulic-Based and TSS-Based Concentration Factors, and Feed Tank TSS Concentration Versus Operational Time For Run 3.

7.0 CONCLUSIONS

The SpinTek centrifugal membrane system successfully concentrated a biological waste that mimicked a biosorbent waste from a decontamination/decommissioning effort. Permeate Flux increased with temperature and rotational speed. Permeate turbidity increased with increasing temperature and decreasing rotational speed. Hydraulic and mass based concentration factors were in good agreement.
but was still

8.0 WORK PLANNED FOR NEXT QUARTER

The following work will be conducted during the third quarter: 1) continue testing technology with return waste activated sludge, 2) test technology using a kaolin clay (mimicking a zeolite sorbent) and 3) test sorbents/cleaning solutions provided by IGT.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

None.

WVHTC Foundation's
Environmental Technology Support Program
METC Task No. 3.1

Quarterly Technical Progress Report
Reporting Period: April - June 1996

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

West Virginia High Technology Consortium Foundation
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July 22, 1996

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ETI - Second Quarterly Report
April 1996 - June 1996

Executive Summary

The second quarter of 1996 was used to complete the development of a formal business plan for the Environmental Technology Incubator. Attendance to the annual National Business Incubator Association conference during this period provided the opportunity to identify a model upon which the business plan has been based. This plan is predicated upon the role of the incubator as a commercialization service organization rather than the traditional incubator model as a property management company as a means of obtaining operating revenue. Additionally, the ETI will operate initially as an "incubator without walls" as a means of providing commercialization services. This will allow the ETI to focus on its mission of commercialization rather than devote a great deal of effort into property management. The ability to accept clients without requiring them to operate out of a specific location also allows the ETI to provide services to a larger number of clients in a broader region.

Consistent with this new direction, efforts are oriented towards using the 3rd and 4th quarters of 1996 as a means of implementing key initiatives to support the commercialization focus. Some of these activities that are being started now for implementation during the final half of 1996 are the following:

- Promotion of the ETI and development of a track record in business management services through a statewide solicitation to select two environmental product or service business plans (advertisement is running in newspapers on June 30 and July 7 and in the WV State Journal on July 15);

- Development of a model for WVU to commercialize WVU academic capital through business management services; this proposal has already been presented to the WVU Research Corporation and is now in negotiation with the WVU Sponsored Programs organization using the Alternative Fuels Program as the first area upon which to focus;

- Development of an Environmental Information Clearinghouse which will provide on-line environmental services in the areas of permitting, planning, and assessing; the ETI team will conduct market research to identify key services to implement; funding for this research will come from an amendment to a grant in place with EPA Region III;

- Development of the Sterling Faucet site as a testbed for environmental remediation with interest in helping to define "brownfields" policy for the state as part of this process (participating expected from METC); and

- Initiation of a program whereby graduating MBAs may apply their initiative in helping to develop new businesses areas in WV; currently negotiating with WVU civil/environmental engineer undergradutate, five years work experience as an

environmental engineer, and graduating MBA was selected for this program; he has tentatively selected a NOAA nitrous oxygen measurement device obtained under CRDA from the NOAA Aeronomy Laboratory in Boulder, Colorado for this purpose and will determine whether a business driven by impending higher stringency Ozone regulations can be developed.

A Board meeting was held on July 12 to review the busines plan and review each of these initiatives.

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. A total of $187,000 in funds for FY '95 and FY '96 has been awarded to the WVHTC Foundation from the Department of Energy to support the management and operation of the Environmental Technology Incubator which has been established in Morgantown, West Virginia. Funds from the U.S. Small Business Administration and the Environmental Protection Agency have also been used to further this initiative.

2.0 Purpose

The WVHTC Foundation's mission is to create a high technology business sector in north central West Virginia. 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 facilitate the pursuit of economic development. The Environmental Technology Incubator (ETI) will foster this effort in the area of environmental technology related business activity. The ETI will serve as a catalyst organization for change, linking entrepreneurs with technology, capital and academic resources in an effort to sustain new high technology environmental business development.

4.0 Methodology

The methodology for the establishment of the Environmental Technology Incubator includes a three phased approach:

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 tasks proposed to be performed during Phase 2 are the following:

Task 1: Start-up Activities

- Form an Advisory Board of DOE staff, community leaders, business experts, and academic representatives.
- Hire the ETI Director
- Define the ETI business plan and exercise key strategies to determine feasability inclusive of incubator services to be offered
- Admit the first cycle of ETI clients
- Begin to build a regionally-based capital network
- Assess DOE technologies
- Develop brochures and other marketing communications products

Task 2: Infrastructure Development

- Obtain and install computer/communications equipment and e-mail and Internet acess
- Furnish the ETI

Task 3: Operating Policies
Develop a comprehensive set of policies, procedures, and metrics for the selection and graduation of incubator clients

It should be noted here that those phases and tasks that stated in the the original proposal for this effort and part of past quarterly, were based upon the premise that the ETI was being created as a traditional incubator. A traditional incubator would include acquiring property and subleasing space as a means of generating the majority of the operating revenue. The current ETI model that has been defined focuses on the need to provide those services necessary to fulfill the ETI's mission (business management services) and generating a revenue stream from providing those services for a fee. This change in direction is the reason that there may be a disconnect between those tasks that have been proposed and planned to be worked on and those tasks have actually been performed during the quarter just completed and tasks planned to be work on.

