WVU Cooperative Agreement

Decontamination Systems, Information and Research Program

Deployment Support Leading to Implementation

Quarterly Technical Progress Report

Reporting Period:
July - September 1997

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For:

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

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EXECUTIVE SUMMARY

The following paragraphs summarize the progress of each research project funded under the WVU Cooperative Agreement during the third quarter of 1997 (July - September 1997). The projects are arranged according to their 1997 WVU task number.

WVU Focus Area 1.0: Subsurface Contaminants, Containment and Remediation

Task No. 1.1: Project discontinued.

Task No. 1.2: Development of Standard Test Protocols and Barrier Design Models for Desiccation Barriers (K. Amininan & S. Ameri):

A number of experiments were performed this period to evaluate the ability of the dried sand-packs to act as a barrier to liquids. Water infiltration tests were done with a constant head, dispersing 80 ml of water, and by adding water in small increments. Results indicate that when the water is spilled over the sand-pack, it has the tendency to channel through the sand-pack, significantly reducing the capacity of the dried zone to retain liquid contaminants. This appears to be largely influenced by particle size. As the particle size is reduced, the capillary forces spread the water and prevent/delay channels from forming. The measured permeability values were in agreement with those measured with air. The water retention capacity and capillary rise were largely influenced by time and showed no sensitivity to channeling. The water retention capacity tests suggest the sand-packs can retain more water than the expected.

Two sets of water infiltration and drying experiments were designed to evaluate the CAB's ability to prevent spills from spreading. Ten ml of water was injected every 20 minutes and 80 ml of water was added at one time. When injected slowly, results showed the drying process to be similar to the original drying process. The second set indicted the drying process follows a slowly declining drying with no break through. Results also suggested that air flow through the sand-pack can remove water infiltration. The air flow appeared to prevent any water channeling and thus should cause lateral distribution of the water.

The large tank that accommodates the sand bed and the necessary plumbing to simulate various well configurations was received. The monitoring equipment and the sensors are currently being installed. The experimental procedures for Phase II experiments are under further investigation and will be initiated upon installation of CATC and assembly of the monitoring system. Due to insufficient operating funds, the large scale experiments will not be done this year.

Task No. 1.3: Technical Support - Development of Standard Test Protocols and Barrier Design Models for In Situ Formed Barriers (B. Overbey & D. Locke, BDM Federal):

The Operating Permit Renewal Request for bench scale operations in the FETC B-17 building was submitted to the FETC Lab Safety Committee for approval on 8/14/97. A review of the revised NEPA documents prepared last year indicates that these documents are still applicable for the current work. The initial design and specifications for the CATC vessel were prepared. Construction of the CATC was initiated in early July, the vessel was received August 15, 1997, and on-site work was completed this quarter.

Process Dynamics Corp. (Pro-Dyn) of Morgantown, WV designed the instrumentation. The Capacitance measurement system provides information on the location and degree of saturation in the test bed with a resolution of 1 meter. Computer programs to control data access are being developed. The system planned will sample the volume of the tank in a specified manner part of the time, followed by random sampling. Initially data will be collected every 30 seconds until a 3-D picture is developed. Depending on the flow rates, sampling time may be lowered. The level of detail that an investigator would like to see cannot be obtained from the planned instrumentation, but it is the best money can buy for the budget allocated.

Revisions are being made to the Process Flow Diagrams developed for the CATC in preparation for the Operating Permit SARS Package. Work is proceeding so when construction is completed, the Permit Application can be submitted. The system should be up and running early next quarter.

The reduced funding for the tank and instrumentation system has resulted in approximately four items not being purchased. These items will have to be procured before testing can begin. A bench scale test has been outlined to determine the rate of heat flow in the subsurface that would interfere with the operations. The report should be completed during the next quarter. An outline of bench scale tests for the CAB/Humasorb-L combination is also in progress.

Task No. 1.4: Laboratory Studies & Field Testing at the DOE/RMI Extrusion Plant, Ashtabula, Ohio (J. Quaranta):

Continuing efforts this period included the following: Review of the site literature to understand the specific problems, groundwater modeling via computer analysis, and laboratory soils testing at WVU. Modeling of parametric remediation scenarios were carried out between the site's proposed corrective actions and the PVD enhanced system. Calibration of the different scenarios was the main focus.

Additional laboratory testing on the soil samples previously collected was initiated. The samples were compacted to predetermined densities to perform hydraulic flow tests using PVDs installed in actual site soil. To date, two cells have been constructed and are undergoing water saturation. Once the soil is saturated, the experiments will begin. Information from these tests will be used to establish baseline operating parameters. Four flexible wall permeameter cells were also established for hydraulic conductivity testing. Column flushing experiments that focus on surfactant selection are underway. The gas chromatograph (GC) used to analyze the samples was moved to another lab within CEMR, due to inadequate exhaust ventilation. Also, a computer was connected to the GC to achieve better results. These incidents have made the GC unavailable for some time, causing a delay in performing TCE batch tests. As a result, the analyses of the batch tests are approximately three months behind schedule. Also, the equipment ordered for the column tests had a delay in arrival due to the United Postal Service (UPS) strike.

Exploratory drilling, to determine contaminant levels, at the RMI site was conducted in the vicinity of the test pad where the PVD demonstration is proposed. RMI Environmental assisted with setting up the field crews for the drilling operations and with handling all of the chemical laboratory analysis subcontracting. Two test holes were made. Split spoon and shelby tube samples were collected.

Interaction continues for setting up the field demonstration with the prefabricated vertical drains. A meeting was held between RMI, DOE, Ohio EPA, and WVU to introduce the project to the regulatory division in Ohio having jurisdiction over the facility. Activities were set into motion for performing the field construction at the RMI facility in support of WVU Task 1.6.

Task No. 1.5: Drain Enhanced Soil Flushing for Contaminants Removal (M.A. Gabr):

The primary goal of this reporting period was to perform the extraction phase of the soil flushing process on one of the full scale test pads constructed at the Weston, WV site. Test pad one was split into two sections in order to complete the testing program as planned. This change resulted because of the amount of vacuum pressure required to overcome the elevation head and hence extract groundwater contaminants.

Currently, four manifold rows are in operation, one at a time, holding vacuum pressure and producing effluent. The average flow rate (to date) is estimated at 100 liters per hour, or 4 ml/s per PVD. This is consistent with the laboratory data. Additional data from the site are still being analyzed and final values will be reported thereafter. Grab samples of the effluent were taken and sent to Ashland's R&D department for laboratory testing. Observations of groundwater table fluctuations versus run time are also being made.

Hydraulic conductivity testing in the WVU laboratory on the Weston site soils was completed. Tests were performed on six samples at two water contents (8.2% and 10.5%) and at three concentrations of surfactant (.1%, .5%, and 1%). Results showed the hydraulic conductivity decreased on samples compacted at a water content of 10.5%. In addition, the micelles formed within the permeant fluid could not get through this soil sample. The sample's compacted at 8.2% water content did not experience any reduction in hydraulic conductivity regardless of the concentration of surfactant.

Additional testing was directed toward the characteristics of the chosen surfactant, Tergitol, when mixed with a contaminant and at various concentrations. Two series of viscosity tests were carried out. The first considered the following three concentrations of Tergitol: 1%, 3%, and 5%. The second considered the same concentrations of surfactant with added ethylbenzene contamination of 1,000 ppm. Results showed that viscosity was not affected by the addition of the ethylbenzene. Also noteworthy, the viscosity increased approximately 30% when a Tergitol solution of 5% was used.

It was speculated that the pH of the Tergitol solution was changing as the concentration of Tergitol in solution was increased. Therefore, solutions of Tergitol at different concentrations were made and the pH and temperature measured. For concentrations of surfactant from 0% to 5% the pH drops from 7 to approximately 4. During this period the temperature remained relatively constant. For concentrations between 5% and 80%, the pH remained relatively constant while the temperature increased. This indicates, for the range studied, the Tergitol is breaking the bond within the water molecule and releasing energy in the form of heat.

WVU Focus Area 2.0: Mixed Wastes, Characterization, Treatment and Disposal

Task No. 2.1: Analysis of the Vortec Cyclone Melting System (CMS™) for Remediation of PCB Contaminated Soils Using CFD (I. Celik):

During this quarter, progress was made on the development of a multi - step chemical kinetic scheme for typical PCB compounds. A kinetic model for dichloroethane ($C_2H_4Cl_2$) was adapted to simulate the destruction of all of the chloromethanes; that also has the ability to predict the formation of heavy hydrocarbons, aromatics, and chloroaromatics in the destruction of halocarbons.

Work was also done on improving the predictions of condensate species inside the recuperator section. The

chemical equilibrium program CET93 was used to predict the condensation of salt species. The program is currently running on the UNIX system to give greater flexibility regarding the number of species and elements to be considered. The new equilibrium phase change calculations with CET93 appear to be much better than the previous ones. CET93 had the ability to run the full H C O N Cl Si Na K Mg Ca elemental system, without memory or algorithmic errors, and it allows for detection of both liquid and solid phases of condensed species. Currently, six species are detected to condense inside the recuperator. The current results agree with Vortec's own observations.

To analyze the results from the output files of CHEMKIN, the software package Xsenkplot was acquired from NIST (National Institute of Standards for Technology). Xsenkplot has the ability to study the sensitivity matrix, which aids in reducing the chemical kinetic mechanism. In addition, the Chemkin postprocessor KINALC, was obtained to help select the species and equations in the reduced mechanism.

The results of this research were presented at the First International Conference on Incineration and Flue Gas Treatment, Organized by Sheffield University, Sheffield, UK, July 8-12, 1997. A paper was published in the conference proceedings.

WVU Focus Area 3.0: Decontamination and Decommissioning

Task No. 3.1: Production and Evaluation of Biosorbents and Cleaning Solutions for Use in Decontamination and Decommissioning (J. Kilbane, IGT):

During the past quarter the biodegradability of various surfactants was investigated, additional contaminant desorption tests were performed using various surfactants, and metal binding tests were performed using biosorbents prepared from byproducts of the paper and food industries. The surfactants being studied focus on those which gave the best results for contaminant desorption, but those that are considered food grade surfactants are of particular interest as they should readily receive regulatory approval for use in environmental remediation applications.

Based on the contaminant desorption data obtained thus far, for PAH desorption, DXP135, DXP207, and Witcamide 5085 show the best performance. Of these only DXP135 can be classified as a food grade surfactant. In addition, it is relatively inexpensive compared to the other products. Additional tests were performed to determine the ability of DXP135 and blends of DXP135 plus other surfactants to desorb PAHs and total petroleum hydrocarbons from two contaminated soils. For the desorption of petroleum hydrocarbons, aqueous solutions of Witconol 2722 are best, but for PAH desorption ethanol solutions of DXP135 work better. Blends of surfactants which contain DXP135 plus other surfactants yield no significant improvements.

The best biodegradation of surfactants is obtained at concentrations below cmc, but surfactants have the greatest capacity to solubilize contaminants when present at concentrations above the cmc. Enrichment culture techniques were used to obtain bacterial cultures which can adapt to utilize/tolerate high concentrations of surfactants. After enrichment, in the presence of surfactants for twelve weeks, bacterial cultures have been obtained which are reasonably well adapted.

Metal binding experiments were performed using waste waters from West Valley Nuclear. Several additional lignin byproduct samples were obtained and tested for their ability to remove radioactive strontium. The level of radioactivity in the wastewater was quite low and required concentration to perform the analyses. Due to

the radioactive nature, they can't be analyzed using the available AA equipment. Scintillation counting, using protocols focused on monitoring the emission spectrum of strontium, is being used for the analysis since it does not require direct contact with the analytical equipment. Lignin biosorbents should be easily removed by ultrafiltration. Wastewater samples were also tested using the industrial byproduct's Marasperse CBA-1 and Borresol HA-1. Excellent removal of radioactivity was observed. These will be tested further to determine their ability to remove strontium from concentrated wastewater.

Task No. 3.2: Use of SpinTek Centrifugal Membrane Technology and Sorbents/Cleaning Solutions in the D & D of DOE Facilities (B. Reed):

A membrane separation study was performed this quarter to test the ability of the SpinTek high-shear rotary ultrafiltration system to concentrate Tween 20, a commercially available surfactant commonly used in soil flushing applications. In this study, a polymeric membrane with a 5,000 MWCO was used to concentrate a 1% Tween 20 solution to a final concentration of 9.26%. The system was operated in semi-batch mode from 0 to 59 hr. Batch-down operation was conducted from 59 hours through the end of the experiment at 76.5 hr. Permeate flux, concentrate and permeate turbidity, temperature, pH, and conductivities were measured.

A rapid decrease in permeate flux was observed over the first 20 hours of operation that became stable throughout the remainder of the semi-batch operation. Permeate flux was then constant throughout. It is hypothesized that the decline in permeate flux was due to the accumulation of solute molecules at the membrane surface. The effect of membrane-induced turbulence was apparently unable to effectively minimize the accumulation of solute molecules. The constant permeate flux demonstrates effective scouring of solute molecules from the membrane surface.

Permeate turbidity was constant throughout the experiment. Concentrate turbidity increased rapidly from 10.0 NTU at 70 hours to a final value of 32 NTU at the end of the run. Concentrate and permeate pH were approximately equal. A decrease in both was observed when the system was operated in recycle mode for approximately 17 hours. Permeate and concentrate conductivities were also constant and approximately equal.

The Tween 20 solution appeared yellow in the feed tank. The permeate was initially clear but turned yellow as the Tween 20 solution was concentrated. At the end of the run, the vessel was opened and observations of the membrane's physical condition were made. Both the top and bottom membranes were stained a light yellow color.

A similar treatment experiment is planned using a CYTEK surfactant and a request was made for acquiring it. A technical difficulty encountered was the failure of the centrifugal feed pump's mechanical seals. These seals were upgraded with double mechanical seals for added durability.

WVU Focus Area 4.0: Cross Cutting Innovative Technologies

Task No. 4.1: Use of Centrifugal Membrane Technology with Novel Membranes to Treat Hazardous/Radioactive Wastes (B. Reed):

The following work was carried out in the third quarter: 1) Continuation of literature search, 2) Investigation of system performance treating freshly prepared oil/water emulsions at an oil package concentration of 15%, and 3) Implementation of a standardized cleaning procedure and tracking of membrane resistance after each experiment.

A comprehensive literature search on membrane technology was conducted and more than 75 articles and reports have been added to the membrane technology literature database. The identifications of wastes and membranes that warrant further study will be ongoing tasks. A virgin ceramic membrane with an average pore size of 0.11 μm was acquired this period. Numerous researchers have investigated the performance of virgin ultrafiltration membranes. Thus, the virgin ceramic membrane can be compared with membranes used in conventional systems. Because of the poor performance of the PV-100K polymeric membrane it was decided that the majority of testing should involve the more promising ceramic membrane.

The treatment of a synthesized oily industrial wastewater using the *SpinTek* high shear rotary ultrafiltration system was investigated. Three experiments were conducted, each containing a forty-liter feed solution of distilled water with an oil package concentration of 15 %. Constant membrane rotational speeds ranging from 1,150 to 1,750 rpm were used with an applied pressure range of 15 to 75 psig to obtain limiting flux data for future use in system performance modeling. A mathematical model was used to correct for the average permeate back pressure due to membrane rotation. The experiments were performed at 110°F in recycle mode using the 0.11 μm average pore size ceramic membrane. Permeate flux, and permeate/concentrate pH and conductivities were measured.

After each oil package/membrane rotational speed experiment, the system was drained, flushed, and cleaned. Each cleaning procedure was followed by a clean water flux measurement at 110 ± 2 °F 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 experiments. It was observed that as the membrane rotational speed was decreased, the limiting flux in the mass transfer controlled region decreased. It is hypothesized that the cause of this behavior was the increase in a gel layer thickness, and subsequent increase in resistance to fluid flow, at the membrane surface as the membrane rotational speed was decreased.

During the next work period, similar experiments will be conducted at higher oil package concentrations (20, 30, and 40% oil package). In addition, the mathematical models used to predict limiting flux behavior will be further investigated.

A technical difficulty was encountered in the performance of the feed pump. The mechanical seals on the centrifugal feed pump failed and had to be replaced. The stock carbide/tungsten carbide seals were retrofitted with higher grade materials.

Task No. 4.2: Environmental Pollution Control Devices Based on Novel Forms of Carbon (A. Brennsteiner, J. Zondol, A. Stiller):

Two varieties of AN-201 carbon fibers obtained from Applied Sciences, Inc. were tested as 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 are referred to as “oxidized” fibers. An equal mass (0.40 grams) of each fiber was used 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. An applied cell potential of -1.00 V was

used and the removal efficiencies compared. The concentration of uranium in the effluent was measured at one-half hour intervals and compared to the concentration of uranium at the inlet. Nearly all of the uranium was removed after one hour in the cell containing oxidized fibers in comparison to about 20% removal using the regular fibers.

The performance of the AN-201 oxidized fibers was further examined. The cell parameter first investigated was the 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. After one hour, both the -0.5V and -1.0V cell produced nearly 100% removal whereas the smaller applied potentials removed significantly less.

The effect of uranium ion concentration at the cell inlet was examined next. Three different concentrations were used: 5.3 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. In all three cases, nearly 100% removal was evident after one hour.

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 one hour stripping step (42 mL) to determine the ability to regenerate the carbon surface for further treatment. Uranium metals are available in non-radioactive isotopes. Atomic absorption cannot 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.

Several new cell geometries and configurations of a larger cell were designed. An additional 200 grams of "oxidized" carbon fibers were obtained from Applied Sciences, Inc. and are currently being prepared. Two new cell geometries will be constructed in the next quarter and their performance will be assessed.

Task No. 4.3: Design of a Rotating Membrane Filtration System for Remediation Technologies (V. Mucino):

During this quarter, work involved the parametric modeling of an actual CAD rendition of the filtration system as it was originally designed. The parametric model allows analysis to be conducted so relationships can be established between specific design parameters and responses of interest. The models supplied by SpinTek™ were imported from AutoCad into IGES files that can be read by the program IDEAS Master Series™. These drawings allowed models to be created in SDRC I-DEAS and Fluent with the correct dimensions. Once the geometry is transferred, the models are parameterized so meshing can be directed. This is to incorporate parameter variations prior to meshing the components of the filtration system, so analysis can be executed to identify trends in the response.

The parametric approach is being used in both the mechanical stress and vibration analyses as well as in the fluid analysis of the fluid chamber being analyzed for turbulence assessment purposes. In the latter case, the geometries from the files supplied by SpinTek are also being used to "extract" the "fluid volume shape." The program FLUENT is being used to model the fluid dynamic behavior of the fluid chamber, with special interest in the gap between the rotating membrane and the turbulence promoter. To this end, fluid models representing the surface of 8", 11", and 24" OD disks were produced in Fluent. For each disk diameter, six modeling cases were produced. Fluid chamber heights of 3/8", 5/8", and 1" were modeled with and without a turbulence

promoter. The Reynolds Shear Model (RSM) in Fluent was used to approximate the highly rotational fluid behavior.

Finite element models for stress were developed for varying disk diameters. Using SDRC I-DEAS these models analyzed the stresses in the rotating disk. These models differed by the diameter of the disk, which varied from the original 8 inches to 24 inches. Models were also created to look at the effects of a multi-disk system and examine the whirl associated with an unbalanced multi-disk system. For the stress analysis of the SpinTek™ water filtration system, SDRC I-DEAS was used to obtain values for the Von Mises stresses and the displacements due to rotation. For the 8-inch disk the stresses obtained were all within the allowable limits for the materials used. Additional refinements to the finite element models will be conducted to obtain more realistic results for the stresses in the membrane.

Results for the remainder of the eighteen three-dimensional cases will be collected and analyzed to identify any trends strongly affecting the fluid shear on the membrane surface. Membrane technical data will be obtained, and axisymmetric fluid models (of 8", 11", and 24" diameter disks) predicting the flow direction through and under the membrane for different radii will be completed. The combined effects of stress, vibration and turbulence will allow the parametric-design sensitivity analysis to be conducted. "Parameter-Response" trends are to be obtained based on the models thus far developed leading to the scaled-up design.

WVU Focus Area 5..0: Outreach

Task 5.1: Small Business Technical Based Support (E. Cook)

During this reporting period additional planning occurred for the clean up of TCE contaminated soil and groundwater at the RMI Extrusion Plant located in Ashtabula, Ohio. All proposals were finalized to cover each part of the pilot scale Prefabricated Vertical Drain field demonstration. A change was made regarding treatment of the extracted fluids that will consist of water, surfactant, contaminant and combination thereof. RMI Environmental Services will be providing expertise in developing unit operations and treatment of all fluids extracted from the subsurface. Due to this modification, minor delays have resulted. Two exploratory test holes were drilled this quarter to discern relevant soil data.

A call for proposals was sent out in August to begin preparation of the 1998 WVU Cooperative Agreement Program, in addition to the new five (5) year program. The focus of the 98 work will be field demonstrations of the developed innovative technologies. Attention will also be directed toward continued support of the small business supported by FETC-Morgantown.

A presentation of the 97 WVU Cooperative Agreement Program was given at the October "Industry Partnerships to Deploy Environmental Technology" conference held at FETC. Posters were displayed and a technical data sheet booklet distributed.

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

- 1.2 DEVELOPMENT OF STANDARD TEST PROTOCOLS & BARRIER DESIGN MODELS FOR DESICCATION BARRIERS
- 1.3 DEVELOPMENT OF STANDARD TEST PROTOCOLS & BARRIER DESIGN MODELS FOR IN-SITU FORMED BARRIERS - TECHNICAL SUPPORT
- 1.4 LABORATORY STUDIES AND FIELD TESTING AT THE DOE/RMI EXTRUSION PLANT (ASHTABULA, OHIO)
- 1.5 USE OF DRAINED ENHANCED SOIL FLUSHING (DESF) FOR CONTAMINANTS REMOVAL

TABLE OF CONTENTS

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

- 3.1 PRODUCTION AND EVALUATION OF BIOSORBENTS AND CLEANING SOLUTIONS FOR USE IN DECONTAMINATION & 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
- 4.3 DESIGN OF ROTATING MEMBRANE FILTRATION SYSTEM FOR REMEDIATION TECHNOLOGIES

FOCUS AREA 5.0: OUTREACH

- 5.1 SMALL BUSINESS TECHNICAL BASED SUPPORT

PROJECT TITLE WITH PRINCIPLE INVESTIGATORS

FOCUS AREA 1.0: SUBSURFACE CONTAMINANTS, CONTAINMENT AND REMEDICATION

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

S. Ameri and K. Aminian, Department of Petroleum Engineering

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

B. Overbey and D. Locke, BDM Federal

1.4 LABORATORY STUDIES AND FIELD TESTING AT THE DOE/RMI EXTRUSION PLANT (ASHTABULA, OHIO)

E. Cook and J. Quaranta, Department of Civil & Environmental Engineering
W. Best, US DOE/RMI Decommissioning Project
J. Henderson, RMI Environmental Services, Inc.

