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EXECUTIVE SUMMARY

The following paragraphs comprise the research efforts during the first quarter of 1998 (January 1 - March 31). These tasks have been granted a continuation from the 1997 work and will all end in June 1998. This report represents the last technical quarterly report deliverable for the WVU Cooperative Agreement - Decontamination Systems Information and Research Program. Final reports for all of the 1997 projects will be submitted afterwards as one document.

*During this period, groundwater extraction operations were completed on **Task 1.6 - Pilot Scale Demonstration of TCE Flushing Through PVDs at the DOE/RMI Extrusion Plant**. The data have been evaluated and graphs are presented. The plot of TCE Concentration versus Time shows that the up-gradient groundwater monitoring well produced consistent levels of TCE contamination. A similar trend was observed for the down-gradient wells via grab samples tested. Groundwater samples from the PVD test pad Zone of Influence showed consistent reductions in TCE concentrations with respect to time. In addition, a natural pulse frequency is evident which will have a significant impact on the efficiency of the contaminant removal under natural groundwater advection/diffusion processes. The relationships between the PVD Extraction Flow Rate versus Cumulative Time shows a clear trend in flow rate. Consistent values between 20 to 30 g.p.m. at the beginning of the extraction duration, to less than 10 g.p.m. by the end of the extraction cycle are observed. As evidenced by the aquifer's diminishing recharge levels, the PVD extraction is affecting the response of the aquifer's natural attenuation capability.*

Progress was also marked on the Injection and Circulation of Potable Water Through PVDs task. Data reduction from this sequence of testing is ongoing. Work planned for next quarter includes completing the Injection / Extraction of potable water task and beginning the Surfactant Injection and removal task.

*Work by The Institute of Gas Technology (IGT) this quarter on **Task 1.7 - Technical Support for Surfactant Flushing through Prefabricated Vertical Drains (PVDs) at the RMI Ashtabula Site** consisted of ordering the materials to prepare 1,400 gallons of surfactant flooding solution for field experimentation. This quantity is the anticipated volume of material needed for the next round of injection/withdrawal tests at the 10 ft by 10 ft test pad and represents about one pore volume. The ingredients delivered to the site include 28 gallons of MA-80-I, 7 gallons of GMO-K, 33.6 pounds of sodium chloride, and 5.6 pounds of xanthan gum. The surfactant solution is best prepared by first dissolving the sodium chloride and the xanthan gum. Vigorous mixing may be required and the surfactants should not be added to the mixture until the xanthan has been fully dissolved. Afterwards, the surfactants can be added either separately or together. Mild agitation at this point will reduce foaming and should be sufficient to get these components into solution.*

IGT received 10 samples from SpinTek for surfactant analysis relating to ultrafiltration testing. Surface tension readings and dilutions were taken to determine the approximate surfactant concentration of these samples in comparison with a standard curve prepared for the four component surfactant mix. Since ultrafiltration can alter the ratio of components of the mix, it is possible that the standard curve is not accurate for each sample. However, tests with control samples suggest that readings should be accurate within a factor of two, and in the worst possible case, a factor of ten. The surfactant concentration anticipated in these filtrate samples after the removal of surfactant micelles is about 10 ppm or less. Results showed that ultrafiltration can reduce surfactant concentrations from 25,000 ppm to about 10 ppm, under some circumstances. These are highly favorable results that suggest ultrafiltration could be used to process the surfactant-containing liquids. Ultrafiltration tests with solutions containing TCE and surfactants were not done, but are clearly needed before drawing any definite conclusions.

Analytical methods for surfactant/TCE mixtures were determined, and several licensed commercial laboratories were contacted to identify their ability to meet the unique needs of this project. The presence of relatively high concentrations of surfactants in combination with contaminants is not typical and methods have not been specifically

developed for the analysis of such samples. EPA SW846 Method 5030B/8260B will be used for the analysis of liquid samples, and 8275A for the analysis of soils containing surfactant/contaminant mixtures. Method 5030B is a purge and trap method while 8260B is a GC/MS method for the analysis of material eluted from the trap. Method 8275A is a thermal desorption method coupled with GC/MS analysis. While these methods are thought to be the most appropriate choices, confirmatory tests with rigorous QA/QC should also be done for verification.

The most helpful labs contacted were Core Labs and DIAL. Core volunteered to perform preliminary tests on soil and water samples that contained surfactants to help select the appropriateness of the methodology. The liquid samples were analyzed by a modified purge and trap technique in which antifoam was added directly to the liquids and GC/MS analysis of contaminants captured in the trap. The soil samples were first extracted with methanol and then the methanol extract was subjected to purge and trap followed by GC/MS. The results were favorable regarding the analysis of liquid samples, but an improved technique is needed for the soil samples.

Tests were performed to see if sodium sulfate can be substituted for sodium chloride in the selected surfactant solution. Sodium sulfate is an essential component for treating technetium in the I-Chrome process. Results indicate that the substitution is acceptable if equivalent concentrations are maintained (0.05 M). However, if sodium sulfate concentrations of 1 M are used, the surfactant solution is negatively affected and therefore not recommended. Surfactant biodegradation experiments were also done. Results showed that complete biodegradation of the four component surfactant mix at a starting concentration of 25,000 ppm can be achieved, but the treatment time could be as long as 60 days. However, if adapted cultures are employed surfactant solutions with a starting concentration of 2,500 ppm can be biodegraded in as little as nine days. The adaptation procedure included the use of surfactants as sole carbon and energy sources for multiple cycles of growth in a chemostat. Surfactant-adapted bacteria are being grown and preserved/frozen for future use. If ultrafiltration is used as a component of the wastewater treatment process, the concentration of surfactant requiring biodegradation should only be about 10 ppm and hence easily biodegraded.

Work this quarter on **Tasks 1.8a and 1.8b - Installation/Operation of PVD System and Design/Construction Support for Wastewater Treatment Associated with the PVD Operation** by RMI Environmental Services (RMIES) are reported together. RMIES intermittently operated the PVD system during the weeks of January 12, January 19, February 17, February 23, March 2, March 9, and March 16, 1998. Approximately 3,000 gallons of water have been extracted to date. A variety of injection/extraction modes were implemented to establish optimum operating conditions. January operations were in an extraction only mode. During the week of February 17, experiments were conducted to evaluate the potential for volatilization of TCE during extraction and the injection system was commissioned.

A total of 265 samples (groundwater and extract water) have been collected. Samples were analyzed for one or more of the following parameters: volatile organics, total uranium, Tc-99, TSS/TDS, specific conductance, pH, and/or temperature. Results from the off-site laboratory for samples collected through February 25 show that TCE concentrations in the extracted groundwater are less than the TCLP limit for TCE. Therefore, the extracted groundwater does not have to be handled or stored as hazardous waste. This alleviates the potential storage capacity limitations for the Hazardous Waste Storage Area. Approximately 6,000 lbs. of soil were collected and packaged for shipment in early April to NCSU for further laboratory studies.

RMIES developed and submitted a de-minimis exemption request to the OEPA for TCE emissions associated with the air stripper that will be used for the Phase I treatment of TCE contaminated groundwater. OEPA granted this exemption in March 1998. An NPDES permit modification was submitted to the OEPA in early February. OEPA approved the NPDES modification request and public noticed it on March 30, 1998. Pending no significant comments from the public, official OEPA approval is expected April 30, 1998 allowing RMIES to treat and discharge the water.

Various pieces of process equipment including the process control panel and miscellaneous hardware (e.g., process piping, valves, instrumentation, and electrical materials), tanks, pumps, filters, air stripper and other similar items

were ordered and/or received this period. Internal work orders were developed to construct the waste water treatment system and it is expected to be built by April 20. This is approximately 30 days behind schedule due to the additional work required to obtain the water permit modification. RMIES continued to investigate other on-site laboratory expansion capabilities to support long term operational needs of the wastewater treatment system. No progress has been marked here.

RMIES worked with IGT to define the technical specifications and received revised bids on a gas chromatograph (GC) to conduct on-site organic analysis of water. The purchase order is scheduled to be placed in early April, and shipment is scheduled for early May. RMIES purchased and received a surface tension meter to conduct on-site surfactant analysis. RMIES will work with IGT to obtain matrix specific calibration curves and operational information.

Task 2.1 - Analysis of the Vortec Cyclone Melting System (CMS™) for Remediation of PCB Contaminated Soils Using Computational Fluid Dynamic Codes (CFD) reports progress on two fronts: 1) The formulation of a reduced chemical kinetics mechanism and 2) Validation of the radiation model. The complex kinetics model used previously was too large for reasons of computational cost and application in the CFD codes used in this study. A reduced mechanism for conversion and destruction of dichloromethane was formulated that reduced the number of reactions from 3430 to 34. The reduced mechanism contains only 21 species as opposed to the 278 reactions involved in the complex mechanism. Results from the reduced and complex mechanism were compared. Comparisons were also made with equilibrium calculations. The performance of the reduced mechanism was favorable for the PCB compounds, but only fair for the intermediate compounds such as CO, HO, O and Cl.

The radiation calculations performed on the recuperator using the FLUENT code were validated this quarter. A test case studied by Staiek and Collins (1992) was selected for this purpose. This case has a similar geometry to the Vortec recuperator and one-dimensional analytical solutions were available for various scenarios with and without radiation. Two typical cases were simulated with the same initial and boundary conditions. Agreement between the results reported in the literature and the FLUENT calculations were good.

Ultrafiltration testing was the main focus of **Task 3.2 - Use of SpinTek Centrifugal Membrane Technology and Sorbent/Cleaning solutions in the Decontamination and Decommissioning of DOE Facilities** this period. CYTEC Aerosol MA 80-I surfactant was treated using a hollow fiber ultrafiltration system designed and constructed by the Membrane Separation Research Group in West Virginia University's Department of Civil and Environmental Engineering. An experimental study on the separation of surfactant micelles using a hollow fiber (HF) membrane system was conducted that employed a hollow fiber membrane module having a molecular weight cutoff of 5,000 (HF 1.0-43-PM5). The HF separation system was also used to recover CYTEC Aerosol MA 80-I surfactant.

Permeate flux, turbidity, pH, conductivity and adsorbance of both permeate and concentrates were measured regularly during the experiment. Permeate flux decreased rapidly over the first 2 hours of operation, and slowly decreased thereafter from approximately 28 hours of operation through the end of experiment. Permeate turbidity was stable throughout along with the pH of the permeate and concentrate. Concentrate turbidity was stable through the first 36 hours of operation, then increased at the end of the experiment. The permeate and concentrate conductivity increased gradually.

A linear relationship between conductivity and MA 80-I concentration was observed. Thus, the MA 80-I concentration could be estimated by measuring the conductivity of the feed and permeate solutions. Low surfactant rejections were observed at low feed concentrations. As the feed concentration increased, surfactant rejection also increased. A surfactant rejection of 89% was observed at a final MA 80-I concentration of 12.9%. The MA 80-I surfactant is proposed for use at the RMI Ashtabula, Ohio site.

Task 4.1 - Use of Centrifugal Membrane Technology With Novel Membranes to Treat Hazardous/Radioactive Wastes continued to work on the following: 1) A literature search, 2) Investigation of system performance treating an oily wastewater at a constant concentration of 30% synthetic oil, membrane rotational speed of 1750 rpm, and applied pressure ranging from 25 to 70 psig; and, 3) Application of a standardized cleaning procedure and tracking of membrane resistance after the oily wastewater experiments. A ceramic membrane with an average pore size of 0.11 μm was used with the SpinTek technology to treat a synthetic oily wastewater. A mathematical model was used to correct for the average permeate back pressure due to centrifugal force.

The permeate flux was stable at each applied pressure condition. The permeate flux was re-investigated after the pressure independent flux was determined. A lower rebound was observed that may be due to membrane pore plugging or adsorption of solute molecules onto the membrane surface. Additionally, it is possible that the thickness of the solute boundary layer was not reduced to its initial value when the applied pressure was decreased. A higher resistance to the hydraulic flow of permeate and thus a lower permeate flux would result from a thicker solute concentration boundary layer. Permeate pH was greater than concentrate pH throughout experiment. Both permeate and concentrate pH followed the same general trend: decreased through the first hour then increased through the end of the experiment. A net decrease in permeate conductivity was observed. Concentrate conductivity was constant. Permeate conductivity was greater than concentrate conductivity through approximately 2.75 hours, then concentrate conductivity exceeded permeate conductivity through the end of the experiment. Distinct step-wise changes in permeate and concentrate pH and conductivity were not observed as applied pressure was increased. No oil was visible on the membrane surface after cleaning.

A technical difficulty experienced during the first quarter was the failure of the mechanical seals on the SpinTek feed pump. Due to the leaking seals, maintaining a constant applied pressure in the membrane vessel was not possible and experimentation was halted. New seals have been ordered from the manufacturer for the Grundfos CRN2-40 pump and will be replaced upon arrival.

The application of Uranium removal and recovery was the primary focus of the work performed on **Task 4.2 - Environmental Pollution Control Devices Based on Novel Forms of Carbon** this quarter, along with the continued evaluation of the cathode carbon materials. It was found previously, that the adsorbed uranium could be stripped easily from the carbon fiber bed by simply reversing the potential to +1.0V and pumping a 0.1N KNO₃ solution through the cell at a flow rate of 0.7 ml/min. Stripping efficiency was further examined by filtration of the solution as well as by direct measurement of uranium concentration in the stripped solution. An electrosorption test was run at -0.3V and the stripping was run after. More than 96% of the adsorbed uranium was stripped and recovered during the first 30 minutes. The precipitates were collected by filtration through a 0.45 μm filter membrane. The uranium in the filtrate is very easy to separate and recover from aqueous solution in the neutral pH range. The solid form eliminates the need to treat a secondary waste.

The concentration of surface functional groups on ASI carbon fibers were determined using wet chemical methods. Selective neutralization by equilibration with a series of bases with increasing strength allows differentiation of various types of surface groups. The results were related to the efficiency of uranium removal by electrosorption on the carbon fibers. This is one approach to clarify chemical reaction of uranium during electrosorption and to explain the great difference between the "as-grown" and "oxidized" ASI carbon fibers. Results obtained so far are not consistent. More tests based on larger carbon samples (up to 5 g) will be run. Meanwhile, instrumental analysis using FTIR, XPS, etc. will be tried to complement the information from chemical analysis.

An attempt was made to remove uranium from drinking water. As a naturally occurring radioactive element, uranium exists in both ground water and surface water. Many drinking water supplies contain 3-500 ppb or even higher uranium concentrations. To comply with the treatment of waters containing ppb level uranium, adjustments to the uranium analysis were necessary. For the previous tests, polarographic data have been obtained using a static mercury drop electrode with a potentiostat. A linear potential scan was applied between 0.0 and -0.6V. This method is sufficiently accurate for samples containing 10-200 ppm uranium but not for 1 ppm or less. By modifying the

technique and using the differential pulse scan mode, the detection limit has been markedly reduced to around 5 ppb. A voltammetric analyzer (Mode EC/225, IBM) was used as the scanning potential source and an X-Y recorder (Model 7035B, HP) as the current recorder. Tests using a feed solution of 1 ppm uranium were made at two different potentials. Results show that up to 63% removal of uranium was reached from a single pass of the solution through the electrochemical cell with ASI oxidized carbon fibers as the cathode. When the applied potential was lowered to -1.0V, the removal efficiency was greatly improved. In two and half hours the uranium concentration was reduced to less than 8 ppb and in three hours the uranium was essentially 0 ppb (below the detectable limit). Using the value of $0.368 \text{ g}_{\text{uranium}}/\text{g}_{\text{c-fiber}}$, 1 gram of ASI carbon fiber can treat almost 100 gallons (368 L) of 1 ppm uranium solution. With its high removal efficiency, great capacity, and convenient separation of adsorbed uranium, the electrosorption technology with the use of ASI carbon fibers may be an effective approach for uranium removal from potable water.

During this reporting period **Task 5.1- Small Business Technical Based Support** focused on completing the new five year proposal for submittal to DOE/FETC. The first year's work will demonstrate innovative remediation technologies in the field developed in the previous agreement. A larger scale field demonstration (0.1 acres) of the Prefabricated Vertical Drain (PVD) Technology at the RMI Ashtabula, Ohio site is planned. The work is a joint effort between DOE-Ashtabula, FETC-Morgantown, West Virginia University (WVU), North Carolina State University (NCSU), RMI Environmental Services (RMIES), The Institute of Gas Technology (IGT), SpinTek and Nilex Corporation. RMIES will provide the treatment scheme and train to treat the extracted fluids to standards allowing re-injection or release to the local sewage treatment plant. Nilex Corporation will be responsible for supplying the materials required and installing the PVDs. IGT will provide the expertise on selecting, mixing and injecting the various chemicals through the PVDs and will address QA/QC issues. The SpinTek Centrifugal Membrane Technology will be used to separate the surfactant from the surfactant/TCE/groundwater mixture so that it can be recycled and reinjected. A great cost savings will be realized by incorporating this technique into the treatment train. Discussions have recently been completed for bringing the 3-M Corporation's Specialized Separation Membrane Technology on line for treating Technetium 99 (T^{99}). The 3M Corporation has developed, through FETC-Morgantown, an adsorbent particle membrane fabricated into small 10-inch cartridges capable of removing T^{99} . Conventional methods are planned for addressing the small quantities of Uranium that may be encountered.

A proposal was also submitted for a research paper on watershed economics to be used as a tool for environmental management. This project was requested by Mr. Karl Stockle and Steve Meador of National Center for Acquisition and Business Excellence (NCAB) at FETC Morgantown. Funding for this work is expected to come from the NCAB.

Plans for the annual WVU Cooperative Agreement Program Review Conference were initiated. Technical data sheets for the new program were developed and work began on designing a proceedings document for the event. The conference was originally planned for April at FETC-Morgantown, but due to scheduling conflicts it has been pushed ahead to June 10, 1998.