5.0 Worked Performed this Period

The following tasks were performed during this period:

- A business plan was developed for the ETI
- A second Advisory Board meeting was postponed from June 20 to July 12 to review progress and approve the business plan
- Several WVU graduate students were hired to support the administrative and functional support needs of the ETI

- A solicitation was placed in nine newspaper publications and the West Virginia State Journal to announce the ETI's Business Management Services promotion
- A proposal was delivered to EPA regarding the creation of an Environmental Information Clearinghouse
- Additional work was performed on a proposal to the WVU Research Corporation to create a model for commercializing WVU environmental ("academic capital") research focusing on a technology derived from WVU's Alternative Fuels Program
- A program was drafted to utilize WVU graduate students who are completing course requirements to provide "sweat equity" towards the creation of new environmental business enterprises
- Work was performed to support the Sterling Faucet site remediation testbed initiative

6.0 Results and Discussion

All tasks performed are now oriented towards commercialization related activities. It is felt that there will be more focus on accomplishments from this point forward now that the business model and key projects have been defined.

7.0 Conclusions - ***not applicable***

8.0 Work Planned for Next Period

The following activities will be performed during the next period:

- Several new WVU graduate students will be interviewed and hired to replace previously employed summer staff to support the administrative and functional support needs of the ETI;
- Two applicants will be chosen and work begun on bringing the business concepts towards successful start-up;
- Work will begin towards the development of a business plan for the Environmental Information Clearinghouse;
- It is expected that after another presentation to the WVU Research Corporation, approval will be granted to the contract with the ETI to commercialize technology within the WVU Alternative Fuels Program and develop as part of this initiative a model for commercialization WVU academic capital;
- It is expected that the WVU graduate student "sweat equity" program will be initiated and the beginnings of a business plan defined; and
- The ETI team will provide support to facilitate the selling of the concept of using the Sterling Faucet site as a remediation testbed.

Budget Summary

As an overall strategy, the METC budget will be conserved as much as possible for pursuing ETI development type activites by the sharing of costs where appropriate with other WVHTC Foundation contracts. For example, the ETI Director is the current program manager for a NOAA sponsored grant and has off-set his direct labor charges to this specific contract. It is anticipated that his role will be reduced to a project manager function in order to devote more time to the ETI development once a replacement program manager is hired in the next reporting period.

As shown below, the Phases 2 and 3, the approved budget totals $119K of which, $12.4K was spent during the first quarter of 1996. An additional $34,222 was spent during the second quarter of 1996 with a cumulative amount of $46,667 spent for the first half of calendar year 1996. This number is estimated as the WVHTCF does not have their books current up to the June period.

ETI Phase 1 Funding Summary

The following budget is for Q2 of 1996.

ETI Phase 2 - Q2 '96 Budget

Total Direct Labor	$12,123	(estimated)
Overhead Rate (80.84%)	$11,022	(estimated)
		$23,146
ETI - Public Information Service	$50	
ETI - Office Supplies	$2,754	
ETI - Technical/Facilities Support	$2,954	
ETI - Travel	$1,768	
Miscellaneous (unpaid lease amount)	$960	
		$8,485
Total Cost Input		$31,631
G&A (.0753%)		$2,591
Total Expended		$34,222

The following budget is a cumulative amount spent for Q1 and Q2 of 1996.

ETI Phase 2 - Q1 & Q2 '96 Cumulative Budget

Total Direct Labor	$17,327	(estimated)
Overhead Rate (80.84%)	$14,007	(estimated)
		$31,334
ETI - Public Information Service	$60	
ETI - Office Supplies	$3,097	
ETI - Technical/Facilities Support	$6,144	
ETI - Travel	$1,795	
Miscellaneous (unpaid lease amount)	$960	
		$12,056
Total Cost Input		$43,390
G&A (.0753%)		$3,267
Total Expended		$46,657

SMALL BUSINESS SUPPORT PROGRAM

SMALL BUSINESS INTERACTION OPPORTUNITIES

SUBTASK 3.2

Quarterly Technical Progress Report
April 1 through June 30, 1996

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
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June 1996

EXECUTIVE SUMMARY
Small Business Support Program

Small Business Interaction Opportunities

Subtask 3.2

- The Environmental technology Incubator (ETI) Advisory Committee did not meet this quarter.