1.5 USE OF DRAINED ENHANCED SOILED SLUSHING (DESF) FOR CONTAMINANTS REMOVAL

M. Gabr, Department of Civil & Environmental Engineering
J. Cramer, Nilex Corporation
R. Freemant & G. Smith, Ashland Petroleum

PROJECT TITLES WITH PRINCIPAL INVESTIGATORS

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)

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

FOCUS AREA 3.0: DECONTAMINATION AND DECOMMISSIONING

- 3.1 PRODUCTION AND EVALUATION OF BIOSORBENTS AND CLEANING SOLUTIONS FOR USE IN DECONTAMINATION & DECOMMISSIONING

J. Kilbane and V. Srivastava, IGT

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

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

PROJECT TITLES WITH PRINCIPAL INVESTIGATORS

FOCUS AREA 4.0: CROSSCUTTING INNOVATIVE TECHNOLOGIES

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

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

4.2 ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

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

4.3 DESIGN OF ROTATING MEMBRANE FILTRATION SYSTEM FOR REMEDIATION TECHNOLOGIES

V. Mucino, Department of Mechanical & Aerospace Engineering

FOCUS AREA 5.0: OUTREACH

5.1 SMALL BUSINESS TECHNICAL BASED SUPPORT

E. Cook, Department of Civil & Environmental Engineering

QUARTERLY
TECHNICAL
PROGRESS REPORTS

FOCUS AREA 1.0

Subsurface Contaminants,
Containment & Remediation

**DEVELOPMENT OF STANDARD TEST PROTOCOLS AND DESIGN MODELS FOR
DESICCATION BARRIERS
FETC Task No. 1.2**

Quarterly Technical Progress Report
Reporting Period: 07/01/97 - 09/30/97

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For:
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ABSTRACT

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

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

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

TABLE OF CONTENTS

	Page No
Abstract	ii
Table of Contents	iii
List of Tables	iv
List of Figures	v
Executive Summary	vi
1.0 Introduction	1
2.0 Purpose	1
3.0 Background	1
4.0 Methodology	2
5.0 Work Performed this Period	4
5.1 Liquid Storage Capacity and Migration Rate	4
5.1.1 Water Infiltration Tets	4
5.1.2 Hydraulic Conductivity Measurements	4
5.1.3 Water Retention Capacity	6
5.1.4 Capillary Rise Measurements	6
5.2. Water Infiltration and Drying	6
5.3. Design and Experimental Plans for Scaled Models	6
6.0 Results and Discussion	9
6.1 Liquid Storage Capacity and Migration Rate	9
6.1.1 Water Infiltration Tets	9
6.1.2 Hydraulic Conductivity Measurements	9
6.1.3 Water Retention Capacity	9
6.1.4 Capillary Rise Measurements	9
6.2 Water Infiltration and Drying	14
6.3 Design and Experimental Plans for Scaled Models	14
7.0 Conclusions	16
7.1 Liquid Storage Capacity and Migration Rate	16
7.2 Water Infiltration and Drying	16
7.3 Design and Experimental Plans for Scaled Models	16
8.0 Work Planned for Next Period	16
8.1 Liquid Storage Capacity and Migration Rate	16
8.2 Water Infiltration and Drying	16
8.3 Design and Experimental Plans for Scaled Models	16
9.0 Technical/Administrative Difficulties	16
10.0 References	17

LIST OF TABLES

	Page No
TABLE 1. Results of the Third Series of Infiltration Experiments	11

LIST OF FIGURES

	Page No
FIGURE 1. Experimental Setup for Water Infiltration Tests	5
FIGURE 2. Experimental Setup for Capillary Rise Measurements	7
FIGURE 3. Experimental Setup for Simultaneous Infiltration and Drying Tests	8
FIGURE 4. Results of the First Series of the Water Infiltration Experiments	10
FIGURE 5. Results of the Second Series of the Water Infiltration Experiments	10
FIGURE 6. Water Hydraulic Conductivities through Different Size Sand-packs	12
FIGURE 7. Comparison of Water and Air Permeability Values for Different Size Sand-packs	12
FIGURE 8. Results of the Water Retention Experiments	13
FIGURE 9. Results of 24-hour Capillary Rise Experiments	13
FIGURE 10. Comparison of the Original Drying with the Drying After Water Infiltration	14
FIGURE 11. Comparison of the Drying with the Simultaneous Water Infiltration and Drying	14

EXECUTIVE SUMMARY

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

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

1.0 INTRODUCTION

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

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

2.0 PURPOSE

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

Among issues that must be settled before it can be decided if CAB technology is applicable to all DOE sites are the influence of the soil characteristics (such as, porosity, permeability, water saturation, grain size distribution, and clay content) on the drying profile and CAB performance. The laboratory study to be undertaken will evaluate the soil characteristics influence on CAB performance and will determine the effects of flow and sweep efficiency for fixed and mixed grain size soils. These experiments will validate and/or improve model predictions of system behavior and drying profiles of different soil types.

3.0 BACKGROUND

The Circulating Air Barrier (CAB) system is a desiccant-type barrier designed to prevent the movement of liquid contaminants toward groundwater, using air circulation and a processing system to lower water saturation in a targeted subsurface zone. The concept of Circulating Air Barrier was introduced in a study (1) that evaluated the barrier systems that could be installed beneath and around the tank farms with a minimum of excavation at DOE's Hanford Site. The CAB can be installed using

either vertical or horizontal wells, establishing a pattern of air injection and extraction wells. The moving air vaporizes water in the zone and carries the water vapor to an extraction well. In time, circulation of the air reduces the water saturation in the swept interval, and continues to remove, by evaporation, liquids that move into the zone such as a leaked plume. No liquids can flow through this interval until a critical saturation is achieved, a saturation level that is well above the initial saturation. In the event that a leak occurs, the CAB system serves as a tool for early leak detection and provides a means to withdraw volatile contaminants for surface treatment. The study concluded that CAB system provided many advantages including non-physical confinement, active monitoring and leak detection, commercially available oil and gas technologies and equipment, emergency response and rapid deployment capability, and high potential for integration with other remediation technologies. However, the concept needs to be demonstrated to develop data needed for scale-up and regulatory acceptance.

A follow up study by K&M/BDM (2) which addressed modeling, cold test design, and surface processing and control design for the CAB demonstration at Hanford concluded that several issues must be settled before it can be decided if CAB technology is applicable to all DOE sites. Key among these issues is the influence of the soil characteristics such as porosity, permeability, water saturation, grain size-distribution, and clay content on the drying profile and CAB performance. This report further recommended a laboratory study to be undertaken to evaluate the soil characteristics influence on CAB performance and to find out the effects of flow and sweep efficiency for fixed grain-size and mixed grain-size soils. This would also serve to validate and/or improve model predictions of system behavior and drying profiles of different soil types. In addition, a range of geologic and climatic environments within which the CAB could successfully operate, baseline equilibrium moisture curve for a specific grain-size, and relative humidity for a specific temperature could be determined.

4.0 METHODOLOGY

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

Bench-scale testing of the CAB process parameters will utilize sand packs to determine the relationship between soil characteristics and in situ barrier quality. Sand packs will be calibrated to determine porosity, permeability, and saturation characteristics. The soil characteristics will be varied by changing grain size and sorting of the pack materials. Residual water saturation of the pack will be established by first saturating the pack with water and then de-saturating the pack by injection of water-saturated air. The pack will then be dried at various rates of air injection to determine drying characteristics as a function of rate, remaining water saturation, and soil characteristics. The final

phase of sand pack testing will be to re-saturate the packs with simulated contaminant fluids injected at low pressure (near atmospheric) at the top while monitoring any effluent at the bottom. This will allow determination of contaminants migration rate as well as total storage capacity of the packs.

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

5.0 WORK PERFORMED THIS PERIOD

5.1. Liquid Storage Capacity and Migration Rate

To evaluate the performance of dried sand-pack as barrier to liquids as well as migration rate of water, a number of experiments were performed during the reporting period. These experiments are described below.

5.1.1 Water Infiltration Tests

Three series of experiments were performed to evaluate the infiltration of water through the sand-pack. Each series of the experiments are described below:

The first type of experiments were conducted using a constant head of water on top of the sand-pack. The CAB small scale setup was modified as illustrated in Figure 1 to perform these series of experiments. The sand-packs were prepared first by compacting the sand at the optimum water content and then by completely drying the sand-packs based on the previously developed protocols. A number of uniform size sand-packs were prepared using various sand sizes. The location of the water front as a function of time was monitored during these experiments. Each experiment was performed at three times to assure the repeatability of the results.

The second series of experiments involved dispersing 80 ml of water on top of the sand-pack. The sand-pack preparation was the same as the first series of the experiments. The water penetration into the sand-pack was monitored during these experiments. Each experiment was performed at three times to assure the repeatability of the results.

The third series of experiments were performed by adding water in small increments such that an infiltration rate of 2.5ml/min was achieved. The sand-pack was prepared in three manners. The first method of preparation was similar to the two previous series of the experiments. The second method of preparation involved compaction of dry sand. The third method simply used loose sand in the chamber. Each experiment was performed at three times to assure the repeatability of the results.

5.1.2. Hydraulic Conductivity Measurements

Sand-pack hydraulic conductivity to water and permeability to water were measured in these series of experiments. The sand-packs were prepared first by compacting the sand at the optimum water content and based on the previously developed protocols. The sand-packs were then saturated with water by flowing 5 pore volumes of water through each sand-pack. The experimental setup illustrated in Figure 1 was utilized to measure the sand-packs hydraulic conductivity under constant head of 3-inch of water. The results were then converted to permeability values for each sand-packs. Each experiment was performed at three times to assure the repeatability of the results.

Figure 1. Experimental Setup for Water Infiltration Tests

5.1.3 Water Retention Capacity

The capacity of the sand-pack to retain water was measure in these series of experiments. The sand-packs were prepared in similar manner as those in previous set of experiments. However, after 3 pore volumes of the water entered the sand-pack the head of the water was removed and the sand-pack was drained. The water that exited the sand-pack at the bottom was collected and measured. The experiment was continued for about 24 hours after which the amount of water that exited the sand-pack declined to such a low level that the measurements were difficult. Then, the amount of water retained by the sand-pack was evaluated. Each experiment was performed at three times to assure the repeatability of the results.

5.1.4 Capillary Rise Measurements

The capillary rise in the various sand-packs were measured using a setup illustrated in Figure 2. The sand-pack was prepared similar to the previous experiments. The height of water in the sand-pack was measured after 24 hours for various sizes of the sands. Each experiment was performed at three times to assure the repeatability of the results.

5.2 Water Infiltration and Drying

These series of experiments were designed to evaluate CAB's ability to prevent spills from spreading. The experimental setup was similar to sand-pack drying however a water injection line was added to the top of the sand-pack as illustrated in Figure 3. The sand-packs were prepared first by compacting the sand at the optimum water content and then by completely drying the sand-packs based on the previously developed protocols. The experiment is similar to the sand-pack drying experiment with exception that every 20 minutes 10ml of water was injected into the top of the sand-pack. A second set of experiments were also conducted in which 80 ml of water was added at one time to the sand pack followed by drying experiment.

5.3 Design and Experimental Plans for the Scaled Models

The large tank that large tank which accommodates the sand bed and the necessary plumbing to simulate various well configurations, has been ordered and received. The monitoring equipment and the sensors are currently being installed in this tank. The experimental procedures for Phase II experiments are under further investigation.

Figure 2. Experimental Setup for Capillary Rise Measurements

Figure 3. Experimental Setup for Simultaneous Infiltration and Drying Tests

6.0 RESULTS AND DISCUSSION

6.1. Liquid Storage Capacity and Migration Rate

6.1.1 Water Infiltration Tests

The results of the first series of the experiments are illustrated in Figure 4. Figure 5 illustrates the results of the second series of the tests. The results of third series of the tests are summarized in Table 1. As it can be seen from the obtained results the particle (sand) size plays a significant role in the water migration and distribution in the sand-pack. The water tends to channel much easier and faster through the sand-packs with larger size sand such as 20/30 or 30/40 mesh sizes. However as the particle size is reduced the capillary forces tend to spread the water better and prevent or delay the channel to form. The channeling can significantly reduce the capacity of the dried zone to retain liquid contaminants. Therefore this phenomenon deserves close scrutiny.

6.1.2. Hydraulic Conductivity Measurements

The results of the water hydraulic conductivity measurements are illustrated in Figure 6. Figure 7 compares the measured water permeability values with the previously measured air permeability values for different sand-packs. As it can be seen, the measured permeability values are in agreement with those measured with air. Therefore, it confirms our previous experimental results.

6.1.3 Water Retention Capacity

The results of water retention capacity experiments are illustrated in Figure 8. The results tend to indicate that the sand-packs can retain significantly more water than the expected 10% (residual saturations) of pore volume. It should however be noted that this test is influenced to a large degree by the duration of the test. For low permeability sands, such as 120 mesh size particles, it may take months before a complete equilibrium is reached. These results may appear to be in conflict with water infiltration experiments. However, it should be noted that these experiments reflect the total amount of water passed through the sand-pack and not the distribution of the water. In other words these experiments are not sensitive to channeling.

6.1.4 Capillary Rise Measurements

The results of capillary rise measurements are illustrated in Figure 9. As with water retention capacity experiments, these measurements are influenced to a large degree by the duration of the test.

Figure 4. Results of the First Series of the Water Infiltration Experiments

Figure 5. Results of the Second Series of the Water Infiltration Experiments

TABLE 1. Results of the Third Series of Infiltration Experiments

SAND TYPE	LOOSE			COMPACTED DRY			AFTER DRYING		
Pore Volume	TIME	MASS OF WATER	SAT	TIME	MASS OF WATER	SAT	TIME	MASS OF WATER	SAT
20-30 SAND 834.21	30 min	75g	8.90%	30min	75g	8.90%	10min	25g	3.00%
	40min	97g	11.63%	35min	75g	8.90%	15min	50g	5.99%
				33min	75g	8.90%			
30-40 SAND 852.98	30min	75 g	8.79%	40 min	100 g	11.99%	35	100	11.99%
	40min	100g	11.99%	35 min	100g	11.99%	30	75	8.79%
	30 min	75g	8.79%	30min	75g	8.79%			
60 SAND 879.2785	180min	375g	42.65%	170 min	400 g	45.49%	170	375	42.65%
	140min	350g	39.81%	171min	425g	48.34%			
80 SAND 896.567	210min	455g	50.75%	200 min	525g	58.25%	195	525	58.25%
	170min	425g	47.40%	190min	500g	55.77%			
120 sand 908.742	400min	850g	93.64%	350 min	900 g	99.03%	355	875	99.03
	330min	825g	90.78	340min	875g	96.28%			
MIXTURE 1 857.8505	30min	75g	8.74%	30min	75g	8.74%	10 min	25g	2.91%
	30min	75g	8.74%	40min	100g	11.66%			
	20min	50g	5.83%	20min	50g	5.83%			
				30min	75g	8.74%			
				30min	75g	8.74%

Figure 6. Water Hydraulic Conductivities through Different Size Sand-packs

Figure 7. Comparison of Water and Air Permeability Values for Different Size Sand-packs

Figure 8. Results of the Water Retention Experiments

Figure 9. Results of 24-hour Capillary Rise Experiments

6.2 Water Infiltration and Drying

The results of these experiments are illustrated in Figures 10 and 11. As it can be seen from Figure 10, the drying process after water infiltration is similar the original drying process. Figure 10 indicates that during simultaneous infiltration and drying, the initial period of the drying follows the original drying behavior. Upon reaching the second phase of drying however the drying process continues to follow the slowly declining drying with no break-through. This obviously is because the water is continuously is being added to sand-pack. During these experiment no water reached the bottom of the sand-pack. The drying process appears to be similar to the drying process in uniformly wet sand which tends to indicate that air flow causes the lateral distribution of the water.

6.3. Design and Experimental Plans for the Scaled Models

Phase II experiments will be initiated upon installation of CATC and assembly of the necessary the monitoring system at B-17 at FETC.

Figure 10. Comparison of the Original Drying with the Drying After Water Infiltration

Figure 11. Comparison of the Drying with the Simultaneous Water Infiltration and Drying

7.0 CONCLUSIONS

7.1. Liquid Storage Capacity and Migration Rate

The experiemntal results indicate that when the water is spilled over the sand-pack, it has tendency to channel through the sand-pack. The channeling appears to be significanlty influenced by particle size. The channeling can significantly reduce the capacity of the dried zone to retain liquid contaminants. Therefore, this phenomenon deserves close scrutiny. The measured permeability values for water flow through the sand-packs are in agreement with those measured for air flow and therefore confirm the previous experimental results. The water retention capacity and capillary rise in the sand-packs are significantly influenced by time.

7.2 Water Infiltration and Drying

The air flow through the sand-pack can remove any water that infiltrated the sand-pack. The drying process appears to be similar to the drying process in uniformly wet sand. The air flow appears to have prevented any water channeling.

7.3. Design and Experimental Plans for the Scaled Models

Phase II experiments will be initiated upon installation of CATC and assembly of the necessary the monitoring system at B-17 at FETC.

8.0 WORK PLANNED FOR NEXT PERIOD

8.1 SARS Activity

Prepare 'Operating Permit' for larger scale experiments in FETC Building B-17.

8.2. Design and Experimental Plans for the Scaled Models

Develop protocols for sand compaction, porosity, and permeability measurements relative to CATC.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

Due to lack of sufficient operating funds we are not able to proceed with the large scale experiments.

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**DEVELOPMENT OF STANDARD TEST PROTOCOLS AND
DESIGN MODELS FOR *IN SITU* FORMED BARRIERS**
FETC Task No. 1.3

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ABSTRACT

The DOE Environmental Management Division is supporting research aimed at examining the installation of barrier systems that can be installed above aquifers to prevent them from being contaminated with radioactive and other toxic materials. The Circulating Air Barrier is a barrier that has high potential because it can function to halt vertical migration of liquids, but does not form a permanent impairment to flow of fluids through the subsurface vadose zone environment.

This work is designed to support the on-going research at West Virginia University (WVU) that is aimed at the development of standard test protocols for installation of in-situ formed barriers for the containment of contaminants released into the subsurface environment. BDM Federal Inc. in previous studies conducted for DOE made recommendations for the continued development of permeation barriers and desiccation barriers. BDM is providing planning assistance and technical support relating to the requirements for barriers to function as required in the subsurface environment under differing geological conditions.

BDM is providing technical support to assist WVU in examining the key questions that must be answered in the current research program that will support the ultimate in-situ field demonstration of a circulating air barrier, and a permeable reactive barrier. Support will also be provided for examining the proposed dual barrier system consisting of a freeze barrier and a circulating air barrier. Both of these barriers can be deployed and demobilized without permanently impacting the hydraulic conductivity of the vadose zone.

TABLE OF CONTENTS

<u>DESCRIPTION</u>	<u>PAGE NOS.</u>
Executive Summary	v
1.0 Introduction	1
2.0 Purpose	1
3.0 Background	1
4.0 Methodology	2
5.0 Work Performed this Period	2
6.0 Results and Discussion	5
7.0 Conclusions	5
8.0 Work Planned for Next Period	5
9.0 Technical/Administrative Difficulties	5
Appendix	
References	6
List of Acronyms	6
Glossary	6
List of Tables	
List of Figures	

Executive Summary

The purpose of the current studies being conducted by West Virginia University is to develop protocols for testing and evaluating barrier materials and barrier deployment processes that may be useful in either saturation (partially or completely)condition.

The DOE in response to requirements of congressional and executive orders has developed a program designed to first contain and then remediate hazardous and mixed waste materials which have moved or are moving towards points where the potential environmental impacts are not acceptable according to federal law.

The Federal Energy Technology Center (FETC) of the DOE has been assigned the tasks of managing one of the five focus areas for the remediation efforts. That focus area is Decontamination and Decommissioning of buildings, reactors, and other contaminated infrastructure on the former weapons sites. FETC also provides project management for procurement for research conducted in the Contaminant Containment Focus area. FETC also in cooperation with West Virginia University has developed a Decontamination and Containment Test Center to examine proof of concept or technical feasibility of new technologies being developed in the Subsurface Containment and Decontamination and Decommissioning focus areas. The center is located in building B-17 on the Morgantown FETC/DOE Campus.

During the past quarter, procurements were made for materials to be used in the development of an instrumentation system to be used on the circulating air test cell (CATC) to monitor water saturation in the test cell and the flow rates of air and water vapor being produced with the air.

The test cell was built and the electrodes for the conductance type measurement system installed. The instruments and the computer program to control the system are under development and are expected to be completed in early to mid-November.

Outlines of tests to be conducted in the CATC are in progress. Proposed test series for evaluating deployment requirements of reactive barrier materials are also in progress.

Planning for technology Transfer via the Internet is in progress.

1.0 Introduction

This report discusses the progress made during the 3rd, quarter of 1997 by BDM in providing technical support to the WVU departments of PNGE and CEE on their tasks to develop test protocols for barrier materials, barrier deployment processes, and barrier design functions

2.0 Purpose

The purpose of the current studies being conducted by West Virginia University is to develop protocols for testing and evaluating barrier materials and barrier deployment processes that may be useful in either saturation (partially saturated vadose zone or completely saturated groundwater aquifer) condition. The application of the testing results will be in moving potential barrier materials or processes to the next phase of demonstration before deployment.

3.0 Background

Across the Department of Energy's (DOE) Nuclear Weapons manufacturing plant complex, most sites disposed of hazardous and mixed waste liquids by dumping them into pits or placing them in specially manufactured steel and concrete tanks with a design life of 30 years. Most of the tanks have exceeded their design life but are still in service. Almost half of them are suspected of leaking contaminated liquids, or are known to have leaked. In some cases the leaked contaminant material has already reached the groundwater and is approaching a point of contact with the biosphere (river bed). The use of barriers to halt movement into the biosphere where humans and animal life forms can contact the materials is an important strategy developed by DOE officials until remediation technologies are developed and implemented.

The DOE has supported testing and evaluation studies of various barrier materials over the past 20 years. Many materials and deployment processes have been tested during this period, but DOE scientists are not convinced that they have found the right barrier material and deployment process for broad scale application to the former weapons sites. A reason for this is the geographic and climatic differences in the sites. Western sites are mostly in semi-arid climates with sediment deposition by mass wasting or catastrophic depositional modes. Eastern sites are located in high rainfall types of climates where sediment cover on bed rock is thin and usually contains more fine grained sediments. Vadose zone soils have higher water saturation's in the east than the dry soils of the west. Barriers are generally considered as containment devices without any particular use as a remediation unit.

The particular materials being tested by West Virginia University are low viscosity permeation grout materials, the desiccation barrier process, and in the near term reactive barrier materials.

4.0 Methodology

The methodology involves the development of NEPA documents and documents for DOE/FETC=s Lab Safety Committee that describe procedures for construction of tanks with instrumentation needed to conduct experiments that involve desiccation of simulated vadose zone soils in the B-17 building on the FETC Morgantown, WV, campus. The work also includes the preparation of line drawings, lists of materials to be utilized, and notes on construction procedures. The work also includes coordinating requests for installation of utilities needed to perform the experiments.

BDM reviews state -of -the-art barrier materials and processes and evaluates the potential for application at the DOE Sites. Evaluation is based on the suggested approach by the National Academy of Science Audit teams which review DOE approaches to containment and remediation.

5.0 Work Performed this Period

Milestones planned for this period were as follows:

- Installation of CATC
- Operating Permit for CATC

Operating Permit Renewal Request for bench scale operations to complete planned experiments in Rm. -16 of B-17 building. The request for renewal was submitted to the FETC Lab Safety Committee for approval on 8/14/97. No response to the request has been received as yet.

Work is proceeding on the Operating Permit so that as soon as the construction of the CATC is completed, the Permit Application will be submitted. to the SARS committee.

The operating permit cannot be submitted until the CATC vessel has been installed and instrumented and is ready to function.

Revisions are being made to the Process Flow Diagrams that have been developed for the CATC in preparation for the Operating Permit SARS Package. As instrumentation is added the process flow diagram is altered to match changes.

Subtask 1.3 (Subcontract) Technical Support to West Virginia University for Standard Test Protocols and Design Models for In Situ Formed Barriers

1.3.0 NEPA Documentation

- 0.1 Prepare NEPA documents required for the modification or continuation of the work.
- 0.2 Constructional and Operational Activities
Prepare and supervise progress and completion of SARS packages to support work on the CATC to be located in B-17 bldg. On FETC Morgantown Campus.