TABLE OF CONTENTS

Executive Summary

Project Titles with Principal Investigators

Administrative Summary

Budget Updates

Schedule Updates

Quarterly Technical Progress Reports

FOCUS AREA 1.0: SUBSURFACE CONTAMINANTS, CONTAINMENT AND REMEDIATION

- 1.6 Pilot Scale Demonstration of TCE Flushing Through PVDs at the RMI Extrusion Plant in Ashtabula, Ohio
- 1.7 Technical Support for Surfactant Flushing Through PVDs at the RMI Extrusion Plant in Ashtabula, Ohio
- 1.8A Technical Support on Installation and Operation of the PVD System at the RMI Extrusion Plant in Ashtabula, Ohio
- 1.8B Design, Procurement, Installation and Operation of a Pilot Scale Wastewater Treatment System to Treat Extracted Groundwater Fluids During Demonstration of the PVDs at the RMI Extrusion Plant in Ashtabula, Ohio

TABLE OF CONTENTS (Continued)

FOCUS AREA 2.0: MIXED WASTE CHARACTERIZATION, TREATMENT AND DISPOSAL

- 2.1 Analysis of the Vortec Cyclone Melting System (CMS™) for Remediation of PCB Contaminated Soils Using Computational Fluid Dynamics (CFD)

FOCUS AREA 3.0: DECONTAMINATION AND DECOMMISSIONING

- 3.2 Use of SpinTek Centrifugal Membrane Technology and Sorbents/Cleaning Solutions in the D & D of DOE Facilities

FOCUS AREA 4.0: CROSS-CUTTING INNOVATIVE TECHNOLOGIES

- 4.1 Use of Centrifugal Membrane Technology with Novel Membranes to Treat Hazardous/Radioactive Wastes
- 4.2 Environmental Pollution Control Devices Based on Novel Forms of Carbon

FOCUS AREA 5.0: OUTREACH

- 5.1 Small Business Technical Based Support

PROJECT TITLES WITH PRINCIPLE INVESTIGATORS

FOCUS AREA 1.0: SUBSURFACE CONTAMINANTS, CONTAINMENT AND REMEDIATION

- 1.6 PILOT SCALE DEMONSTRATION OF TCE FLUSHING THROUGH PVDs AT
THE RMI EXTRUSION PLANT IN ASHTABULA, OHIO

M. Gabr and J. Quaranta, Department of Civil & Environmental Engineering
North Carolina State University (NCSU)

- 1.7 TECHNICAL SUPPORT FOR SURFACTANT FLUSHING THROUGH PVDs AT
THE RMI EXTRUSION PLANT IN ASHTABULA, OHIO

J. Kilbane, Institute of Gas Technology (IGT)

- 1.8A TECHNICAL SUPPORT ON INSTALLATION AND OPERATION OF THE PVD
SYSTEM AT THE RMI EXTRUSION PLANT IN ASHTABULA, OHIO

E. Marsh and J. Hughes, RMI Environmental Services (RMIES)

- 1.8B DESIGN, PROCUREMENT, INSTALLATION AND OPERATION OF A PILOT
SCALE WASTEWATER TREATMENT SYSTEM TO TREAT EXTRACTED
FLUIDS DURING DEMONSTRATION OF THE PVDs AT THE RMI
EXTRUSION PLANT IN ASHTABULA, OHIO

E. Marsh and J. Hughes, RMI Environmental Services (RMIES)

FOCUS AREA 2.0: MIXED WASTE CHARACTERIZATION TREATMENT AND DISPOSAL

- 2.1 ANALYSIS OF THE VORTEC CYCLONE MELTING SYSTEM (CMS) FOR
REMEDICATION OF PCB CONTAMINATED SOILS USING COMPUTATIONAL
FLUID DYNAMICS (CFD)

I. Celik, Department of Mechanical & Aerospace Engineering, WVU
J. Gnat and J. Santoriani, Vortec Corporation

PROJECT TITLES WITH PRINCIPAL INVESTIGATORS

FOCUS AREA 3.0: DECONTAMINATION AND DECOMMISSIONING

- 3.2 USE OF SPINTEK CENTRIFUGAL MEMBRANE TECHNOLOGY AND
SORBENTS/CLEANING SOLUTIONS IN THE D & D OF DOE FACILITIES

B. Reed, Department of Civil & Environmental Engineering, WVU
W. Green and R. Hayes, SPINTEK

FOCUS AREA 4.0: CROSSCUTTING INNOVATIVE TECHNOLOGIES

- 4.1 USE OF CENTRIFUGAL MEMBRANE TECHNOLOGY WITH NOVEL
MEMBRANES TO TREAT HAZARDOUS/RADIOACTIVE WASTES

B. Reed, Department of Civil & Environmental Engineering, WVU
W. Green and R. Hayes, SPINTEK

- 4.2 ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL
FORMS OF CARBON

J. Zondlo and A. Stiller, Department of Chemical Engineering, WVU
B. Alig, Applied Sciences, Inc.

FOCUS AREA 5.0: OUTREACH

- 5.1 SMALL BUSINESS TECHNICAL BASED SUPPORT

E. Cook, Department of Civil & Environmental Engineering, WVU

QUARTERLY
TECHNICAL
PROGRESS REPORTS

FOCUS AREA 1.0

Subsurface Contaminants,
Containment & Remediation

Pilot Scale Demonstration of TCE Flushing Through PVDs at the DOE/RMI Extrusion Plant 1997 FETC Task No. 1.6

Quarterly Technical Progress Report

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April 1998

ABSTRACT

Continuing development on the use of Prefabricated Vertical Drains for Enhanced Soil Flushing technology is progressing with application of the technology at a private-sector site that was a former uranium processing facility for the US Department of Energy. The site, located in Ashtabula Ohio, is owned by the RMI Titanium Corporation. It has both radiological and hazardous materials contamination in soil and groundwater mediums which are limited to a 7 acre area of a 26 acre site. The facility terminated all production operations in 1988 and since then has focused efforts on the decontamination and decommissioning of the facility which includes remediation of the soil and groundwater contaminated by low-level uranium and Trichloroethylene (TCE).

North Carolina State University Department of Civil Engineering is working with RMI Environmental Services through support from DOE's Federal Energy Technology Center - Morgantown and DOE's Ashtabula Area Office - RMI Decommissioning Project, and West Virginia University (WVU). Current work for 1998 consists of continuing with the field work initiated in 1997 on the field pilot study on the use of PVDs enhanced with a surfactant flushing solution for removal of TCE from contaminated fine-grain fraction soil and groundwater.

TABLE OF CONTENTS

Abstract	ii
Executive Summary	1
Introduction	1
Purpose	2
Background	2
Methodology	2
Work Performed this Period	3
Conclusions / Next Period Work Plan	4

List of Figures

Figure #1	PVD Test Pad	5
Figure #2	TCE Concentration vs PVD Extraction Duration	6
Figure #3	PVD Extraction Flowrate vs Cumulative Week Time Task 1, Sequence 2: Extraction Only, Day 1 to 4	7
Figure #4	PVD Extraction Flowrate vs Cumulative Week Time Task 1, Sequence 2: Extraction Only, Day 5 to 8	8

EXECUTIVE SUMMARY

This project was brought on-line during the fourth quarter of 1997. The project scope is to demonstrate the effectiveness of the PVD enhanced soil flushing technology at the RMI site. This research program includes all activities associated with the design, installation, operation, data gathering and interpretation, and site closure for performing a small- scale (10 ft x 10 ft area) clean-up of TCE contaminated soils at the RMI facility. The research objectives are to investigate the performance of the prefabricated vertical drains used for enhanced soil flushing operating under an injection/extraction mode in a glacial till soil.

Regular monthly project coordination meetings continue to be held between the key researchers, industry partners, and funding representatives in order to maintain project communication and progress.

INTRODUCTION

This project is a concerted effort between North Carolina State University Department of Civil Engineering, U.S. Department of Energy's (DOE) Federal Energy Technology Center - Morgantown and DOE's Ashtabula Area Office - RMI Decommissioning Project, RMI Environmental Services, and WVU's Civil and Environmental Engineering Department. The goal of the work during Phase I efforts consist of performing field research into the use of the Prefabricated Vertical Drain Enhanced Soil Flushing technology enhanced with surfactant solutions at the RMI facility located in Ashtabula, Ohio. This report discusses the progress made for the current reporting period.

PURPOSE

As environmental remediation technologies progress through the research process, it is important to continually evaluate the research goals and determine the value-added of the developing technology. For this project, the research objectives of Phase I are three-fold: The first is to perform a limited extraction of the subsurface groundwater to establish the aquifer response to the PVD vacuum extraction system. The second is to demonstrate the injection and flushing with potable water, and the third sequence of testing is to inject the surfactant solution and demonstrate a clean-up at the site. This research is specific to addressing key issues necessary for the design, installation, and operation of a one-tenth acre field remediation of the TCE contaminated soils and groundwater.

BACKGROUND

The RMI Titanium Company (RMI) Extrusion Plant is located in Ashtabula County, Ohio. The facility consists of 25 buildings and occupies 7 acres of a 26 acre site. The facility is contaminated with both radiological and hazardous materials resulting from previous operations for the US Department of Energy. The primary function of RMI, since 1962, has been the extrusion and closed-die forging of metallic depleted, natural, and

slightly enriched uranium (U) used in the production of nuclear fuel elements for defense production reactors, extrusion operations for other government agencies, and the private-sector. Extrusion operations ceased in 1990, since then the Nuclear Regulatory Commission (NRC) has required the facility to implement accelerated site clean-up pursuant to its Site Decommissioning Management Plan. The US Environmental Protection Agency has issued RMI a Resource Conservation Recovery Act (RCRA) Hazardous Waste Management Permit with conditions mandating clean-up of an existing Corrective Action Management Unit. DOE's office of Environmental Restoration and Waste Management (EM) has contracted RMI to conduct the RMI Decommissioning Project by removing all radiological and hazardous contaminants to levels which permit the facility and adjacent areas to be released for unrestricted use.

The principal contaminant on equipment, buildings, and surrounding open space areas is uranium. In addition to the uranium, soil and groundwater are contaminated with Trichloroethylene (TCE) and Technetium 99 in limited areas of the site. Clean-up of the facility is slated to continue for the next several years due to technology limitations and the unique challenges which face RMI in handling the large physical size of the manufacturing equipment and facility.

METHODOLOGY

Phase I efforts for the Laboratory Studies and Field Testing at the RMI Extrusion Plant project involves the field demonstration of the PVD enhanced soil flushing technology. The purpose of this phase of the project focuses on the *in situ* field demonstration of the flushing system configured using with two injection and six extraction PVDS. The schematic of the final constructed test pad is illustrated in Figure #1. The three testing phases are discussed as follows.

Task 1 : System Operation Sequence 1 - Groundwater Extraction

Operate the eight PVDS in a full extraction mode only. This entails calibrating the extraction flow rate equal to the aquifer recharge in the vicinity of the test pad. The extraction will remove only site groundwater contaminated with TCE, no injection of liquids will be performed during this phase. During this operation, a set number of pore volumes of groundwater will be passed through the site soil where desorption of the TCE contaminant into the groundwater is expected to take place. Field sampling was performed on retrieved groundwater specimens for laboratory analysis of TCE, and real-time monitoring of the discharged air from the venturi system for volatile organics.

Task 2: Injection and Circulation of Potable Water Through PVDS Sequence II

During this phase of the testing, potable water will be introduced to the injection PVDS and a flushing operation between the injection and extraction PVDS will be performed. Modifications to the PVD collector piping will be

made for proper operation of the system. The groundwater sampling protocol followed for the first Task will be used during this phase. It is expected that the injection phase will run for approximately ten days. During this period liquids will not be reintroduced to the aquifer.

Task 3 : Surfactant Augmented Injection / Circulation Sequence III

This will be the final process for removal of the TCE contaminants from the soil and groundwater. A surfactant will be introduced to the groundwater for removal of the residual soil-bound contaminants using the injection/extraction mode of operation followed in Task 2. Revised operational, sampling, and analysis protocol will be developed for this phase of the work. It is expected that this task will operate for approximately 8 weeks.

WORK PERFORMED THIS PERIOD

During this period, Task 1, Extraction Only operations were completed. The data has been evaluated and representative graphs are presented in Figures #2- #4. Progress has been made with testing on Task 2, Injection and Circulation of Potable Water Through PVDs. The data obtained and reduced from this sequence of testing is on-going.

Interpretation of Figure #2 TCE Concentration versus Time shows that the Up-gradient groundwater monitoring well produced consistent levels of TCE contamination on the order of 8,000 ppb. A similar trend is observed for the Down-gradient well, where the TCE concentration in recovered grab samples showed consistent concentrations of 100 to 200 ppb. Analyzed samples of groundwater recovered from the PVD extraction hose showed consistent reductions in concentrations during the ten test periods. The frequency of the TCE rebound and attenuation level indicates that as the PVD system is operated in an extraction only mode, a natural pulse cycle is evident. This pulse cycle characterizes the response of the contaminant removal through advective transport and diffusion mechanisms.

Figures #3 and #4 present the relationships between the PVD Extraction Flowrate versus Cumulative Week Time. The significance of these graphs is the clear trend in flowrate from consistent values between 20 to 30 g.p.m. at the beginning of the extraction duration, to less than 10 g.p.m. by the end of the extraction cycle. Evidence of the aquifer's diminishing recharge levels indicates that the PVD extraction is effecting the response of the aquifer's natural attenuation capability.

CONCLUSIONS/WORK PLANNED FOR NEXT PERIOD

The preliminary conclusions which may be drawn from this initial testing is that the PVD system operating in a extraction only mode influences the attenuation of the aquifer to naturally recover; and that recovered Groundwater specimens from the PVD test pad Zone of Influence showed consistent reductions in TCE concentration with time; and that a natural pulse frequency is evident which will have a significant impact on the efficiency of the contaminant removal under natural groundwater advection/diffusion processes.

Research planned for the next quarter includes completion of Task 2, Injection / Extraction of potable water and beginning with Task 3 Surfactant Injection and removal. There are no outstanding issues on this work and the project is on schedule and budget.

Figure #1, PVD Test Pad

Task 1: Extraction Only

Figure #2 TCE Concentration vs PVD Extraction Duration

Task 1, Sequence 2: Extraction Only

Day #1 - Day #4
(Jan. 12, 1998 - Jan. 15, 1998)

FWS2D1_4.spw

Figure #3PVD Extraction Flowrate vs Cumulative Week Time

Task 1, Sequence 2: Extraction Only, Day 1 to 4

Task 1, Sequence 2: Extraction Only

Day #5 - Day #8
(Jan. 19, 1998 - Jan. 22, 1998)

FWS2D5_9.spw

Figure #4PVD Extraction Flowrate vs Cumulative Week Time

Task 1, Sequence 2: Extraction Only, Day 5 to 8

**Technical Support for Surfactant Flushing through Prefabricated Vertical Drains (PVDs)
at the RMI Ashtabula Site**

FETC Task No. 1.7

Quarterly Technical Progress Report
Reporting Period:

January 1, 1998 to March 31, 1998

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

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

By
Institute of Gas Technology
1700 South Mount Prospect Road
Des Plaines, Illinois 60018

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ABSTRACT

West Virginia University will perform a field experiment to test the ability of wick drains to be used as a tool to deliver surfactant solutions to the subsurface for remediation of trichloroethylene (TCE) contamination at the DOE/RMI site in Ashtabula, Ohio. The objective of this proposal is to supply technical support for that field experiment in surfactant flooding by performing laboratory tests to select an appropriate surfactant product and the correct concentration of surfactant, obtain a sufficient quantity of the appropriate surfactant for use in the field experiment, assist in field operations, recruit industrial partners, and to provide field services for the in situ biodegradation of residual TCE and surfactant.

The overall objective of the project is to demonstrate the use and versatility of wick drains for the in situ remediation of contaminated aquifers. The specific objective of this proposal is to identify and supply appropriate solutions for two remediation approaches: surfactant flooding, and in situ biodegradation.

During the past quarter the ingredients of the four component surfactant solution (2% MA-80, 0.5% Mazol GMOK, 0.3% NaCl, and 0.05% xanthan gum) were ordered and delivered to RMI for use in field experiments. The quantity of materials obtained are sufficient to prepare 14,000 gallons of surfactant flooding solution, which is the anticipated volume of material needed for the next round of injection/withdrawal tests at the 10 ft by 10 ft test site in Ashtabula.

Samples received from SpinTek resulting from ultrafiltration tests were analyzed to determine the concentration of residual surfactants. The details of the ultrafiltration tests will be reported by SpinTek, but these results indicated that ultrafiltration is capable of reducing surfactant concentrations from 25,000 ppm to about 10 ppm, at least under some circumstances. These are highly favorable results and suggest that ultrafiltration could be considered as a means of processing surfactant-containing liquids produced in this project. Ultrafiltration tests with solutions containing TCE as well as surfactants were not performed, but would clearly be indicated for future experiments.

Analytical methods appropriate for surfactant/TCE mixtures were determined, and several commercial analytical labs were contacted to identify labs capable of meeting the specialized analytical needs of this project. The presence of relatively high concentrations of surfactants in combination with contaminants is not typically encountered and methods have not been specifically developed for such samples. However, after extensive discussion with project personnel, commercial analytical labs, and regulators appropriate methods were identified. EPA SW846 Method 5030B/8260B will be used for the analysis of liquid samples, and 8275A for the analysis of soils containing surfactant/contaminant mixtures.

The surfactant mixture contains sodium chloride, but tests were performed to see if sodium sulfate can be substituted. Sodium sulfate is an essential component for treatment of technetium in wastewater using the I-Chrome process. Results indicate that sodium sulfate can be substituted for sodium chloride in the surfactant mix as long as equivalent sodium concentrations are maintained (0.05 M); however, if sodium sulfate concentrations of 1 M are used, as recommended by I-Chrome then the surfactant solution is negatively effected. It is suggested that if these high sodium sulfate concentrations are needed that they should be added to collected liquids undergoing treatment, but should not be included in the surfactant flooding solution.

Surfactant biodegradation experiments were also performed which indicated that complete biodegradation of the four component surfactant mix at a starting concentration of 25,000 ppm can be achieved, but the treatment time could be as long as 60 days. However, if adapted cultures are employed surfactant solutions with a starting concentration of 2,500 ppm can be biodegraded in as little as 9 days.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1.0 Introduction	1
2.0 Purpose	1
3.0 Background.....	2
4.0 Methodology.....	2
5.0 Work Performed This Period.....	2
6.0 Results and Discussion	3
7.0 Conclusions.....	7
8.0 Work Planned for Next Period.....	7

1.0 Introduction

The DOE/RMI site in Ashtabula, Ohio is a former uranium processing facility whose operations resulted in significant contamination of soil and groundwater at the site. The contaminants of chief concern are trichloroethylene (TCE) and technetium, and the site soil has regions of relatively low permeability. Groundwater contamination is of particular concern due to the possibility of contaminants migrating offsite. TCE is a highly recalcitrant environmental contaminant with low aqueous solubility and a density greater than water. Because TCE is a dense non-aqueous phase liquid with low solubility it tends to sink to the bottom of aquifers and dissolve slowly serving as a source of groundwater contamination for decades. Various approaches for the remediation of aquifers contaminated with chlorinated solvents include soil vapor extraction/air sparging, bioventing/biosparging, steam injection/thermal desorption, surfactant flooding, and excavation. In situ technologies are preferred as are low cost but effective technologies. A problem common to the in situ remediation of a contaminated aquifer by any approach is the need to efficiently deliver and/or recover solutions/agents to the subsurface. The problem of efficiently delivering solutions to the subsurface is even more challenging in soils with relatively low permeability.

To address the problem of in situ remediation of the subsurface West Virginia University is developing a novel versatile technology for the delivery and withdrawal of solutions using wick drains. Wick drains have been used for decades in the construction industry to dewater soil. Wick drains consist of corrugated plastic wicks encased in permeable fabric. Water movement through the soil is facilitated by the extremely high hydraulic conductivity of the wick drain material. They are typically installed by hydraulic rams to depths of 50 feet or more, and are often spaced only a few feet apart. Installation of wick drains at a one acre site can generally be accomplished within about a week. This inexpensive technology which has proven to be so successful for dewatering soils has not yet been adapted for the remediation of contaminated sites, but that will be the chief objective of the West Virginia University research and field demonstration program. Wick drains will be installed at the DOE/RMI site in Ashtabula, Ohio in the vicinity of a TCE-contaminated aquifer having a hydraulic conductivity of about 10^{-5} cm/sec. These drains will then be used to inject surfactant solutions to mobilize TCE for subsequent recovery by other wick drains. Additionally the wick drains will be used to inject nutrient solutions to stimulate the in situ biodegradation of residual TCE and surfactant. The goal of this portion of the project is to supply support services for these field tests by selecting appropriate surfactants, supplying surfactants, and supplying nutrient solutions for the in situ biodegradation of residual contaminants.

2.0 Purpose

The overall objective of the project is to demonstrate the use and versatility of wick drains for the in situ remediation of contaminated aquifers. The specific objective of this proposal is to identify and supply appropriate solutions for two remediation approaches: surfactant flooding, and in situ biodegradation.

3.0 Background

IGT has experience in the production and use of surfactants for removing contaminants from solids, and in the biodegradation of chlorinated solvents. The West Virginia University (WVU) has experience in the application of prefabricated vertical drains for environmental remediation applications. IGT and WVU are collaborating on this project to combine their areas of expertise to develop improved processes for the in situ treatment of TCE contaminated soil and groundwater at the RMI Ashtabula site.

4.0 Methodology

Biodegradation Experiments

Anaerobic digester sludge obtained from the Woodridge, IL municipal wastewater treatment plant was used as an inoculum to provide anaerobic cultures for biodegradation studies. Experimental samples were amended with mineral salts medium containing at least 20 ppm sulfate. Experimental samples were incubated statically at room temperature for various periods at which time TCE biodegradation was assessed by quantifying chloride ion concentrations. Surfactant biodegradation studies were performed under aerobic conditions and utilized microbial cultures specifically adapted to the presence of high concentrations of surfactants.

Analytical Procedures

Chloride ion concentrations are determined using a chloride specific electrode (Orion). Phase behavior experiments for surfactants are performed by mixing equal volumes of aqueous solutions and TCE in sealed test tubes. After agitation the mixtures are observed initially and after coming to equilibrium after 12 to 24 hours. The volume and appearance of aqueous phase, microemulsion and oil phase are recorded. Solutions are preincubated in water baths prior to agitation and during the equilibration period when tests were performed at temperatures other than room temperature.

Surface Tension Measurements

The surface tension of surfactant solutions were determined using a Fisher 21 tensiometer and a 6 cm circumference platinum ring. Various dilutions of surfactant solutions were prepared and their surface tension was determined according to the manufacturers instruction.