- A new Subtask 1.6 "Chemically Enhanced In Situ Bioremediation of Chlorinated Solvents" was initiated this period involving both INTERA Corp. and the USDOE Portsmouth facility.

- More interactions occurred this period with SPINTEK Corp. Their successful venture with the Institute of Gas Technology on the recent METC Research Opportunity Announcement will provide more opportunities to assist in the development of that technology for remediation use.

- Other contacts made were with Concurrent Technologies Corporation in hopes of leveraging research funds and opportunities.

1.0 Introduction

Subtask 3.2 "Small Business Interaction Opportunities" was initiated to address the technical problems or barriers to commercialization of innovative site remediation technologies. Through METC, a very large percentage of the USDOE innovative remediation technologies being developed is done by small businesses. Small business owners are creative thinkers usually technically competent beyond their resource base. At times they find technical problems and their lack of highly technical personnel creates an unsurpassable barrier for the small business to get their innovative technologies developed and commercialized. By ferreting out these problems, this program will allow teaming of a faculty member with the small business to solve the problem allowing further development of the innovative technology to occur.

2.0 Purpose

The Small Business Interaction Opportunities 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 three years the WVU Cooperative Agreement has funded numerous projects at WVU and Marshall University. This has resulted in defining at least four 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 include:

* Remediation processes such as surfactant flushing of soils and chemical and biological destruction of polyaromatic chlorinated hydrocarbons

* Confinement Barriers such as the Circulating (Desiccation) Air Barrier and Chemical Grouting Barriers

* Fluid Recirculating Systems such as the Drain Enhanced Soil Flushing using Prefabricated Vertical Drains (PVD's)

* Separation processes using novel membranes and novel forms of carbon

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 USDOE 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

The Environmental Technology Incubator (ETI) Advisory Committee did not meet this quarter. Meetings were scheduled but for a number of reasons were not conducted.

The interaction with GeneSyst (a company with a supercritical water oxidation system known as a Supercritical Gravity Pressure Vessel) came to a halt on June 27, 1996. Their contact person, Don Bogner, provided me with a letter from GeneSyst indicating he was to "cease and desist" from representing GeneSyst.

A new Subtask 1.6, "Chemically Enhanced In Situ Bioremediation of Chlorinated Solvents", was begun this period. It is a continuation of the bioremediation work being done by Dr. Sack and Dr. Carriere of the Dept. of Civil & Environmental Engineering. The work has been focused and it involves interaction with INTERA corp. and the Portsmouth (PORTS) facility. It is to be a polishing step following INTERA's surfactant flush which will be conducted in the very near future to clean a DNAPL contaminated site at the PORTS facility.

During late May a visit was made to SPINTEK Inc. at Huntington Beach, CA to discuss the direction of research to take in next years (97) program. Great progress is being made getting SPINTEK incorporated into a number of USDOE's separation process applications. This interaction between METC, SPINTEK, UNDEERC and WVU is most likely our greatest success to date arising from the WVU Cooperative Agreement.

In mid June Dr. John Zondlo and I visited Concurrent Technologies Corp. (CTC) in Johnstown, PA. Dr. Zondlo presented his work on using novel forms of carbon for pollution control and I presented an overview of the WVU Cooperative Agreement. It appears there are areas of mutual interest and Zondlo's work as well as SPINTEK's centrifugal membrane

technology has been included in a preproposal to the US Navy indicating those capabilities and the willingness of WVU to work together with CTC.

A proposal for internal USDOE funding was submitted during the latter part of June. It involved a cooperative effort between METC, faculty members from the WVU Dept. of Civil and Environmental Engineering and SPINTEK Corp. Its objective was to investigate utilization of the centrifugal membrane technology in separation processes in various USDOE remediation applications.

At the close of June, METC presented their EM program to Dr. Clyde Frank, head of EM50. During the presentation of the exsitu vitrification technology of Vortec Corporation, Dr. Frank inquired as to the effect of lithium hydroxide on the quality of glass being produced by the vitrifier. He indicated there are large amounts of this material which must go to disposal. This opportunity will be pursued during the next quarter.

6.0	Results and Discussion	N/A
7.0	Conclusion	N/A

APPROACH FOR ASSESSING POTENTIAL VOLUNTARY ENVIRONMENTAL PROTECTION, KANAWHA VALLEY AREA

Quarterly Technical Progress Report
for Period April 1 through June 30, 1996

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

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P. O. Box 880, Collins Ferry Road
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July 1996

ABSTRACT

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

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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

A meeting was held with the State of West Virginia Division of Environmental Protection regarding the establishment of a memorandum of understanding with EPA on the issue of voluntary clean-ups. They were interested, we are awaiting a copy of another MOU to use as a model, it has not arrived yet.

The companies were briefed on our meetings with EPA and the State and are interested in going further.

3.0 WORK PLANNED FOR NEXT PERIOD

Begin MOU development and discuss implementation with the companies. Link companies to DOE.

4.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES - None.