A review of the revised NEPA documents prepared last year indicate that the documents are still applicable for the current work. The document will have to be revised if a new direction in the experimentation occurs such as work on reactive barrier materials planned for the next phase of experiments.

An initial design and specifications for the CATC vessel was prepared and sources sought. Construction of the CATC was initiated in early July. The vessel was received in Morgantown at the FETC Campus on August 15, 1997. Installation of the electrodes for the instrumentation package was started shortly thereafter. The work on the CATC vessel was completed on 9/30/97.

The instrumentation system should be completed and installed early next quarter

1.3.1.0 Planning and Technology Transfer

- 1.1 Plan Bench scale tests for a Dual Barrier System in B-17
 - a. CAB and Freeze Barriers
 - b. CAB and Humasorb Barriers
- 1.2 Plan a series of experiments for reactive barrier materials
 - a. Humic acid type materials
 - b. Zeolites
 - c. Zero valence iron materials
- 1.3 Design a series of scale up experiments for reactive barriers
- 1.4 Transfer Technology results of Bench Scale Tests on the CAB

A bench scale test has been outlined to determine the rate of heat flow in the subsurface that would interfere with the operations with either the Freeze or the CAB barrier. The report should be completed during the next quarter.

An outline of bench scale tests for the CAB/Humasorb-L combination is also in progress. Humasorb

-L is a liquid form of humic acid. The tests will be conducted as column tests in which the Humasorb will saturate an upper section of the column and air is circulated through the column and the liquids removed. A contaminant surrogate will then be allowed to drain into the column and the amount of contaminant that moves entirely through the column will be measured.

BDM is planning to test a technology transfer medium with an Internet page that presents the results of several projects for DOE in which there is a requirement for technology transfer. Design of the web site is in progress, and should be completed early next quarter. BDM plans to add the Technology Transfer material to its own web page.

1.3.2.0 Circulating Air Barrier Pilot Scale Tests

2.1 Purchase and install CATC vessel in B-17

2.1.1 Install simulated horizontal well system of injection and production wells

2.1.2 Develop protocol for installation and compaction of sand in the CATC

2.1.3 Develop protocol for reduction of water saturation for a specific deployment process.

The CATC vessel was purchased and received in August. Modifications for instrumentation were made

Plastic pipe for use in simulating the horizontal wells has been purchased and designs for the horizontal well system are being prepared. The design calls for equal flow rates from one end of the well to the other which means that there will have to be some difference in the hole sizes used to compensate for decreasing air pressure at the far end of the well. The sizes and numbers and spacing of the perforations is being calculated.

The initial discussions on protocols for partially saturating the sand in the CATC have not been very rewarding. The reduction in height of the CATC reduced the space available for use of mechanical equipment to saturate the test bed. The injection of vapor laden air may be the best way to condition the reservoir before starting the desiccation process.

2.2 Design and purchase instrumentation system for CATC vessel

2.1 Design instrumentation system for CATC series of experiments to evaluate position of saturation zone of CATC as a function of time.

Process Dynamics Corp. (Pro-Dyn) of Morgantown, WV completed design of the instrumentation system during the quarter. A report describing the design work is in progress. Actual work on the

instrumentation system was initiated and nearly completed. The system should be installed and tested by mid quarter. There have been some delays due to procurement activities.

21 Install and test instrumentation system in test vessel

The Capacitance measurement system was designed to provide information on the location and degree of saturation in the test bed with a resolution of 1 meter. A higher resolution system is possible but the costs would far exceed the budget provided. Operations to install components of the instrumentation system were initiated in September and are expected to be completed in early November. Computer programs to control data access and the instrumentation system are being developed.

6.0 Results and Discussion

The CATC as delivered seems to be adequate for the use designed although the tank suffered stress cracking in the area where the lifting lugs are located. The cracks did not penetrate through the entire thickness of the tank wall.

The pilot scale Circulating Air Barrier test in the Circulating Air Test Cell (CATC) will be most useful if we can determine if there is good sweep efficiency in a system that is nearly ideal. This is the case that is planned with a homogeneous grain size and high permeability to air reservoir. After the test zone has been desiccated, then a scaled volume of contaminant liquid will be released and its distribution within the test cell will be determined by the Capacitance instrumentation system.

The instrumentation system will be controlled by a computer which will sample the volume of the tank in a specified manner part of the time and with random sampling part of the time. Initially data will be collected every 30 seconds until a 3-D picture is developed and then sampling time may be lowered depending upon the flow rates during the process.

7.0 Conclusions

The level of detail that an investigator would like to see cannot be obtained from the planned instrumentation system, but the system planned is the best money can buy for the budget allocated.

8.0 Work Planned For Next Quarter

Work planned for next quarter is the completion of the instrumentation system and obtaining approval of the operating permit, so that experiments can be initiated by the end of the quarter.

9.0 Technical/Administrative Difficulties

Delay of receipt of funding by 4 months had a major impact on the proposed schedule. It forced us to begin work at the end of the semester instead of at the beginning.

BDM is in the midst of a change in its procurement bookkeeping system which has forced the local office to wait in Que. for procurement action that we were able to accomplish locally for the past 10 years. This delay has had minimal impact to date but could get worse as time goes on.

The reduced funding for the tank and instrumentation system has resulted in approximately four items not being purchased. These items will have to be procured before the testing can be initiated.

Appendix

References

List of Acronyms

CAB - Circulating Air Barrier

DOE -Department of Energy

FETC-Federal Energy Technology Center

CATC -Circulating Air Test Cell

Glossary

Vadose zone - Soil zone in which there is a mixed saturation of fluids in the pore space which includes water and air.

Capillarity - the action by which the surface of a liquid is elevated or depressed depending upon the relative attraction of the liquid for the solid travel higher in small tubes or pore spaces than in large tubes or pore spaces.

Biosphere -The zone on the planet in which most life occurs.

Laboratory Studies & Field Testing at the DOE/RMI Extrusion Plant 1997 FETC Task No. 1.4

Quarterly Technical Progress Report

Reporting Period:

July - September 1997

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

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ABSTRACT

Continuing development of 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 have focused efforts on the decontamination and decommissioning of the facility which includes remediation of the soil and groundwater contaminated by low-level uranium and TCE.

WVU's Civil and Environmental Engineering Department work with RMI Environmental Services is made possible through support from DOE's Federal Energy Technology Center - Morgantown and DOE's Ashtabula Area Office - RMI Decommissioning Project. WVU, DOE-Ashtabula, and RMI are working together in problem identification and with bringing WVU's technical resources in technology development to bear on several of RMI's decontamination and decommissioning projects. Current work for 1997 consists of performing a groundwater modeling study of the site and a treatability study using surfactants to remove TCE from contaminated fine-grain fraction soil and groundwater.

TABLE OF CONTENTS

Abstract	ii
Executive Summary	1
Introduction	1
Purpose	1
Background	2
Methodology	2
Work Performed this Period	3
Conclusions / Next Period Work Plan	4
Appendix A: Subtask 1.4 Lab Scale Chemical Testing	5

EXECUTIVE SUMMARY

Efforts this period focused on continuation of the groundwater modeling, continuing with contaminated soils and groundwater field investigations, attending meetings with the Ohio EPA, and performing laboratory soils tests at WVU which focused on surfactant selection. Continued research on batch scale testing of the selected surfactants was delayed however column flushing experimentation were set-up and are underway. Field drilling at the RMI site was performed to determine contaminant levels at the proposed test pad location for FETC Task 1.6.

A meeting was held between RMI, DOE, Ohio EPA, and WVU to introduce the project to the regulatory division in Ohio having jurisdiction over the facility. Activities were set into motion for performing the field construction at the RMI facility in support of FETC Task 1.6.

INTRODUCTION

The research activities presented in this report are part of the WVU Cooperative Agreement's initiative for bringing innovative environmental remediation technologies to field-scale demonstrations. This project is a concerted effort between WVU's Civil and Environmental Engineering Department, U.S. Department of Energy's (DOE) Federal Energy Technology Center - Morgantown and DOE's Ashtabula Area Office - RMI Decommissioning Project, and RMI Environmental Services. The goal of the work during Phase I efforts consist of performing preliminary engineering studies necessary for subsequent design and installation of the Prefabricated Vertical Drain Enhanced Soil Flushing technology at the RMI facility located in Ashtabula, Ohio. This report discusses the progress made for the current reporting period.

The Phase I research includes: an information review of previous engineering studies/reports performed at the RMI facility regarding the site corrective measures; groundwater modeling to characterize a TCE contaminant plume; laboratory bench-scale testing to investigate performance requirements of the prefabricated vertical drains in site soil, and chemical laboratory analysis as part of a treatability study addressing the site contaminated soil. Results of the Phase I efforts will produce: identification of candidate locations for installation of a PVD test pad area; characterization of the PVD performance requirements necessary for operation at the site; and determination of contaminant clean-up levels achieved using RCRA approved, food-grade surfactants on TCE contaminated site soils.

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 two-fold: The first is to perform a limited groundwater model of the RMI Ashtabula site for identifying candidate locations suitable for the Phase II field test pad research; The second objective is to perform laboratory bench-scale experiments for the design of the PVD system used in the field application, and to perform treatability studies to determine clean-up levels achieved using RCRA approved, food-grade surfactants on the TCE

contaminated soils at the RMI facility. This research is specific to addressing key issues necessary for the design, installation, and operation of the test pad experiment, and remediation of the TCE contaminated soils proposed for a subsequent Phase II.

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

The project objectives for Phase I are two fold: The first is to perform a limited groundwater model of the RMI Ashtabula site for identifying candidate locations suitable for the Phase II field test pad research; The second objective is to perform laboratory experiments for the design of the PVD system for the field application, and to perform treatability studies to determine clean-up levels achieved using RCRA approved, food-grade surfactants on the TCE contaminated soils at the RMI facility. This research is specific to addressing key issues necessary for the design, installation, and operation of the test pad experiment, and remediation of the TCE contaminated soils proposed for Phase II.

The work scope of the first phase activities is broken down into the following subtasks:

Subtask 1.1 Site Data Evaluation

Subtask 1.2 Predictive Modeling

Subtask 1.3 Lab Scale Physical Testing

Subtask 1.4 Lab Scale Chemical Testing

Subtask 1.5 RMI Environmental Site Support

WORK PERFORMED THIS PERIOD

Accomplishments made during this period are reported by subtask in the following discussions.

Subtask 1.1 Site Data Evaluation

Work continued with review of the site literature and with performing literature searches necessary for work under subtasks 1.2 to 1.4. This effort is an on-going activity focused on understanding the site problems.

During this reporting period a comprehensive field soil study was undertaken which consisted of drilling two exploratory bore holes and obtaining split spoon and Shelby tube type samples from soil in the vicinity of the proposed PVD test pad. Results of the field and laboratory chemical data were not available at the time of this writing but will be included in the next quarterly report submittal.

Subtask 1.2 Predictive Modeling

During this period significant work was completed with development of the groundwater characterization and flow predictions. Accomplishments were limited to performing modeling of parametric remediation scenarios between the site's proposed corrective actions and a PVD enhanced system. Modeling results to date have focused on calibration of the different scenarios and no reliable results are available.

Subtask 1.3 Lab Scale Physical Testing

During this reporting period the lab scale soil testing was begun. Soil obtained from earlier site excavations has been processed and compacted into containers at established soil properties in order to perform hydraulic flow tests using PVDs installed in actual site soil. To date, the two cells have been constructed and are undergoing water saturation. Once the soil specimens have been saturated, operation of the experiments will begin. Information from these tests will be used to establish baseline operating parameters for follow-on field work.

Subtask 1.4 Lab Scale Chemical Testing

Research during this period was limited to setting up four flexible wall permeameter cells in order to begin hydraulic conductivity testing on the site soil. Information regarding this portion of the work is included in

Attachment A.

Subtask 1.5 RMI Environmental Site Support

During this period RMI assisted with setting up the field crews for performing the site drilling operations and with handling all of the chemical laboratory analysis subcontracting. Interaction continues as preliminary work has been performed on setting up for the field operations to be carried out under FETC Task 1.6. A meeting was held between RMI, DOE, Ohio EPA, and WVU to introduce the project to the regulatory division in Ohio having jurisdiction over the facility. Activities were set into motion for performing the field construction at the RMI facility in support of FETC Task 1.6.

CONCLUSIONS/WORK PLANNED FOR NEXT PERIOD

During the next period, work will continued to completion all of the subtasks required under this project's scope of work. Conclusions and carry-over work into FETC Task 1.6 will be identified and the complete result of this project will be summarized.

APPENDIX A

SUBTASK 1.4 Lab Scale Chemical Testing

1. BACKGROUND AND LITERATURE REVIEW

Surfactant Enhanced Soil Flushing

In situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions (such as surfactants). Soil flushing is accomplished by passing the extraction fluid through the site soils using an injection process. At the end of the process, extraction fluids must be recovered from the underlying aquifer and if possible, recycled.

The conventional soil flushing process involves four major steps that are effective in this remediation technique. These are:

- 1) Contaminant solubilization by the flushing fluid (surfactant),
- 2) Extraction of the solubilized contaminants,
- 3) Treatment of the spent flushing fluid, and
- 4) Disposal/reuse of the treatment residuals.

The applicability and effectiveness of the process can be limited, due to the following reasons:

- Low permeability soils are difficult to treat.
- Surfactants can be bound to the soil and reduce effective soil porosity. [The mass of hydrophobic organic contaminants (HOCs) sorbed onto soil is an increasing function of the soil/water (weight-to-volume) ratio. As the soil/water ratio is increased, the mass of surfactant available in the bulk solution for micelle formation decreases because of increased surfactant sorbed onto soil, which also affects HOC sorption.]
- Reactions of flushing fluids with soil can reduce contaminant mobility. (1)

During water flooding at sites, the rate of removal of the organic species has been observed to decrease substantially over time, suggesting that there are physical or chemical processes limiting the exchange of mass from the non-aqueous phase liquid (NAPL) to the aqueous phase. Two properties of the entrapped NAPL that may change over the period of remediation are the NAPL composition and the interfacial area across which mass transfer can occur. Mass transfer may become rate limited as NAPL saturations decrease, or under high aqueous phase flow conditions typically encountered during pump-and-treat remediation. Also, the pore structure of a medium is a critical parameter which controls mass transfer rates during the initial period of dissolution. Experiments have revealed that large NAPL blobs, with relatively small interfacial areas, are entrapped in coarse media. These smaller interfacial areas limit steady state mass transfer rates. (2)

Characteristics effecting the soil flushing process are shown in Table 1.

Table 1. Characteristics Affecting the Soil Flushing Process

Characteristics	Reason for Potential Impact
<i>Unfavorable Waste Characteristics:</i> <ul style="list-style-type: none"> Mixed Waste types Variable Waste composition 	<ul style="list-style-type: none"> Flushing solution difficult to formulate Frequent formulation of solution
<i>Unfavorable Soil Characteristics:</i> <ul style="list-style-type: none"> Variable soil conditions Low permeability High soil humic content Soil-solvent interactions 	<ul style="list-style-type: none"> Inconsistent flushing Movement of flushing solution hampered Desorption difficult Desorption inhibition
<i>Unfavorable Flushing Solution Characteristics:</i> <ul style="list-style-type: none"> Solution recovery difficult Solution toxicity Soil permeability reduction Poor solution treatability. 	<ul style="list-style-type: none"> High Costs Replacement of solution Health risks Chemicals reduce porosity

[Source: *Technology Screening Guide for Treatment of CERCLA Soils and Sludges*, U.S. EPA (1988)]

2. OBJECTIVE AND PURPOSE

The overall project objectives are supported by this component of the research by identifying the surfactant that displays the highest effectiveness in removing trichloroethylene (TCE) contamination from subsurface soils. The research undertaken and reported here deals with first investigating the movements of liquid through the site soil, as measured by hydraulic conductivity.

3. METHODOLOGY

The column tests are set-up and operated according to the ASTM method D 5084. (4) This method is utilized for testing undisturbed or compacted specimens with a hydraulic conductivity less than or equal to 1×10^{-3} centimeters/second (cm/s), in a flexible wall permeameter. The procedure of the column tests conducted is divided into 5 parts:

Part 1-Specimen Preparation:

The tests are conducted on soil specimens obtained from the RMI site. For specimen preparation purposes, four samples are taken and their water contents adjusted to 15.95%, 17.7%, 19.63%, and 21.67%, by the addition of a calculated amount of water. The samples are then placed in a compaction mold (4" diameter) in order to obtain the necessary soil densities (113.25 lb/ft³, 111.74 lb/ft³, 115.8 lb/ft³, and 113.47 lb/ft³ for the water contents mentioned above, respectively) corresponding to the molded water contents. After the soil is compacted, the specimens are removed from the mold and trimmed to dimensions of 4" diameter by 1" thickness.

Part 2-Column Set-Up:

The permeameter tests are set-up following a falling head approach under a steady flow rate condition.

In order to supply the permeameter cells with a constant flow rate, a syringe pump is used (kdScientific-Model 230). This pump can hold up to 10 syringes. The syringes used in the experiments have a volume of 10 milliliters (ml). With syringes this size, the pump can handle a flow rate ranging from 0.001 microliters/hour ($\mu\text{L/hr}$) to 20.91 milliliters/minute (ml/min). The syringe has 5 modes of operation: infusion, withdrawal, infusion followed by withdrawal, withdrawal followed by infusion, and continuous. The desired volume and flow rate of fluid to be injected can be entered digitally. (3)

The porous stones to be placed in the permeameters are boiled for 15 minutes to achieve saturation. One of the porous stones is placed on the base of the permeameter cell, followed by filter paper and the soil sample. Another filter paper is placed on top of the sample, followed by the second porous stone and the top cap of the permeameter. To cover the arranged specimen, a membrane is expanded by a membrane expander, placed around the specimen, and sealed to the bottom and end caps by O-rings. The flow tubing is attached to the top cap, the permeameter cell is assembled (providing a tight seal), and then filled with water. Each of the four cells are connected to a pressure board to apply the confining pressure of 8.5 psi to the cells.

After the set-up of the permeameters are completed, the experiments are conducted according to the three sequences explained in parts 3, 4, and 5.

Part 3-Flushing with DI Water (Non-Contaminated Soil):

The soil specimens in the cells are permeated with DI water in order to establish base-line conditions. The syringe pump provides an injection flow rate of 0.010 milliliters/minute (ml/min) to the cells. The DI water that has gone through the soil specimen is collected in a 30 ml sealed bottle that is connected to the outlet port of the cell. One of the lines leading to one of the cells has a water pressure gage attached to it for measuring the pressure the syringe pump applies to the liquid to be injected. With the flow rate provided, the syringe pump is capable of pumping 7 ml of liquid in 12 hours. The pump automatically stops when this is accomplished. Therefore, the syringes are then replaced with new filled ones and the process continued. During the experiment, the water collected, and the pressure gage are observed to record the amount of water and pressure of the pump. These recorded values are then used to perform mass balances and calculate the hydraulic conductivity of the soil specimen.

Part 4-Flushing with DI Water:

This sequence deals with permeating TCE-contaminated soil species in order to investigate the attenuation of TCE with water as the only permeant fluid. The procedure followed is basically the same as that explained in part 3, with the differences being that the soil is contaminated and the water collected at the outlet is analyzed for TCE [by the gas chromatograph (GC)].

Part 5-Flushing with Surfactants:

In this sequence, a surfactant solution is used as the permeating liquid to solubilize the TCE on the soil. The TCE in the solubilized form is present in the solution leaving the cell, and is collected in a sealed bottle. The TCE is then analyzed by a gas chromatograph. According to the data collected, the surfactant that reveals the best treatment efficiency is chosen.

4. WORK PERFORMED THIS PERIOD

Research undertaken during this report period dealt mainly with obtaining the permeameter cell and pump equipment, set-up of these equipments, determination of experimental protocol, and initiating testing on part 3 of the methodology mentioned above.

5. PLANS FOR NEXT PERIOD

It is anticipated that parts 3, 4, and 5 of the methodology will be completed. Before starting the last step (flushing with surfactants), the batch tests mentioned in the previous report will be accomplished, in order to make use of the results of these batch tests in the last step of the column tests. The batch tests were not completed previously, due to technical difficulties.

6. TECHNICAL DIFFICULTIES

The gas chromatograph (GC) used to analyze the samples in the experiments was required to be moved to another lab within the WVU College of Engineering, due to inadequate laboratory exhaust ventilation. Also, a computer was connected to the GC in order to achieve better results. These incidents have made the GC unavailable for use for some time, causing the delay in performing analysis of TCE batch tests. As a result of these delays, the analysis of the batch tests is approximately 3 months behind schedule. Also, the equipment ordered for the column tests had a long delay in arrival due to the United Postal Service (UPS) strike.

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DRAIN-ENHANCED SOIL FLUSHING(DEF) FOR CONTAMINANTS REMOVAL

Quarterly Report XX for Period
July 1 through September 30, 1997

Work Performed Under Contract
No. DE-FC21-92MC29467
FETC 97 Task 1.5

For:

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

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ABSTRACT

The main objective of this research is to investigate major parameters affecting the efficiency of contaminant extraction using PVD systems. The concept aims at enhancing the effectiveness of the soil flushing process by installing the PVD to shorten the drainage path of the flow and provide redundancy and wide coverage to capture the subsurface pollutants. The laboratory phase and pilot scale field test have proven the feasibility of the concept. The objective of this proposed phase is to prove and evaluate the technology performance in the field on a full scale. Hence, the overall cleanup of a chosen site in accordance with acceptable groundwater standards. In addition, a comparison with the conventional vapor extraction system, proposed at the same test site, will be conducted.

Work conducted so far on the project included laboratory tests, pilot scale testing and analytical model development. Laboratory tests included flexible wall permeability tests on soil specimens with and without a PVD installed. Bench-scale tests using large scale reactors, referred to as Smear Cells, were conducted to evaluate the equivalent diameter, long term performance, and zone of influence of the PVDs. In addition, several pilot scale Contaminant Recovery Cells (CRCs) were used to evaluate the flow characteristics of the soil samples and the concept of soil flushing using the PV drains in various installation arrangements. Sodium chloride (NaCl) tracer (100 and 1,000 mg/l) was used for discerning the concept of contaminant recovery using the PVDs system. Soil samples were prepared from sand and a mixture of 80% Ottawa sand and 20% kaolinite. An analytical model for the design of PVD systems for soil remediation was also developed. The field site selection and investigation was done following procurement of a site in Weston, WV. This site is owned by Ashland Petroleum Co. and has LNAPL and DNAPL contamination present in the groundwater. A Pilot Scale field experiment was performed to find air and fluid flowrates per PVD. Also, several grab samples were acquired during testing and tested for BTEX concentrations.

TABLE OF CONTENTS

Abstract	ii
Introduction	1
Purpose	1
Background	1
Work Performed This Period	2
Conclusions	4
Work Planned For Next Period	4

1.0 INTRODUCTION

Work in this project researches the use of Prefabricated Vertical Drain (PVD) systems for remediation of contaminated sites with fine-grained soils. PVD systems are relatively simple in operation and installation. This type of system can be expected to reduce remediation costs while at the same time increase the efficiency of the remediation effort.

Currently, PVDs are used for soil improvement and consolidation. Other than the work performed in the first two phases of this project, no research has been done to test the feasibility of using PVDs for enhanced soil flushing.