5.0 Work Performed This Period

During the past quarter the ingredients of the four component surfactant solution (2% MA-80, 0.5% Mazol GMOK, 0.3% NaCl, and 0.05% xanthan gum) were ordered and delivered to RMI for use in field experiments, samples received from SpinTek resulting from ultrafiltration tests were analyzed, analytical methods appropriate for surfactant/TCE mixtures were determined, and surfactant biodegradation experiments were performed.

6.0 Results and Discussion

During the past quarter the ingredients of the four component surfactant solution (2% MA-80, 0.5% Mazol GMOK, 0.3% NaCl, and 0.05% xanthan gum) were ordered and delivered to RMI for use in field experiments. The quantity of materials obtained are sufficient to prepare 1,400 gallons of surfactant flooding solution, which is the anticipated volume of material needed for the next round of injection/withdrawal tests at the 10 ft by 10 ft test site in Ashtabula. The volume of 1,400 gallons was selected because it represents about one pore volume for the test site, plus a bit more. The amounts of ingredients needed to prepare a 1,400 gallon batch are 28 gallons of MA-80-I, 7 gallons of GMO-K, 33.6 pounds of sodium chloride, and 5.6 pounds of xanthan gum. The surfactant solution is best prepared by first dissolving the sodium chloride and the xanthan gum. Vigorous mixing may be required and it is best not to have the surfactants in the mixture until the xanthan has been fully dissolved. After the salt and xanthan have been fully dissolved the surfactants can be added either separately or together, and mild agitation should be sufficient to get these components into solution and foaming can be avoided.

IGT received 10 samples from SpinTek for surfactant analysis. The origins of the samples will be described by SpinTek, but they relate to ultrafiltration testing of the surfactant mixture intended for use at the RMI, Ashtabula site. Surface tension readings were taken of the samples and dilutions of each sample in order to determine the approximate surfactant concentration of these samples in comparison with a standard curve prepared with the 4 component surfactant mix. From 4 to 6 independent surface tension readings were performed for each sample in order to insure that accurate data was obtained. Since ultrafiltration can alter the ratio of the components of the surfactant mix it is possible that the standard curve we used was not completely appropriate/accurate for each of these samples; however, our tests with control samples indicate that these readings should be accurate to within a factor of two, and in the worst possible case accuracy is within a factor of ten.

Feed	25,000ppm
LIU-003	5ppm
LIU-007	5ppm
LIU-015	10ppm
LIU-040	88ppm
LIU-060	3065ppm
LIU-100	122ppm
TC-2K	0.25ppm
TC-15K	1ppm
CE007	1063ppm

The surfactant concentration anticipated to be in filtrate samples (of this particular surfactant mix) after the removal of surfactant micelles is 10 ppm or less. We would recommend that future experiments also include retentate samples.

These results indicated that ultrafiltration is capable of reducing surfactant concentrations from 25,000 ppm to about 10 ppm, at least under some circumstances. These are highly favorable results and suggest that ultrafiltration could be considered as a means of processing surfactant-containing liquids produced in this project. Ultrafiltration tests with solutions containing TCE as well as surfactants were not performed, but would clearly be indicated for future experiments.

Analytical methods appropriate for surfactant/TCE mixtures were determined, and several commercial analytical labs were contacted to identify labs capable of meeting the specialized analytical needs of this project. The Ashtabula/RMI site is unusual in having radionuclides (uranium and technetium) possibly present in soil and water samples in addition to TCE. Additionally, the use of surfactant flooding as a remediation treatment in this project introduces further complications. Because of the possible presence of radionuclides it is necessary to deal with labs licensed to receive such samples. The list of licensed labs includes:

Core Laboratories Inc.
420 West First Street
Casper, WY 82601
Phone 800-666-0306

Diagnostic Instrumentation and Analysis Laboratory (DIAL)
205 Research Blvd.
Starkville, MS 39759
Phone 601-325-7380

McDermott Technology Inc.
Research and Development Division
Mt. Athos Rd.
P. O. Box 11165
Lynchburg, VA 24506-1165
Phone 804-522-6755

Quanterra Environmental Services
13705 Rider Trail North
Earth City, MO 63045
Phone 314-298-8566

Each of the labs listed above are licensed to receive samples which contain radionuclides, but the analysis of surfactant/contaminant mixtures presents unique problems. The presence of relatively high concentrations of surfactants in combination with contaminants is not typically encountered and methods have not been specifically developed for such samples. Each of the labs listed above was not equally willing to discuss the unusual analytical needs of this project, particularly as regards the analysis of surfactant/contaminant mixtures which is non-routine. The most helpful labs in this regard were Core Labs and DIAL. Core volunteered to perform preliminary analyses on soil and water samples that contained surfactants to help decide on the appropriateness of methodology. Two liquid samples were prepared using the full strength four-component surfactant mixture but spiked to contain 10 or 200 ppm TCE. Similarly two 100 g samples of clean soil from the Ashtabula site were intentionally contaminated with 200 ppm TCE in the presence of surfactant solution wetting the soil. The liquid samples were analyzed by a modified purge and trap technique in which antifoam was added directly to the liquids and GC/MS analysis of contaminants captured in the trap. Analysis showed that the sample spiked with 10 ppm contained 9 ppm, while the sample spiked with 200 ppm was found to contain 150

ppm. The soil samples were first extracted with methanol and then the methanol extract was subjected to purge and trap followed by GC/MS. The soil samples which were spiked with 200 ppm were found to contain 39 and 47 ppm TCE according to these analyses. These results are favorable as regards the analysis of liquid samples using a purge and trap technique, but an improved methodology is apparently required for the accurate analysis of soil samples. After extensive discussion with project personnel, commercial analytical labs, and regulators appropriate methods were identified. EPA SW846 Method 5030B/8260B will be used for the analysis of liquid samples, and 8275A for the analysis of soils containing surfactant/contaminant mixtures. Method 5021 which is a headspace gas analytical technique could be used for the analysis of both soil and water samples, but it's accuracy is less certain than alternative methods for the analysis of difficult samples such as surfactant/contaminant mixtures. Method 5030B is a purge and trap method while 8260B is a GC/MS method for the analysis of material eluted from the trap. Method 8275A is a thermal desorption method coupled with GC/MS analysis. While these methods are thought to be the most appropriate choices for use in this project confirmatory tests with rigorous QA/QC should be performed as a component of future work to verify this.

The surfactant mixture contains sodium chloride, but tests were performed to see if sodium sulfate can be substituted. Sodium sulfate is an essential component for treatment of technetium in wastewater using the I-Chrome process. Results indicate that sodium sulfate can be substituted for sodium chloride in the surfactant mix as long as equivalent sodium concentrations are maintained (0.05 M); however, if sodium sulfate concentrations of 1 M are used, as recommended by I-Chrome then the surfactant solution is negatively effected. It is suggested that if these high sodium sulfate concentrations are needed that they should be added to collected liquids undergoing treatment, but should not be included in the surfactant flooding solution.

Surfactant biodegradation experiments were also performed which indicated that complete biodegradation of the four component surfactant mix at a starting concentration of 25,000 ppm can be achieved, but the treatment time could be as long as 60 days. However, if adapted cultures are employed surfactant solutions with a starting concentration of 2,500 ppm can be biodegraded in as little as 9 days. Figure 1 illustrates the results of surfactant biodegradation of a 2,500 ppm surfactant mixture using surfactant degrading bacteria versus bacterial cultures specifically adapted to the degradation of this surfactant mixture. The surface tension of the surfactant solution is about 35 while the surface tension of bacterial growth medium is about 65. The results shown in Figure 1 clearly illustrate that a mixture of surfactant degrading microorganisms adapted to fully degrade this surfactant mixture yields superior performance. The adaptation procedure included the use of surfactants as sole carbon and energy sources for multiple cycles of growth in a chemostat. The chemostat was initially supplied with surfactant at 25,000 ppm and the effluent of the chemostat was recycled as the feed until surface tension readings indicated that the entirety of the surfactant had been degraded. What was observed was that different populations of bacteria were required for the initial attack on surfactant molecules versus the final degradation of surfactants. Surfactant-adapted bacteria are being grown and preserved/frozen for future use to assist in the start-up of a future wastewater treatment process to treat surfactant-containing water resulting from this project. If ultrafiltration is used as a component of the wastewater treatment process then the concentration of surfactant requiring biodegradation should be in the range of 10 ppm which should be easily biodegraded.

Figure 1. Surfactant Biodegradation by Regular Versus Adapted Bacterial Cultures

7.0 Conclusions

The project is proceeding as scheduled. Food grade surfactants which yield good TCE solubilization were identified and the composition of a surfactant formulation for use in preliminary field tests of surfactant flooding was determined: 2% MA-80, 0.5% Mazol GMOK, 0.3% NaCl, and 0.05% xanthan gum, and sufficient quantities of the materials to prepare 1,400 gallons of surfactant solution were obtained and shipped to Ashtabula. 1 M sodium sulfate should not be included in the surfactant mix. Ultrafiltration appears to be an appropriate technology for the removal of surfactant from solution. After extensive discussion with project personnel, commercial analytical labs, and regulators appropriate methods were identified. EPA SW846 Method 5030B/8260B will be used for the analysis of liquid samples, and 8275A for the analysis of soils containing surfactant/contaminant mixtures. Biodegradation with adapted cultures can be used to biodegrade the surfactant mixture used in this project.

8.0 Work Planned for Next Period

Support of field tests of surfactant flooding are planned.

**Installation/Operation of PVD System and
Design/Construction Support for Wastewater Treatment
Associated with the PVD Operation**

1997 FETC Tasks 1.8a & 1.8b

**Quarterly Technical Progress Report
Reporting Period:**

January 1, 1998 to March 31, 1998

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Office of Fossil Energy
Federal Energy Technology Center
Morgantown, West Virginia

By:
RMI Environmental Services
P.O. Box 579
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April, 1998

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ABSTRACT

RMI Environmental Services (RMIES) is working cooperatively with US Department of Energy (DOE)-Federal Energy Technology Center (FETC), US DOE, Ashtabula Area Office - RMI Decommissioning Project, West Virginia University (WVU), North Carolina State University (NCSU), and the Institute of Gas Technology (IGT) to support development and deployment of a groundwater and soil remediation technology called Drain Enhanced Soil Flushing (DESF) utilizing Prefabricated Vertical Drains (PVD). RMIES's responsibilities include providing the site for the demonstration project, providing installation and operations support for the test pad area, and the design, construction, and operation of the wastewater treatment plant to treat the extracted groundwater.

During the report period, RMIES intermittently operated the PVD system. Approximately 3,000 gallons of groundwater was extracted from the study area. A variety of injection/extraction modes were implemented to establish optimum operating conditions. Approximately 260 samples were collected and analyzed for various parameters during the report period. All data received was forwarded to NCSU for review. RMIES completed a DESF Field Demonstration Project Engineering Report and Project Plan which defines the design basis for the water treatment system.

RMIES submitted a NPDES water permit modification to the Ohio EPA during the report period. The modification was public noticed on March 30, 1998. An air permit exemption request for the air stripper was submitted to and approved by the OEPA during the report period.

RMIES continued work on the engineering/design of the water treatment system and various pieces of process equipment including tanks, pumps, filters, air stripper and other similar items were ordered and/or received during the report period.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1.0 Introduction	1
2.0 Purpose	1
3.0 Background	1
4.0 Methodology	2
5.0 Work Performed This Period	3
6.0 Results and Discussion	4
7.0 Conclusions	5
8.0 Work Planned For Next Period	5
9.0 Technical Difficulties	6
10.0 Drawings	6

1.0 Introduction

The activities presented in this quarterly report are part of the WVU Cooperative Agreement's initiative for bringing environmental remediation technologies to field scale demonstration. This project is a concerted effort between RMI Environmental Services, WVU's Civil and Environmental Engineering Department, US Department of Energy's (DOE) Federal Energy Technology Center (Morgantown), North Carolina State University (NCSU), DOE's Ashtabula Area Office and the Institute of Gas Technology (IGT). The goals of the portion of the work performed by RMIES consists of 1) providing the site to perform the Prefabricated Vertical Drain (PVD) investigations 2) providing installation and operation support for a 10' x 10' test pad area and 3) providing engineering, design, procurement, installation, and operational support for a wastewater treatment system for treatment of extracted groundwater.

This report discusses the progress made during the current reporting period.

2.0 Purpose

The overall objective of this project is to demonstrate the applicability of prefabricated vertical drains for remediation of contaminated groundwater and associated soils. The project will evaluate removal efficiency of contaminated groundwater through simple extraction, injection and extraction of potable water only, and injection and extraction of a surfactant solution.

3.0 Background

The RMI Titanium Company (RMI) Extrusion Plant is located in Ashtabula County, Ohio. The facility consists of 25 buildings and occupies 7 acres of a 32 acre site. The facility is contaminated with both radiological and hazardous materials resulting from previous operations for the US Department of Energy. The primary function of RMI, since 1962, has been the extrusion and closed-die forging of metallic depleted, natural, and slightly enriched uranium (U) used in the production of nuclear fuel elements for defense production reactors, extrusion operations for other government agencies, and the private-sector. Extrusion operations ceased in 1990, since then the Nuclear Regulatory Commission (NRC) has required the facility to implement accelerated site clean-up pursuant to its Site Decommissioning Management Plan. The US Environmental Protection Agency has issued RMI a Resource Conservation Recovery Act (RCRA) Hazardous Waste Management Permit with conditions mandating clean-up of an existing Corrective Action Management Unit. DOE's office of Environmental Restoration and Waste Management (EM) has contracted RMI to conduct the RMI Decommissioning Project by removing all radiological and hazardous contaminants to levels which permit the facility and adjacent areas to be released for unrestricted use.

The principal contaminant on equipment, buildings, and surrounding open space areas is uranium. In addition to the uranium, soil and groundwater are contaminated with Trichloroethylene (TCE) and Technetium 99 in limited areas of the site. Clean-up of the facility is slated to continue for the next several years due to technology limitations and the

unique challenges which face RMI in handling the large physical size of the manufacturing equipment and facility. The use of the PVD technology has been targeted for demonstration on the portion of the site within the CAMU which has TCE, uranium, and technetium 99 contamination.

4.0 Methodology

Task 1.8a Installation/Operation of the PVD System

RMI Environmental Services has been tasked with supporting WVU for installation and operation of a 10' x 10' test pad area. As such there are no specific or unique methodologies required to construct this system. However, as part of the operations portion of this task, extracted groundwater was analyzed via the following methods.

Analytical Methodologies

- Volatile Organic Analysis (VOA) - EPA SW846 Method 8240
- Total Uranium - EPA 908.1
- Technetium 99 - HASL 300 (beta scintillation)
- Suspended Solids
- Dissolved Solids
- Specific Conductance
- pH
- Temperature

Task 1.8b Design, Procurement, Construction and Decontamination Associated with Operation of the PVD System

RMI Environmental Services has been tasked with design, construction, operation, and decontamination of a wastewater treatment system to treat extracted wastewater. During the report period, preliminary design of the wastewater treatment system was completed. This included defining the problem and work scope, identifying contaminants, treatment standards, performing academic and industry research to evaluate treatment options, development of a project plan, cost estimate, and process flow diagram. The following design criteria were established for the process:

- Equipment sized to treat water generated during the project.
- Modification to existing Wastewater Treatment Plant (WWTP) required since it is not designed to remove TCE or tolerate surfactant.
- Minimize use/cost of surfactant via recovery and recycling.
- Develop unit operations which can be readily scaled-up.
- Identify and develop analytical protocol required to support operation and evaluate process performance.
- Safely and efficiently treat wastewater within license and permit limits.

5.0 Work Performed This Period

Work accomplished during this period consisted of:

Task 1.8a

- Operation of the PVD System during the weeks of January 12, January 19, February 17, February 23, March 2, March 9, and March 16, 1998. Approximately 3,000 gallons of water have been extracted to date.
- January operations were in an extraction only mode.
- During the week of February 17, experiments were conducted to evaluate the potential for volatilization of TCE during extraction and the injection system was commissioned.
- During the week of February 23, the PVD system was operated under a continuous injection/continuous extraction mode for 8 hours per day.
- During March operations, a variety of injection/extraction sequences were performed to support the optimization of injection and extraction rates.
- A total of 265 samples (groundwater and extract water) have been collected since field operations commenced in December, 1997. Samples were analyzed for one or more of the following parameters: volatile organics, total uranium, Tc-99, TSS/TDS, specific conductance, pH, and/or temperature. Data for samples collected through February 25 and sent to the off-site laboratory for analysis have been received. A summary spreadsheet listing sample number, type and result was prepared.
- Approximately 6,000 lbs of soil were collected and packaged for shipment to NCSU for further laboratory studies. The soil is scheduled to be shipped in early April.

Task 1.8b

- A de-minimus air exemption request was submitted to the OEPA for the air stripper which will be used for the Phase I treatment of the TCE contaminated groundwater. Approval was received during March, 1998.
- A National Pollutant Discharge Elimination System (NPDES) permit modification application was completed and submitted to the OEPA for approval. The OEPA public noticed the permit modification on March 30, 1998.

- RMIES developed technical specifications and received bids on a gas chromatograph (GC) to conduct on-site organic analysis of water to support the project. A purchase order is expected to be issued in early April.
- RMIES developed the DESF Field Demonstration Project Engineering Report and Project Plan which defines the design basis and approach for the water treatment system. A copy of this plan was submitted to the OEPA along with additional design and equipment information in support of the NPDES permit modification application.
- RMIES continued work on the engineering/design of the wastewater treatment system to treat extracted contaminated water. Major process equipment (e.g., pumps, tanks, filters and air stripper) was previously ordered. During this period, the process control panel and miscellaneous hardware (e.g., process piping, valves, instrumentation, and electrical materials) was ordered. The equipment either has already arrived or is scheduled to arrive by early April.
- RMIES has initiated the electrical and mechanical work orders to allow construction of the wastewater treatment system to begin in early April. Construction of the system is scheduled to be completed by April 20, 1997.
- RMIES worked with IGT to define the technical specifications and received revised bids on a gas chromatograph (GC) to conduct on-site organic analysis of water to support the project. The purchase order is scheduled to be placed in early April, and shipment scheduled for early May.
- RMIES purchased a surface tension meter to conduct on-site surfactant analysis, and it was received in late March. RMIES will work with IGT to obtain matrix specific calibration curves and operational information.
- RMIES continued to investigate various other on-site laboratory expansion capabilities such as surface tension measurement, wet chemistry, etc to support long term operational needs of the wastewater treatment system. No progress.

6.0 Results and Discussion

Task 1.8a

The PVD system was intermittently operated during January, February, and March. Approximately 3,000 gallons of water was extracted and 265 samples collected for various on-site and off-site analysis. Based on a review of the data, RMIES determined that TCE concentrations in the extracted groundwater are less than the TCLP limit for TCE. Therefore, the extracted groundwater does not have to be handled or stored as hazardous

waste. This determination alleviates the potential constraint on operations imposed by storage capacity limitations for the Hazardous Waste Storage Area. No significant operational issues or delays occurred during the period.

Task 1.8b

During the report period, RMIES continued to focus on permitting various activities associated with the on-site treatment of contaminated groundwater design and procurement of the water treatment system. Specifically, a NPDES permit modification was submitted to the OEPA in early February. RMIES met with OEPA shortly thereafter and OEPA requested additional information on design and equipment specifications. Additional time was needed for RMIES to supply this information which was provided to OEPA in early March. OEPA reviewed this and then requested a piping and instrumentation diagram which was immediately provided. OEPA approved the NPDES modification request and public noticed it on March 30, 1998. Pending no significant comments from the public, official OEPA approval would be April 30, 1998. At this time, RMIES would be authorized to treat and discharge the water.

RMIES developed and submitted a de-minimus exemption request to the OEPA for TCE emissions associated with the air stripper. OEPA granted this exemption in March 1998.

Detailed engineering and design work has been completed for the water treatment system. Various pieces of equipment including the air stripper, pumps, tanks, filters, process control panels, and hardware were ordered. Internal work orders were developed to construct the system which is expected to be built by April 20th, 1998. This is approximately 30 days behind because of additional work required to obtain the water permit modification. RMIES continued to work with IGT, 3M, and others in support of treatment of water.

7.0 Conclusions

No significant conclusions were reached during this report period.

8.0 Work Planned For Next Period

Task 1.8a

- Intermittently operate the PVD system injecting/extracting potable water.
- Intermittently operate the PVD system injecting/extracting surfactant mixture.
- Collect and analyze samples.
- Complete operation of the 10' x 10' test.
- Demobilize if applicable.

Task 1.8b

- Construct the water treatment system.
- Operate the water treatment system for treatment of 3,000-5,000 gallons of extracted water only.

- Operate the water treatment system for treatment of surfactant containing water.
- Procure necessary instrumentation and develop analytical protocol to support on-site analytical requirements.
- Finalize the water treatment operations work plan including details of system operations, sampling and analysis, QA/QC, and health and safety.
- Receive approved NPDES permit modification.
- Complete operation of the water treatment system.
- Demobilize if applicable.

9.0 Technical Difficulties

None identified during the report period.

10.0 Drawings

- Drawing E-1269, PVD Piping and Instrumentation Diagram for Phase I
- Drawing E-1270, PVD Piping and Instrumentation Diagram for Phase II

FOCUS AREA 2.0

Mixed Waste Characterization,
Treatment & Disposal

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

FETC Task No. 2.1

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Quarterly Technical Progress Report
Reporting Period: January 1 to March 31, 1998

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

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

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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 CMSTM of Vortec Corporation. The results are summarized in the executive summary section as they become available for each quarterly reporting period.

TABLE OF CONTENTS

Abstract	iii
List of Tables	v
List of Figures	vi
Executive Summary	vii
1.0 Introduction	1
2.0 Purpose	2
3.0 Background	3
4.0 Methodology	3
5.0 Work Performed this Period	4
6.0 Results and Discussion (Current Period)	4
7.0 Conclusions (Current Period)	11
8.0 Work Planned for Next Period	12
Appendices	
A. References	13
B. Figures	16

LIST OF TABLES

	<u>Page</u>
Table 6.1 Species Involved in the Reduced Mechanism	6
Table 6.2 Reaction Included in the Reduced Mechanism	7
Table 6.3 Comparison of Equilibrium Concentrations from two Different Models	9
Table 6.4 Boundary Conditions for the Short Tube, $L = 1$ m, $D = 0.2$ m	10
Table 6.5 Boundary Conditions for the Long Tube, $L = 1$ m, $D = 0.0625$ m	10
Table 6.6 Energy Balance for the FLUENT Calculations: Short Tube	10
Table 6.7 Energy Balance for the FLUENT Calculations: Long Tube	11

LIST OF FIGURES: Appendix B

	<u>Page</u>
Figure 1 Vortec's CMS TM System Sketch	17
Figure 6.1 Comparison of the Complex and Reduced Mechanisms for the Destruction of CH ₂ Cl ₂	18
Figure 6.2 Comparison of the Complex and Reduced Mechanisms for the Destruction of CH ₂ Cl	19
Figure 6.3 Comparison of the Complex and Reduced Mechanisms for the Formation and Destruction of Major Species at 0.001 s	20
Figure 6.4 Comparison of the Complex and Reduced Mechanisms for the Formation and Destruction of Major Species at 0.01 s	21
Figure 6.4 Comparison of the Complex and Reduced Mechanisms for the Formation and Destruction of Major Species at 0.1 s	22
Figure 6.6 Validation Results for a Short Tube	23
Figure 6.7 Validation Results for a Long Tube	24

* All figures are given in Appendix B unless otherwise noted.

EXECUTIVE SUMMARY (current period)

During this quarterly period progress has been made on two topics, namely (i) formulation of a reduced chemical kinetics mechanism, (ii) validation of the radiation model. The complex kinetics model that was used in the previous quarterly period is too large for reasons of computational cost and implementation in computational fluid dynamics (CFD) codes such as FLUENT used in this study. We embarked on formulating a reduced mechanisms for conversion and destruction of dichloromethane and succeeded to reduce the number of reactions from 3430 to 34. The reduced mechanism contains only 21 species as opposed to the 278 reactions involved in the complex mechanism. Results from the reduced and complex mechanism are compared in addition to the comparison with equilibrium calculations. The performance of the reduced mechanism is good for the PCB compounds but only fair for the intermediate compounds such as CO, HO, O and Cl.

Another issue was the validation of the radiation calculations performed for the recuperator using the FLUENT code. For this a test case which was studied by Staiek and Collins (1992) was selected. This case has a similar geometry to the Vortec recuperator and one-dimensional analytical solutions are available for various scenarios with and without radiation. Two typical cases were simulated with the same initial and boundary conditions. The agreement between the results reported in the literature and our FLUENT calculations are good.

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 1.0). 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 CMSTM 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 (CMSTM), separation reservoir, recuperator base (or residence chamber), and recuperator (see Figure 1.0). 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 CMSTM 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-V4.4, 1996) 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. Two other equilibrium chemistry codes are also used, namely, CET93 (McBride et al., 1994), and STANJAN (Reynolds, 1986). The later codes are the updated versions of the earlier ones and they have a relatively broader data base compared to the earlier versions. The CET93 version runs on UNIX systems.

5.0 WORK PERFORMED THIS PERIOD

During this quarterly period progress has been made on two topics, namely (i) formulation of a reduced chemical kinetics mechanism, (ii) validation of the radiation model. The complex kinetics model that was used in the previous quarterly period is too large for reasons of computational cost and implementation in computational fluid dynamics (CFD) codes such FLUENT used in this study.

Another issue was the validation of the radiation calculations performed for the recuperator using the FLUENT code. For this a test case which was studied by Stasiak and Collins (1992) was selected. This case has a similar geometry to the Vortec recuperator and one-dimensional analytical solutions are available for various scenarios with and without radiation. Two typical cases were simulated with the same initial and boundary conditions.

6.0 RESULTS AND DISCUSSION

6.1 Reduced Chemical Kinetic Model Formulation

The complex kinetic model suggested by Senkan (1990) that was used in the previous quarterly reports is too large (due to computational overhead) to use in conjunction with a CFD code like FLUENT. On the other hand, a one step global model could not capture any intermediate species that occur during the destruction of CH_2Cl_2 because the reactants are converted directly to end products. A model that has more reactions and species than the global model but much less than the complex model is needed. There are many types of analysis that could be applied to reduce the complex model, but there is no well defined method for reduction of mechanisms. The detailed assessment of the methods for the reduction of kinetic models is beyond the scope of this work. The reader is referred to Turanyi (1998) for the current information on the reduction of kinetic models. Unfortunately, these reduction methods are not automatic, and must be inspected and verified before they can be accepted. To reduce the complex

chemical kinetic model suggested by Senkan, Xsenkplot (1996) was used to find the most important species and reactions from the previous Senkin run. The utility program Mechmod (Turanyi, 1996) was used to convert the equilibrium kinetic reaction into pairs of forward and backward reactions. Equilibrium kinetic reactions are not usually an input option in CFD codes, and usually only one side of the kinetic reaction dominates the destruction / production process. So by converting the equilibrium reactions into pairs, an additional computational savings can be achieved. Using Xsenkplot we were able to create a set with a reduced number of species and reactions. This reaction set was created by ordering the reactions that destroyed or produced the largest amount of species. The species set was ordered by the species mole amounts with respect to the reduced reaction set. This was dependent on a reduction time integration parameter. This reduction time integration controlled the reduction of the mechanism. Different reduction time integrations produce different reduced schemes because at different times different reactions and species are dominant. The reduction time integration that took place for the reduction of the complex mechanism was 0.001 s ($t_{\min} = 0$ s, $t_{\max} = 0.001$ s). This time was considered the most appropriate by inspecting various reduced mechanisms at varying time integrations. Reduction with a short time interval produced a reaction set that did not include any end products. Reduction over the entire time span of 2.0s (the longest time step that could be analyzed because of memory requirements) produced a mechanism that did not have any intermediate species. After a final inspection of the mechanism that was produced at a time integration of 0.001 s, one intermediate species and one reaction was dropped because of no destruction pathway. The Zeldovich NO_x mechanism was added because this mechanism dominates the NO_x formation at the time and temperature scales at which the destruction occurs. The species for the final reduced mechanism are given in Table 6.1 and the corresponding reactions are listed in Table 6.2.

Table 6.1 Species Involved in the Reduced Mechanism

Number	Species
1	CH ₂ CL
2	CH ₂ CL ₂
3	CH ₂ O
4	CH ₃ O
5	CHO
6	CL
7	CLO
8	CO
9	CO ₂
10	H
11	H ₂
12	H ₂ O
13	HCL
14	HO ₂
15	HOCL
16	N
17	N ₂
18	NO
19	O
20	O ₂
21	OH

Table 6.2 Reaction Included in the Reduced Mechanism

Number	Reaction	A Mole*cm ³ *sec	n	T cal/mole
1	O+H2O => 2OH	1.487E+11	0.87	17818.09
2	2OH => O+H2O	1.510E+09	1.14	99.40
3	CL+H2O => OH+HCL	7.807E+13	-0.24	17269.99
4	H2O+H => OH+H2	7.955E+10	0.97	19595.56
5	OH+H2 => H2O+H	1.170E+09	1.30	3626.00
6	OH+HCL => CL+H2O	1.450E+12	0.00	660.00
7	H+O2 => OH+O	1.590E+17	-0.93	16873.00
8	OH+O => H+O2	4.124E+14	-0.52	-312.05
9	CH2CL2 => CH2CL+CL	1.020E+16	0.00	76800.00
10	CH2CL+CL => CH2CL2	1.928E+07	1.88	-6005.93
11	CO2+H => CO+OH	3.640E+13	0.21	26587.27
12	CO+OH => CO2+H	6.320E+06	1.50	497.00
13	OH+CL => O+HCL	3.974E+11	0.54	5591.30
14	O+HCL => OH+CL	7.270E+11	0.50	6700.00
15	CHO+M => H+CO+M	7.100E+14	0.00	16802.10
	H2/1.87/ O2/0.99/ H2O/5./ CO/2.1/ CO2/4.3/			
16	CH2O+OH => CHO+H2O	7.230E+05	2.46	-970.40
17	H2+CL => HCL+H	1.418E+12	0.39	4440.43
18	HOCL+M => OH+CL+M	1.000E+18	0.00	55000.00
19	HCL+H => H2+CL	1.790E+12	0.30	3800.00
20	HO2+OH => H2O+O2	2.890E+13	0.00	497.00
21	OH+CL+M => HOCL+M	1.507E+16	0.27	-7.98
22	CH2CL+O2 => CH2O+CLO	3.600E+20	-3.00	1720.00
23	OH+H => O+H2	3.534E+04	2.62	4529.87
24	O+H2 => OH+H	5.120E+04	2.67	6279.00
25	CH3O+M => CH2O+H+M	1.900E+26	-2.70	30600.00
	H2/2.9/ O2/1.2/ H2O/18.50/ CO/2.1/ CO2/4.3/			
26	CH2CL+OH => CH3O+CL	2.000E+12	0.29	3270.00
27	CH2CL+OH => CH2O+HCL	1.240E+22	-2.72	3860.00
28	OH+CLO => CL+HO2	2.897E+11	0.42	-1247.89
29	O+N2 => NO+N	1.820E+14	0.00	76250.00
30	NO+N => O+N2	8.997E+13	-0.10	1325.60
31	NO+O => N+O2	3.790E+09	1.00	41370.00
32	N+O2 => NO+O	4.316E+10	0.90	9725.08
33	NO+H => N+OH	1.740E+14	0.00	48810.00
34	N+OH => NO+H	5.140E+12	0.30	-19.96
note: reaction rates are in Arrhenius form i.e., $k = AT^n \exp(-E/RT)$				

The final reduced mechanism involves 21 species and 34 reactions. This is a great reduction in size and computational cost compared to the original complex mechanism, which had 1715 equilibrium reactions (3430 non - reversible reactions) and 278 species.

Validation of the Reduced Mechanism

The reduced mechanism shown in Tables 6.1 and 6.2 needs to be validated before it can be considered a good approximation of the complex mechanism. The reduced mechanism was implemented into Senkin with the same parameters as the complex mechanism. The transient results of the calculations are shown in Figures 6.1 – 6.5 in Appendix B. Figure 6.1 shows the destruction of CH_2Cl_2 and the formation of CH_2Cl . Only minor discrepancies can be found for formation of CH_2Cl_2 and destruction of CH_2Cl between the complex and reduced kinetic models. Figure 6.2 shows the destruction of CH_2Cl . The reduced model takes a slightly small time for destruction of CH_2Cl , but the agreement is still good. There is a very good agreement between the formation and destruction of species like Cl , CO , H_2 , HCl , and O . Figure 6.3 shows the formation and destruction of major species (Cl , CO , H_2 , HCl , and O) at 1 ms of the destruction process. There is a good agreement between the two models for Cl , H_2 , and O , but there exists a moderate difference for CO prediction. Figure 6.4 shows the formation and destruction of major species at 10 ms. The reduced mechanism reaches equilibrium at approximately 5 ms (the destruction time), while the reaction process is still proceeding for the complex model. Figure 6.5 shows the formation and destruction of major species at 100 ms. The complex mechanism proceeds until approximately 100 ms. The discrepancies between the reduced and complex models past approximately 1 ms are probably caused by the integration time step of 1 ms to create the reduced mechanism. But as stated previously, this time was chosen after inspection of various proposed reduced mechanisms. General discrepancies are probably caused by the loss of information as the complex model is reduced to a simpler model. In all, discrepancies between the reduced and the complex mechanisms are small considering the amount of reduction that took place. A final test for the reduced model is to compare it with the previous equilibrium results. The reduced model was run until a time at which equilibrium, or steady state is reached. This time for the reduced model is approximately 1000 s. A comparison between the two models is shown in Table 6.3.

Table 6.3 Comparison of Equilibrium Concentrations from two Different Models

Species	Reduced Model	Equilibrium	Difference Between Reduced and Equilibrium
	Mole fraction	Mole fraction	%
CL	1.48E-05	8.43E-06	75.56
CO	1.54E-04	5.15E-05	199.03
CO2	1.24E-01	1.24E-01	0.00
H2	5.90E-05	1.93E-05	205.70
H2O	1.57E-01	1.57E-01	0.00
HCL	3.37E-04	3.34E-04	0.90
N2	6.93E-01	6.94E-01	0.14
NO	9.58E-04	8.85E-04	8.25
O	1.89E-05	6.35E-06	197.64
O2	2.32E-02	2.32E-02	0.00
OH	4.49E-04	2.58E-04	74.03

The agreement between the equilibrium and reduced model calculations are good except for intermediate (unstable) species such as Cl, CO, O, and OH. However, the overprediction of H₂ concentration by the reduced model was unexpected. These results are encouraging considering the loss of information, and the significant uncertainty involved in the reduced model coefficients. The differences in the amount of NO_x predicted are because the Zeldovich mechanism is no longer valid at large time scales. From the comparison of transient and the equilibrium calculations, it can be seen that the reduced model can be used for prediction of the emissions of CH₂Cl₂ inside the residence chamber.

6.2 Validation of the FLUENT Radiation Model

The radiation heat transfer results from FLUENT cannot be used with confidence until they are compared with a valid test case. This is mostly due to the numerical errors and limitations of the mathematical models that FLUENT uses. The one - dimensional cooled tube analysis of Stasiek and Collins (1992) is used to verify the FLUENT results. FLUENT was run using the same boundary conditions as Stasiek and Collins for two cooled tube results (Table 6.4 and 6.5).

Here t is the non - dimensional temperature, q is the heat flux at the wall, σ is the Stephan - Boltzmann constant, and T is the temperature. The non - dimensional temperature is defined by

$$t = T \left(\frac{\sigma}{q} \right)^{1/4}$$

Table 6.4 Boundary Conditions for the Short Tube, L = 1 m, D = 0.2 m

	T	q	sigma	T
		W/m ²		K
Inlet	1.5	50000	5.67E-08	1453.58
Outlet	1.4727	50000	5.67E-08	1427.12
Wall In	1.3284	50000	5.67E-08	1287.29
Wall Out	1.2936	50000	5.67E-08	1253.56
Rad In	1.5	50000	5.67E-08	1453.58
Rad Out	1.4727	50000	5.67E-08	1427.12

Table 6.5 Boundary Conditions for the Long Tube, L = 1 m, D = 0.0625 m

	T	q	Sigma	T
		W/m ²		K
Inlet	1.5	50000	5.67E-08	1453.58
Outlet	1.382	50000	5.67E-08	1339.23
Wall In	1.3275	50000	5.67E-08	1286.42
Wall Out	1.1621	50000	5.67E-08	1126.13
Rad In	1.5	50000	5.67E-08	1453.58
Rad Out	1.382	50000	5.67E-08	1339.23

Table 6.6 Energy Balance for the FLUENT Calculations: Short Tube

	Convection & Conduction	Radiation	
	W	W	
Inlet	0.00	0.00	
Outlet	0.00	0.00	Total Heat Transfer
Symmetry	0.00	0.00	W
Wall	-2430.00	-2760.00	-5190.60
	Enthalpy		
	W		
inlet	1.02e+05		
outlet	9.67e+04		
Delta H	-5193.00		
	W	%	
Difference	-2.40	0.05	

Table 6.7 Energy Balance for the FLUENT Calculations: Long Tube

	Convection & Conduction	Radiation	
	W	W	
inlet	0	0	
outlet	0	0	Total Heat Transfer
symmetry	0	0	W
wall	-940.00	-766.00	-1705.96
	Enthalpy		
	W		
inlet	9.95E+03		
outlet	8.29E+03		
Delta H	-1664.10		
	W	%	
Difference	41.86	2.52	

As a consistency check, the overall energy balance was checked for the FLUENT calculations. As seen from Tables 6.6 and 6.7, energy conservation is achieved in the calculations for both cases. Figures 6.5 and 6.6, in Appendix B, show the non - dimensional temperature results from FLUENT and Stasiek and Collins at the tube centerline and within the tube walls. In Figures 6.5 and 6.6 the short tube results are denoted by #8, and long tube results are denoted by #11. These figures show that there are very little differences between the non - dimensional temperatures for the gas given by FLUENT and Stasiek and Collins one - dimensional results. The results for the non - dimensional temperature at the wall show that even though there are minor discrepancies between the FLUENT results and Stasiek and Collins results, FLUENT is able to predict the general trend of the non - dimensional temperature at the wall. It should be noted that Stasiek and Collins model is only one - dimensional, but the FLUENT runs were 2D (axisymmetric) where the cross - stream variations are accounted for. In this regard, we have more confidence in the results from FLUENT

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

A reduced mechanisms for conversion and destruction of dichloromethane has been formulated. The number of reactions have been reduced from 3430 to 34. The reduced mechanism contains only 21 species as opposed to the 278 reactions involved in the complex mechanism. Results from the reduced and complex mechanism are compared in

addition to the comparing them with equilibrium calculations. The performance of the reduced mechanism is good for predicting the conversion rates of the PCB compounds but only fair for predicting the concentration levels of the intermediate compounds such as CO, HO, O and Cl. More work is necessary to fine tune the reaction rate constants to improve the predictions quantitatively.

The radiation calculations using the FLUENT code have been validated for this a test case which was studied by Staiek and Collins (1992) was selected. This case had a similar geometry to the Vortec recuperator and one-dimensional analytical solutions are available for various scenarios with an without radiation. Two typical cases were simulated with the same initial and boundary conditions. The agreement between the results reported in the literature and our FLUENT calculations are good thus building confidence on the previously reported FLUENT radiation heat transfer results for the recuperator.

8.0 WORK PLANNED FOR NEXT PERIOD

The final report will be prepared.

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APPENDIX B: Figures

Figure 1 Vortec CMS TM System Sketch

Complex Mechanism

Reduced Mechanism

Figure 6.1 Comparison of the Complex and Reduced Mechanisms for the Destruction of CH_2Cl_2

Complex Mechanism

Reduced Mechanism

Figure 6.2 Comparison of the Complex and Reduced Mechanisms for the Destruction of CH_2Cl

Complex Mechanism

Reduced Mechanism

Figure 6.3 Comparison of the Complex and Reduced Mechanisms for the Formation and Destruction of Major Species at .001 s

Figure 6.4 Comparison of the Complex and Reduced Mechanisms for the Formation and Destruction of Major Species at .01 s

Complex Mechanism

Reduced Mechanism

Figure 6.5 Comparison of the Complex and Reduced Mechanisms for the Formation and Destruction of Major Species at .1 s

FIG. 10. Effect of tube length on the tube wall and temperature distributions. $q(x) = \text{const}$; $\epsilon = 1.0$; $k = 0$

Figure 6.6 Validation Results for a Short Tube

FLUENT Long Tube Validation Results

Results from Stasiek and Collins

FIG. 10. Effect of tube length on the tube wall and temperature distributions. $q(x) = \text{const}$; $\epsilon = 1.0$; $k = 0$

Figure 6.7 Validation Results for a Long Tube

FOCUS AREA 3.0

Decontamination & Decommissioning

**USE OF *SPINTEK* CENTRIFUGAL MEMBRANE TECHNOLOGY AND
SORBENT/CLEANING SOLUTIONS IN THE DECONTAMINATION AND
DECOMMISSIONING OF DOE FACILITIES**

FETC Task No. 3.2

Quarterly Technical Progress Report
Reporting Period: 1/1/98 – 3/31/98

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, chelating agents) to decontaminate surfaces such as pipes and walls represents a unique and cost-effective method for remediating DOE facilities. As envisioned, the sorbent or cleaning agent 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 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 conventional membrane processes. The *SpinTek* centrifugal membrane separation (CMS) 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 surface 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, thus decreasing cleaning chemical use and maintenance and increasing the volume of waste treated per area of membrane.