2.0 PURPOSE

The primary goal of the work performed in the past quarter was the construction and connection of the manifold network to the PVDs at the Ashland site in Weston, West Virginia. A secondary goal was the investigation of adsorption and desorption characteristics of ethylbenzene, as a representative contaminant of BTEX, using soil collected from Weston, and Tergitol as the chosen surfactant.

3.0 BACKGROUND

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

Previous work conducted on the project included laboratory tests, pilot scale testing and analytical model development. Laboratory tests included flexible wall permeability tests on soil specimens with and without a PVD installed. Bench-scale tests using large scale reactors, referred to as Smear Cells, were conducted to evaluate the equivalent diameter, long term performance, and zone of influence of the PVDs. In addition, several pilot scale Contaminant Recovery Cells (CRCs) were used to evaluate the flow characteristics of the soil samples and the concept of soil flushing using the PV drains in various installation arrangements. Sodium chloride (NaCl) tracer (100 and 1,000 mg/l) was used for discerning the concept of contaminant recovery using the PVDs system. Soil samples were prepared from sand and a mixture of 80% Ottawa sand and 20% kaolinite. An analytical model for the design of PVD systems for soil remediation was also developed. The field site selection and investigation was done following procurement of a site in Weston, WV. This site is owned by Ashland Petroleum Co. and has LNAPL and DNAPL contamination present in the groundwater. A Pilot Scale field experiment was performed to find air and fluid flowrates per PVD. Also, several grab samples were acquired during testing and tested for BTEX concentrations.

4.0 WORK PERFORMED THIS PERIOD

The primary goal of this reporting period was performing the extraction phase of soil flushing on one of the full scale pads constructed at the Weston site. Test pad 1, 18 ft x 18 ft, having seven rows with connected PVDs was split in two sections. One section containing four rows and the other section consisted of the remaining three rows.

The manner in splitting Test pad 1 was decided due to the amount of vacuum pressure required to overcome the elevation head and extract groundwater and contaminants. The PVDs throughout the Weston site, on average, were installed approximately 5m(15 ft) below the ground surface. According to previous work performed, the selected vacuum pressure required ranges from 25-30 kPa. Using the venturi vacuum system, the original pipe network plan required too much air flow for the vacuum system to create the necessary pressure, hence the change in pipe arrangement. However, it was found after the changes were made that the new set up was too much for the vacuum system also. Therefore, the running situation was altered due to time constraints brought about by the delay in the water discharge permit.

Having the split in the pipe network, two venturi vacuums were connected: one to the four-pipe and one to the three-pipe. The running plan comprised of turning on one row at a time for each vacuum system for a predetermined length of time. The length of run time for each row usually consisted of 1 or 2 hours. After each row completed the run time, it was shut off and the next row was turned on.

Due to vacuum shortages, some rows did not produce an effluent. The vacuum shortages were originally thought to be at the PVD-manifold connection but could not be solved or no apparent leaks were actually discovered at the connections. From the delay, the system remained dormant for an extended period, approximately two months. The vacuum shortages were thought to come from weathered silicone used in the sealing of the connections. The connections involving silicone were completely torn down and resealed but to no avail, the vacuum loss remains.

There are four rows holding vacuum pressure and producing effluent. Although the data obtained from the site is still being analyzed, an estimation of flowrate was generated. The average flowrate for the working rows is approximately 100 liters per hour per row or 4 ml/s per PVD which is consistent with laboratory work. Grab samples of the effluent have been taken and sent to Ashland's R&D lab for testing but no results have been obtained.

Observations of groundwater table fluctuations versus run time have been taken. Although still being analyzed, certain trends have developed which are intrinsic to the site subsurface and geology.

The secondary goal focuses on the chemical aspect of this remediation project. This quarter, the work on hydraulic conductivity was completed for the Weston site. Hydraulic conductivity tests were performed on six samples at two different water contents, 8.2% and 10.5%, and at three concentrations of surfactant, .1%, .5%, and 1%. As can be seen in the enclosed graphs, the hydraulic

conductivity decreased for samples which were compacted at a water content of 10.5%. This decrease in hydraulic conductivity can be attributed to the decrease in size of the voids within the soil sample. This decrease in void size was enough as to not allow the micelles formed within the permeant fluid to get through the soil sample. The samples which were compacted at 8.2% water content did not experience any reduction in hydraulic conductivity regardless of what concentration of surfactant was used.

Additional testing this quarter focused on the characteristics of the chosen surfactant, Tergitol when it is mixed in a variety of concentrations. Testing of this kind focused on determining the viscosity and the pH of Tergitol when mixed at various concentrations. For the viscosity tests, two tests were conducted. One test consisted of three concentrations of Tergitol, (1%, 3%, and 5%) without contamination by ethylbenzene. The other test consisted of the same concentrations of surfactant solutions, but also with an ethylbenzene contamination of 1000 ppm. As can be seen by the enclosed graphs, the viscosity was not affected by the addition of the ethylbenzene. Also of note, is the fact that the viscosity increases approximately 30% when a Tergitol solution of 5% was used.

It was speculated that the pH of the Tergitol solution was changing as the concentration of Tergitol in solution was increased. In order to investigate this idea, pH testing was performed. This included making solutions of Tergitol at different concentrations and determining their pH as well as their temperature. From the enclosed graphs, one can see that for concentrations of surfactant from 0% to 5% the pH drops from 7 to approximately 4. During this period the temperature remains relatively constant at a value of 20 C. For concentrations between 5% and 80%, the pH remains relatively constant while the temperature increases to approximately 26 C. It is suggested that during this range, the Tergitol is breaking the bond within the water molecule and releasing this energy in the form of heat.

5.0 CONCLUSIONS

The Drain Enhanced Soil Flushing technique, although still being debugged, has successful traits. These traits comprised of significant groundwater extraction, vacuum pressure, and observations of the groundwater table are the cornerstone for the soil flushing process. There are changes needed or alterations in the design, but these necessary changes will only increase efficiency and do not change the original idea.

6.0 WORK PLANNED FOR NEXT PERIOD

Injection process is to be performed during the next quarter at the Weston site. When injection will be performed will be determined using two sets of criteria: location of the groundwater table and contaminant concentration in the effluent.

Additional testing in the laboratory will consist of the completion of the batch testing at various retention times. Also, the flushing efficiency of the Tergitol solution have been started and will be completed during the next quarter. Solutions of Tergitol include concentrations of 1% and 2%.

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: July 1 - September 30, 1997

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For
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Office of Fossil Energy
Federal Energy Technology Center
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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	viii
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)	5
7.0 Conclusions (Current Period)	8
8.0 Work Planned for Next Period	8
Appendices	
A. References	9
B. Figures	11
C. Example Input data for CET93	14
D. Example output data from CET93	15

LIST OF TABLES

	<u>Page</u>
Table 6.1 Species Considered for Condensation	5
Table 6.2 Condensed Species for Scenario #1 from 1600 – 800K	6
Table 6.3 Condensed Species for Scenario #2 from 1600 – 800K	6
Table 6.4 Possible Problem Species for Scenario #1 from 1600 –800K	7
Table 6.5 Possible Problem Species for Scenario #2 from 1600 –800K	7

LIST OF FIGURES: Appendix B

	<u>Page</u>
1.0 Vortec CMS TM System Sketch	12
6.1 Illustration of the Condensed Species Inside the Recuperator	13

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

EXECUTIVE SUMMARY (current period)

The results of the research conducted under this contract was presented by Dr. Celik at the First International Conference on Incineration and Flue Gas Treatment, Organized by Sheffield University, Sheffield, UK, July 8-12, 1997. The paper was also published in the conference proceedings.

During this quarterly period progress has been made on the development of a multi - step chemical kinetic scheme for typical PCB compounds. In order to develop such a scheme, an extensive survey of past work needed to be done. The kinetic model suggested by Dr. Selim Senkan of UCLA, CA. for dichloroethane ($C_2H_4Cl_2$) was adapted. The model has the ability to simulate the destruction of the following compounds that are of interest: all of the chloromethanes; mono, di, and trichloroethane; benzene; and chlorobenzene. It also has the unique ability to predict the formation of heavy hydrocarbons, aromatics, and chloroaromatics in destruction of halocarbons.

Work has also been done on improving our predictions of condensate species inside the recuperator section. The chemical equilibrium program CET93 (McBride et al., 1994) was used to predict the condensation of salt species like NaCl, $MgCl_2$, and other similar salt species that can be found in soil. This program is currently running on UNIX systems which gives us greater flexibility in terms of the number of species and elements to be considered. Furthermore, to analyze the results from the output files of CHEMKIN the software package, Xsenkplot, has been acquired from NIST (National Institute of Standards for Technology). Xsenkplot also has the ability to study the sensitivity matrix, which aids in reducing the chemical kinetic mechanism. The Chemkin postprocessor KINALC, was also acquired from Leeds University, England, to help in the selection of the species and equations in the reduced mechanism.

The new equilibrium phase change calculations with CET93 appear to be much better than the calculations that were previously reported. CET93 had the ability to run the full H C O N Cl Si Na K Mg Ca elemental system, without memory or algorithmic errors. We were able to detect both liquid and solid phases of condensed species. Currently, six species are detected to condense inside the recuperator (not including the separate condensed phases of each species. Our communication with Vortec engineers indicate that the current results appear to agree with Vortec's own observations. Because of the small mole fractions (less than 10 PPM) of each of the species, condensation is not expected to be a problem in the recuperator in the short run.

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

The results of the research conducted under this contract was presented by Dr. Celik at the First International Conference on Incineration and Flue Gas Treatment, Organized by Sheffield University, Sheffield, UK, July 8-12, 1997. The paper was also published in the conference proceedings (see Celik et al., 1997)

During this quarterly period progress has been made on the development of a reduced multi - step chemical kinetic scheme for typical PCB compounds. In order to develop such a scheme, an extensive survey of past work needed to be done. An important piece of information from this survey came from Dr. Selim Senkan of UCLA, CA. who suggested a detailed dichloroethane ($C_2H_4Cl_2$) kinetic model which includes over 500 species, and 1200 reactions and appears to be the most up to date of all published mechanisms. (The chemical kinetics code, Chemkin II, was used by Dr. Senkan to run the model .) The model has the ability to simulate the destruction of the following compounds that are of interest: all of the chloromethanes; mono, di, and trichloroethane; benzene; and chlorobenzene. Concerning the reliability of the mechanism, the model includes the same published detailed reaction steps of methane and higher hydrocarbon oxidation and the mechanism for the rest of a C \ O \ H \ Cl system. It also has the unique ability to predict the formation of heavy hydrocarbons, aromatics, and chloroaromatics in destruction of halocarbons.

Work has also been done on improving our predictions of condensate species inside the recuperator section. The chemical equilibrium program Stanjan (Reynolds, 1986) was used to predict the condensation of salt species like NaCl, $MgCl_2$, and other similar salt species that can be found in soil. Stanjan has been successfully run on DOS. Results from these runs have been inconclusive. Because of the need for including more species and phases a similar equilibrium code CET93 (McBride et al., 1994) was purchased and made operational on our work stations. This program is currently running on UNIX systems.

The software package, Xsenkplot, has been acquired from NIST to help us in

visualizing the large output files of Chemkin. Xsenkplot also has the ability to study the sensitivity matrix, which aids in reducing the chemical kinetic mechanism. The Chemkin postprocessor KINALC, was obtained from Leeds University, England, to help in the selection of the reduction of species and equations.

6.0 RESULTS AND DISCUSSION

6.1 Equilibrium Phase Change Calculations for the Recuperator

The large temperature drop inside of the recuperator may cause some species to condense. This condensation may decrease recuperator efficiency, contribute to corrosion, and increased maintenance done on the recuperator. To analyze the recuperator section, chemical equilibrium calculations had to be performed. The software packages CET89 (PC version, NASA), CET93 (NASA), and STANJAN (Stanford Univ.) were used to perform these calculations. Several different software packages had to be used because of the complexity of the elemental system comprising more than six elements. This complex, large elemental system had two effects: 1) a large number of species had to be considered during equilibrium calculations, requiring a computer that had a large memory size; 2) an equilibrium code had to be used that could accurately predict phase changes. Preliminary calculations using CET89 or Stanjan on a PC were not successful in this respect. Attempts were made to port Stanjan to UNIX, but it could not be done due to the limited time constraints. After that, CET93 running on UNIX machines was purchased. After consultation with the Vortec engineers, the major components consisting of salts and particulate matter which might result from the remediation of contaminated soil species was determined. The species that are considered for condensation are listed in Table 6.1

Table 6.1 Species Considered for Condensation

Species Name	Chemical Formula
Magnesium Chloride	MgCl ₂
Potassium Chloride	KCl
Sodium Chloride	NaCl
Silicon Dioxide (Quartz, sand)	SiO ₂
Calcium Chloride	CaCl ₂

The amount of the possible species to be considered was assumed to be the same as the amount of particulate matter considered by Vortec's engineers. These species were distributed according to two possible scenarios, namely, (1) even mole fraction distributions, (2) SiO₂ to be 50% of the particulate matter, and even distributions of remaining salts. Unfortunately, the actual amounts of each species present in the flue gas are not known at this stage. However, sensitivity analysis can be performed by varying the concentrations. CET93 was then run at a temperature range between 1600 and 800K.

This range was determined from previous heat transfer analysis for the recuperator.

Input data for CET93 is listed in Appendix C, and output data is listed in Appendix D. The condensed species (solid and liquid) concentrations resulting from our equilibrium calculations for the two cases are shown in Tables 6.2 and 6.3, respectively. The location of the condensed species inside the recuperator is illustrated in Figure 6.1 in Appendix B.

Table 6.2 Condensed Species for Scenario #1 from 1600 – 800K

Species	1600K	1200K	800K
	Mole fraction	Mole fraction	Mole fraction
CaCO ₃ (caL)	0.0000	0.0000	1.14E-05
CaO(s)	1.08E-05	1.14E-05	0.0000
KCL(s)	0.0000	0.0000	1.67E-05
MgSiO ₃ (I)	0.0000	0.0000	1.33E-05
MgSiO ₃ (II)	0.0000	1.33E-05	0.0000
MgSiO ₃ (III)	1.33E-05	0.0000	0.0000
NaCL(s)	0.0000	0.0000	2.15E-05
SiO ₂ (Lqz)	0.0000	0.0000	7.77E-06
SiO ₂ (hqz)	7.79E-06	7.77E-06	0.0000

Table 6.3 Condensed Species for Scenario #2 from 1600 – 800K

Species	1600K	1200K	800K
	Mole fraction	Mole fraction	Mole fraction
CaCO ₃ (caL)	0.0000	0.0000	7.13E-06
CaO(s)	6.54E-06	7.12E-06	0.0000
KCL(s)	0.0000	0.0000	1.03E-05
MgSiO ₃ (I)	0.0000	0.0000	8.32E-06
MgSiO ₃ (II)	0.0000	8.32E-06	0.0000
MgSiO ₃ (III)	8.30E-06	0.0000	0.0000
NaCL(s)	0.0000	0.0000	1.34E-05
SiO ₂ (Lqz)	0.0000	0.0000	4.43E-05
SiO ₂ (hqz)	4.44E-05	4.43E-05	0.0000

The chemical equilibrium analysis also calculates certain species which may cause corrosion over a given period of time. These species are not condensed, and are species that were not previously discussed in previous reports. The possible problematic species are listed in Tables 6.4 and 6.5, for the two scenarios, respectively.

Table 6.4 Possible Problem Species for Scenario #1 from 1600 –800K

Species	1600K	1200K	800K
	Mole fraction	Mole fraction	Mole fraction
CaCL2	1.173E-07	1.168E-08	
CaO2H2	4.789E-07		
KCL	1.01E-05	1.06E-05	2.34E-07
KOH	5.500E-07	1.737E-08	
NaCL	1.28E-05	1.35E-05	8.55E-08
NaOH	7.480E-07	2.267E-08	

Table 6.5 Possible Problem Species for Scenario #2 from 1600 –800K

Species	1600K	1200K	800K
	Mole fraction	Mole fraction	Mole fraction
CaCL2	1.331E-7	1.321E-8	
CaO2H2	4.789E-7		
KCL	1.61E-05	1.69E-05	2.34E-07
KOH	8.279E-7	2.609E-8	
NaCL	2.05E-05	2.15E-05	8.55E-08
NaOH	1.126E-6	3.401E-8	

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

The new equilibrium phase change calculations with CET93 appear to be much better than the calculations that were previously reported. CET93 had the ability to run the full H C O N Cl Si Na K Mg Ca elemental system, without memory or algorithmic errors. We were able to detect both liquid and solid phases of condensed species. Currently, six species are detected to condense inside the recuperator (not including the separate condensed phases of each species). Six species are also reported to be of concern for that they may cause corrosion. Our communication with Vortec engineers indicate that the current results appear to agree with Vortec's own observations. Because of the small mole fractions (less than 10 PPM) of each of the species, condensation is not expected to be a problem in the recuperator in the short run. Long term operation of the system may result in some problems, because 10 PPM may induce fouling overtime. This conclusion was inferred from steam-water systems, in which the water must usually be cleaner than 10 PPM to avoid long term fouling.

8.0 WORK PLANNED FOR NEXT PERIOD

In the next quarterly period we shall revisit the detailed chemical kinetics mechanism that was reported in the previous quarterly. The task will be to reduce that detailed mechanism to a much simpler mechanism with 15 to 20 reactions which will involve only the major species and reactions of interest. The reduced mechanism will be validated against the detailed mechanism.

Also some transient analysis will be conducted to investigate the influence of system transients such as the change in combustion properties of contaminated soils that may lead to a fluctuation in temperature of the effluent gas entering the residence chamber. The impact of such temperature fluctuations on the conversion rate of selected PCB compounds will be investigated.

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APPENDIX B: Figures

Figure 1. Vortec's CMS™ system sketch

Figure 6.1 Illustration of the Condensed Species Inside of the Recuperator

APPENDIX C: Input file to CET93

REACTANTS

C 1.	O 1.	00	.0016	G1600	J
C 1.	O 2.	00	12.4	G1600	J
CL1.		00	.00057	G1600	J
H 1.	CL1.	00	.0347	G1600	J
H 2.		00	.000678	G1600	J
H 2.	O 1.	00	15.8	G1600	J
N 1.	O 1.	00	.0606	G1600	J
N 2.		00	69.4	G1600	J
O 1.		00	.00022	G1600	JO
O 1.	H 1.	00	.0131	G1600	JO
O 2.		00	2.34	G1600	JO
NA1.	CL1.	00	.0047	S298	J
MG1.	CL2.	00	.0047	S298	J
CA1.	CL2.	00	.0047	S298	J
K 1.	CL1.	00	.0047	S298	J
SI1.	O 2.	00	.0047	S298	J

INSERT SiO2(hqz)

INSERT MgSiO3(III)

NAMELISTS

&inpt2 kase=631,tp=t,p=1.0,t=1600,1200,800, trace=1D-07,
siunit=t, &end

APPENDIX D: Output from CET93

REACTANTS

C	1.0000	O	1.0000	0.0000	0.0000	00	0.0000	0.0016	0.000G	1600.000J
C	1.0000	O	2.0000	0.0000	0.0000	00	0.0000	12.4000	0.000G	1600.000J
CL	1.0000		0.0000	0.0000	0.0000	00	0.0000	0.0006	0.000G	1600.000J
H	1.0000	CL	1.0000	0.0000	0.0000	00	0.0000	0.0347	0.000G	1600.000J
H	2.0000		0.0000	0.0000	0.0000	00	0.0000	0.0007	0.000G	1600.000J
H	2.0000	O	1.0000	0.0000	0.0000	00	0.0000	15.8000	0.000G	1600.000J
N	1.0000	O	1.0000	0.0000	0.0000	00	0.0000	0.0606	0.000G	1600.000J
N	2.0000		0.0000	0.0000	0.0000	00	0.0000	69.4000	0.000G	1600.000J
O	1.0000		0.0000	0.0000	0.0000	00	0.0000	0.0002	0.000G	1600.000JO
O	1.0000	H	1.0000	0.0000	0.0000	00	0.0000	0.0131	0.000G	1600.000JO
O	2.0000		0.0000	0.0000	0.0000	00	0.0000	2.3400	0.000G	1600.000JO
NA	1.0000	CL	1.0000	0.0000	0.0000	00	0.0000	0.0047	0.000S	298.000J
MG	1.0000	CL	2.0000	0.0000	0.0000	00	0.0000	0.0047	0.000S	298.000J
CA	1.0000	CL	2.0000	0.0000	0.0000	00	0.0000	0.0047	0.000S	298.000J
K	1.0000	CL	1.0000	0.0000	0.0000	00	0.0000	0.0047	0.000S	298.000J
SI	1.0000	O	2.0000	0.0000	0.0000	00	0.0000	0.0047	0.000S	298.000J

INSERT SiO2(hqz)
 INSERT MgSiO3(III)

NAMELISTS

INPT2

KASE = 631 IDEBUG = 0 TRACE = 0.10000D-06 IONS = F SIUNIT = T

TP = T HP = F SP = F TV = F UV = F SV = F RKT = F SHOCK = F DETN = F

TRANSPT = F

OF = F FA = F FPCT = F ERATIO = F PHI = F

S0 = 0.000000000E+00 UR = 0.000000000E+00 HR = 0.000000000E+00

P = 0.100000E+01

NSQM = F PSIA = F INHG = F MMHG = F ATM = F BAR = T

T = 1.600000E+03 1.200000E+03 8.000000E+02

NO INPT2 VALUE GIVEN FOR OF, EQRAT, FA, OR FPCT

MIX = 0.000000E+00

SPECIES BEING CONSIDERED IN THIS SYSTEM

L11/88 C	J12/69 CCL	J12/68 CCL2
J 6/70 CCL3	L12/81 CCL4	TPIS79 CH
TPIS79 CHCL	X 6/81 CHCL3	L11/89 CH2
L12/81 CH2CL2	L11/89 CH3	L12/81 CH3CL
L12/92 CH2OH	L10/92 CH3O	L 8/88 CH4
L 8/88 CH3OH	TPIS91 CN	L12/89 CNN
TPIS79 CO	J12/65 COCL	TPIS91 COCL2
L 7/88 CO2	TPIS91 COOH	TPIS91 C2
J12/68 C2CL2	L10/87 C2CL4	L10/87 C2CL6
L 1/91 C2H	TPIS91 C2HCL	L 6/89 CHCO,ketyl
L 1/91 C2H2,acetylene	L12/89 C2H2,vinylidene	L 5/90 CH2CO,ketene
L 2/92 C2H3,vinyl	L12/92 CH3CN	BUR 84 CH3CO,acetyl
L 1/91 C2H4	L 8/88 C2H4O,ethylen o	L 8/88 CH3CHO,ethanal
L 8/88 CH3COOH	BUR 92 (HCOOH)2	L12/92 C2H5
L 8/88 C2H6	L 8/88 CH3N2CH3	L12/92 CH3OCH3
L 8/88 C2H5OH	L12/92 CCN	TPIS91 CNC
TPIS79 C2N2	L12/89 C2O	TPIS79 C3
BUR 92 C3H3,propargyl	L12/92 C3H4,allene	L12/92 C3H4,propyne
L 5/90 C3H4,cyclo-	BUR 92 C3H5,allyl	L 7/90 C3H6,propylene
L 1/93 C3H6,cyclo-	L 6/90 C3H6O	L 6/90 C3H7,n-propyl
L 9/85 C3H7,i-propyl	L 6/90 C3H8	L 9/88 C3H8O,1propanol
L 9/88 C3H8O,2propanol	L 7/88 C3O2	L 7/88 C4
L 2/93 C4H2	L 5/90 C4H4,1,3-cyclo-	X10/92 C4H6,butadiene
X10/88 C4H6,2-butyne	L 5/90 C4H6,cyclo-	X 4/88 C4H8,1-butene
X 4/88 C4H8,cis2-buten	X 4/88 C4H8,tr2-butene	X 4/88 C4H8,isobutene
L 5/90 C4H8,cyclo-	L 6/90 (CH3COOH)2	X10/84 C4H9,n-butyl
X10/84 C4H9,i-butyl	L 1/93 C4H9,s-butyl	L 1/93 C4H9,t-butyl
L 6/90 C4H10,isobutane	L 6/90 C4H10,n-butane	J 3/61 C4N2
L 7/88 C5	L 5/90 C5H6,1,3cyclo-	L 1/93 C5H8,cyclo-
X 4/87 C5H10,1-pentene	L 6/90 C5H10,cyclo-	X10/84 C5H11,pentyl
L 1/93 C5H11,t-pentyl	X10/85 C5H12,n-pentane	X10/85 C5H12,i-pentane
X10/85 CH3C(CH3)2CH3	L 2/93 C6H2	L 1/91 C6H5,phenyl
L 6/90 C6H5O,phenoxy	L 1/91 C6H6	L 6/90 C6H5OH,phenol
L 1/93 C6H10,cyclo-	X 4/87 C6H12,1-hexene	L 6/90 C6H12,cyclo-
X10/83 C6H13,n-hexyl	L 1/93 C7H7,benzyl	L 1/93 C7H8
L 1/93 C7H8O,cresol mx	X 4/87 C7H14,1-heptene	X10/83 C7H15,n-heptyl
X10/85 C7H16,n-heptane	X 4/89 C8H8,styrene	X10/86 C8H10,ethylbenz
X 4/87 C8H16,1-octene	X10/83 C8H17,n-octyl	X 4/85 C8H18,isooctane
X 4/85 C8H18,n-octane	X10/83 C9H19,n-nonyl	L 8/93 C10H8,naphthale
X10/83 C10H21,n-decyl	L12/84 C12H9,o-bipheny	L12/84 C12H10,bipheny