The objective of Task 3.2 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 (D&D) 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 residuals (*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 the CMS system. 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 prepared to obtain funding for D&D research through existing DOE ROAs and PERDAs.

TABLE OF CONTENTS

Item	Page
Title Page	i
Disclaimer	ii
Abstract	iii
Table of Contents	iv
List of Tables	v
List of Figures/Illustrations	vi
Executive Summary	vii
Introduction	1
Purpose	2
Background	3-6
Methodology	7-8
Work Performed During This Period	9
Results and Discussion	10-19
Conclusions	20
Work Planned for Next Quarter	21
Technical/Administrative Difficulties	22

LIST OF TABLES

Table #		Page
1	Surfactant concentrations in permeate and concentrate and surfactant rejections.	12

LIST OF FIGURES/ILLUSTRATIONS

Figure #		Page
1	Schematic of the <i>SpinTek</i> centrifugal membrane separation (CMS) system.	6
2	Schematic of the hollow fiber (HF) membrane separation system.	13
3	Permeate and concentrate temperature versus operational time.	14
4	Permeate flux and concentration factor versus operational time.	15
5	Permeate and concentrate turbidity versus operational time.	16
6	Permeate and concentrate pH versus operational time.	17
7	Permeate and concentrate conductivity versus operational time.	18
8	Permeate MA 80-I concentration and concentration factor versus operational time.	19

EXECUTIVE SUMMARY

In the reporting period from 1/1/98 to 3/31/98, CYTEC Aerosol MA 80-I surfactant was treated using a hollow fiber ultrafiltration system designed and constructed by the Membrane Separation Research Group in West Virginia University's Department of Civil and Environmental Engineering. The hollow fiber UF system was to recover/retain surfactants such as the CYTEC MA 80-I proposed for use in the RMI soil remediation project at Ashtabulah, Ohio.

1.0 INTRODUCTION

The use of sorbents (biosorbents, powdered activated carbon) and cleaning agents (surfactants, chelating 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 contaminated surfaces. For example, a pipe that is contaminated with inorganic and organic contaminants can be contacted with a solution containing a surfactant (for 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 processes. 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 surface by centrifugal and hydraulic action. Permeate is forced through the membrane is collected in the hollow shaft and is discharged. The concentrate exits at the edge of the membrane pack. The centrifugal action continuously cleans the membrane surface thus 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 processes.

2.0 PURPOSE

The purpose of this research is to investigate the feasibility of using sorbents (biosorbents and powdered activated carbon) and cleaning agents (surfactants and chelating agents) to decontaminate surfaces (*e.g.*, pipes) and then to separate the sorbents/cleaning solutions from the aqueous phase using the *SpinTek* centrifugal membrane separation system. 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 and use of sorbents/cleaning solutions.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon conventional membrane separation processes. The *SpinTek* system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The feed 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 contaminants) exits at the edge of the membrane disk packs. A schematic of the *SpinTek* centrifugal membrane separation (CMS) system is presented in Figure (1). Figures are presented at the end of the text portion of Section 3.0.

With time, solute molecules will accumulate at the membrane surface resulting in a decrease in the permeate flow rate. The accumulation of solute molecules at the membrane surface is known as concentration polarization. To reduce the effects of concentration polarization 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 high velocities increase hydraulic turbulence which reduces the thickness of the concentration polarization layer. In the CMS system, the rotation of the membrane disk induces the hydraulic turbulence required to minimize the thickness of the solute concentration boundary layer. In conventional membrane systems, maximum surface velocities of ~15 ft/s are possible while surface velocities of ~60 ft/s are typical in the CMS system. As the concentrate thickens with treatment time, conventional systems are not able to maintain high velocities because of the difficulty in pumping viscous material at large flow rates. Because the CMS 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 semi-batch mode or batch-down mode. In semi-batch mode, fresh waste is added to the system at a rate equal to the permeate production rate. In 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. During batch-down, large concentration factors are achieved (permeate is still being produced, thus reducing the concentrate volume).

All membrane separation processes are volume reduction technologies because contaminants are not degraded or destroyed. Thus, an important measure of membrane technology efficiency is the concentration factor (CF). The CF during semi-batch and batch-down operation are calculated using the following two equations:

Semi-Batch Operation

$$CF_{SB} = 1 + V_{perm}/V_{feed} \quad (1)$$

Batch-Down Operation

$$CF_{BD} = CF_{SB} \times [V_{feed}/(V_{feed} - V_{perm})] \quad (2)$$

where CF_{SB} = concentration factor during semi-batch operation; V_{perm} = volume of permeate produced, gal.; V_{feed} = feed tank volume, gal; CF_{BD} = concentration factor during batch-down operation. Concentration factors are expressed as 1X, 2X, *etc.*, and increase with treatment time during semi-batch and batch-down operation. CFs in excess of 100X are obtainable with membrane technology. Another measure of treatment efficiency is the permeate flux (volume of permeate produced per membrane area per time). The permeate flux for a given membrane and depends upon waste viscosity, solids content, and temperature. Waste characteristics can also change during treatment due to the effects of mechanical shear and thermal stress.

Membranes used in ultrafiltration are characterized by the molecular weight of a molecule that is retained by the membrane. Compounds having a molecular weight greater than the membrane's molecular weight cut-off (MWCO) would theoretically 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 of the unique three dimensional particle geometry.

Surfactants, or surface-active agents, are substances that have amphiphilic molecules which have both hydrophilic head groups and a hydrophobic hydrocarbon chain. When dissolved in water, the amphiphilic surfactants have a tendency to collect at any interface where the hydrophobic groups can be partially or completely separated from contact with water and the hydrophilic groups can remain wetted. The same dual tendencies of molecules will cause the formation of particles of colloidal dimensions which are termed micelles when the surfactant concentration is in excess of a certain value. In micelle formation, the molecules undergo self-association in solution to produce aggregates in which the hydrocarbon chains are put together so that the total contact area of the hydrophobic groups of the surfactant molecules with water is reduced. The typical aggregation number of micelles is in the range of 50-300. The concentration at which micelles form is termed the critical micelle concentration (CMC). The CMC of a surfactant is determined by its molecular structure and is also affected by additives and temperature. When the surfactant concentration is beyond the CMC, the concentration of monomers (single molecules in the surfactant solution) may remain relatively constant at the CMC value for some types of surfactant and may increase for other types of surfactant.

For an aqueous surfactant solution, the hydrocarbon core of micelles provide a

hydrophobic pseudophase in a polar environment. When organic substances insoluble or sparingly soluble in water are mixed with surfactant solution, hydrophobic molecules will be repelled by water molecules and tend to be incorporated by the hydrocarbon core of the micelles. Superficially, the solubility of these substances is increased. The phenomenon is termed solubilization. Solubilized organic substances reside within the surfactant micelles. Solubilized organic molecules are then separated from water with the surfactant micelles when the solution is passed through an ultrafiltration membrane (because most surfactant micelles are large enough in size to be retained by ultrafiltration membranes).

Figure (1)-Schematic Of The *SpinTek* Centrifugal Membrane Separation (CMS) System.

4.0 METHODOLOGY

A hollow fiber (HF) membrane separation system, designed and constructed by the Membrane Separation Research Group in West Virginia University's Department of Civil and Environmental Engineering was used to separate surfactant micelles from solution. A hollow fiber membrane module with a MWCO of 5,000 (Model number HF 1.0-43-PM5) was used in the experiment.

Aerosol MA 80-I, obtained from CYTEC Industries, is an anionic surfactant. The main component of MA 80-I is 78 to 80% sodium dihexyl sulfosuccinate (SDS). The critical micelle concentration (CMC) of the MA 80-I surfactant is 1.2 to 1.6% (wt.) according to information provided by CYTEC. The purpose of this experiment is to investigate the effectiveness of the HF membrane separation process in recovering/retaining the MA 80-I surfactant from an aqueous solution.

A clean water flux (CWF) was measured for (1) the virgin HF membrane and (2) after the membrane was cleaned. The CWF: (1) served as a baseline indicator of membrane condition in the case of the virgin membrane and (2) to determine if the membrane was sufficiently cleaned after an experiment. In this experiment, a 1% Aerosol MA 80-I surfactant solution was concentrated using the HF separation system. The HF membrane system was operated in batch-down (direct concentration) mode. The following parameters were monitored during the experiment:

1. Permeate flux
2. Feed and permeate temperature
3. Inlet and outlet pressures
4. Turbidity, pH, conductivity, and light adsorbance of the feed and permeate solutions.

Conductivity was measured using a ACCUMET[®] Model 30 conductivity meter which was calibrated regularly during the experiment. All conductivity measurement was presented in the units of micromhos per centimeter ($\mu\text{S}/\text{cm}$). pH was measured using an ORION Model 520 pH meter. The pH meter was calibrated regularly during the experiment. Turbidity was measured using an ORBECO-HELLIGE Model 965-10A turbidimeter. The turbidimeter was calibrated regularly during the experiment. All turbidity measurements were presented in nephelometric turbidity units (NTUs).

A Milton Roy SPECTRONIC[®] GENESIS[™] 5 Spectrophotometer was used to determine the Aerosol MA 80-I surfactant concentration by measuring the light adsorbance of the surfactant at a wavelength of 300 nm. The wavelength for the surfactant was determined by performing a wavelength scan and determining the wavelength at which the maximum adsorbance was observed. After the wavelength was determined, a calibration curve was developed for the Aerosol MA 80-I surfactant to correlate surfactant concentration and

adsorbance.

Permeate flux, surfactant concentration in the permeate, operational ease, and the membrane's physical/chemical resistance and cleanability were used to judge the effectiveness of the HF separation process.

5.0 WORK PERFORMED DURING THIS PERIOD

During the period from 1/1/98 to 3/31/98, an experimental study on the separation of surfactant micelles using a hollow fiber (HF) membrane system was conducted. The HF system was designed and constructed by the Membrane Separation Research Group in West Virginia University's Department of Civil and Environmental Engineering. A hollow fiber membrane module having a molecular weight cutoff of 5,000 (HF 1.0-43-PM5) was employed in the experiment. The HF separation system was to recover/retain CYTEC Aerosol MA 80-I surfactant (78-80% sodium dihexyl sulfosuccinate as the effective component). The MA 80-I surfactant has been proposed for use in the RMI soil remediation project at Ashtabula, Ohio.

6.0 RESULTS AND DISCUSSION

In this chapter, results from the surfactant separation experiment will be presented and discussed. The experiment was conducted using CYTEC Aerosol MA 80 I surfactant. A schematic of the hollow fiber (HF) separation system is presented in Figure (2). Figures and tables are presented at the end of the text portion of Section 6.0.

A virgin hollow fiber membrane was installed and a clean water flux (CWF) of 4500 L/m²-day was measured. A 180 L feed solution of 1% Aerosol MA 80-I surfactant was treated under the following operational conditions: inlet pressure = 27 psi; outlet pressure = 13 psi; concentrate return flow = 2.5 gal/min; feed temperature = 110 ± 2 °F; and operational mode = batch-down. The system was briefly operated in recycle mode (*i.e.*, constant concentration) from 30 to 34 hours.

The system was started and the feed tank temperature was increased to 110 ± 2 °F. Permeate and concentrate temperature versus operational time are presented in Figure (3). The permeate temperature was typically 9 to 10 °F lower than the concentrate temperature. The temperature difference was due to permeate heat loss during flux measurement.

Permeate flux; turbidity; pH; conductivity; and adsorbance of both permeate and concentrate were measured regularly during the experiment. Permeate flux and concentration factor versus operational time is presented in Figure (4). Permeate flux decreased rapidly over the first 2 hours of operation, decreasing from 2,700 L/m²-d to approximately 1,250 L/m²-d. Permeate flux decreased to ~1,000 L/m²-d from ~28 hr. of operation through the end of experiment. Permeate and concentrate turbidity versus operational time is presented in Figure (5). Permeate turbidity was stable at ~0.6 NTU throughout the experiment. Concentrate turbidity was stable at ~45 NTU through the first 36 hr. of operation, then increased to ~65 NTU at the end of the experiment. Permeate and concentrate pH versus operational time is presented in Figure (6). The pH of the permeate and concentrate remained stable at ~6.20 throughout the experiment. The permeate and concentrate conductivity versus operational time is presented in Figure (7). The permeate and concentrate conductivity increased gradually through the experiment.

The final system volume was 14 L; thus, the hydraulically based MA 80-I concentration at the end of experiment was 12.9%. The system was shut down and cleaned by running 120 L of hot (110 °F) distilled water through the system.

A linear relationship between conductivity and MA 80-I concentration was observed. Thus, it was concluded that the MA 80-I concentration could be estimated by measuring the conductivity of a solution. Permeate surfactant concentration and hydraulic concentration factor versus operational time are presented in Figure (8). Surfactant concentrations in permeate and concentrate and surfactant rejections are presented in

Table (1). Low surfactant rejections (25 to 49%) were observed at low feed concentrations (1 and 2%). As the feed concentration increased, surfactant rejection also increased to 89% rejection at 12.9% MA 80-I feed concentration.

**Table (1)-Surfactant Concentrations In Permeate And Concentrate And
Surfactant Rejections.**

Concentrate Concentration (% wt.)	Permeate Concentration (% wt.)	Rejection (%)
1	0.75	25
2	1.02	49
3	1.06	65
4	1.16	71
5	1.16	77
6	1.33	78
7	1.35	81
8	1.41	82
9	1.42	84
10	1.43	86
11	1.48	87
12	1.48	88
12.9	1.44	89

Figure (2)-Schematic of Hollow Fiber (HF) Separation System.

Figure (3)-Permeate and Concentrate Temperature Versus Operational Time.

Figure (4)-Permeate Flux and Concentration Factor Versus Operational Time.

Figure (5)-Permeate And Concentrate Turbidity Versus Operational Time.

Figure (6)-Permeate And Concentrate pH Versus Operational Time.

Figure (7)-Permeate And Concentrate Conductivity Versus Operational Time.

Figure (8)-Permeate MA 80-I Concentration And Concentration Factor Versus Operational Time.

7.0 CONCLUSIONS

A hollow fiber (HF) separation system was designed and constructed by researchers from the Membrane Separation Research Group in West Virginia University's Department of Civil and Environmental Engineering. The HF separation system was used to retain/recover CYTEC Aerosol MA 80-I surfactant proposed for use in the RMI soil remediation project at Ashtabulah, Ohio. The MA 80-I concentration was proportional to solution conductivity. Thus, solution conductivity was used to determine surfactant concentration in the feed and permeate solutions. A surfactant rejection of 89% was observed at a final MA 80-I concentration of 12.9%.

8.0 WORK PLANNED FOR NEXT QUARTER

Further testing of the hollow fiber (HF) separation system will be conducted. Additional experiments will be conducted to test the ability of the HF separation system to recover/retain MA 80-I surfactant micelles.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

There were no technical difficulties to report during the first quarter of '98.

FOCUS AREA 4.0

Cross Cutting
Innovative Technologies

**USE OF CENTRIFUGAL MEMBRANE TECHNOLOGY WITH NOVEL MEMBRANES
TO TREAT HAZARDOUS/RADIOACTIVE WASTES**

FETC Task No. 4.1

Quarterly Technical Progress Report
Reporting Period: 1/1/98 - 3/31/98

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ABSTRACT

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon conventional membrane processes. 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 a hollow center shaft and is discharged. The concentrate exits at the edge of the membrane packs.

The centrifugal action continuously cleans the membrane surface, thus decreasing cleaning chemical use and maintenance and increasing the volume of waste treated per unit membrane area. 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 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 obtain training on the use of *SpinTek* technology, and 4) test and evaluate *SpinTek* technology and specialty membranes. These experiments will provide baseline system performance data using a controlled feed solution. The following variables will be monitored as a function of run time: 1) permeate flux, 2) temperature and pressure, and 3) conductivity and pH of all liquids.

The result of this work will be a technology that can treat a variety of wastewaters such as contaminated groundwater, mixed-waste process water, and existing waste residual (*e.g.*, low-level radioactive 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 the centrifugal membrane separation technology will be high and a relatively low amount of residual requiring additional treatment will be produced.

TABLE OF CONTENTS

Item	Page
Title Page	i
Disclaimer	ii
Abstract	iii
Table of Contents	iv
List of Tables	v
List of Figures/Illustrations	vi
Executive Summary	vii
Introduction	1
Purpose	2
Background	3-8
Methodology	9
Work Performed During This Period	10
Results and Discussion	11-16
Conclusions	17
Work Planned for Next Quarter	18
Technical/Administrative Difficulties	19

LIST OF TABLES

Table #		Page
1	Average permeate backpressures at common membrane rotational speeds.	8
2	Characteristics of the ceramic membrane.	13

LIST OF FIGURES/ILLUSTRATIONS

Figure #		Page
1	Schematic of the <i>SpinTek</i> centrifugal membrane separation (CMS) system.	7
2	Permeate flux versus time for the 30%-1750 rpm experiment.	14
3	Average permeate flux versus average transmembrane pressure for the 30%-1750 rpm experiment.	15
4	Average permeate flux versus average transmembrane pressure for the 30%-1750 rpm clean water flux experiment.	16

EXECUTIVE SUMMARY

In the first quarter of '98, the treatment of an oily wastewater was investigated using the *SpinTek* centrifugal membrane separation system. An experiment was conducted at a synthetic oil concentration of 30% at a constant membrane rotational speed of 1750 rpm to obtain pressure-independent permeate flux data. Applied pressure ranged from 25 to 70 psig in this experiment. The experiment was performed at 110 °F in recycle mode using a 0.11 µm average pore size ceramic membrane. Permeate flux, and permeate/concentrate pH and conductivity were measured regularly. The applied pressure was corrected for permeate backpressure using the mathematical model presented in the first quarterly technical progress report of '97. After the constant synthetic oil concentration/membrane rotational speed experiment, the *SpinTek* system was drained, flushed, and cleaned using a standardized cleaning procedure consisting of a surfactant and NaOH solution adjusted to pH 11.8 followed by an H₂SO₄ solution adjusted to pH 2.2, as presented in the second quarterly technical progress report of '97. The cleaning procedure was followed by a clean water flux measurement at 110 °F, 1750 rpm, at three applied pressures ranging from 25 to 75 psig. The membrane resistance was then calculated and tracked to monitor the condition of the membrane throughout the course of the study. The primary technical difficulty encountered in the first quarter was a leaking mechanical seal on the *SpinTek* system feed pump. Mechanical seals have been ordered and will be replaced prior to continuing the study.

1.0 INTRODUCTION

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon conventional membrane separation processes. The *SpinTek* centrifugal membrane separation (CMS) 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 discharged. The concentrate exits at the edge of the membrane packs. The centrifugal action continuously cleans the membrane surface, thus 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.*, increasing the volume reduction factor). *SpinTek's* CMS 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 effects of system operating parameters (membrane rotation and transmembrane pressure) on the treatment of a synthetic oily wastewater using *SpinTek's* centrifugal membrane separation system. Additionally, a mathematical model is used to correct for the average permeate backpressure due to centrifugal force.

The result of this work will be a further step toward optimizing the centrifugal membrane separation (CMS) technology for the treatment of a variety of waste streams such as: DOE decontamination/decommissioning wastes; 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 volume reduction factors for the CMS technology will be high and a relatively 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 conventional membrane separation processes. The *SpinTek* system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The feed 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 contaminants) exits at the edge of the membrane disk packs. A schematic of the *SpinTek* centrifugal membrane separation (CMS) system is presented in Figure (1). Figures and tables are presented at the end of the text portion of Section 3.0.