L 6/88 Jet-A(g)	L 3/93 Ca	J 6/70 CaCL
J 6/70 CaCL ₂	J12/74 CaO	J12/75 CaOH
J12/75 CaO ₂ H ₂	J 9/83 Ca ₂	J 6/82 CL
J 6/66 CLCN	J 6/61 CLO	L 7/93 CLO ₂
TPIS89 CL ₂	J12/65 CL ₂ O	L 5/93 H
L 7/88 HCN	L12/89 HCO	TPIS91 HCCN
J 9/64 HCL	L11/92 HNC	J12/70 HNCO
L12/89 HNO	TPIS89 HNO ₂	L 4/90 HNO ₃
J 3/79 HOCL	L 5/89 HO ₂	TPIS78 H ₂
L 8/88 HCHO,formaldehy	L 8/88 HCOOH	L 8/89 H ₂ O
L 2/93 H ₂ O ₂	L 8/88 (HCOOH) ₂	L 4/93 K
J 3/66 KCN	J 3/66 KCL	J 3/63 KH
J12/67 KO	J12/70 KOH	J12/83 K ₂
J 3/66 K ₂ C ₂ N ₂	J 3/66 K ₂ CL ₂	J12/70 K ₂ O ₂ H ₂
J 9/83 Mg	J 3/66 MgCL	J12/69 MgCL ₂
J12/66 MgH	J 3/64 MgN	J12/74 MgO
J12/75 MgOH	J12/75 MgO ₂ H ₂	J 9/83 Mg ₂
L 6/88 N	L12/89 NCO	L11/89 NH
L12/89 NH ₂	TPIS89 NH ₃	TPIS89 NH ₂ OH
TPIS89 NO	L12/86 NOCL	L 7/88 NO ₂
L12/86 NO ₂ CL	J12/64 NO ₃	TPIS78 N ₂
L12/89 NCN	L 5/90 N ₂ H ₂	TPIS89 NH ₂ NO ₂
L 5/90 N ₂ H ₄	L 7/88 N ₂ O	L 4/90 N ₂ O ₃
TPIS89 N ₂ O ₄	L 4/90 N ₂ O ₅	TPIS89 N ₃
L 7/88 N ₃ H	L 4/93 Na	J3/66 NaCN
J12/64 NaCL	J 3/63 NaH	J12/67 NaO
J12/70 NaOH	J12/83 Na ₂	J 3/66 Na ₂ C ₂ N ₂
J12/64 Na ₂ CL ₂	L10/74 Na ₂ O	J12/70 Na ₂ O ₂ H ₂
L 1/90 O	TPIS78 OH	TPIS89 O ₂
L 5/90 O ₃	J 3/83 Si	J 3/67 SiC
J 3/67 SiC ₂	J12/60 SiC ₄ H ₁₂	J12/76 SiCL
J12/77 SiCL ₂	J12/77 SiCL ₃	J12/70 SiCL ₄
J12/76 SiH	J12/76 SiHCL ₃	TPIS79 SiH ₂
J12/76 SiH ₂ CL ₂	TPIS79 SiH ₃	J12/76 SiH ₃ CL
J 6/76 SiH ₄	J 3/67 SiN	J 9/67 SiO
J 9/67 SiO ₂	J 3/67 Si ₂	J 3/67 Si ₂ C
J 3/67 Si ₂ N	J 3/67 Si ₃	X 4/83 C(gr)
X10/86 C ₆ H ₆ (L)	X10/86 C ₇ H ₈ (L)	X10/76 C ₈ H ₁₈ (L),n-octa
L 6/88 Jet-A(L)	SRD 93 Ca(a)	SRD 93 Ca(b)
SRD 93 Ca(L)	BAR 89 CaCO ₃ (caL)	J 6/70 CaCL ₂ (s)
J 6/70 CaCL ₂ (L)	J 6/73 CaO(s)	J 6/73 CaO(L)
J12/75 CaO ₂ H ₂ (s)	L 8/89 H ₂ O(s)	L 8/89 H ₂ O(L)
CODA89 K(cr)	CODA89 K(L)	J 3/66 KCN(s)
J 3/66 KCN(L)	J 3/66 KCL(s)	J 3/66 KCL(L)
J12/70 KOH(a)	J12/70 KOH(b)	J12/70 KOH(L)
J 6/71 KO ₂ (s)	J 3/66 K ₂ CO ₃ (s)	J 3/66 K ₂ CO ₃ (L)

J 6/63 K2O(s)	J 9/63 K2O2(s)	SRD 93 Mg(cr)
SRD 93 Mg(L)	J12/66 MgCO3(s)	J12/65 MgCL2(s)
J12/65 MgCL2(L)	J12/74 MgO(s)	J12/74 MgO(L)
J12/75 MgO2H2(s)	J12/67 MgSiO3(I)	J12/67 MgSiO3(II)
J12/67 MgSiO3(III)	J12/67 MgSiO3(L)	J12/67 Mg2SiO4(s)
J12/67 Mg2SiO4(L)	BAR 73 NH4CL(a)	BAR 73 NH4CL(b)
CODA89 Na(cr)	CODA89 Na(L)	J 3/66 NaCN(s)
J 3/66 NaCN(L)	J 9/64 NaCL(s)	J 9/64 NaCL(L)
J12/70 NaOH(a)	J12/70 NaOH(L)	J 6/63 NaO2(s)
J 3/66 Na2CO3(I)	J 3/66 Na2CO3(II)	J 3/66 Na2CO3(L)
J 6/68 Na2O(c)	J 6/68 Na2O(a)	J 6/68 Na2O(L)
J 6/68 Na2O2(a)	J 6/68 Na2O2(b)	TPIS91 Si(cr)
TPIS91 Si(L)	J 3/67 SiC(b)	J 6/67 SiO2(Lqz)
J 6/67 SiO2(hqz)	J 6/67 SiO2(L)	L 1/84 Si2N2O(s)
J 3/67 Si3N4(a)		
SiO2(hqz)	INSERTED	
MgSiO3(III)	INSERTED	

OF = 0.024082

	EFFECTIVE FUEL	EFFECTIVE OXIDANT	MIXTURE
ENTHALPY	HPP(2)	HPP(1)	HSUB0
(KG-MOL)(DEG K)/KG	-0.18917605E+03	0.16863998E+03	-0.18076181E+03

KG-FORM.WT./KG	B0P(I,2)	B0P(I,1)	B0(I)
C	0.28838291E-02	0.00000000E+00	0.28160143E-02
O	0.14764152E-01	0.62481723E-01	0.15886258E-01
CL	0.13248651E-04	0.00000000E+00	0.12937101E-04
H	0.17966243E-01	0.32730597E-03	0.17551454E-01
N	0.50723431E-01	0.00000000E+00	0.49530640E-01
Na	0.82295959E-06	0.00000000E+00	0.80360723E-06
Mg	0.50515268E-06	0.00000000E+00	0.49327372E-06
Ca	0.43336021E-06	0.00000000E+00	0.42316949E-06
K	0.64513941E-06	0.00000000E+00	0.62996859E-06
Si	0.80047183E-06	0.00000000E+00	0.78164827E-06

POINT ITN	T	C	O	CL	H
	N	NA	MG	CA	K
	SI				
1 33	1600.000	-30.750	-15.962	-25.542	-15.097
	-13.309	-30.393	-39.670	-38.574	-34.286
	-47.898				
ADD CaO(s)					
1 3	1600.000	-30.750	-15.962	-25.527	-15.097
	-13.309	-30.407	-39.670	-41.506	-34.300
	-47.898				

PHASE CHANGE, REPLACE MgSiO3(III) WITH MgSiO3(II)

2	4	1200.000	-40.160	-15.501	-24.270	-17.822
		-12.879	-35.143	-54.840	-56.474	-39.866
		-69.829				

PHASE CHANGE, REPLACE SiO2(hqz) WITH SiO2(Lqz)

PHASE CHANGE, REPLACE MgSiO3(II) WITH MgSiO3(I)

3	7	800.000	-59.370	-14.954	-22.175	-23.529
		-12.362	-47.458	-85.900	-87.153	-53.181
		-114.393				

ADD CaCO3(caL)

3	4	800.000	-64.946	-14.915	-22.116	-23.509
		-12.323	-47.476	-85.940	-87.192	-53.197
		-114.472				

REMOVE CaO(s)

3	7	800.000	-59.370	-14.954	-22.175	-23.529
		-12.362	-47.458	-85.900	-92.650	-53.181
		-114.393				

ADD NaCL(s)

3	3	800.000	-59.370	-14.954	-22.175	-23.529
		-12.362	-50.598	-85.900	-92.650	-53.181
		-114.393				

ADD KCL(s)

3	3	800.000	-59.370	-14.954	-22.175	-23.529
		-12.362	-50.598	-85.900	-92.650	-55.732
		-114.393				

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED
TEMPERATURE AND PRESSURE

CASE NO. 631

CHEMICAL FORMULA

			WT FRACTION	ENERGY	STATE	TEMP
			(SEE NOTE)	KJ/KG-MOL		DEG K
FUEL	C	1.00000	O 1.00000			
			.0000164	-68197.750	G	1600.00
FUEL	C	1.00000	O 2.00000			
			0.126891	-326041.750	G	1600.00
FUEL	CL	1.00000				
			.0000058	150247.531	G	1600.00
FUEL	H	1.00000	CL 1.00000			
			0.000355	-51387.051	G	1600.00

FUEL	H	2.00000				
			.0000069	39589.480	G	1600.00
FUEL	H	2.00000	O	1.00000		
				0.161684	-188802.938	G 1600.00
FUEL	N	1.00000	O	1.00000		
				0.000620	134549.531	G 1600.00
FUEL	N	2.00000				
				0.710180	41861.203	G 1600.00
OXIDANT	O	1.00000				
				.0000935	276559.375	G 1600.00
OXIDANT	O	1.00000	H	1.00000		
				0.005567	79533.344	G 1600.00
OXIDANT	O	2.00000				
				0.994340	44233.074	G 1600.00
FUEL	NA	1.00000	CL	1.00000		
				.0000481	-411138.781	S 298.00
FUEL	MG	1.00000	CL	2.00000		
				.0000481	-641632.625	S 298.00
FUEL	CA	1.00000	CL	2.00000		
				.0000481	-795823.438	S 298.00
FUEL	K	1.00000	CL	1.00000		
				.0000481	-436701.688	S 298.00
FUEL	SI	1.00000	O	2.00000		
				.0000481	-910863.688	S 298.00

O/F= 0.024082 % FUEL= 97.648445 EQUIVALENCE RATIO= 0.906764 PHI=-0.011143

THERMODYNAMIC PROPERTIES

P, BAR	1.0000	1.0000	1.0000
T, DEG K	1600.00	1200.00	800.00
RHO, KG/CU M	2.0258-1	2.7011-1	4.0519-1
H, KJ/KG	-1503.40	-2084.97	-2625.27
U, KJ/KG	-1997.04	-2455.18	-2872.07
G, KJ/KG	-16825.9	-13075.7	-9515.54
S, KJ/(KG)(K)	9.5765	9.1589	8.6128

M, MOL WT	26.949	26.950	26.952
(DLV/DLP)T	-1.00002	-1.00000	-1.00000
(DLV/DLT)P	1.0007	1.0000	1.0000
CP, KJ/(KG)(K)	1.5038	1.4050	1.2886
GAMMA (S)	1.2586	1.2814	1.3148
SON VEL,M/SEC	788.2	688.7	569.6

MOLE FRACTIONS

CO	1.079 -5	9.377 -9	6.594-15
CO2	7.5876-2	7.5890-2	7.5880-2
CaCL2	1.331 -7	1.321 -8	3.900-13
CaO2H2	4.789 -7	6.501-10	4.487-18
CL	3.9582-6	3.6338-7	3.1580-9
CL2	1.2976-9	5.9122-9	1.1404-7
H	1.817 -7	2.878-11	8.527-19
HCL	3.0772-4	3.0968-4	3.0979-4
H2	1.118 -5	2.127 -8	8.667-14
H2O	2.3625-1	2.3635-1	2.3635-1
KCL	1.6149-5	1.6906-5	2.3364-7
KOH	8.279 -7	2.609 -8	3.765-13
NO	5.4494-4	5.5456-5	5.6857-7
NO2	6.7414-7	2.8974-7	5.4259-8
N2	6.6711-1	6.6739-1	6.6742-1
NaCL	2.0511-5	2.1510-5	8.5484-8
NaOH	1.126 -6	3.401 -8	1.294-13
O	2.034 -6	3.538 -9	1.128-14
OH	1.505 -4	2.554 -6	7.447-10
O2	1.9664-2	1.9938-2	1.9966-2
CaCO3(caL)	0.0000 0	0.0000 0	1.1404-5
CaO(s)	1.0792-5	1.1391-5	0.0000 0
KCL(s)	0.0000 0	0.0000 0	1.6659-5
MgSiO3(I)	0.0000 0	0.0000 0	1.3294-5
MgSiO3(II)	0.0000 0	1.3294-5	0.0000 0
MgSiO3(III)	1.3278-5	0.0000 0	0.0000 0
NaCL(s)	0.0000 0	0.0000 0	2.1535-5
SiO2(Lqz)	0.0000 0	0.0000 0	7.7717-6
SiO2(hqz)	7.7858-6	7.7716-6	0.0000 0

PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS
WERE LESS THAN 1.000000E-07 FOR ALL ASSIGNED CONDITIONS

C	CCL	CCL2	CCL3
CCL4	CH	CHCL	CHCL3
CH2	CH2CL2	CH3	CH3CL
CH2OH	CH3O	CH4	CH3OH
CN	CNN	COCL	COCL2
COOH	C2	C2CL2	C2CL4
C2CL6	C2H	C2HCL	CHCO,ketyl
C2H2,acetylene	C2H2,vinylidene	CH2CO,ketene	C2H3,vinyl
CH3CN	CH3CO,acetyl	C2H4	C2H4O,ethylen o
CH3CHO,ethanal	CH3COOH	(HCOOH)2	C2H5
C2H6	CH3N2CH3	CH3OCH3	C2H5OH
CCN	CNC	C2N2	C2O

C3	C3H3,propargyl	C3H4,allene	C3H4,propyne
C3H4,cyclo-	C3H5,allyl	C3H6,propylene	C3H6,cyclo-
C3H6O	C3H7,n-propyl	C3H7,i-propyl	C3H8
C3H8O,1propanol	C3H8O,2propanol	C3O2	C4
C4H2	C4H4,1,3-cyclo-	C4H6,butadiene	C4H6,2-butyne
C4H6,cyclo-	C4H8,1-butene	C4H8,cis2-buten	C4H8,tr2-butene
C4H8,isobutene	C4H8,cyclo-	(CH3COOH)2	C4H9,n-butyl
C4H9,i-butyl	C4H9,s-butyl	C4H9,t-butyl	C4H10,isobutane
C4H10,n-butane	C4N2	C5	C5H6,1,3cyclo-
C5H8,cyclo-	C5H10,1-pentene	C5H10,cyclo-	C5H11,pentyl
C5H11,t-pentyl	C5H12,n-pentane	C5H12,i-pentane	CH3C(CH3)2CH3
C6H2	C6H5,phenyl	C6H5O,phenoxy	C6H6
C6H5OH,phenol	C6H10,cyclo-	C6H12,1-hexene	C6H12,cyclo-
C6H13,n-hexyl	C7H7,benzyl	C7H8	C7H8O,cresol mx
C7H14,1-heptene	C7H15,n-heptyl	C7H16,n-heptane	C8H8,styrene
C8H10,ethylbenz	C8H16,1-octene	C8H17,n-octyl	C8H18,isooctane
C8H18,n-octane	C9H19,n-nonyl	C10H8,naphthale	C10H21,n-decyl
C12H9,o-bipheny	C12H10,bipheny	Jet-A(g)	Ca
CaCL	CaO	CaOH	Ca2
CLCN	CLO	CLO2	CL2O
HCN	HCO	HCCN	HNC
HNCO	HNO	HNO2	HNO3
HOCL	HO2	HCHO,formaldehy	HCOOH
H2O2	(HCOOH)2	K	KCN
KH	KO	K2	K2C2N2
K2CL2	K2O2H2	Mg	MgCL
MgCL2	MgH	MgN	MgO
MgOH	MgO2H2	Mg2	N
NCO	NH	NH2	NH3
NH2OH	NOCL	NO2CL	NO3
NCN	N2H2	NH2NO2	N2H4
N2O	N2O3	N2O4	N2O5
N3	N3H	Na	NaCN
NaH	NaO	Na2	Na2C2N2
Na2CL2	Na2O	Na2O2H2	O3
Si	SiC	SiC2	SiC4H12
SiCL	SiCL2	SiCL3	SiCL4
SiH	SiHCL3	SiH2	SiH2CL2
SiH3	SiH3CL	SiH4	SiN
SiO	SiO2	Si2	Si2C
Si2N	Si3	C(gr)	C6H6(L)
C7H8(L)	C8H18(L),n-octa	Jet-A(L)	Ca(a)
Ca(b)	Ca(L)	CaCL2(s)	CaCL2(L)
CaO(L)	CaO2H2(s)	H2O(s)	H2O(L)
K(cr)	K(L)	KCN(s)	KCN(L)
KCL(L)	KOH(a)	KOH(b)	KOH(L)

KO ₂ (s)	K ₂ CO ₃ (s)	K ₂ CO ₃ (L)	K ₂ O(s)
K ₂ O ₂ (s)	Mg(cr)	Mg(L)	MgCO ₃ (s)
MgCL ₂ (s)	MgCL ₂ (L)	MgO(s)	MgO(L)
MgO ₂ H ₂ (s)	MgSiO ₃ (L)	Mg ₂ SiO ₄ (s)	Mg ₂ SiO ₄ (L)
NH ₄ CL(a)	NH ₄ CL(b)	Na(cr)	Na(L)
NaCN(s)	NaCN(L)	NaCL(L)	NaOH(a)
NaOH(L)	NaO ₂ (s)	Na ₂ CO ₃ (I)	Na ₂ CO ₃ (II)
Na ₂ CO ₃ (L)	Na ₂ O(c)	Na ₂ O(a)	Na ₂ O(L)
Na ₂ O ₂ (a)	Na ₂ O ₂ (b)	Si(cr)	Si(L)
SiC(b)	SiO ₂ (L)	Si ₂ N ₂ O(s)	Si ₃ N ₄ (a)

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

FOCUS AREA 3.0

Decontamination & Decommissioning

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

FETC Task No. 3.1

Quarterly Technical Progress Report
Reporting Period:

July 1,1997 to September 30,1997

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
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October 1997

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ABSTRACT

The objectives of this project are to prepare and to evaluate biosorbents and cleaning solutions that may be useful in the decontamination and decommissioning (D&D) of U.S. Department of Energy facilities. In this collaborative project, the Institute of Gas Technology will make available to researchers at West Virginia University (WVU) biosorbents and cleaning solutions that are useful for D&D activities, but require filtration/liquid processing in order to be used in a practical process. Filtration tests will be performed by WVU.

Previous studies have identified surfactant solutions which are good for the desorption of polyaromatic hydrocarbons (PAHs) from soils, and during this quarter additional contaminant desorption studies were performed to determine the ability of surfactants to desorb petroleum hydrocarbons from contaminated soil and to further refine the choice of surfactants for use in environmental remediation applications. The surfactants that are being studied focus on those which gave the best results for contaminant desorption, but those that are considered food grade surfactants are of particular interest as they should readily receive regulatory approval for use in environmental remediation applications. The surfactants being studied include DXP135, DXP207, MA80-I, Rewoteric AMB14, Standapol ES2, Witconol 2722, and Witcamide 5085. Based on the contaminant desorption data obtained thus far it was suggested that for PAH desorption DXP135, DXP207, and Witcamide 5085 show the best performance. However, of these only DXP135 can be classified as a food grade surfactant and is relatively inexpensive compared to the other products. Unfortunately, while Witcamide 5085 desorbs PAHs well it is considered to be relatively toxic and will no longer be included in these investigations. Witconol 2722 and MA80-I are also food grade surfactants. Additional contaminant desorption tests were performed to determine the ability of DXP135 and blends of DXP135 plus other surfactants to desorb PAHs and total petroleum hydrocarbons from several contaminated soils. DXP135 in ethanol-based solutions appears to yield the best performance for the desorption of PAHs from coal tar-contaminated soil from a former manufactured gas plant site, while Witconol 2722 in water-based solutions yields the best performance for the desorption of petroleum hydrocarbons from soil.

Preliminary results of surfactant biodegradation tests indicate that surfactants present at high concentrations (500ppm) are generally inhibitory to microbial growth. Mixtures of two or more surfactants uniformly yields greater inhibition of bacterial growth. Enrichment culture techniques were used to obtain bacterial cultures which are adapted to utilize/tolerate high concentrations of surfactants. Bacterial cultures which can tolerate high concentrations of surfactants were used to examine the biodegradation of PAHs present in surfactant/contaminant mixtures. Excellent rates and extents of PAH biodegradation were obtained even in the presence of 2,000 ppm surfactant; however, the amount of surfactant biodegradation was minor. These results show that contaminants present in contaminant/surfactant mixtures can be efficiently biodegraded, but the biodegradation of surfactants is significantly slower and less complete. This would suggest the possible use of a biotreatment step to degrade contaminants in contaminant/surfactant mixtures so that the surfactant solution can be reused. These results also indicate that the biodegradation of residual surfactants used in environmental remediation processes could be problematic.

Additionally during the past quarter metal binding tests were performed with several biosorbent materials prepared from byproducts of the paper and food processing industries. Previous tests have shown that removal by biosorbents of many metals from simulated D&D wastewater is quite good. However the removal of strontium is problematic. To address this issue several additional lignin byproduct samples were obtained and tested for their ability to remove radioactive strontium from an actual contaminated wastewater sample obtained from the West Valley Nuclear facility. Two of the industrial byproduct samples in particular (Marasperse CBA-1 and Borresal HA-1) showed excellent removal of radioactivity from this wastewater (100% and 86% respectively) and offer real potential for use in conjunction with ultrafiltration for the treatment of wastewater.

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.....	4
6.0 Results and Discussion	4
7.0 Conclusions.....	11
8.0 Work Planned for Next Period.....	11

1.0 Introduction

The decontamination and decommissioning (D&D) of the Department of Energy facilities can result in the production of large volumes of wastewater containing metals, radionuclides, organic contaminants, and particulate material. Treatment of these wastewater streams is highly problematic because of their complexity and toxicity. Treatments appropriate for the removal of particulate material, such as filtration, are generally ineffective for the removal of soluble contaminants in D&D wastes such as metals and radionuclides. Techniques commonly used for the removal of metals and radionuclides from wastewater include the use of ion exchange resins; however, particulate material and organic contaminants present in D&D waste are incompatible with the use of ion exchange columns because of plugging/fouling. Biosorbents are biologically derived substances that can be used to sorb metals/radionuclides in a manner analogous to ion exchange resins, and biosorbents may be inexpensive in comparison with ion exchange resins.

The approach that is being tested in this project is the use of biosorbents, in a powdered form, added directly to D&D wastewater for the removal of metals and radionuclides. The use of biosorbents as powders rather than as ion exchange columns avoids the plugging/fouling problems associated with ion exchange columns. Also the powdered biosorbent should provide better contact and therefore more rapid metal/radionuclide binding than with ion exchange columns or immobilized biosorbent columns. D&D wastewaters require filtration in order to remove particulates and the same filtration step can be used to remove biosorbent particles and metals/radionuclides bound to them. It is expected that this approach will simplify and decrease the cost of treatment of D&D wastewater.

A related issue in D&D activities is the use of effective cleaning solutions, and the ultimate fate of used/spent cleaning solutions. The Institute of Gas Technology (IGT) has developed novel surfactant formulations that are highly efficient in the removal of organic and inorganic contaminants from solids. Ordinarily surfactants are discarded in spent D&D solutions. However, these surfactants can inhibit the subsequent treatment of these solutions and if not completely destroyed can contribute to the mobility of contaminants and thereby pose an environmental risk. This project will examine the possibility of using filtration to remove surfactants from D&D solutions, and possibly aid in the recovery/reuse of those surfactants, as well as aid in the treatment of D&D wastewater. A related issue is the biodegradation of surfactants and surfactant/contaminant mixtures. The biodegradation of surfactants is crucial to insure that after remediation that contaminant-laden surfactant solutions can be efficiently and effectively decontaminated and that residual surfactants and contaminants will be destroyed restoring the soil to a pristine state.

2.0 Purpose

The purpose of this project is to evaluate the use of biosorbents in conjunction with filtration to treat D&D wastewater. An additional purpose of the project is to evaluate the removal of surfactants from D&D solutions by biodegradation and by filtration.

3.0 Background

IGT has experience in the production and use of biosorbents, and in the production and use of surfactants for removing contaminants from solids. The West Virginia University (WVU) has experience in filtration and possesses a bench-scale model of a novel centrifugal filtration device developed by SpinTek Corporation. IGT and WVU are collaborating on this project to combine their areas of expertise to develop improved processes for the treatment of D&D wastewater.

4.0 Methodology

Bacterial Strains and Culture Media

Escherichia coli (ATCC 23724) was grown in nutrient broth (Difco) while *Zoogloea ramigera* 115 (ATCC 25935) was grown in nutrient broth supplemented with 25 g glucose per liter. Cultures were incubated at 30°C and the production of exopolysaccharide by *Z. ramigera* was monitored spectrophotometrically, and by measuring the viscosity of the medium. *Z. ramigera* cultures were harvested when viscosities exceeding 600 centipoise were achieved.

Immobilization of Dried Biomass

Biomass (cells plus exopolysaccharides if present) was harvested by centrifugation at 10,000 X g for 10 minutes and dried under vacuum in a rotary evaporator at 65°C. The dried biomass was ground to a uniform fine powder using a mortar and pestle. Dried, powdered biomass was used as is for metal-binding experiments.

Industrial Byproducts

Protein samples were obtained from American Protein Corp. (Ames, IA), while lignin products were obtained from Lignotech USA (Rothschild, WI) and Repap Technologies (Valley Forge, PA). These products were used as received from the suppliers in metal binding tests.

Analytical Procedures

Atomic Absorption Spectrophotometry (AAS) (Model: 403, Perkin-Elmer Co.) Inductively Coupled Plasmic Emission Spectroscopy (ICPAES) (Model: Atom Scan 25, Thermo Jaorell Ash Co.) and ion exchange chromatography (Model DX-100, Dionex Corp.) were used for metal concentration analyses. Samples were diluted to 0.1-1.0 ppm to ensure accurate analysis. To remove the interference from suspended particles, samples were centrifuged (600 rpm, 5 min) and filtered by a 0.45-µm filter before injection into the AAS, ion exchange chromatography, or ICPAES apparatus. Radioactivity was quantified using a scintillation counter programmed to monitor the emission spectrum of the radionuclide(s) of interest.

Metal Adsorption Studies

Batch studies were performed using 100 mg of biomass in a 250-ml Erlenmeyer shaker flask containing 100 ml of 10 to 100 ppm metal solution (adjusted to pH 6.0 or 4.0 using HCl) and shaken for 15 minutes to 24 hours at a speed of 160 rpm at room temperature. Biomass was removed by centrifugation, the supernatant was decanted, filtered, and metal ions were then analyzed by AAS, ion exchange chromatography, or ICPAES.

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 biodegradability of various surfactants was investigated, additional contaminant desorption tests were performed using various surfactants, and metal binding tests were performed using biosorbents prepared from byproducts of the paper and food industries. These metal binding experiments were performed using wastewaters obtained from an actual nuclear industry operation.

6.0 Results and Discussion

The surfactants that are being studied focus on those which gave the best results for contaminant desorption, but those that are considered food grade surfactants are of particular interest as they should readily receive regulatory approval for use in environmental remediation applications. The surfactants being studied include DXP135, DXP207, MA80-I, Rewoteric AMB14, Standapol ES2, Witconol 2722, and Witcamide 5085. Based on the contaminant desorption data obtained thus far it was suggested that for PAH desorption DXP135, DXP207, and Witcamide 5085 show the best performance. However, of these only DXP135 can be classified as a food grade surfactant and is relatively inexpensive compared to the other products. Unfortunately, while Witcamide 5085 desorbs PAHs well it is considered to be relatively toxic and will no longer be included in these investigations. Witconol 2722 and MA80-I are also food grade surfactants. Additional contaminant desorption tests were performed to determine the ability of DXP135 and blends of DXP135 plus other surfactants to desorb PAHs and total petroleum hydrocarbons from two contaminated soils: a coal tar contaminated soil from a former manufactured gas plant site, and a petroleum hydrocarbon contaminated soil from a natural gas exploration and production site. Figure 1 illustrates the results of desorption experiments with exploration and production (E&P) site soil #3. The surfactant solutions tested contained 4% surfactant in the presence of 40% ethanol with the exception of some solutions which were prepared using water, which are indicated as, (W), in Figure 1. The best desorption of petroleum hydrocarbons from this soil was obtained with water-based solutions and Witconol 2722 yielded the best results with about 44% desorption. This is in contrast to the results shown in Figures 2 and 3 in which PAH desorption from coal tar contaminated soil from the Vandalia MGP site was tested. These results show that as much as 90% removal of PAHs from this soil can be obtained and that ethanol-based solutions containing DXP135 yield the best results. Blends of surfactants which contain DXP135 plus other surfactants yield no significant improvements.

It seems then, that for the desorption of petroleum hydrocarbons aqueous solutions of Witconol 2722 are best, but for PAH desorption ethanol solutions of DXP135 are best.

Figure 1.

Figure 2.

Figure 3.

It has been found that the best biodegradation of surfactants is obtained at concentrations below cmc, while surfactant concentrations above cmc can be inhibitory to bacteria; however, surfactants have the greatest capacity to solubilize contaminants when present at concentrations above the cmc. Preliminary results of surfactant biodegradation tests indicate that surfactants at concentrations greater than 500 ppm are generally inhibitory. Mixtures of two or more surfactants uniformly yields greater inhibition of bacterial growth. Nonetheless, enrichment culture techniques were used to obtain bacterial cultures which are adapted to utilize/tolerate high concentrations of surfactants. Bacterial cultures which can efficiently biodegrade surfactants and surfactant/contaminant mixtures are essential to the success of any remediation approach which employs surfactants. The ability of microbial cultures to utilize surfactants as sole sources of carbon and energy is indicated in Figure 4. Initial experiments failed to yield any appreciable biodegradation of the surfactants used in this project at concentrations of 500 ppm or greater; however, after enrichment in the presence of surfactants for twelve weeks bacterial cultures have been obtained which are reasonably well adapted to the presence of surfactants. These cultures are now capable of growing using surfactants as their sole source of carbon and energy, albeit at only about half the efficiency with which preferred carbon sources, such as glucose, are utilized. These surfactant tolerant microbial cultures were tested for their ability to biodegrade PAHs within a surfactant/contaminant mixture. Radioactively labeled phenanthrene was added to solutions containing 2000 ppm DXP135 and then inoculated with PAH-degrading, surfactant tolerant, microbial cultures. The biodegradation of the phenanthrene was then monitored by the release of radioactively labeled carbon dioxide, which unequivocally indicates mineralization of phenanthrene. These results are illustrated in Figure 5.

Figure 4.

Surfactant-Adapted Cultures Biodegrade Phenanthrene Even in the Presence of 2000ppm Surfactant

Figure 5.

Additionally during the past quarter metal binding tests were performed with several biosorbent materials prepared from byproducts of the paper and food processing industries. Previous tests have shown that removal by biosorbents of many metals from simulated D&D wastewater is quite good. However the removal of strontium is problematic. To address this issue several additional lignin byproduct samples were obtained and tested for their ability to remove radioactive strontium from an actual contaminated wastewater sample obtained from the West Valley Nuclear facility. The level of radioactivity in this wastewater is quite low (30 DPM per ml above background) requiring concentration so that accurate analyses can be performed conveniently. Atomic absorption spectroscopy can be used to accurately quantify the levels of strontium in these samples, but because they are radioactive they can't be analyzed using the available AA equipment. Scintillation counting is what is being used for the analysis of strontium as that does not require direct contact with the analytical equipment. Concentrated samples were prepared by evaporation of the wastewater to yield samples with about 200 DPM per ml above background. Biosorbent binding experiments were performed using 100 mg of sorbent per ml of wastewater. The sorbent was mixed thoroughly for one minute and then removed from the sample by centrifugation at 10,000 x gravity for ten minutes. The residual radioactivity in the supernatant was then determined by scintillation counting using a protocol focused on monitoring the emission spectrum of strontium. The results are graphically summarized in Figure 6.

Industrial Byproduct Biosorbents Allow Excellent Removal of Strontium from West Valley Nuclear Wastewater

Figure 6.

The use of industrial byproducts to treat wastewater should result in an economical process as lignin byproducts are readily available from the paper industry and are inexpensive. Moreover, lignin biosorbents should be easily removed by ultrafiltration. This should be confirmed in subsequent testing to be performed by WVU.

7.0 Conclusions

The project is proceeding as scheduled. Food grade surfactants which yield good contaminant desorption were identified. The most promising surfactant in terms of PAH desorption, food grade status and cost is DXP135. This surfactant is not readily biodegradable, but it is also not particularly inhibitory to bacterial growth. Bacterial cultures with improved abilities to biodegrade surfactants and surfactant/contaminant mixtures are needed and experiments to obtain such cultures are currently underway. However, contaminants within contaminant/surfactant mixtures can be biodegraded. For desorption of petroleum hydrocarbons aqueous solutions of the food grade surfactant Witconol 2722 yielded the best results.

Industrial byproducts of the paper industry were found which exhibit good metal binding ability and may be useful in a process for the treatment of D & D and/or industrial wastewater. Wastewater samples received from West Valley Nuclear were tested and the industrial byproducts Marasperse CBA-1 and Borresol HA-1 yielded excellent removal of radioactivity.

8.0 Work Planned for Next Period

Further tests are planned to determine the biodegradability of surfactants and surfactant/contaminant mixtures. Enrichment culture experiments will also be performed to obtain cultures with improved abilities to biodegrade surfactants. Industrial byproduct samples, particularly Marasperse CBA-1 and Borresol HA-1, will be tested further to determine their ability to remove strontium from concentrated West Valley Nuclear wastewater.

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

METC Task No. 3.2

Quarterly Technical Progress Report
Reporting Period: 7/1/97 - 9/30/97

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, walls, *etc.* represents a unique and cost-effective method for remediating DOE facilities. As envisioned, the sorbent or cleaning agents would be added to a liquid (most likely water) and the solution would be contacted with the contaminated surface. For example, a pipe that is contaminated with inorganic and organic contaminants can be contacted with a solution containing a surfactant (for organics) and a chelating agent (for inorganics). After removal of the surface-bound contamination by the cleaning agents, a solid sorbent can be added to the liquid to bind the cleaning agent-contaminant compound. A major problem associated with this approach is the efficient separation of the sorbent/cleaning agent from the liquid phase using conventional separation techniques.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and discharged. The concentrate exits at the edge of the membrane packs. The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance and increasing the volume of waste treated per area of membrane.

The objective of this Task 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 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 centrifugal membrane process. The following tasks will be completed by IGT: 1) identification and formulation of synthetic wastes and 2) selection and evaluation of sorbents and cleaning solutions. WVU-CEE and IGT will submit separate quarterly reports. A joint proposal will be 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 Figures/Illustrations	v
Executive Summary	vi
Introduction	1
Purpose	2
Background	3
Methodology	5
Work Performed During This period	6
Results and Discussion	7
Conclusions	14
Work Planned for Next Quarter	15
Technical/Administrative Difficulties	16

LIST OF FIGURES/ILLUSTRATIONS

Figure #		Page
1.	Schematic of experimental apparatus.	9
2.	Permeate flux and concentration factor versus time.	10
3.	Concentrate and permeate turbidity and concentration factor versus time.	11
4.	Concentrate and permeate pH versus time.	12
5.	Concentrate and permeate conductivity versus time.	13

EXECUTIVE SUMMARY

Tween 20, a commercially available surfactant was concentrated from 1% (wt.) to 9.26% (wt.) using the SpinTek high-shear rotary ultrafiltration system. The system performance was studied using a PV-5k. In this experiment, the permeate flux initially declined then was stable during semi-batch operation. The permeate flux decreased rapidly during batch-down operation.

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 liquid to bind the cleaning agent-contaminant compound. A major problem associated with this approach is the efficient separation of the sorbent/cleaning agent from the liquid phase using conventional separation techniques.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane 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 treatment.

2.0 PURPOSE

The purpose of this research is to investigate the feasibility of using sorbents (biosorbents, powdered activated carbon) and cleaning agents (surfactants, 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 technology. The result of this work will be an effective decontamination/decommissioning process that can be used for inorganic (*e.g.* radionuclides and heavy metals) and organic contaminants.

3.0 BACKGROUND

Background information contained in this report pertains only to membrane technology. The Institute of Gas Technology (IGT) will provide, in a separate report, the required background information on the development/use of sorbents/cleaning solutions.

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The fluid stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate (“clean” liquid) is forced through the membrane and is collected in the hollow shaft and then discharged. The concentrate (liquid containing the contaminants) exits at the edge of the membrane packs.

With time, the membrane surface will become fouled resulting in a decrease in the permeate flow rate. To reduce fouling in conventional membrane systems, a large portion of the concentrate is recycled back to the membrane unit producing large liquid velocities near the membrane surface. The large velocities increase turbulence which reduces the thickness of the fouling layer. In centrifugal membrane systems, the rotation of the membrane disk induces the turbulence (*i.e.*, shear force near membrane surface) required to minimize the thickness of the fouling layer. In conventional membrane systems, maximum surface velocities of about 15 ft/s are possible while with centrifugal systems surface velocities of 60 ft/s are typical. As the concentrate thickens with treatment time, conventional systems are not able to maintain the high velocities because of the difficulty in pumping viscous material at large flow rates. Because the centrifugal membrane system does not rely on pumping to produce the required surface velocities, extremely concentrated wastes can be treated.

Membrane systems are typically operated in either the semi-batch mode or the batch mode. In the semi-batch mode, fresh waste is added to the system at a rate equal to the permeate production rate. In the batch-mode, which normally occurs at the end of semi-batch operation, no fresh waste is added to the system and the concentrate remaining from semi-batch operation is concentrated further (“batch-down”). During batch-down, large concentration factors are achieved (permeate is still being produced reducing the concentrate volume).

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

Semi-Batch Operation

$$CF_{SB} = 1 + V_{perm}/V_{feed\ tank}$$

Batch-Down Operation

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

where,

CF_{SB} = hydraulic-based concentration factor during semi-batch operation.

V_{perm} = volume of permeate produced, gal.

$V_{feed\ tank}$ = volume of the feed tank, gal.

CF_{BD} = hydraulic-based concentration factor during batch-down operation.

Concentration factors are expressed as 1X, 2X, *etc.*, and increase with treatment time. CFs in excess of 100X are obtainable with the membrane technology. Another measure of treatment efficiency is the permeate flux (volume of permeate/membrane area per time). The permeate flux for a given membrane is dependent on the waste's viscosity, solids content, and temperature. These waste characteristics can also change during treatment.

Membranes that are used for ultrafiltration are characterized by the molecular weight of a molecule that is not allowed to pass through the membrane. For example, the membrane used in this quarter's research had a molecular weight cut-off (MWCO) of 100,000 and 50,000. In theory, compounds having a molecular weight greater than the MWCO would be retained by the membrane and compounds with molecular weights less than the MWCO would pass through the membrane and be contained in the permeate. It should be noted that the MWCO designation is somewhat misleading because a molecule having a molecular weight less than the membrane's MWCO may still be retained by the membrane because its unique geometry.

4.0 METHODOLOGY

Centrifugal membrane technology was tested for separation of Tween 20, a commercially available surfactant. A polyvinylidene fluoride membrane with a MWCO of 5k was used in this experiment. A clean water flux (CWF) was determined for the virgin membrane. For this waste-membrane combination, the SpinTek system was operated in semi-batch then batch-down modes to test the ability of the SpinTek system to concentrate the Tween 20 solution. The following variables were monitored during the technology testing:

1. Permeate flux
2. Permeate and feed pH
3. Permeate and feed conductivity
4. Permeate and feed turbidity
5. Applied pressure

5.0 WORK PERFORMED DURING THIS PERIOD

During the period from 7/1/97 to 9/30/97, a membrane separation study was performed to test the ability of the SpinTek high-shear rotary ultrafiltration system to concentrate Tween 20, a commercially available surfactant commonly used in soil flushing applications. In this study, a polymeric membrane with a 5,000 MWCO was used to concentrate a 1% Tween 20 solution to a final concentration of 9.26%.

6.0 RESULTS AND DISCUSSION

In this chapter, results of the Tween 20 surfactant experiment will be presented and discussed. A schematic of the experimental apparatus is provided in Figure 1. Figures and tables are presented at the end of the text portion of Section 6.0.

Tween 20--5,000 MWCO Polymeric Membrane

A 190L solution of 1% (wt.) Tween 20 in distilled water was treated using a PV-5k membrane under the following conditions: vessel pressure = 40psi, rotational speed = 1750 rpm, feed temperature = 110 ± 2 °F, return flow = 1.0 ± 0.2 gal/min, and operational mode = semi-batch to batch-down. The pH and conductivity of the distilled water used to make the 1% (wt.) Tween 20 solution were 6.93 and 3.70 $\mu\text{S}/\text{cm}$, respectively. Before the run, a CWF of 360 gal/ft² day was measured for the virgin PV-5k polymeric membrane. The system was started and the feed tank temperature was stabilized at 110 ± 2 °F. The system was operated in semi-batch mode from 0 to 59 hr. Batch-down operation was conducted from 59 hr. through the end of the experiment at 76.5 hr. Permeate flux, concentrate and permeate turbidity, temperature, pH, and conductivity were measured regularly.

Permeate flux and concentration factor versus time are presented in Figure 2. A rapid decrease in permeate flux from 190 to ~25 gal/ft²-d was observed over the first 20 hr. of operation. Permeate flux was then constant at ~25 gal/ft²-d through 72 hr. Over the period of constant permeate flux, the feed solution was concentrated from 2 to 7.5X. The permeate flux then declined to a minimum value of 11.5 observed at the end of the run. It is hypothesized that the decline in permeate flux through 20 hr. was due to the accumulation of solute molecules at the membrane surface. Additionally, the constant permeate flux of ~25 gal/ft²-d observed from 2 to 7.5X was due to the effective scouring of solute molecules from the membrane surface. As the concentration of solute molecules in the feed was increased above 7.5X, the effect of membrane rotation was unable to effectively minimize the accumulation of solute molecules at the membrane surface and a decrease in permeate flux was observed.

Concentrate and permeate turbidity versus time are presented in Figure 3. Permeate turbidity was constant throughout the experiment. Permeate turbidity averaged 1.94 NTU and ranged from 1.30 to 4.02 NTU. Concentrate turbidity was constant at an average of 7.75 NTU through ~70 hr. Over this time period, concentrate turbidity ranged from 4.20 to 13.84 NTU. Concentrate turbidity increased rapidly from 10.0 NTU at 70 hr. to a final value of 32 NTU at the end of the run.

Concentrate and permeate pH versus time are presented in Figure 4. Concentrate and permeate pH were approximately equal in this experiment. A decrease in both concentrate and permeate pH was observed when the system was operated in recycle mode for ~17 hr. Permeate pH averaged 7.02 and ranged from 9.72 to 7.31 from 0 to 43 hr. Concentrate pH averaged 6.98 and ranged from 6.70 to 7.23 from 0 to 43 hr. Permeate pH averaged 6.63 and ranged from 5.33 to 5.88 from 43 to 76.5 hr. Concentrate pH averaged 5.49 and ranged from 5.24 to 5.72 from 43 to 76.5 hr.

Concentrate and permeate conductivity versus time are presented in Figure 5. Permeate and concentrate conductivity were constant and approximately equal in this experiment. Concentrate conductivity averaged 422 $\mu\text{S}/\text{cm}$ and ranged from 333 to 478 $\mu\text{S}/\text{cm}$. Permeate conductivity averaged 431 $\mu\text{S}/\text{cm}$ and ranged from 368 to 458 $\mu\text{S}/\text{cm}$.

The Tween 20 solution appeared yellow in the feed tank. The permeate was initially clear but turned yellow as the Tween 20 solution was concentrated to $\sim 3\text{X}$. At the end of the run, the vessel was opened and observations of the membrane's physical condition were made. Both the top and bottom membranes were stained a light yellow color.

Figure 1-- Schematic of experimental apparatus.

Figure 2—Permeate flux and concentration factor versus time.

Figure 3— Concentrate and permeate turbidity and concentration factor versus time.

Figure 4—Concentrate and permeate pH versus time.

Figure 5--Concentrate and permeate conductivity versus time.