With time, solute molecules will accumulate at the membrane surface resulting in a decrease in the permeate flow rate. The accumulation of solute molecules at the membrane surface is known as concentration polarization. To reduce the effects of concentration polarization 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 high velocities increase turbulence which reduces the thickness of the concentration polarization layer. In the CMS system, the rotation of the membrane disk induces the turbulence required to minimize the thickness of the solute concentration boundary layer. In conventional membrane systems, maximum surface velocities of ~15 ft/s are possible while with the CMS systems, surface velocities of ~60 ft/s are typical. As the concentrate thickens with treatment time, conventional systems are not able to maintain high velocities because of the difficulty in pumping viscous material at large flow rates. Because the CMS 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 semi-batch mode or batch mode. In semi-batch mode, fresh waste is added to the system at a rate equal to the permeate production rate. In 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. During batch-down, large concentration factors are achieved (permeate is still being produced thus reducing the concentrate volume).

All membrane separation processes are volume reduction technologies because contaminants are not degraded or destroyed. Thus, an important measure of membrane technology efficiency is the concentration factor (CF). The CF during semi-batch and batch-down operation are calculated using the following two equations:

Semi-Batch Operation

$$CF_{SB} = 1 + V_{perm}/V_{feed} \quad (1)$$

Batch-Down Operation

$$CF_{BD} = CF_{SB} \times [V_{feed}/(V_{feed} - V_{perm})] \quad (2)$$

where CF_{SB} = concentration factor during semi-batch operation; V_{perm} = volume of permeate produced, gal.; V_{feed} = feed tank volume, gal; CF_{BD} = concentration factor during batch-down operation. Concentration factors are expressed as 1X, 2X, *etc.*, and increase with treatment time during semi-batch and batch-down operation. CFs in excess of 100X are obtainable with membrane technology. Another measure of treatment efficiency is the permeate flux (volume of permeate per membrane area per time). The permeate flux for a given membrane and depends upon waste viscosity, solids content, and temperature. Waste characteristics can also change during treatment.

Membranes used in ultrafiltration are characterized by the molecular weight of a molecule that is retained by the membrane. Compounds having a molecular weight greater than the membrane's molecular weight cut-off (MWCO) would theoretically 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 of the unique particle geometry.

A backpressure results from permeate pooling at the outer perimeter of the disk pack as centrifugal force is exerted on the permeate through membrane rotation. A mathematical correction for the average permeate backpressure is presented in Equation (3):

$$P_{back-avg} = [\rho(I\omega)^2]/2 \quad (3)$$

where $P_{back-avg}$ = average permeate backpressure; ρ = permeate mass density = 1 kg/L; I = radius of gyration; and ω = angular velocity.

In the centrifugal membrane separation system, the permeate backpressure is a direct function of membrane rotational speed, feed solution density, and the radius of gyration. The explicit form the radius of gyration is:

$$I = [(R_i^2 + R_o^2)/2]^{1/2} \quad (4)$$

where R_i = inner disk radius = 0.975 in. = 2.48 cm and R_o = outer disk radius = 3.625 in. = 9.21 cm.

The average transmembrane pressure is the difference between the gauge pressure and the average permeate backpressure:

$$P_{tmp-avg} = P_{gauge} - P_{back-avg} \quad (5)$$

where $P_{tmp-avg}$ = average transmembrane pressure and P_{gauge} = gauge pressure. A summary of average permeate backpressures at common membrane rotational speeds is presented in Table (1).

Membrane resistance is an intrinsic material property of a membrane. Darcy's Law, presented in Equation (6), is used to calculate the membrane resistance (determined using a virgin membrane with a clean water feed solution):

$$J = P_{\text{tmp}}/\mu R_m \quad (6)$$

where J = permeate flux; P_{tmp} = transmembrane pressure; μ = permeate absolute viscosity; R_m = membrane resistance. The slope of a regression line through the origin on a plot of permeate flux versus transmembrane pressure is inversely proportional to the product of the absolute feed viscosity and the resistance of the membrane:

$$R_m = 1/(\mu \text{slope}) \quad (7)$$

For clean water and feeds at low concentrations and low transmembrane pressures with high cross-flow velocities, the Hagen-Poiseuille model for stream-line flow in an ideal membrane system is generally accepted as the best description of fluid flow through a microporous membrane:

$$J = \varepsilon r^2 P_{\text{tmp}}/8\nu \Delta x \quad (8)$$

where J = permeate flux; ε = membrane surface porosity; r = mean pore radius; P_{tmp} = transmembrane pressure permeate; ν = permeate kinematic viscosity; and Δx = membrane thickness.

As the transmembrane pressure or the solute concentration are increased, or the hydraulic turbulence is decreased, the flux becomes independent of transmembrane pressure due to a buildup of solute molecules at the membrane surface when compared to the bulk solution. In this case, the film theory model is used to predict the pressure independent permeate flux:

$$J^* = k_s \ln(C_m/C_b) \quad (9)$$

where J^* = pressure independent permeate flux; k_s = solute mass transfer coefficient; C_m = solute concentration at the membrane surface; and C_b = solute concentration in the bulk solution. J^* is determined experimentally from the pressure independent region on a flux versus $\ln(\text{transmembrane pressure})$ curve. In the pressure independent region, permeate flux can only be improved by increasing the mass transfer coefficient:

$$k_s = D/\delta \quad (10)$$

where k_s = solute mass transfer coefficient; D = solute diffusion coefficient; and δ = thickness of concentration polarization layer. Two methods of increasing the mass transfer coefficient include increasing D by increasing feed temperature and decreasing δ by increasing turbulence. Several semi-empirical relationships have been developed for turbulent hydraulic flow conditions ($Re > 4000$). One representative relationship is:

$$k_s d_h / D = 0.023(Re)^{0.8}(Sc)^{0.33} \quad (11)$$

where d_h = hydraulic diameter of the flow channel and D = solute diffusion coefficient, Re = Reynolds Number, and Sc = Schmidt Number. The power-law relationship presented in Equation (12) is used to judge the effect of turbulence on the pressure independent permeate flux:

$$J^* = f(\text{turbulence})^n \quad (12)$$

where J^* = pressure independent permeate flux and n = slope of the line fitted to experimental data in a plot of $\log(J^*)$ versus $\log(\text{turbulence})$. Typical values of n range from 0.3 to 0.6 for laminar flow and from 0.8 to 1.2 for turbulent flow conditions. The magnitude of n is an indicator of the effect of hydraulic turbulence on pressure independent permeate flux. In Equation (___), turbulence can be expressed in terms of Reynolds Number or cross-flow velocity. In the CMS system, hydraulic turbulence can be expressed in terms of membrane rotational speed since the Reynolds Number is a direct function of membrane rotation. [Cheryan, M. (1986). Ultrafiltration Handbook, Technomic Publishing Corp., Inc., Lancaster, PA.]

Figure (1)-Schematic Of The SpinTek Centrifugal Membrane Separation (CMS) System.

Table (1)-Average Permeate Backpressures At Common Membrane Rotational Speeds.

Rotational Speed (rpm)	P _{back-avg} (psi)
1750	11.1
1450	7.6
1250	5.7
1150	4.8
850	2.6
750	2.0
250	0.3

4.0 METHODOLOGY

The *SpinTek* ST-II centrifugal membrane separation (CMS) system was used to treat a synthetic oily wastewater. A ceramic membrane with an average pore size of $0.11\ \mu\text{m}$ was used in this study. The experiment was conducted at a membrane rotational speed of 1750 rpm and a constant feed concentration of 30% synthetic oil. The experiment was conducted in recycle mode, at $110 \pm 2\ ^\circ\text{F}$, with a 40 L feed volume of freshly prepared synthetic oily wastewater. A 1.0 ± 0.2 gpm concentrate return flow rate was maintained throughout the experiment. The permeate flux was measured at an increasing applied pressure ranging from 25 to 70 psig. Permeate backpressure as a function of rotational speed was taken into account to ensure a positive net transmembrane pressure. Additionally, the transmembrane pressure was corrected to account for the average permeate backpressure due to permeate pooling at the outer perimeter of the membrane disk under centrifugal force.

The following variables were monitored during testing:

1. Applied pressure.
2. Membrane rotational speed.
3. Concentrate return flow rate.
4. Permeate flux.
5. Concentrate and permeate temperature.
6. Concentrate and permeate conductivity and pH.

The following standardized cleaning procedure was applied after the experiment: The system was stopped, the lines were drained, and the system was flushed with hot tap water. Five gallons of distilled water was adjusted to pH 11.8 using NaOH (from a 1M stock NaOH solution stored with a soda scrubber.) Additionally, 30 mL *Dawn* dishwashing detergent was added to the NaOH solution. The pH and conductivity of the cleaning solution were measured and recorded. The cleaning solution was heated to $135 \pm 2\ ^\circ\text{F}$ and the membrane was cleaned for 30 minutes at 1750 rpm and 40 psig. Permeate flux was measured and recorded during the base/surfactant cleaning cycle. The system was then drained and flushed with hot tap water. An additional 5 gallons of distilled water was adjusted to pH 2.2 using a stock 1M H_2SO_4 solution. The pH and conductivity of the cleaning solution were measured and recorded. The cleaning solution was heated to $135 \pm 2\ ^\circ\text{F}$ and the membrane was cleaned for 30 minutes at 1750 rpm and 40 psig. The permeate flux was measured and recorded during the acid cleaning cycle. The system was then flushed with hot tap water. A clean water flux (CWF) was measured at $110 \pm 2\ ^\circ\text{F}$, 1750 rpm, at three pressures ranging from 25 to 75 psig using a distilled water feed. The average permeate flux versus the average transmembrane pressure was plotted and the membrane resistance was determined (see Equation [7]).

5.0 WORK PERFORMED DURING THIS PERIOD

The following work was conducted during the period from 1/1/98 to 3/31/98: 1) continuation of literature search; 2) investigation of system performance treating an oily wastewater at a constant concentration of 30% synthetic oil, membrane rotational speed of 1750 rpm, and applied pressure ranging from 25 to 70 psig; and 3) application of a standardized cleaning procedure and tracking of membrane resistance after the oily wastewater experiment.

Literature Search

A comprehensive literature search on membrane technology was conducted and over 75 articles and reports have been added to the membrane technology literature database. As new relevant documents come to light the material will be requested through West Virginia University's Interlibrary Loan program.

Waste and Membrane Identification and Acquisition

The identification of wastes and membranes that warrant further study is an on ongoing task for this research project. In this quarter, a ceramic membrane with an average pore size of 0.11 μm was used to treat a synthetic oily wastewater. Numerous researchers have investigated the performance of ultrafiltration membranes; thus the behavior of the ceramic membrane used in the *SpinTek* CMS system can be compared with data from other conventional and mechanically enhanced systems. Due to the poor performance of the PV-100K polymeric membrane it was decided that the majority of testing should involved the more promising ceramic membrane.

Technology Evaluation

In the first quarter, the *SpinTek* technology with a ceramic membrane (0.11 μm pore size) was used to process a 30% synthetic oily wastewater. Results and discussion are presented in Section 6.0.

6.0 RESULTS AND DISCUSSION

In this section results from the treatment of freshly prepared synthetic oily wastewater using a ceramic membrane with an average pore size of $0.11\ \mu\text{m}$ will be presented and discussed. A schematic of the *SpinTek* centrifugal membrane separation (CMS) system was presented previously in Figure (1). Figures and tables are included at the end of the text portion of Section 6.0.

A ceramic membrane was obtained from the *SpinTek* Corporation. Characteristics of the ceramic membrane are presented in Table 2. Prior to being used in the synthetic oily wastewater experiments, the membrane resistance was determined using Equation (7) as presented in the first through fourth quarterly reports of '97.

In the experiment, a forty liter feed solution consisting of 30% synthetic oil in distilled water. The distilled water was obtained from the West Virginia University Department of Civil and Environmental Engineering's house supply. The experiment was conducted in recycle mode, at $110 \pm 2\ ^\circ\text{F}$, with a 1.0 ± 0.2 gpm concentrate return flow.

Permeate flux versus time for the 30%-1750 rpm experiment is presented in Figure (2). The system was operated over an applied pressure range of 25 to 70 psig. Permeate flux was stable at each applied pressure condition. The average permeate backpressure was 11.1 psi at a membrane rotational speed of 1750 rpm. The permeate flux was $44\ \text{gal/ft}^2\text{-d}$ when the 25 psig applied pressure condition was re-investigated after the pressure independent flux was determined. The permeate flux at the initial 25 psig condition was $56\ \text{gal/ft}^2\text{-d}$. The lower "rebound" may have been due to membrane pore plugging or adsorption of solute molecules onto the membrane surface. Additionally, it is possible that the thickness of the solute boundary layer was not reduced to its initial value when the applied pressure was decreased. A higher resistance to the hydraulic flow of permeate and thus a lower permeate flux would result from a thicker solute concentration boundary layer. Average permeate flux versus average transmembrane pressure for the 30%-1750 rpm experiment is presented in Figure (3). A pressure independent flux of $97\ \text{gal/ft}^2\text{-d}$ was observed at the 25 to 70 psig applied pressure conditions. The slope of the regression line fitted to the pressure-controlled data from 0 to 25 psig was $3.832\ \text{gal/ft}^2\text{-d-psi}$. Thus, the total resistance to hydraulic flow in the pressure-controlled region was $6.15 \times 10^{12}\ \text{m}^{-1}$.

Permeate pH ranged from 6.20 to 7.41 and averaged 6.74. Concentrate pH ranged from 5.91 to 7.25 and averaged 6.57. Permeate pH was greater than concentrate pH throughout the 30%-1750 rpm experiment. Both permeate and concentrate pH followed the same general trend in this experiment: pH decreased through 1 hr. then increased from 1 hr. through the end of the experiment. Permeate and concentrate pH values were then approximately equal from 2.5 hr. through the end of the experiment. Permeate conductivity ranged from 868 to $1164\ \mu\text{S/cm}$ and averaged $965\ \mu\text{S/cm}$. Concentrate conductivity ranged from 880 to $976\ \mu\text{S/cm}$ and averaged $936\ \mu\text{S/cm}$. A net decrease in permeate conductivity was observed. Concentrate conductivity was constant. Permeate conductivity was greater than concentrate conductivity through ~ 2.75 hr. Concentrate conductivity then exceeded permeate conductivity from ~ 2.75 hr. through the end of

the experiment. Distinct step-wise changes in permeate and concentrate pH and conductivity were not observed as applied pressure was increased.

The system was cleaned using the standardized cleaning procedure presented in Chapter 4.0. The pH and conductivity of the distilled water used to determine the membrane resistance after cleaning were 6.93 and 3.83 $\mu\text{S}/\text{cm}$, respectively. No oil was visible on the membrane surface after cleaning. Average permeate flux versus average transmembrane pressure for the 30%-1750 rpm clean water flux experiment is presented in Figure (4). The resistance of the membrane was determined to be $2.42 \times 10^{12} \text{ m}^{-1}$ after cleaning.

Table (2)-Characteristics Of Ceramic Membrane.

Manufacturer	TRUMEM
Lot number	CRM-011M-TA
Chemical composition	TiO ₂ /Al ₂ O ₃
Mean pore size	0.11 μm
Maximum pore size	0.70 μm
Total membrane area	492 cm ² (0.53 ft ²)
Maximum operating temperature	> 70 °C (> 158 °F)
Maximum operating pressure	> 150 psi
Thickness	240 μm
Inner radius	2.48 cm (0.98 in.)
Outer radius	9.21 cm (3.63 in.)
Radius of gyration	6.75 cm (2.65 in.)

Figure (2)-Permeate Flux Versus Time For The 30%-1750 Rpm Experiment.

Figure (3)-Average Permeate Flux Versus Average Transmembrane Pressure For The 30%-1750 Rpm Experiment.

Figure (4)- Average Permeate Flux Versus Average Transmembrane Pressure For The 30%-1750 Rpm Clean Water Flux Experiment.

7.0 CONCLUSIONS

The treatment of a 30% synthetic oil wastewater was studied using the *SpinTek* centrifugal membrane separation system. The experiment was conducted at a membrane rotational speed of 1750 rpm and an applied pressure range of 25 to 70 psig to obtain permeate flux data. A mathematical model was used to correct for the average permeate back pressure due to centrifugal force.

8.0 WORK PLANNED FOR NEXT QUARTER

The following work will be conducted during the second quarter of '98: 1) experiments at 30% synthetic oil will be conducted at 1450 and 1150 rpm; 2) a further investigation of mathematical models used to predict permeate flux behavior in ultrafiltration systems will be performed; and 3) a summary of membrane resistance throughout the course of all synthetic oily wastewater experiments will be presented.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

The primary technical difficulty during the first quarter was the failure of the mechanical seals on the *SpinTek* feed pump. Due to the leaking seals, it was not possible to maintain a constant applied pressure in the membrane vessel. New seals have been ordered from the manufacturer for the *Grundfos* CRN2-40 pump and will be replaced upon arrival.

ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

Report for Period
ending March 31, 1998

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Federal Energy Technology Center
Morgantown, West Virginia

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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. 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 carbonaceous materials 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 been demonstrated. Removal efficiencies above 90% have been observed for the reductive removal of Cd, Pb, Cu and Ni. Removal of U via electrolytic precipitation was 99% effective. The removal of Sr utilized electrosorption and a removal efficiency of 68.0% was obtained using a coating of MnO_2 .

A parametric study of removal efficiency versus cell variables of current, pH and flow rate was completed. Flow rate had the most significant effect on the removal of lead. The method worked well over the pH range of 3.5 to 7.0. At a pH below 3.5, the oxidation of the plated lead by the acid in solution becomes significant, thus decreasing the efficiency of the electrolytic cell. The scaled-up remediation cell was put to use treating 32.4 liters of a 100 ppm lead solution over a period of 54 hours. Removal efficiencies remained at 98% or greater for the study.

The continuous removal of lead was demonstrated over a 72 hour period. The removal of lead over this period was continually greater than 90%. This corresponds to an effluent concentration of less than 10 ppm for an inlet solution feed of 100 ppm.

A scaled-up version of the prototype was constructed and tested to handle even greater flow rates of contaminated wastes. After several modifications, a removal efficiency of 99% was achieved for lead. A "real" sample obtained from the EPA's cleanup process at Fort Benjamin Harrison was treated. 95% removal of lead from this sample was achieved for a single pass through the electrolytic cell. The final objective is to transfer this technology for "on-site" use in industrial applications.

TABLE of CONTENTS

A. <u>Prefatory Material</u>	
Cover	i
Disclaimer	ii
Abstract	iii
Table of Contents	iv
List of Tables	v
List of Figures	vi
Executive Summary	viii
 B. <u>Body of Report</u>	
Introduction	1
Purpose	1
Background	1
Experimental Methodology	3
Carbon Samples	4
Work Performed	6
Analytical Methods	6
Anodic Stripping Voltammetry	6
Polarography	6
Atomic Absorption	7
Experimental	7
Reagents	7
Surface Area Measurements	7
7	
Construction of Small-Scale Remediation Cell	8
Evaluation Of Carbonaceous Material	8
Construction of the Scaled-Up Remediation Cell	9
Work Performed This Quarter	12
Experimental	12
Results and Discussion	13
Industrial Application	15
Radionuclides	16
Prototype Remediation Cell	17
This Quarter's Work	21
Conclusion	22
 C. <u>Appendix</u>	

References

50

LIST of TABLES

Table I	Standard Reduction Potentials of the Metals	44
Table II	Properties of Carbon Materials (Surface Areas)	45
Table III	Removal Efficiencies for Cadmium and Lead	46
Table IV	Immediate Industrial Application (Nickel Removal)	47
Table V	Doe Application (Strontium Removal)	48
Table VI	Project Completion	49

LIST of FIGURES

Figure 1	Schematic of Electrochemical Remediation Cell	25
Figure 2	Schematic of Scaled-Up 3-inch Remediation Cell	26
Figure 3	Schematic of 1.5-inch Galvanic Remediation Cell	27
Figure 4	Long-Term Removal of Lead using Electroplating	28
Figure 5	Long-Term Removal of Lead using Electrosorption	29
Figure 6	Long-Term Removal of Uranium	30
Figure 7	Effect of Plating Current on Removal Efficiency	31
Figure 8	Effect of pH on Removal Efficiency	32
Figure 9	Effect of Flow Rate on Removal Efficiency	33
Figure 10	Long-Term Removal of Lead Using Scaled-Up Cell	34
Figure 11	Treatment of a Mixed-Metal (Cu-Pb) Solution using Small-Scale Remediation Cell	35
Figure 12	Treatment of a Mixed-Metal (Pb-Ni) Solution using Small-Scale Remediation Cell	36
Figure 13	Affect of pH on the Treatment of a Mixed-Metal (Pb-Ni) Solution using Small-Scale Remediation Cell	37
Figure 14	Comparison of AN-210 Regular and “Oxidized” Carbon Fibers for the Removal of Uranium.	38
Figure 15	Effect of Applied Cell Potential on the Removal of Uranium Using Oxidized Carbon Fibers.	39
Figure 16	Effect of Uranium Feed Concentration on Removal.	40
Figure 17	Schematic of Scaled-Up 1.5-Inch Remediation Cell -Replacing Pt Wire with Conductive Carbon (Graphite) Rods.	41
Figure 18	Schematic of Scaled-Up 1.5-Inch Reme diation Cell	

	with Multiple Cathode Compartments.	42
Figure 19	Removal of Uranium by Electrosorption from a 1ppm solution.	43

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 $1.025 \text{ g}_{\text{Pb}}/\text{g}_{\text{carbon fibers}}$ was 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 ($7.1 \times 10^{-4} \text{ g}_{\text{Pb}}/\text{g}_{\text{carbon fibers}}$ 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 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 68.0%.

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 $0.15 \text{ g}_{\text{uranium}}/\text{g}_{\text{carbon}}$.

A scaled-up version of the prototype was constructed and tested to handle even greater flow rates of contaminated wastes. After several modifications, a removal efficiency of 99% was achieved for lead. A "real" sample obtained from the EPA's cleanup process at Fort Benjamin Harrison was treated. 95% removal of lead was achieved for a single pass through the electrolytic cell.

A parametric study of removal efficiency versus cell variables of current, pH and flow rate was completed. Flow rate had the most significant effect on the removal of lead. The method worked well over the pH range of 3.5 to 7.0. At a pH below 3.5, the oxidation of the plated lead by the acid in solution becomes significant, thus decreasing the efficiency of the electrolytic cell. The scaled-up remediation cell was put to use treating 32.4 liters of a 100 ppm lead solution over a period of 54 hours. Removal efficiencies remained at 98% or greater for the study.

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 adsorption and/or electrochemical reduction of the metal ions. In this procedure, a conductive surface acts as an 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 choose 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 FETC 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 small-scale 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 (15). 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 ($0.09 \text{ m}^2/\text{gram}$). 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). 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 (17)

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 μm . 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 (18-19). 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 or chemical methods were employed. A potential of +1.0 V was applied to the carbon surface for 10 minutes to remove contaminants and produce oxidized sites on the carbon surface. This was followed by applying a potential of -1.0 V for 10 minutes to condition the surface prior to use.

WORK PERFORMED

ANALYTICAL METHODS:

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 Perkin-Elmer "Analytical Methods of Atomic Absorption Spectrophotometry" Cookbook (20). All standards and samples were matrix-matched prior to analysis.

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 $\text{Hg}(\text{NO}_3)_2$ 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 Small-Scale Remediation Cell:

The small-scale 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 KNO₃ 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).

Construction of the Scaled-Up Remediation Cell:

Construction of the 3-inch prototype remediation cell has been completed. A schematic of the apparatus is shown in Figure 2. 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 was established in the same manner used in the smaller cell. The prototype has been assembled and parametric studies have begun. Several problems were encountered with this model (see Results and Discussion).

A redesigned version of the remediation cell (Figure 3) was designed and constructed to compensate for the problems associated with the above cell. This new galvanic cell utilizes a two electrode system. The anode reaction was separate from the cathode reaction using a porous ceramic cylinder (0.2 μm pores). The inner chamber contained the carbonaceous material (97.5 grams, WVU foam for this study) where the removal of metal ions takes place. The cathode material can be varied up to 8 inches in length. Upon passing through the cathodic chamber, the treated effluent was directed to the inlet of the anode chamber. No decrease in removal efficiency was noted and the need for the anolyte solution was eliminated. The electrode system was enclosed in a Plexiglas® tube. A solution flow rate of 10.0 mL/min was used for the sample and a flow rate of 60 mL/min was used for the anolyte solution. The pH of the lab prepared solutions was adjusted using nitric acid prior to testing.

Initial removal efficiencies for the scaled-up remediation cell were lower than expected. It was believed that the surface area of the platinum wire used as the anode was insufficient to carry the necessary current. The outer (anode) chamber of the electrolytic cell was filled with the same mass of carbonaceous material (97.5 grams, WVU foam for this study) to ensure an anode surface area equivalent to that of the cathode. The use of the carbonaceous anode boosted

charge transfer and thus removal efficiencies. Removal efficiencies above 90% were easily obtained for lead with this setup.

The above setup was used to perform a study of several parametric variables. These included plating current, solution pH and solution flow rate. Samples containing 100 ppm lead were passed through the cell as each parameter was varied. The concentration of lead in the effluent was measured and the effect of each parameter determined.

The presence of excess cations (i.e. Na^+ and K^+) in the solution from added electrolyte was examined to determine if they affect removal efficiencies. These spectator ions are present at concentrations up to 1000X greater than the target ion (i.e. Pb^{2+}). Successive experiments were carried out with increasing electrolyte concentrations (0.01, 0.05, 0.10 and 0.50 M NaNO_3 and KNO_3). The removal of lead ions from these samples was monitored, as well as any changes in solution conductivity.

Solutions containing 50 ppm copper and 50 ppm lead were prepared in 0.05M potassium nitrate and 0.02M potassium chloride electrolyte solution. The pH of these solutions was 3.5 and was not adjusted prior to use.

Carbon fibers (Oak Ridge National Laboratories) were prepared as previously described and placed into the small-scale remediation cell. The mixed-metal (Cu-Pb) solution was passed through the cell (0.87 mL/min) and the desired potential (-0.50 V, -0.80 V or -1.00 V) was applied. The effluent was collected at predetermined time intervals (usually 30 minutes) and the concentration of the two metal ions was determined using atomic absorption spectroscopy.

Solutions containing 50 ppm lead and 50 ppm nickel were prepared in 0.05M potassium nitrate and 0.02M potassium chloride electrolyte solution. The pH of this solution was 5.1.

The mixed-metal (Pb-Ni) solution was passed through the remediation cell. Three different potentials (-0.50 V, -0.80 V and -1.00 V) were applied and the effluent collected and analyzed as previously discussed. Following this study, the pH was adjusted to 3.5 using nitric acid and metal ion removal was re-examined at -0.80 V.

The carbon fibers were cleaned prior to each study by imposing a positive potential (+1.00 V) to the cell while the blank electrolyte solution was passed through it. This insured the removal of any metal that had been previously deposited onto the carbon surface. This cleaning was performed prior to each testing.

The long-term application of the 1.5-inch remediation cell was tested over a period of 54 hours using a 100 ppm lead solution. 100 mL aliquot samples were collected at selected time intervals and the concentration of the lead ions was measured. The total volume treated was 33 liters of 100 ppm lead solution over a 54 hour time period.

The sample obtained from the Fort Benjamin Harrison Site was pumped through the scaled-up remediation cell without any prior treatment. The Ft. Ben Harrison sample contained 279 ppm Pb and had a pH of 4.7. A constant plating current of 60 mA was employed to remove the lead.

Two varieties of AN-201 carbon fibers obtained from Applied Sciences, Inc. were tested as the cathode material. The first fibers were as-grown and are of the "regular" composition and surface states. The second fibers were surface oxidized during the production stage and shall hence be referred to as "oxidized" fibers. Both types of fibers were washed with nitric acid and prepared as previously discussed. An equal mass (0.40 grams) of each fiber was utilized in the small electrochemical cell and a solution containing 100 ppm uranium was passed through the cell at a flow rate of 0.70 mL/min with an applied cell potential of -1.00 V. The concentration of uranium in the effluent was measured at one-half hour intervals and compared to the concentration of uranium at the inlet. The removal efficiencies of the two types of fibers were compared.

The performance of the AN-201 oxidized fibers in the above study was further examined. The cell parameter first investigated was applied cell potential. A solution containing 100 ppm uranium was passed through the cell at -0.20 V, -0.30 V, -0.50 V and -1.00 V. The uranium concentration in the effluent was measured and the effect of the applied cell potential determined.

Next, the effect of uranium ion concentration at the cell inlet was examined. Three different concentration were used: 5 ppm, 20 ppm and 100 ppm. The removal efficiencies were obtained for each of these concentrations at -1.00 V and a flow rate of 0.70 mL/min.

The mass of uranium removed during the 4 hour electrochemical treatment of a 100 ppm uranium solution (168 mL) was compared to the mass of uranium recovered in the 1 hour stripping step (42 mL). The masses were compared in order to determine the ability to regenerate the carbon surface for further treatment.

Several new cell geometries and configurations of a yet larger cell were designed and the components have been obtained or fabricated. 200 grams of "oxidized" carbon fibers have been obtained from Applied Sciences, Inc. and are being prepared for utilization. Two new cell geometries will be constructed in the next quarter and their performance will be assessed.

A highly concentrated solution of uranium, 1000 ppm, was treated using AN-201 oxidized fibers in the small remediation cell. This concentration corresponds to 1 mg of uranium per milliliter of solution. Removal was carried performed over a 6 hour period. The treated solution (252 ml) contained a total of 252 mg of uranium. The concentration of uranium in the resulting effluent was monitored and removal efficiencies calculated.

A carbon nanofiber sample from ORNL (#UK-25-2) was also examined for its ability to remove uranium. This sample was able to remove over 99% of lead ions from an aqueous sample in previous studies due to its high electrical conductivity. This is believed to be due to the highly graphitic properties of this sample. The uranium in the effluent was measured and compared to the removal demonstrated by the above sample (AN-201, oxidized).

A second batch of "oxidized" fibers was obtained from Applied Sciences Inc. These fibers were post oxidized and should work well for the removal of uranium in the large scale remediation cell. A small sample (0.242 grams) of these fibers were tested in the small scale remediation cell and their ability to remove uranium from a 100 ppm U solution was examined. The surface properties of these fibers should be very suitable for the removal of uranium.

A larger scale (1.5 inch i.d. by 12 inch length) prototype has been designed and constructed with help from our machine shop (see Figure 17). This design allows for easy replacement of the cathode material via switching of the porous ceramic tube containing the various cathode materials to be tested.

WORK PERFORMED THIS QUARTER

EXPERIMENTAL

It was found from previous studies that the adsorbed uranium could be stripped easily from the carbon fiber bed by simply reversing the potential to +1.0V and pumping a 0.1N KNO₃ solution through the cell at a flow rate of 0.7 ml/min. A yellow-colored precipitate was observed in the solution. Stripping efficiency was further examined by filtration of the solution as well as by direct measurement of uranium concentration in the stripped solution as done before. The precipitate was either dissolved with a tiny drop (0.03 ml; negligible change to the sample volume) of concentrated nitric acid for the measurement of uranium concentration or was filtered through a 0.45- μ m filter paper, washed with water and air-dried for structural analysis.

The concentration of surface functional groups on ASI carbon fibers was determined using wet chemical methods. Selective neutralization by

equilibration with a series of bases with increasing strength (i.e., sodium bicarbonate, sodium carbonate and sodium hydroxide) allows differentiation of various types of surface groups on carbon fibers. Sodium bicarbonate neutralizes carboxylic groups; sodium carbonate neutralizes carboxylic groups and also allows lactone groups to open and form carboxylic groups which are neutralized; sodium hydroxide neutralizes carboxylic, lactone, and phenolic groups. The three bases were reacted with carbon fiber samples for 24 hours. The supernatant from the base-carbon mixture was titrated with hydrochloric acid. The volume of the acid solution was compared with that used for blank base solution to obtain the equivalents of carboxylic, lactone and phenolic groups. The results will be related to the efficiency of uranium removal by electrosorption on the carbon fibers. This is one of the approaches to clarify chemical reaction of uranium during electrosorption and to explain the great difference between the "as-grown" and "oxidized" ASI carbon fibers.

Previous study of electrosorption on ASI carbon fibers for the removal of uranium has been focused on waste waters containing uranium in the range of 20 to 100 ppm. An attempt was made recently to apply this technology to the removal of uranium from drinking water. As a naturally occurring radioactive element, uranium exists in both ground water and surface water. The concentration of uranium in seawater is usually less than 3 ppb. It has been found, however, that many drinking water supplies contain 3-500 ppb or even higher uranium. There has been increased interest in uranium removal from drinking water. Although the permitted level of uranium in potable water has not been established, EPA expects to propose regulations for uranium by December 2000.

In order to comply with the treatment of waters containing ppb level uranium, adjustment to the uranium analysis was necessary. For the previous tests, polarographic data have been obtained using a static mercury drop electrode in conjunction with a potentiostat. A linear potential scan was applied in the range of 0.0 to -0.6V. This method is sufficiently accurate for samples containing 10-200 ppm uranium but not for 1 ppm or less. By modifying the technique and using the differential pulse scan mode, the detection limit has been markedly reduced to around 5 ppb. A voltammetric analyzer (Mode EC/225, IBM) was used as the scanning potential source and an X-Y recorder (Model 7035B, HP) as the current recorder.

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. 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 sufficiently negative to reduce the metal ions, electroplating removes 89% at 0.60 V, 91% at 0.80 V and nearly all (99%) at -1.00 V.

The removal of lead was conducted 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 of time demonstrates a removal capacity of $1.025 \text{ g}_{\text{Pb}}/\text{g}_{\text{carbon fibers}}$, 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 $1.9 \times 10^{-4} \text{ g}_{\text{Pb}}/\text{g}_{\text{carbon fibers}}$ is obtained. At 57 hours this capacity increases to 7.1×10^{-4}

$\text{gPb/g}_{\text{carbon fibers}}$. 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 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 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 also 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 for 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 isotopes. 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 was 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 assembled and tested.

No removal of strontium was observed using the untreated WVU foam. This was expected due to the relatively low surface area ($0.5 \text{ m}^2/\text{g}$) 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. A coating of MnO_2 on the carbon surface improved the removal efficiency in a pH 11.0 solution to 68.0%.

The removal of uranium was examined using ASI carbon nanofibers. No removal was observed for adsorption alone (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 9.

Prototype Remediation Cell:

Several problems became apparent with the 3-inch diameter prototype electrolytic cell. Due to the increased distance between the electrodes and the large amount of carbon material used, a very large potential drop was experienced. This large potential drop was sufficient to prohibit the potential on the carbon material from becoming adequately negative to reduce the metal ions. Also the diameter of the carbon bed was increased but the depth of the bed was not. Even though more carbon cathode was used, the residence time in the cathode material was not increased. An improvement would be to increase the diameter less while increasing the depth of the bed. Also it was believed that the surface area of the auxiliary electrode was insufficient to handle the current necessary to reduce the metal ions. Therefore, a redesigned electrolytic cell (Figure 3) was developed to address these problems. The new cell utilizes a two electrode system. The cell employed the carbon material as a cathode to remove the metal ions from solution. The material was also used as the anode and was isolated from the cathode using the porous ceramic tube. A flow rate of 10 mL/min was used in the initial tests with this new cell design. Removal efficiencies for lead of lab generated samples was 99%. This is comparable to those obtained using the small remediation cell with a 10-fold increase in throughput.

A sample was provide by Dr. Szlag of the EPA from the lead solution generated by the treatment of contaminated soil at the Fort Benjamin Harrison Site. The concentration of lead in the sample as received was determined to be 279 ppm. Following a single pass through the scaled-up version of the electrolytic cell and with no sample pretreatment, the concentration of lead was lowered to 14 ppm. This corresponds to a 95% removal of lead from the waste sample.

Examination of several key experimental parameters was performed. The effect of pH, flow rate and galvanic current was investigated. Figure 6 shows the dependence of the removal efficiency for lead on the current used to plate the metal ions from solution. At 30 mA and above, 99% of the lead ions are removed.

Another parameter that was addressed was solution pH. Waste streams generated by various processes can have varying pH values. In order for this treatment method to be useful, it must be applicable over a wide range of pH's. This will eliminate the need for the addition of chemicals to adjust the pH. In Figure 7 the results of this study are shown. The low removal at pH=2.6 is

caused by the chemical oxidation of the plated lead by the acid solution. This reaction occurs simultaneously with the plating reaction. Therefore, minimal adjustment of the pH may be necessary for certain highly acidic waste streams. Lead hydroxide $[\text{Pb}(\text{OH})_2 (\text{s})]$ is precipitated at a pH of 8.2 and above for the 100 ppm lead solution. Therefore, the lead is not in the ionic state in solution and an alternative removal method is needed.

Results for the above parametric studies indicate percentage removal of lead based on the effluent concentration at 2 hours. For each parametric study, the effluent concentration was measured every 15 minutes over the three hour period of the study. Similar trends were clearly apparent throughout the experiments.

The lead ions must spend a sufficient amount of time (residence time) in the carbon bed in order to be reduced. Residence time is a function of flow rate and the void volume of the packed carbon bed. By increasing the flow rate, the ions spend less time in the carbon bed. It is necessary to determine the flow rate at which the maximum amount of solution can be treated without sacrificing removal efficiency. Figure 8 demonstrates the expected decrease in removal efficiency with increased flow rate. In order to remove 99% of the lead ions from the waste sample, a flow rate of $0.10 \text{ mL/min/g}_{\text{carbon foam}}$ is needed. If a removal efficiency of only 80% is required, the flow rate can be increased to $\sim 0.20 \text{ mL/min/g}_{\text{carbon foam}}$.

The concentration of added electrolyte had a small, but positive effect on the removal of lead ions. The electrolyte ions (Na^+ and K^+) did not compete with the lead ions for the electrode surface. The presence of these ions reduced solution resistance and even improved removal efficiencies for lead. The conductivity of the solutions containing 0.01M, 0.05M and 0.10M sodium nitrate, increased from 1.31 S, to 4.76 S and 8.95 S, respectively. This increase in conductivity resulted in the following lead removal efficiencies: 94.6%(0.01M), 98.6%(0.05M) and 99.6%(0.10M). These ions improved the electrical conductivity of the solution leading to decreased iR drop and lower parasitic power losses, which in turn was believed to improve the electron transfer rates.

The long-term removal of lead using the scaled-up 1.5-inch prototype was superb. The improvements to the cell design resulted in the ability to remove lead ions at a 98% efficiency for a period of 54 hours (see Figure 10). A total solution volume of 32.4 liters was treated over this time period.

The removal of metal ions from aqueous mixed-metal solutions was studied. Two metal ion systems were examined: Cu-Pb and Pb-Ni. The desired objective was to examine the experimental parameters that influence the simultaneous removal and separation of the two metal ions from solution.

The first solution contained a mixture of copper and lead at a concentration of both metal ions of approximately 50 ppm. Samples were treated using the small-scale remediation cell and the graphitic carbon nanofibers obtained from Oak Ridge National Laboratories. Three different cell potentials were imposed: -0.50 V, -0.80V and -1.00V (See Figure 11). Separation improved from -0.50 V (inset A) to -1.00 V (inset C), although the separation is not apparent at -0.80 V (inset B) until after 3 hours. Good separation was observed at -1.00 V. The effluent stream after 4 hours contained 46.0 ppm Pb and 1.8 ppm Cu. This represents only a 3.8 % contamination of lead by copper in the effluent. The metal accumulated on the carbon surface consists of 98.2% of removed copper contaminated by only 6.3% lead. These contamination percentages may be further decreased by optimization of cell parameters, such as cell potential, pH, flow rate, carbon material, etc. This study does demonstrate a clear proof of concept for the treatment of solutions contaminated by mixed-metal ions.

The next metal system examined was Pb-Ni. The same cell potentials were imposed (Figure 12). There is a definite difference in the deposition of the two metal ions, even though they have similar reduction potentials (see Table 1). This difference was evident in the initial studies using nickel solutions and may make it possible to separate lead and nickel ions from solution. The improved removal of nickel from -0.50 V (inset A) and -1.00 V (inset C) may be caused by two separate factors: 1) increasingly negative potential forcing the reduction of nickel ions, and 2) co-deposition of lead and nickel ions (or deposition of Ni onto deposited Pb already on the cathode surface).