7.0 CONCLUSIONS

The SpinTek high-shear rotary ultrafiltration unit was able to concentrate a 1% (wt.) Tween 20 solution to a final concentration of 9.26% (wt.) Permeate flux decreased rapidly over the first ~ 20 hr. of operation then became stable through the remainder of semi-batch operation. It is hypothesized that the decline in permeate flux through 20 hr. was due to the accumulation of solute molecules at the membrane surface. The constant permeate flux of ~25 gal/ft²-d observed from during semi-batch operation was due to the effective scouring of solute molecules from the membrane surface. Permeate flux decreased rapidly during batch-down operation. In this case, the effect of membrane-induced turbulence was unable to effectively minimize the accumulation of solute molecules at the membrane surface and a decrease in permeate flux was observed.

The accumulation of Tween 20 on the membrane surface was visually observed after the experiment was completed.

8.0 WORK PLANNED FOR NEXT QUARTER

A similar treatment experiment is planned using a CYTEK surfactant.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

The primary technical difficulty encountered in the third quarter was the failure of the centrifugal feed pump's mechanical seals. These seals were upgraded with double mechanical seals for added durability. Additionally, a surfactant was requested from CYTEK during the third quarter but has not been received.

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: 7/1/97 - 9/30/97

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

For:
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Office of Fossil Energy
Federal Energy Technology Center
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ABSTRACT

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and discharged. The concentrate exits at the edge of the membrane packs.

The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance and increasing the volume of waste treated per area of membrane. Because of the reactive nature of most DOE wastewaters, the use of conventional membrane materials may not be viable. Thus, specialty membranes that can separate hazardous contaminants from the permeate stream and are chemically and radiologically stable will also be tested.

The objective of this research is to investigate the feasibility of using centrifugal membrane technology combined with innovative membranes for the treatment of hazardous/radiological wastes. The following tasks will be completed during this research: 1) perform extensive literature review on membrane technology, 2) identify and acquire waste and membranes, 3) modify, acquire, and be trained in the use of SpinTek technology, and 4) test and evaluate SpinTek technology and specialty membranes. These experiments will provide baseline membrane performance data. 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 wastes such as contaminated groundwater, mixed-waste process water, and existing waste residual (*e.g.*, low-level waste). The process can be used for both inorganic (*e.g.* radionuclides and heavy metals) and organic contaminants. It is envisioned that the volume reduction factors for this technology will be high and a relatively 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	9-10
Work Performed During This Period	11
Results and Discussion	12-28
Conclusions	29
Work Planned for Next Quarter	30
Technical/Administrative Difficulties	31

LIST OF TABLES

Table #		Page
1	Average permeate backpressures at common rotational speeds.	7
2	Viscosity of water at 110 and 135 °F.	8
3	Summary of oil package/rotational speed combinations.	10
4	Characteristics of ceramic membrane.	15

LIST OF FIGURES/ILLUSTRATIONS

Figure #		Page
1	Schematic of Experimental Apparatus.	16
2	Permeate flux versus time for the 15% MW Fluid--1750 rpm experiment.	17
3	The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1750 rpm experiment.	18
4	Permeate and concentrate pH versus time for the 15% MW Fluid--1750 rpm experiment.	19
5	Permeate and concentrate conductivity versus time for the 15% MW Fluid--1750 rpm experiment.	20
6	Permeate flux versus time for the 15% MW Fluid--1450 rpm experiment.	21
7	The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1450 rpm experiment.	22
8	Permeate and concentrate pH versus time for the 15% MW Fluid--1450 rpm experiment.	23
9	Permeate and concentrate conductivity versus time for the 15% MW Fluid--1450 rpm experiment.	24
10	Permeate flux versus time for the 15% MW Fluid--1150 rpm experiment.	25
11	The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1150 rpm experiment.	26
12	Permeate and concentrate pH versus time for the 15% MW Fluid--1150 rpm experiment.	27
13	Permeate and concentrate conductivity versus time for the 15% MW Fluid--1150 rpm experiment.	28

EXECUTIVE SUMMARY

In the third quarter, the treatment of a synthesized oily industrial wastewater using the *SpinTek* high shear rotary ultrafiltration system was investigated. A total of three experiments were conducted at an oil package concentration 15% and at constant membrane rotational speeds ranging from 1150 to 1750 rpm to obtain pressure-independent limiting flux data. Applied pressure ranged from 20 to 75 psig in these experiments. These experiments were performed at 110°F in recycle mode using an 0.11 μm average pore size ceramic membrane. Permeate flux, and permeate/concentrate pH and conductivity were measured periodically. The gauge pressure was corrected for permeate backpressure using a mathematical model presented in the first quarterly technical report of '97. After each oil package/membrane rotational speed experiment, the system was drained, flushed, and cleaned using the standardized cleaning procedure consisting of a surfactant and NaOH solution adjusted to pH 11.8 followed by an H_2SO_4 solution adjusted to pH 2.2, as presented in the previous quarterly report. Each cleaning procedure was followed by a clean water flux measurement at 110 ± 2 °F 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 these oil experiments. The primary technical difficulty during the third quarter was the deterioration and subsequent failure of the mechanical seals on the feed pump.

1.0 INTRODUCTION

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The waste stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate is forced through the membrane and is collected in the hollow shaft and discharged. The concentrate exits at the edge of the membrane packs. The centrifugal action continuously cleans the membrane surface decreasing cleaning chemical use and maintenance, increasing the volume of waste treated per area of membrane, and increasing the contaminant/solids concentration in the residual (*i.e.* increases volume reduction factor). *SpinTek's* centrifugal membrane technology represents an improvement over conventional ultrafiltration technology and increases the number of waste streams that can be treated using membrane treatment.

2.0 PURPOSE

The purpose of this research is to investigate the effects of membrane rotation and transmembrane pressure on the treatment of a synthetic oily wastewater using *SpinTek's* high shear rotary ultrafiltration system. Additionally, a mathematical model used to correct for the average permeate backpressure due to membrane rotation is tested for an oil contaminated feed solution.

The result of this work will be a further step toward optimizing this technology for the treatment of a variety of wastes such as waste from DOE decontamination/decommissioning efforts, biological wastes, and waste with a high solids content (*e.g.*, low level tank waste), contaminated groundwater, mixed-waste process water, and existing waste residual. The process can be used for both inorganic (*e.g.* radionuclides and heavy metals) and organic contaminants. It is envisioned that the volume reduction factors for this technology will be high and a relatively a low amount of residual requiring additional treatment will be produced.

3.0 BACKGROUND

SpinTek, a California-based company, has developed and patented a cross-flow technology that improves upon the conventional membrane process. The SpinTek system uses a series of flat, round membrane disks packs set on a hollow rotating shaft inside a cylindrical housing. The fluid stream enters the membrane chamber under pressure and is distributed across the membrane surfaces by centrifugal and hydraulic action. Permeate (“clean” liquid) is forced through the membrane and is collected in the hollow shaft and is discharged. The concentrate (liquid containing the contaminants) exits at the edge of the membrane packs. A schematic of the SpinTek system is presented in Figure 1.

With time, the membrane surface will become fouled resulting in a decrease in the permeate flow rate. To reduce fouling in conventional membrane systems, a large portion of the concentrate is recycled back to the membrane unit producing large liquid velocities near the membrane surface. The large velocities increase turbulence which reduces the thickness of the fouling layer. In centrifugal membrane systems, the rotation of the membrane disk induces the turbulence required to minimize the thickness of the fouling layer. In conventional membrane systems, maximum surface velocities of about 15 ft/s are possible while with centrifugal systems surface velocities of 60 ft/s are typical. As the concentrate thickens with treatment time, conventional systems are not able to maintain the high velocities because of the difficulty in pumping viscous material at large flow rates. Because the centrifugal membrane system does not rely on pumping to produce the required surface velocities, extremely concentrated wastes can be treated.

Membrane systems are typically operated in either the semi-batch mode or the batch mode. In the semi-batch mode, fresh waste is added to the system at a rate equal to the permeate production rate. In the batch-mode, which normally occurs at the end of semi-batch operation, no fresh waste is added to the system and the concentrate remaining from semi-batch operation is concentrated further (“batch down”). During batch-down, large concentration factors are achieved (permeate is still being produced reducing the concentrate volume).

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

Semi-Batch Operation

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

Batch-Down Operation

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

where,

CF_{SB} = concentration factor during semi-batch operation.

V_{perm} = volume of permeate produced, gal.

V_{feed} = volume of the feed tank, gal.

CF_{BD} = concentration factor during batch-down operation.

Concentration factors are expressed as 1X, 2X, *etc.*, and increase with treatment time. CFs in excess of 100X are obtainable with the membrane technology. Another measure of treatment efficiency is the permeate flux (volume of permeate/membrane area per time). The permeate flux for a given membrane is dependent on the waste's viscosity, solids content, and temperature. These waste characteristics can also change during treatment.

Membrane's that are used for ultrafiltration are characterized by the molecular weight of a molecule that is not allowed to pass through the membrane. For example, the membrane used in this quarter's research had a molecular weight cut-off (MWCO) of 100,000. In theory, compounds having a molecular weight greater than the MWCO would be retained by the membrane and compounds with molecular weights less than the MWCO would pass through the membrane and be contained in the permeate. It should be noted that the MWCO designation is somewhat misleading because a molecule having a molecular weight less than the membrane's MWCO may still be retained by the membrane because its unique geometry.

A backpressure results from permeate pooling at the outer perimeter of the disk pack as centrifugal force is exerted on the permeate by the rotating membrane. A mathematical correction for the average permeate backpressure has been developed by the SpinTek Corporation. This expression is given in Equation (III). In this equation, the permeate backpressure is a direct function of membrane rotational speed, feed solution density, and the radius of gyration which is explicitly stated in Equation (IV). The average transmembrane pressure is the difference between the gauge pressure and this average permeate backpressure as indicated in Equation (V). A summary of average permeate backpressures at common operating rotational speeds is presented in Table 1.

The membrane resistance is an intrinsic material property of the membrane must be determined using a virgin membrane with a clean water feed solution. Darcy's Law, given in Equation (VI) is used to calculate the resistance of the membrane for the case of a virgin membrane with a clean water feed. The slope of a regression line through the origin on a plot of permeate flux -v- transmembrane pressure is inversely proportional to the product of the absolute feed viscosity and the resistance of the membrane, $R_{mem.}$, as shown in Equation (VII). The transmembrane pressure, P , is corrected for permeate backpressure as outlined in Equations (III) and (V). Since the $R_{mem.}$ is a material property of the membrane, the change in the magnitude of the slope of the line fitted to the flux versus transmembrane pressure data should be proportional to the magnitude of the change in $1/\mu$ (in the absence of membrane fouling). The viscosities of water at 110 and 135 °F and the theoretical changes in $1/\mu$ with temperature are shown in Table 2.

$$P_{\text{back}} = [\rho(J^* \omega)^2]/2 \quad (\text{III})$$

$$J = [(R_i^2 + R_o^2)/2]^{1/2} \quad (\text{IV})$$

$$P_{\text{tmp}} = P_{\text{gauge}} - P_{\text{back}} \quad (\text{V})$$

where,

P_{back} = average permeate backpressure

ρ = permeate mass density = 1 kg/L

J = radius of gyration

ω = angular velocity

R_i = inner disk radius = 0.975 in.

R_o = outer disk radius = 3.625 in.

P_{tmp} = transmembrane pressure

P_{gauge} = gauge pressure

$$J = P_{\text{tmp}}/\mu R_{\text{mem}} \quad (\text{VI})$$

$$R_{\text{mem.}} = 1/\mu * \text{slope} \quad (\text{VII})$$

where,

J = permeate flux

P_{tmp} = transmembrane pressure

μ = absolute feed viscosity

$R_{\text{mem.}}$ = membrane resistance

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 through channels in an ideal membrane system is generally accepted as the best description of fluid flow through a microporous membrane:

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

where J = permeate flux, ε = membrane surface porosity, r = mean pore radius, ΔP_T = hydraulic pressure difference between the feed and the permeate, ν = viscosity of fluid permeating the membrane, and Δx = membrane thickness.

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

$$J^* = k_s \ln(C_m/C_b) \quad (\text{X})$$

where J^* = permeate flux in the mass transfer controlled region, 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 plateau portion on a flux versus transmembrane pressure curve. In the pressure independent region, permeate flux can only be improved by increasing the mass transfer coefficient, k_s :

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

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

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

where d_h = hydraulic diameter of the flow channel and D = diffusion coefficient, Re = Reynolds Number, and Sc = Schmidt Number. A power-law relationship can be used to judge the effect of turbulence on permeate flux:

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

where n = slope of the line fitted to experimental data in a plot of $\log(J)$ versus $\log(\text{turbulence})$. The magnitude of n is an indicator of the effect of turbulence on flux. In this model, turbulence can be expressed in terms of Reynolds Number or cross flow velocity. In a rotary ultrafiltration unit, the turbulence can also be expressed in terms of membrane rotational speed since the Reynolds Number is a direct function of membrane rotation. 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. [Cheryan, M., (1986). Ultrafiltration Handbook, Technomic Publishing Corp., Inc., Lancaster, PA.]

Table 1--Average permeate backpressures at common rotational speeds.

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

Table 2-- Viscosity of water at 110 and 135 °F.

Temp. (°F)	μ (cP)	$1/\mu$ (cP ⁻¹)	% change in $1/\mu$ from 110 to 135 °F	% change in $1/\mu$ from 135 to 110 °F
110	0.6178	1.619	27	21
135	0.4884	2.048		

4.0 METHODOLOGY

The *SpinTek* ST-II high shear rotary ultrafiltration system was used to treat a synthetic, “virgin,” emulsified coolant oil. A ceramic membrane with an average pore size of 0.11 μm was used in these experiments. Rotational speeds ranging from 1150 to 1750 rpm for a feed concentration of 15% oil package were examined in this study. Individual experiments were performed according to the oil package concentration/membrane rotational speed combinations and applied pressure ranges outlined in Table (3). All experiments were conducted in recycle mode, at 110°F, with a 40 L feed volume of freshly prepared oil/water emulsion. A 1.0 ± 0.20 gpm return flow rate was maintained in each experiment. The permeate flux was measured at increasing gauge pressures ranging from 20 to 75 psig, depending on membrane rotational speed. (Permeate backpressure as a function of rotational speed was taken into account to ensure a net positive transmembrane pressure.) A mathematical correction for the average permeate backpressure as a function of membrane rotation was used in these experiments.

The following variables were monitored during testing:

1. Gauge pressure.
2. Membrane rotational speed.
3. Permeate flux.
4. Concentrate and permeate temperature.
5. Concentrate and permeate conductivity and pH.

A standardized cleaning procedure was used and clean water flux measurements were made after each experiment to monitor the membrane's condition. After completing an experiment, the rotor 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* detergent was added to this solution. The pH and conductivity of the cleaning solution were measured and recorded. This cleaning solution was heated 135°F and the membrane was cleaned for 30 minutes at 1750 rpm and 40 psig. Permeate flux was measured and recorded during cleaning. The system was then drained and flushed with hot tap water. An additional 5 gallons of distilled water was pH adjusted 2.2 using a stock 1M $\text{H}_2(\text{SO})_4$ solution. The pH and conductivity of this cleaning solution were measured and recorded. The cleaning solution was heated to 135°F and the membrane was cleaned for 30 minutes at 1750 rpm and 40 psig. The permeate flux was measured and recorded during cleaning. The system was flushed with hot tap water. A clean water flux (CWF) was measured at 110°F, 1750 rpm, at three pressures ranging from 25 to 75 psig using a distilled water feed. The average permeate flux versus the corrected pressure was plotted and the slope of the line was determined.

Details on how each run was conducted will be provided in Chapter 6--Results and Discussion.

Table 3--Individual oil package concentration/rotational speed combinations and applied pressure ranges.

% oil package	Rotational speed (rpm)	Applied pressure range (psig)
15%	1750	20 - 75
15%	1450	15 - 70
15%	1150	15 - 70

5.0 WORK PERFORMED DURING THIS PERIOD

The following work was conducted during the period 7/1/97 to 9/30/97: 1) continuation of literature search, 2) investigation of system performance treating freshly prepared oil/water emulsions at an oil package concentration of 15%, membrane rotational speeds from 1150 to 1750 rpm, and gauge pressures ranging from 20 to 75 psig, and 3) implementation of a standardized cleaning procedure and tracking of membrane resistance after each experiment.

5.1 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.

5.2 Waste and Membrane Identification and Acquisition

The identification of wastes and membranes that warrant further study will be an ongoing task for this research project. In this quarter a virgin ceramic membrane with an average pore size of 0.11 μm was acquired. Freshly prepared oil/water emulsions were used as the feed solution. Numerous researchers have investigated the performance of virgin ultrafiltration membranes. Thus, the virgin ceramic membrane used in the SpinTek system can be compared with membranes used in conventional systems. Because of the poor performance of the PV-100K polymeric membrane it was decided that the majority of testing should involve the more promising ceramic membrane.

5.3 Technology Evaluation

In the second quarter, the SpinTek technology with a ceramic membrane (0.11 μm pore size) was used to process freshly prepared oil/water emulsions of 15% oil package. Results and discussion are presented in Section 6.0.

6.0 RESULTS AND DISCUSSION

In this chapter results from the treatment of freshly prepared oil/water emulsions using a ceramic membrane having an average pore size of $0.11\ \mu\text{m}$ will be presented and discussed. A schematic of the experimental apparatus is provided 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 4. Prior to being used in these oil-contaminated feed experiments, the membrane's resistance was determined as presented in the previous quarterly report.

In each experiment, a forty liter feed solution consisting of a 15 vol. % oil package in distilled water was used. The distilled water was obtained from the West Virginia University Department of Civil and Environmental Engineering's house supply. These experiments were all conducted in recycle mode, at $110 \pm 2\ ^\circ\text{F}$, with a $1.0 \pm 0.2\ \text{gpm}$ return flow.

15% MW Fluid--1750 rpm

Permeate flux versus time for the 15% MW Fluid--1750 rpm experiment is presented in Figure (2). Permeate flux was stable at each applied pressure condition. The system was operated over an applied pressure range of 20 to 70 psig. The average permeate backpressure was 11.1 psi for a membrane rotational speed of 1750 rpm. The permeate flux was $90\ \text{gal/ft}^2\text{-d}$ when the 25 psig applied pressure condition was re-investigated after the limiting permeate flux was determined. The permeate flux at the initial 25 psig condition was $61\ \text{gal/ft}^2\text{-d}$. It is hypothesized that the higher "rebound" flux was due to the effects of membrane-induced turbulence effectively removing solute molecules from the membrane surface when the applied pressure was decreased resulting in a decreased resistance to hydraulic flow of permeate. The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1750 rpm experiment is presented in Figure (3). A limiting flux of $305\ \text{gal/ft}^2\text{-d}$ was observed at the 65 to 70 psig applied pressure conditions. The slope of the regression line fitted to the pressure-controlled data from 0 to 55 psig was $6.188\ \text{gal/ft}^2\text{-d-psi}$. The total resistance to hydraulic flow in the pressure-controlled region, R , was $3.81 \times 10^{12}\ \text{m}^{-1}$.

Permeate and concentrate pH versus time for the 15% MW Fluid--1750 rpm experiment are presented in Figure (4). The permeate pH ranged from 5.83 to 7.19 and averaged 6.31. The concentrate pH ranged from 5.95 to 7.36 and averaged 6.34. A net decrease in both permeate and concentrate pH was observed in this experiment. Permeate and concentrate pH values were approximately equal and followed the same general trend: Both permeate and concentrate pH decreased through $\sim 3\ \text{hr.}$ then increased through the end of the experiment. Permeate and concentrate conductivity versus time for the 15% MW Fluid--1750 rpm experiment are presented in Figure (5). The permeate conductivity ranged from 362 to $520\ \mu\text{S/cm}$ and averaged $448\ \mu\text{S/cm}$. The concentrate conductivity ranged from 459 to $564\ \mu\text{S/cm}$ and averaged $534\ \mu\text{S/cm}$. Permeate conductivity was greater than concentrate conductivity through $\sim 1\ \text{hr.}$ Concentrate conductivity exceeded permeate conductivity from $\sim 1\ \text{hr.}$ 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 membrane was cleaned using the standardized cleaning procedure discussed in Section 4.0. No oil was visible on the membrane surface after cleaning. The pH and conductivity of the distilled water used to determine the membrane resistance after cleaning were 6.93 and 3.84 $\mu\text{S}/\text{cm}$, respectively. The resistance of the membrane measured after cleaning was $2.06 \times 10^{12} \text{ m}^{-1}$.

15% MW Fluid--1450 rpm

Permeate flux versus time for the 15% MW Fluid--1450 rpm experiment is presented in Figure (6). Permeate flux was stable at each applied pressure condition. The system was operated over an applied pressure range of 25 to 70 psig. The average permeate backpressure was 7.6 psi for a membrane rotational speed of 1450 rpm. The permeate flux was 107 $\text{gal}/\text{ft}^2\text{-d}$ when the 25 psig applied pressure condition was re-investigated after the limiting permeate flux was determined. The permeate flux at the initial 25 psig condition was also 107 $\text{gal}/\text{ft}^2\text{-d}$. It is hypothesized that the gel layer returned to its initial thickness when the applied pressure was decreased to 25 psig and that solute molecules were not forced into the membrane pores and were not adsorbed onto the membrane surface. The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1450 rpm experiment is presented in Figure (7). A limiting flux of 266 $\text{gal}/\text{ft}^2\text{-d}$ was observed at the 55 to 70 psig applied pressure conditions. The slope of the regression line fitted to the pressure-controlled data from 0 to 45 psig was 6.940 $\text{gal}/\text{ft}^2\text{-d-psi}$. The total resistance to hydraulic flow in the pressure-controlled region, R , was $3.39 \times 10^{12} \text{ m}^{-1}$.

Permeate and concentrate pH versus time for the 15% MW Fluid--1450 rpm experiment are presented in Figure (8). The permeate pH ranged from 6.10 to 6.58 and averaged 6.30. The concentrate pH ranged from 6.10 to 7.01 and averaged 6.30. The permeate and concentrate pH were approximately equal in this experiment and followed the same general trend: A decrease in both permeate and concentrate pH was observed through the first 1 hr. then the permeate and concentrate pH then remained constant at ~ 6.30 from 1 hr. through the end of the experiment. Permeate and concentrate conductivity versus time for the 15% MW Fluid--1450 rpm experiment are presented in Figure (9). The permeate conductivity ranged from 348 to 534 $\mu\text{S}/\text{cm}$ and averaged 433 $\mu\text{S}/\text{cm}$. The concentrate conductivity ranged from 394 to 579 $\mu\text{S}/\text{cm}$ and averaged 514 $\mu\text{S}/\text{cm}$. A net decrease in permeate conductivity and a net increase in concentrate conductivity were observed. Permeate conductivity was greater than concentrate conductivity through ~ 1.5 hr. The concentrate conductivity then exceeded the permeate conductivity from ~ 1.5 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 membrane was cleaned using the standardized cleaning procedure discussed in Section 4.0. No oil was visible on the membrane surface after cleaning. The pH and conductivity of the distilled water used to determine the membrane resistance after cleaning were 6.91 and 2.89 $\mu\text{S}/\text{cm}$, respectively. The resistance of the membrane measured after cleaning was $2.15 \times 10^{12} \text{ m}^{-1}$.

15% MW Fluid--1150 rpm

Permeate flux versus time for the 15% MW Fluid--1150 rpm experiment is presented in Figure (10). Permeate flux was stable at each applied pressure condition. The system was operated over an applied pressure range of 15 to 70 psig. The average permeate backpressure was 4.8 psi for a membrane rotational speed of 1150 rpm. The permeate flux was 50 gal/ft²-d when the 15 psig applied pressure condition was re-investigated after the limiting permeate flux was determined. The initial permeate flux at the initial 15 psig condition was 54 gal/ft²-d. The lower “rebound” flux could 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 gel layer was not reduced to its initial value when the applied pressure was decreased. A higher resistance to hydraulic flow of permeate and thus a lower permeate flux would result from a thicker gel layer. The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1150 rpm experiment is presented in Figure (11). A limiting flux of 190 gal/ft²-d was observed at the 35 to 70 psig applied pressure conditions. The slope of the regression line fitted to the pressure-controlled data from 0 to 25 psig was 6.164 gal/ft²-d-psi. The total resistance to hydraulic flow in the pressure-controlled region, R , was $3.82 \times 10^{12} \text{ m}^{-1}$.