Adjustment of the pH can be used to affect metal ion removal. This was demonstrated at a cell potential of -0.80 V. Initial studies carried out at the natural (unadjusted) solution pH of 5.1 for the lead-nickel solution (inset A, Figure 13) demonstrated some separation of lead and nickel, although the deposited lead was contaminated with nickel. By changing the pH to 3.1, it was possible to remove lead without removing nickel (inset B). Even though the removal efficiency of lead is decreased from that seen at a pH of 5.3, no nickel is removed at these conditions. Subsequent cycling of the effluent through the cell should decrease the concentration of lead in solution down to any desired level.

Judicial adjustment of the experimental parameters will allow control of the removal efficiencies in such a way to successfully separate and remove multiple metal ions from solution.

The performance of the oxidized AN-201 carbon fibers was far superior to that of the regular fibers (Figure 14). The removal of uranium using the "oxidized" fibers immediately resulted in removal of over 95% of the uranium from the solution being treated. The regular fibers obtained a maximum removal efficiency of only 20%. This difference is believed to be caused by the

modification of the carbon fiber surface during oxidation. Changes in the properties of the carbon fibers significantly influence the removal of uranium from the solution. Careful control of the carbon surface can be utilized to improve metal ion removal. The surface conditions necessary are dependent upon the metal ion and the removal mechanism. It is believed that the oxidation state of uranium changes during electrosorption and such a change may be enhanced by the presence of polar oxygen-containing groups on the carbon surface.

Removal of uranium was examined using the oxidized fibers at various applied potentials (Figure 15). The plot exhibits two distinctly different types of removal behavior. The first, demonstrated at low potentials (-0.2 and -0.3 V) has a marked drop-off in removal, typically after 30 minutes. This drop-off in removal is believed to be due to the uranium being solely removed by electrosorption. Once the capacity of the carbon fibers is reached (~30 minutes), the fibers can no longer remove uranium efficiently and the removal decreases. At more negative potentials (-0.50 and -1.00 V), it is believed that the potential is sufficiently negative to produce a secondary reaction (i.e. the formation of a uranium complex or precipitate) on the carbon surface. Once this secondary reaction takes place, more uranium can be removed from the solution. This is supported by the fact that the removal efficiency remains high until clogging of the carbon bed with the precipitate occurs.

The removal of uranium was investigated at three different initial feed concentrations: 5, 20 and 100 ppm. The concentration of uranium in the effluent was consistently reduced to below 2 ppm (See Figure 16). The feed concentration may remain at this level due to equilibrium factors associated with the reaction product formed on the carbon fiber cathode surface. Further studies will determine if even more concentrated solutions (i.e. 1000 ppm) can be remediated in a comparable fashion.

Recovery of the uranium from the solution using oxidized carbon fibers was studied. The mass of uranium removed from the feed solution was compared to the mass of uranium liberated in the stripping/recovery step. Over the 4 hour period of this study, a 100 ppm uranium solution was treated and an average removal efficiency of 80% was observed. This corresponds to 13.44 mg of uranium being removed from 168 mL of solution. The solution produced during the stripping step (42 mL) contained 13.61 mg of uranium. The uranium is removed from the feed solution and concentrated by a factor of 4. This slightly larger mass (0.17 mg) of recovered uranium is most likely due to uranium ions that were present in the system (i.e. dead volume) (This would be equivalent to contamination by only 1.7 mL of the feed solution). Therefore, good agreement was shown between the mass of uranium removed and recovered from the feed solution.

Recovery of uranium using the regular AN-210 fibers, although demonstrating only a 20% removal, also presented good correlation between the mass of uranium removed (0.405 mg) and that recovered (0.411).

Two new cell designs have been developed. These designs address scale-up to treat large volumes of waste at even greater flow rates while maintaining low capital costs. The first design (Figure 17) maintains the size of the larger remediation cell currently being utilized, but replaces the expensive platinum wire used for electrical contact with electrically conductive graphite rods. This realizes a major decrease in capital costs. The second design (Figure 18) provides for increased solution throughput. The feed stream is split to several parallel channels in a “shell-and-tube” arrangement within the electrochemical cell. Each channel can treat the same volume of contaminated waste stream. Therefore, the volume of waste that the cell can effectively treat should be equal to the volume treated by each individual channel multiplied by the total number of channels.

The treatment of the highly concentrated solution of uranium, 1000 ppm, using the small remediation cell was successful. Removal efficiencies for uranium of 56.9% to 62.0% were maintained over 6 hours of treatment. The treated solution (252 ml) contained 252 mg of uranium. The mass of uranium removed was estimated to be approximately 149 mg. This corresponds to a value of $0.368 \text{ g}_{\text{uranium}} / \text{g}_{\text{c-fiber}}$. Although the carbon fibers have not yet reached capacity, this value is far greater than that expected using a typical ion exchange resin ($0.05 \text{ g}_{\text{uranium}} / \text{g}_{\text{resin}}$).

A carbon nanofiber sample from ORNL (#UK-25-2) was also examined for its ability to remove uranium. Although this sample was able to remove over 99% of lead ions from an aqueous sample, only 10% removal of uranium was accomplished. This is believed to be due to the highly graphitic properties of this sample. The absence of surface oxidation sites greatly hinders the removal of uranium on such samples.

The batch of “oxidized” fibers (PR-18) obtained from Applied Sciences Inc. worked well for the removal of uranium. A small sample (0.242 grams) of these fibers were tested in the small scale remediation cell and efficiencies of 99% were realized for uranium. The surface properties of these fibers of very suitable for uranium removal. Comparison to the non-oxidized counterpart is planned.

This Quarter's Work

The adsorbed uranium can be stripped from the ASI carbon fiber electrode by reversing the charge at +1.0V and passing a with 0.1N KNO_3

solution through the cell. Yellow-colored precipitates were observed from the stripping solution. These precipitates are readily dissolved by a drop of 1N HCl. An electrosorption test was run at -0.3V. The total uranium removed in 3 hours was 2.71 mg. The stripping was run after this test. The concentration of uranium in the three 30-minute intervals were 124.8, 6.1 and 2.4 ppm respectively. This corresponds to a total uranium recovery of 2.62, 0.13, and 0.05 mg. Therefore, over 96% of the adsorbed uranium was stripped and recovered during the first 30 minutes.

The precipitates were also collected by filtration through a 0.45 μm filter membrane. The concentration of uranium in the filtrate was less than 0.4 ppm. Thus the stripped uranium is very easy to separate and recovery from aqueous solution in the neutral pH range. The solid form of the recovered uranium eliminates the need to treat a secondary waste.

The results obtained so far from the surface functional group analysis by acid-base titration are not very consistent. This was caused by the trace amount the surface groups and limited amount of samples of carbon (0.3-0.4 g). More tests based on larger carbon sample (up to 5 g) will be run. Meanwhile, instrumental analysis using FTIR, XPS, etc. will be tried to complement the information from chemical analysis.

A few tests using a feed solution of 1 ppm uranium were made at two different potentials. The results are show in Figure 19. At -0.5V, up to 63% removal of uranium was reached from a single pass of the solution through the electrochemical cell in which ASI carbon fiber (oxidized) was packed as the cathode. When the applied potential was lowered to -1.0V, the removal efficiency was greatly improved. In two and half hours the uranium concentration was reduced to less than 8 ppb and in three hours the uranium was essentially 0 ppb (below the detectable limit). Long-term test results reported in the last quarter already showed that the ASI carbon fiber has extremely high electrosorption capacity of uranium. Using the value of 0.368g $\text{uranium/g}_{\text{c-fiber}}$ (which is in fact less than its capacity), 1 gram of ASI carbon fiber can treat almost 100 gallons (368 L) of 1 ppm uranium solution. With its high removal efficiency, great capacity and convenient separation of adsorbed uranium, the electrosorption technology with the use of ASI carbon fibers may become a effective approach for uranium removal from potable water.

CONCLUSION

All proposed objectives have been met (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 performance of the commercially available RVC as a cathode was satisfactory. Improved removal efficiencies were obtained with the novel carbon materials utilized in this study. Loose carbon nanofibers with a relatively large surface area ($200 \text{ m}^2/\text{g}$) 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-plating 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 68.0%.

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 $0.15 \text{ g}_{\text{uranium}}/\text{g}_{\text{carbon}}$. The use of the 1.5-inch remediation cell and larger quantities of carbon will allow for the treatment of larger volumes of low level radioactive wastes.

The utility of this technique has been demonstrated on actual samples obtained from the cleanup of lead from soil at Fort Benjamin Harrison. The aqueous waste was generated by washing the lead from the contaminated soil with acetic acid. The decontaminated soil was returned to the site as clean fill. The aqueous waste generated was contaminated with lead (279 ppm). This

aqueous waste was purified using the electrolytic cell to remove 95% of the lead.

Mixed-metal waste streams have been treated with successful separation for two metal system. Removal of copper in the presence of lead and removal of lead in the presence of nickel has been achieved. This demonstrates the ability of this system to selectively remove and recover individual metal ions from aqueous samples.

The experimental variables under which removal is carried out can widely affect the performance of the electrolytic cell. However, when the optimal operating conditions have been determined, maximum removal is achieved. By paying careful attention to the experimental parameters, this process can be modified to obtain maximum removal efficiencies and throughput while minimizing energy and chemical demand.

The electrosorption of uranium from a 1 ppm solution produced essentially complete removal of uranium from the water. It is likely that the electrosorption technology with the use of ASI carbon fiber may become an effective approach to uranium removal from potable water.

Figure 1. Schematic of Electrochemical Remediation Cell.

Figure 2. Schematic of Scaled-Up 3-inch Remediation Cell.
 (1-Flowmeter; 2-Cell; 3-Manometer; 4-Pump; 5- Auxiliary Electrode;
 6-Pt Contact to Working Electrode; 7-Reference Electrode.)

Figure 3. Schematic of 1.5-inch Galvanic Remediation Cell.

Electroplating

Capacity @ 72 hours > 1.025 grams Pb/ gram of carbon
 (**NOT at Saturation**)

Flow Rate = 3.1 mL/min/(gram carbon)

Figure 4. Long-Term (72 hr) Removal of Lead Using Carbon Nanofibers. ($E_{\text{CELL}} = -1.0 \text{ V}$)

Figure 5. Long-Term (102 hr) Removal of Lead via Electrosorption.
(Conditions: same, $E_{\text{CELL}} = -0.40 \text{ V}$)

Electrolytic Removal of Uranium

Figure 6. Long-Term 48 hr) Removal of Uranium.
(Conditions: same, $E_{\text{CELL}} = -1.00 \text{ V}$)

Figure 7. Effect of Plating Current on Removal Efficiency.
(1.5-Inch scaled-up remediation cell. Conditions: pH=5.3, 0.10 mL/min/g_{carbon})

Figure 8. Effect of pH on Removal Efficiency.
(Conditions: same as Figure 7; 30 mA, 0.10 mL/min/g_{carbon})

Figure 9. Effect of Flow Rate on Removal Efficiency.
(Conditions: same as Figure 7; 30 mA, pH=5.3)

Long-Term Removal of Lead

Figure 10. Long-Term Removal of Lead Using Scaled-Up Cell.
(Conditions: same as Figure 7; 30 mA, pH=5.3)

Figure 11: Treatment of a Mixed-Metal (Cu-Pb) Solution using Small-Scale Remediation Cell.

(Conditions: ORNL carbon fibers, 0.87 mL/min/g_{carbon}, Feed: 50 ppm Cu and 50 ppm Pb, pH=3.5)

Figure 12: Treatment of a Mixed-Metal (Pb-Ni) Solution using Small-Scale Remediation Cell.

(Conditions: Same as Figure 11, Feed: 50 ppm Cu and 50 ppm Pb, pH=5.1)

Figure 13: Affect of pH on the Treatment of a Mixed-Metal (Pb-Ni) Solution using Small-Scale Remediation Cell.
(Conditions: Same as Figure 12)

Figure 14: Comparison of AN-210 Regular and "Oxidized" Carbon Fibers for the Removal of Uranium.

(Conditions: ASI AN-201 carbon fibers, -1.00 V, 0.70 mL/min)

Figure 15: Effect of Applied Cell Potential on the Removal of Uranium Using Oxidized Carbon Fibers.

Conditions: ASI AN-201 “oxidized” carbon fibers, 0.70 mL/min)

Figure 16: Effect of Uranium Feed Concentration on Removal.
(Conditions: ASI AN-201 “oxidized” carbon fibers, -1.00 V, 0.70 mL/min)

**Figure 17: Schematic of Scaled-Up 1.5-Inch Remediation Cell.
-Replacing Pt Wire with Conductive Carbon (Graphite) Rods.**

Figure 18: Schematic of Scaled-Up 1.5-Inch Remediation Cell with Multiple Cathode Compartments.

Figure 19: Removal of uranium from a 1ppm solution by electrosorption

(Conditions: ASI oxidized carbon fibers, 0.70 mL/min)

TABLE I: STANDARD REDUCTION POTENTIALS OF THE METAL IONS OF INTEREST

Reduction Reaction	E, V (vs. Ag/AgCl)
ELECTROSORPTION	
$\text{Sr}^{+2} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Sr} (\text{s})$	-3.108
$\text{U}^{+2} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{U} (\text{s})$	-2.022
$2\text{H}_2\text{O} (\text{l}) + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^{-} (\text{aq})$	-1.050
ELECTROPLATING	
$\text{Cd}^{+2} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cd} (\text{s})$	-0.624
$\text{Ni}^{+2} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ni} (\text{s})$	-0.453
$\text{Pb}^{+2} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Pb} (\text{s})$	-0.348
$\text{Cu}^{+2} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$	+0.115

TABLE II: PROPERTIES of CARBON MATERIALS

Surface Areas

Material	Surface Area (m²/gram)	
	BET	Langmuir
Vapor Grown Carbon Fibers (ASl)		
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

<u>Cathode Material</u>		<u>Metal Removed</u>	
	<u>Cathode Potential, V</u>	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)

$$E^\circ = -1.050 \text{ V}$$

$$E^\circ = -0.453 \text{ V}$$

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

TABLE V: DOE APPLICATION
REMOVAL OF STRONTIUM VIA ELECTROSORPTION

$$E^{\circ} = -3.108\text{V}$$

$$E^{\circ} = -1.050 \text{ V}$$

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

<u>Task #</u>	<u>ID</u>	<u>Task Name</u>	<u>Duration</u>	<u>% Complete</u>
1	138	Task 4.2 Environmental Pollution Control Devices	52w	
2	139	Industrial Contacts	52w	100%
3	140	Define Industrial Needs	52w	100%
4	141	Test Removal Efficiencies Using Small Cell	52w	100%
5	142	Optimize Experimental Parameters	52w	100%
6	143	Study Affect of Interfering Ions	16w	100%
7	144	Design and Construct Large Prototype	12w	100%
8	145	Apply Large-Scale Prototype	24w	100%
9	146	Test Carbon Materials	52w	100%
10	147	Develop Recommendations	4w	100%
11	148	Quarterly Report #1	1w	100%
12	149	Quarterly Report #2	0.2w	100%
13	150	Quarterly Report #3	0.2w	100%
14	151	Quarterly Report #4	0.2w	100%
15	152	Final Report	4w	-
16	153			

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FOCUS AREA 5.0

Outreach

Small Business Technical Based Support

1997 FETC Task No. 5.1

Quarterly Technical Progress Report

Reporting Period:
January - March 1998

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

For:

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

By:

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April 1998

EXECUTIVE SUMMARY

During this reporting period, the new five year proposal was completed and submitted to DOE/FETC for approval. The focus of the first year of the new program is to demonstrate innovative remediation technologies in the field that were developed in the previous agreement. The Prefabricated Vertical Drains (PVDs) technology will be deployed on a larger scale at the RMI Extrusion Plant in Ashtabula, Ohio. In addition, the SpinTek Centrifugal Membrane Technology is planned for separating the fluids extracted from the PVDs to allow for recycling and permit reinjecting of the surfactant. This represents a unique scheme of events affording a great cost savings in the overall clean up effort. Discussions are ongoing for bringing the adsorbent particle membrane technology on line, developed by the 3M Corporation, for removing Technetium.

TABLE OF CONTENTS

<u>DESCRIPTION</u>	<u>PAGE NO.</u>
Executive Summary	ii
Disclaimer	iv
Introduction	1
Purpose	1
Background	1
Methodology	2
Work Performed This Period	2, 3
Conclusions/Work Planned for Next Period	3

DISCLAIMER

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INTRODUCTION

Subtask 5.1, “Small Business Technology Base Support” was initiated to address the technical problems or barriers to commercialization of innovative site remediation technologies. Through FETC, a very large percentage of the US DOE innovative remediation technologies being developed are 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.

PURPOSE

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

BACKGROUND

Over the past five years the WVU Cooperative Agreement has funded numerous projects that have resulted in defining at least four areas of core competencies at WVU that may be called upon to provide assistance to the small businesses that FETC 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 (PVDs)
- Separation processes using novel membranes and novel forms of carbon

METHODOLOGY

By attending the kickoff meetings and other periodic meetings of the small businesses funded by FETC, 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. For the long range research opportunities, the initiative at US DOE HQ level bringing together elements from DOE, DOD, NASA, Commerce and others to coordinate interagency site remediation capabilities and needs will be very helpful. Also, attendance at various meetings and conferences on site remediation provides insights into research needs.

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

WORK PERFORMED THIS PERIOD

During this quarter, the new five year program was completed and submitted to DOE/FETC for approval. The focus of the first years work is on a larger scale field demonstration (0.1 acres) of the Prefabricated Vertical Drain (PVD) Technology at the RMI Ashtabula, Ohio site. The work is a joint effort between DOE-Ashtabula, FETC-Morgantown, West Virginia University (WVU), North Carolina State University (NCSU), RMI Environmental Services (RMIES), The Institute of Gas Technology (IGT), SpinTek and Nilex Corporation. RMIES will provide the treatment scheme and train to treat the extracted fluids to standards allowing re-injection or release to the local sewage treatment plant. Nilex Corporation will be responsible for supplying the materials required and installing the PVDs. IGT will provide the expertise on selecting, mixing and injecting the various chemicals through the PVDs and will address QA/QC issues. The SpinTek Centrifugal Membrane Technology will be used to separate the surfactant from the surfactant/TCE/groundwater mixture so that it can be recycled and reinjected. A great cost savings will be realized by incorporating this technique into the treatment train. Discussions have been completed for bringing the 3-M Corporation Specialized Separation Membrane Technology on line for treating Technetium 99 (T^{99}). The 3M Corporation has developed, through FETC-Morgantown, an adsorbent particle membrane fabricated into small 10-inch cartridges capable of removing T^{99} . Conventional methods are planned for addressing the small quantities of Uranium that may be encountered.

WVU participated in several telephone conference calls with all of the team members listed above. These calls are scheduled regularly to keep everyone informed of the project status and to identify any key issues and/or concerns.

Additional proposals were submitted this quarter, as an amendment to the first increment of funding, for the new five-year program. These include the following:

<u>TASK</u>	<u>DESCRIPTION</u>	<u>PI/CONTRACTOR</u>
Subtask 1.5	Removal of Surfactants and Trichloroethylene (TCE) From Extracted Groundwater at the RMI Ashtabula, Ohio Site	William Green SpinTek Corporation
Subtask 3.1	Watershed Economics: An Overview Research Project	Dr. Jack A. Fuller College of Business and Economics, WVU

Funding for Subtask 3.1 will come from the National Center for Acquisition and Business Excellence (NCAB). This project is a research paper on watershed economics to be used as a tool for environmental management and was requested by Mr. Karl Stockle and Steve Meador of NCAB at FETC Morgantown.

Plans for the annual WVU Cooperative Agreement Program Review Conference were initiated. Technical data sheets for the new program were developed and work began on designing a proceedings document for the event. The conference was originally planned for April at FETC-Morgantown, but due to scheduling conflicts it has been pushed ahead to June 10, 1998. Final details and arrangements for this meeting will occur during the upcoming quarter.

CONCLUSIONS/WORK PLANNED FOR NEXT PERIOD

Beginning the large scale demonstration at the RMI Ashtabula, Ohio site will be the main focus of the work planned for next quarter. Streamlining participation by the 3M Corporation will also be an issue in addition to finalizing the plans for the Waste Water Treatment Facility. New invitations will be sent out for the Annual Program Review Conference and all arrangements for this meeting will be made. The old Agreement will come to a close June 30, 1998 and all associated business and administrative issues will be addressed. A final report for each project will be submitted and an overall summary for the entire 5-year program will be generated.