Permeate and concentrate pH versus time for the 15% MW Fluid--1150 rpm experiment are presented in Figure (12). The permeate pH ranged from 5.84 to 7.60 and averaged 6.33. The concentrate pH ranged from 5.89 to 7.54 and averaged 6.42. The permeate and concentrate pH were approximately equal and followed the same general decreasing trend with time. Permeate and concentrate conductivity versus time for the 15% MW Fluid--1150 rpm experiment are presented in Figure (13). Permeate conductivity ranged from 282 to 540 $\mu\text{S/cm}$ and averaged 395 $\mu\text{S/cm}$. Concentrate conductivity ranged from 346 to 583 $\mu\text{S/cm}$ and averaged 527 $\mu\text{S/cm}$. A net decrease in permeate conductivity and a net increase in concentrate conductivity were observed in this experiment. Permeate conductivity was greater than concentrate conductivity through ~1.75 hr. Concentrate conductivity then exceeded the permeate conductivity from ~1.75 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 membrane was cleaned using the standardized cleaning procedure discussed in Section 4.0. No oil was visible on the membrane surface after cleaning. The pH and conductivity of the distilled water used to determine the membrane resistance after cleaning were 6.98 and 3.98 $\mu\text{S/cm}$, respectively. The resistance of the membrane measured after cleaning was $2.09 \times 10^{12} \text{ m}^{-1}$.

Table 4--Characteristics of ceramic membrane.

Lot Number	CRM-011M-TA
Chemical composition	TiO ₂ /Al ₂ O ₃
Mean pore size	0.11 μm
Thickness	240 μm
Inner radius	0.975 in.
Outer radius	3.625 in.

Figure (1)-- Schematic of experimental apparatus.

Figure (2)-- Permeate flux versus time for the 15% MW Fluid--1750 rpm experiment.

Figure (3)-- Average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1750 rpm experiment.

Figure (4)-- Permeate and concentrate pH versus time for the 15% MW Fluid--1750 rpm experiment.

Figure (5)-- Permeate and concentrate conductivity versus time for the 15% MW Fluid--1750 rpm experiment.

Figure (6)-- Permeate flux versus time for the 15% MW Fluid--1450 rpm experiment.

Figure (7)-- The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1450 rpm experiment.

Figure (8)-- Permeate and concentrate pH versus time for the 15% MW Fluid--1450 rpm experiment.

Figure (9)-- Permeate and concentrate conductivity versus time for the 15% MW Fluid--1450 rpm experiment.

Figure (10)-- Permeate flux versus time for the 15% MW Fluid--1150 rpm experiment.

Figure (11)-- The average permeate flux at each applied pressure versus average transmembrane pressure for the 15% MW Fluid--1150 rpm experiment.

Figure (12)-- Permeate and concentrate pH versus time for the 15% MW Fluid--1150 rpm experiment.

Figure (13)-- Permeate and concentrate conductivity versus time for the 15% MW Fluid--1150 rpm experiment.

7.0 CONCLUSIONS

The treatment of a 15 % oil package feed solution was studied using the *SpinTek* high shear rotary ultrafiltration system. Experiments were conducted over a membrane rotational speed range of 1500 to 1750 rpm and an applied pressure range of 15 to 75 psig to obtain limiting flux data for future use in system performance modeling. A mathematical model was used to correct for the average permeate back pressure due to membrane rotation. It was observed that that as the membrane rotational speed was decreased, the limiting flux in the mass transfer controlled region decreased. It is hypothesized that the cause of this behavior was the increase in gel layer thickness, and subsequent increase in resistance to fluid flow, at the membrane surface as the membrane rotational speed was decreased.

8.0 WORK PLANNED FOR NEXT QUARTER

The following work will be conducted during the third quarter: 1) similar experiments will be conducted at higher oil package concentrations (20, 30, and 40% oil package), 2) a further investigation of mathematical models used to predict limiting flux behavior in ultrafiltration systems will be performed, and 3) a comprehensive summary and discussion of membrane resistance throughout the course of all oil experiments will be presented.

9.0 TECHNICAL/ADMINISTRATIVE DIFFICULTIES

The primary technical difficulty was the performance of the feed pump. The mechanical seals on the centrifugal feed pump failed and had to be replaced. The stock carbide/tungsten carbide seals were retrofitted with higher grade tungsten carbide/tungsten carbide materials.

ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

Report for Period
ending September 30, 1997

Work Performed Under FETC Task 4.2
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For :
US Department of Energy
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	vii
 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
Construction of Small-Scale Remediation Cell	8
Evaluation Of Carbonaceous Material	8
Construction of the Scaled-Up Remediation Cell	9
Work Performed This Quarter	10
Experimental	10
Results and Discussion	11
Industrial Application	12
Radionuclides	13
Prototype Remediation Cell	14
Previous Quarter's Work	16
Conclusion	17
 C. <u>Appendix</u>	
References	46

LIST of TABLES

Table I	Standard Reduction Potentials of the Metals	40
Table II	Properties of Carbon Materials (Surface Areas)	41
Table III	Removal Efficiencies for Cadmium and Lead	42
Table IV	Immediate Industrial Application (Nickel Removal)	43
Table V	Doe Application (Strontium Removal)	44
Table VI	Project Completion	45

LIST of FIGURES

Figure 1	Schematic of Electrochemical Remediation Cell	22
Figure 2	Schematic of Scaled-Up 3-inch Remediation Cell	23
Figure 3	Schematic of 1.5-inch Galvanic Remediation Cell	24
Figure 4	Long-Term Removal of Lead using Electroplating	25
Figure 5	Long-Term Removal of Lead using Electrosorption	26
Figure 6	Long-Term Removal of Uranium	27
Figure 7	Effect of Plating Current on Removal Efficiency	28
Figure 8	Effect of pH on Removal Efficiency	29
Figure 9	Effect of Flow Rate on Removal Efficiency	30
Figure 10	Long-Term Removal of Lead Using Scaled-Up Cell	31
Figure 11	Treatment of a Mixed-Metal (Cu-Pb) Solution using Small-Scale Remediation Cell	32
Figure 12	Treatment of a Mixed-Metal (Pb-Ni) Solution using Small-Scale Remediation Cell	33
Figure 13	Affect of pH on the Treatment of a Mixed-Metal (Pb-Ni) Solution using Small-Scale Remediation Cell	34
Figure 14	Comparison of AN-210 Regular and "Oxidized" Carbon Fibers for the Removal of Uranium.	35
Figure 15	Effect of Applied Cell Potential on the Removal of Uranium Using Oxidized Carbon Fibers.	36
Figure 16	Effect of Uranium Feed Concentration on Removal.	37
Figure 17	Schematic of Scaled-Up 1.5-Inch Remediation Cell -Replacing Pt Wire with Conductive Carbon (Graphite) Rods.	38
Figure 18	Schematic of Scaled-Up 1.5-Inch Remediation Cell with Multiple Cathode Compartments.	39

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.

WORK PERFORMED THIS QUARTER

EXPERIMENTAL

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.

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 g_{Pb}/g_{carbon fibers}, but it should be stressed that even at 72 hours, the carbon showed no signs of saturation (see Figure 4).

Removal of lead ions via electrosorption was carried out using a potential of -0.40 V. For an inlet lead ion concentration of 100 ppb, good removal efficiencies (90%) were obtained for the first 12 hours (see Figure 5). After that time a noticeable decrease in efficiency is evident. The removal efficiency drops to less than 50% after 57 hours. This decrease in removal efficiency is expected due to the neutralization of charge on the electrode surface. Regeneration of the carbon nanofibers would be required to maintain high removal efficiencies. For the first 12 hours of removal a capacity of 1.9×10^{-4} g_{Pb}/g_{carbon fibers} is obtained. At 57 hours this capacity increases to 7.1×10^{-4} g_{Pb}/g_{carbon fibers}. Electrosorption of lead using a 100 ppm lead feed was attempted. Due to the smaller capacity of the carbon nanofibers when using electrosorption, the efficiency should drop off very quickly. As expected, within the first two hours the removal efficiency dropped to less than 20%.

The final desire is to recover the metals once they have been removed from the aqueous stream. It is possible to recover the metal ions plated on the electrode simply by reversing the potential. The metal ion concentration in the resulting effluent is 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 WV U 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.

Previous Quarter's Work

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.

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.

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.

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	80%
3	140	Define Industrial Needs	52w	80%
4	141	Test Removal Efficiencies Using Small Cell	52w	80%
5	142	Optimize Experimental Parameters	52w	85%
6	143	Study Affect of Interfering Ions	16w	95%
7	144	Design and Construct Large Prototype	12w	100%
8	145	Apply Large-Scale Prototype	24w	80%
9	146	Test Carbon Materials	52w	75%
10	147	Develop Recommendations	4w	60%
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	-
15	152	Final Report	4w	-
16	153			

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Design of Rotating Membrane Filtration System for Remediation Technologies

1997 FETC Task No. 4-3

Quarterly Technical Progress Report
July – Sept. 1997

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

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October 1997

Abstract

This project involves the development of a scaled-up design of a centrifugal membrane filtration system. This system is to be used in water remediation of liquid mixed-waste streams. The new design will be based on an existing 8 inch SpinTek™ rotary membrane system, currently being utilized at WVU for DOT-FETC, in the treatment of contaminated water. In the new design, finite element analyses of the rotating disk-membrane, the overhung rotating shaft, the attachment between disk and shaft, and the location of bearings for a multi-disk assembly will be considered. Mechanical and functional failure, as well as material selection, will be considered as the main criteria to develop the scaled-up design. The target new diameter for the disk will be 24 inches, and the features of the IGT™ ceramic/metal membranes will be considered in the new design configuration. The use of alternate materials will be considered for improved performance and ease of manufacturing. The shaft design will consider the possibility of stacking several disks on the same shaft to improve packing density. Rotor dynamics of the shaft with multiple disks will be assessed to ensure safe and stable operation.

An assessment will be made of the turbulence promoters of the system (wagon wheels) to determine their effectiveness in promoting shear force on the membrane surfaces. These turbulence promoters will be dimensioned based on the existing design. Then they will be modeled and analyzed through computational fluid dynamics (CFD) codes to determine fluid velocities, pressure distributions, shear rate distributions on the membrane surfaces and the torque transmitted to the shaft of the system.

An optimization function will be derived from the results of the above modeling. From this function a new scaled-up system will be designed. A series of CAD drawings will be produced with dimensions and material specifications as well as graphic descriptions of the computer analyses conducted to support the design.

Table of Contents

<u>Description Nos.</u>	<u>Page</u>
Abstract	-ii-
List of Figures	-iv-
Executive Summary	-v-
1.0 Introduction	1
2.0 Purpose	2
3.0 Background	2
4.0 Methodology	2-3
5.0 Work performed this period	3-4
6.0 Results and Discussion	4-8
7.0 Conclusions	9
8.0 Worked Planned for Next Period	9

List of Figures

<u>Description Nos.</u>	<u>Page</u>
Figure 1: Von Mises stresses due to rotation in the 8 inch disk	4
Figure 2: Displacements due to rotation in the 8 inch disk	5
Figure 3: Von Mises stresses due to rotation in the 24 inch disk	5
Figure 4: Displacements due to rotation in the 24 inch disk	6
Figure 5: Fluent model without turbulence promoter	7
Figure 6: Fluent model with turbulence promoter	8

Executive Summary

During this quarter, the work developed involved the parametric modeling of an actual CAD rendition of the filtration system as it has been originally designed. The parametric model allows analysis to be conducted in such a way that relationships can be established between specific design parameters and those responses of interest. First the models supplied by SpintekTM imported from the AutoCad format into the IGES files that can be read by the program IDEAS Master SeriesTM. Once the geometry is transferred into IDEAS, the models are to be parameterized so that the meshing can be directed. The objective of this task is to incorporate parameter variations prior to meshing the various components of the filtration system so that various analysis runs can be executed to identify the trends in the response.

This parametric approach is being used in both the mechanical stress and vibration analyses as well as in the fluid analysis of the fluid chamber being analyzed for turbulence assessment purposes. In this latter case, the geometry from the files supplied by SPINTEK are also being used to "extract" the "fluid volume shape". The program FLUENT is being used to model the fluid dynamic behavior of the fluid chamber, with special interest in the gap between the rotating membrane and the wagon wheel (turbulence promoter). In the next quarter, the parametric trends are to be used to identify the parameters that can provide improvements in the operation of the filtration system.

1.0 Introduction

The system whose design is being considered, involves an innovative concept for water remediation, which uses centrifugal force, turbulence and membrane filtration to separate suspended matter from liquid waste streams, producing a filtered permeate stream and a low-volume concentrate stream. Potential applications for this technology includes the treatment of contaminated process waters at DOE facilities, the remediation of groundwater contaminants and industrial processes which require efficient and cost effective remediation technologies.

The existing design (8 inch diameter disk) has been shown to be effective in the treatment of contaminated waters at WVU-FETC. However, there is a need for greater capacities and for greater efficiencies, which call for redesign considerations. Scaling up the system (to just make it bigger) is not a trivial exercise, as multiple mechanical and fluid-dynamics considerations need to be incorporated into the analysis and design of the system. Although there is a target dimension to expand the rotating disk (up to 24 inches in diameter), several models and analyses will be needed to determine the most appropriate dimensions from a systems perspective. Optimization concepts will be applied to determine the configuration that offers the greatest potential performance.

In developing the design of the new system, four main areas will be addressed as follows:

1. Geometry: In this area we will deal with all the geometric features dimensions and attributes, which fully characterize the key mechanical components and overall system configuration. Particular attention will be given to constraints in parametric relationships due to function, size, space, or weight limitations.
2. Materials: This aspect relates to the characteristics of engineering materials required to perform mechanically and functionally, within the operational requirements and conditions of operation. The material properties of concern involve elastic, strength, and physical properties. These properties will be needed to predict the response of the system and the mechanical failure envelopes of the system.
3. Operating Requirements and Conditions: This aspect deals with the determination of loads to be used to predict the systems response. That depends on the operational requirements and capacities of the system as well as the operating conditions, such as temperatures, pressures, etc.
4. Failure Criteria: Two types of failure criteria will be considered. Mechanical failure including stress, fatigue, vibration, instability of systems etc. The second type is functional failure, in which an assessment will be made of the level of performance rendered by the system as compared with accepted benchmark levels of performance.

2.0 Purpose

The objective of this work is to expand the capacity of centrifugal membrane filtration systems, by scaling up the current design. This involves the following specific objectives:

1. To increase the disk diameter (to a target value of 24 in.) based on stress distributions.
2. Design the shaft to carry a multiple set of disks, based on rotor dynamic response.
3. Design the attachments for membrane to disk and shaft, based on load transfer stresses.
4. Consider a ceramic-metallic IGT™ disk by conducting a stress/vibration analyses.
5. To study the performance of the turbulence promoters by means of CFD modeling.
6. To perform optimization studies to determine optimum parametric brackets.

Mechanical and functional failure criteria together with the predicted responses will allow for the definition of the design configuration.

3.0 Background

The rotating-membrane filtration system, is unique, in the fact that the rotation and subsequent turbulence, promotes extended filtration function by avoiding the formation of the so called "cake" on the membrane. The current design of this system, performs in a satisfactory manner. However, in order to increase the capacity of the system (more volume of processed fluid per unit time) while maintaining the quality of the permeate, it is desired to scale-up the current design.

Several approaches can be followed to attain the previously mentioned purpose. One such scenario is to increase the diameter of the membrane-disk assembly in order to increase the filtration surface. Another approach is to mount several disks on the same shaft. However, both scenarios require the considerations of disk stresses, disk-shaft vibration and wagon wheel turbulence promotion effectiveness. An appropriate design of a scaled-up version of the SpinTek™ System will require models to assess the responses (stress, vibration, and turbulence).

4.0 Methodology

The design characterization will be based on the results produced by the finite element models developed. The design and associated models will be developed according to the following task:

Sub-Task 1. Parametric CAD representation. For each part, a CAD rendition will be made to capture the geometric features and to associate them with specific system parameters.

Sub-Task 2. A finite element model will be developed based on the geometry captured in the previous task. The type of mesh will depend on the component and the type of analysis of interest, to produce the responses sought.

Sub-Task 3. Analyses will be conducted to simulate the response of the system. The response (most likely a non-linear physical behavior) will be conducted considering various scenarios, such as steady state and transient conditions.

Sub-Task 4. Post-processing of analysis results will be conducted to identify critical areas, and to visualize responses. The behavior at the interfaces between the various components will be of interest to determine the likelihood of mechanical or functional failures.

Sub-Task 5. Validation of results will be conducted by means of simplified models aimed at validating the response trends. This will be done through quantitative and qualitative assessments.

Sub-Task 6. Parametric variations will then be conducted to determine the sensitivity of the systems responses of interest to parametric variations. This type of analysis will allow the selection of critical parameters needed prior to conducting system optimization.

Sub-Task 7. Design definition of the increased diameter system. This task will produce CAD renditions of the geometric features of components and system, for further analysis or for manufacturing purposes.

Sub-Task 8. Analysis of the new system and prediction of its functional performance. This system simulation will involve the new design dimensions and only slight parametric variations would be expected for final dimensions.

Sub-Task 9. Modeling of the fluid flow and pressure distributions in the chamber through the turbulence promoters. CFD codes would be used for this simulation.

Sub-Task 10. Report and present results to interested parties.

5.0 Work Performed this Period

During this quarter the detailed drawings of the SpinTek™ water filtration system were imported into SDRC I-DEAS from AutoCad. These drawings allowed models to be created in SDRC I-DEAS and Fluent with the correct dimensions. Using SDRC I-DEAS several FE models were created to analyze the stresses in the rotating disk. These models differed by the diameter of the disk, which varied from the original 8 inches to 24 inches. Using SDRC I-DEAS models were created to look at the effects of a multi-disk system. These models will be used to examine the whirl associated with an unbalanced multi-disk system.

Also using the AutoCAD drawings fluid models representing the conditions at the surface of 8", 11", and 24" OD disks were produced in Fluent. For each disk diameter, six modeling cases were produced -- for fluid chamber heights of 3/8", 5/8", and 1" each of these modeled with and without a turbulence promotor. The geometry was modeled as a three-dimensional, 45-degree sector, with cyclic boundaries and a structured (quadrilateral) grid. The turbulence promotor, or wagon wheel, has been modeled with a constant rectangular cross-section. The Reynolds Shear Model (RSM) in Fluent was used to approximate the highly rotational fluid behavior.

6.0 Results and Discussion

For the stress analysis of the SpinTek™ water filtration system, SDRC I-DEAS was used to obtain values for the Von Mises stresses and the displacements due to rotation. For the 8 inch disk the stresses obtained were all within the allowable limits for the materials used. The stresses and displacements results can be seen in Figures 1 and 2 respectively. The results for the 24 inch disk is also shown in Figures 3 and 4 respectively. The results show high stresses on the inner diameter of the membrane. These are due to errors in coupling the thin members and material selection, these parts of the models will be redone for better results.

Figure 1: Von Mises Stresses in the 8 inch disk

Figure 2: Displacements due to rotation in the 8 inch disk

Figure 3: Von Mises stresses due to rotation in the 24 inch disk

Figure 4: Displacements due to rotation in the 24 inch disk

Eighteen total cases representing these geometric variations have been produced, and results have been obtained for ten cases using Fluent. These initial results have predicted increased shear at the membrane surface with the presence of the turbulence promoter, for a given disk diameter and chamber height. Detailed analysis and comparison of the results has yet to be performed. One set of results is shown in Figures 4 and 5 without and with the turbulence promoter respectively.

Figure 5: Fluent model without the turbulence promoter

Figure 6: Fluent model with the turbulence promoter

7.0 Conclusion

This quarter finite element models for stress were developed for varying disk diameters. Currently a model for the assessment of whirl in multi disk systems is being developed. Fluent models were also developed to examine the conditions at the surface of the disk. Three different diameters were used with six modeling cases. The combined effects of stress, vibration and turbulence will allow the parametric-design sensitivity analysis to be conducted in the subsequent tasks. "Parameter-Response" trends are to be obtained based on the models thus far developed leading to the scaled-up design.

8.0 Work Planned for Next Period

Additional refinements to the FE models developed will be conducted in order to obtain more realistic results for the stresses in the membrane. Models have been started to look into the whirl due to unbalance disk in a multi disk system. The geometry for these models was done in SDRC I-DEAS and ANSYS will be used for the analysis.

Results for the remainder of the eighteen three-dimensional cases will be collected and analyzed to identify any trends strongly affecting the fluid shear on the membrane surface. Membrane technical data will be obtained, and axis symmetric fluid models (of 8", 11", and 24" diameter disks) predicting the flow direction through and under the membrane for different radii will be completed.

FOCUS AREA 5.0

Outreach

Small Business Technical Based Support

1997 FETC Task No. 5.1

Quarterly Technical Progress Report

Reporting Period:
July - September 1997

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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October 1997

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EXECUTIVE SUMMARY

The Small Business Support program was initiated to address problems encountered by the small businesses funded by Federal Energy Technology Center (FETC) to develop innovative site remediation technologies. During this reporting period the Institute of Gas Technology initiated studies on surfactants and chemicals to be used in cleaning the TCE plume at the RMI Ashtabula site. Planning continued on installation of the prefabricated vertical drains and treatment of the extracted water at the site.

Preparations were made for a program presentation at the 97 FETC Industry Partnerships meeting and the 98 WVU Cooperative Agreement Program is being prepared.

TABLE OF CONTENTS

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

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 is done by small businesses. Small business owners are creative thinkers usually technically competent beyond their resource base. At times they find technical problems and their lack of highly technical personnel creates an unsurpassable barrier for the small business to get their innovative technologies developed and commercialized. By ferreting out these problems, this program will allow teaming of a faculty member with the small business to solve the problem allowing further development of the innovative technology to occur.

PURPOSE

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

BACKGROUND

Over the past four years the WVU Cooperative Agreement has funded numerous projects which has resulted in defining at least four areas of core competencies at WVU which may be called upon to provide assistance to the small businesses that 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 (PVD's)
- 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 reporting period further planning occurred for clean up of the TCE contaminated RMI site at Ashtabula, Ohio. Proposals were prepared to cover each part of the Phase I clean up effort for the pilot scale demonstration. Some changes have occurred in the participants causing minor delays in the project. West Virginia University will still provide expertise and installation of the eight prefabricated vertical drains. The Institute of Gas Technology has initiated work on selection of the surfactant and other chemicals. RMI Environmental Services will now provide expertise in development of unit operations and treatment of all fluids extracted from the subsurface.

A call for proposals was sent out in August to begin preparation of the 1998 WVU Cooperative Agreement Program and the new five (5) year program as well.

Preparation was also begun for presentation of the 97 WVU Cooperative Agreement Program at the Oct. 21-23, 1997 "Industry Partnerships to Deploy Environmental Technology" technical exchange meeting.

CONCLUSIONS/WORK PLANNED FOR NEXT PERIOD

During late October the initiation of the pilot scale demonstration project will begin at Ashtabula, Ohio. It will involve placement of eight (8) prefabricated vertical drains (PVD's) at the contaminated site, extraction of groundwater through the PVDs and treatment of the extracted water to clean it up.