# Environmental Management Technology Demonstration and Commercialization Tasks 2, 3, 4, and 8

## Semiannual Report
## October 1994 - March 1995

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Jan W. Nowok
Debra Pflughoeft-Hassett
John P. Hurley
Edward N. Steadman

May 1995

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Work Performed Under Contract No.: DE-FC21-94MC31388

For

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Office of Technology Development
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Washington, DC 20585

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May 1995

# TASK 2

# EXTRACTION AND ANALYSIS OF POLLUTANT ORGANICS FROM CONTAMINATED SOLIDS USING OFF-LINE SUPERCRITICAL FLUID EXTRACTION (SFE) AND ON-LINE SFE–INFRARED SPECTROSCOPY

Semiannual Report

*for the period October 1, 1994, through March 31, 1995*

*Prepared by:*

Steven B. Hawthorne

May 1995

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# TASK 2 – EXTRACTION AND ANALYSIS OF POLLUTANT ORGANICS FROM CONTAMINATED SOLIDS USING OFF-LINE SUPERCRITICAL FLUID EXTRACTION (SFE) AND ON-LINE SFE–INFRARED SPECTROSCOPY

## 1.0 INTRODUCTION/BACKGROUND

Several field-portable (e.g., gas chromatography [GC], GC/mass spectrometry [MS]) instruments are available for the measurement of organic pollutants. However, analytes on solid samples such as soils, sludges, and sediments must first be extracted before analyses can be performed. Conventional extraction methods using liquid solvents (e.g., Soxhlet extraction) are not practical in the field because of the difficulties in transporting the large volumes of solvents required as well as the clumsy apparatus and glassware. However, supercritical fluid extraction (SFE) has been demonstrated in several studies by the Energy & Environmental Research Center (EERC) to extract a broad range of organic pollutants from soils and sediments successfully. Of the approximately 100 major organic pollutants identified as problems for U.S. Department of Energy (DOE) sites, our SFE laboratory has demonstrated efficient SFE recoveries for about half of them, and published SFE literature has addressed an additional 40%. SFE in the "off-line" mode (i.e., collection of extracted organics in a small volume of liquid solvent) has also been demonstrated to be easily performed in the field supported only by a generator for electrical power. Recent advances in flow restrictor design have virtually eliminated the mechanical problems previously associated with the performance of SFE in the field.

## 2.0 OBJECTIVES

The specific objectives of this task are to demonstrate, develop, and evaluate the use of SFE to extract organic contaminants rapidly and efficiently for analysis at DOE and related sites. This objective is divided into the following two areas:

- To perform and evaluate off-line SFE on-site using conventional portable instrumentation (i.e., a portable GC) for analysis of the extracts and to compare the results with conventional laboratory methods.

- To evaluate the use of on-line SFE with infrared (IR) detection (based on a fiber-optic interface recently built at the University of North Dakota [UND] Chemistry Department in collaboration with the EERC) for an inexpensive (less than $20,000) and simple-to-operate field instrument. This evaluation will include determining the ability of this SFE–IR instrument to perform screening surveys at relevant (i.e., ppm to ppb) detection levels.

# 3.0 ACCOMPLISHMENTS/WORK PERFORMED

## 3.1 Selection of Field Sites

Several local sites contaminated with polycyclic aromatic hydrocarbons (PAHs) and fuel spills (petroleum hydrocarbons [TPHs]) have been surveyed and will be used for the local field demonstrations. Unfortunately, field sites for polychlorinated biphenyl (PCB) contamination have been difficult to find, since U.S. companies that have been contacted are not willing to allow us to demonstrate the SFE technique on their sites. Fortunately, a field site for PCBs has been found at Manitoba Hydro (Winnipeg, Canada).

## 3.2 Preliminary Field Demonstration

A preliminary field demonstration of a commercially available SFE unit was performed on local field sites contaminated with PAHs. Three sites were selected and sampled, and quadruplicate samples were extracted at each site using only a portable electric generator for field support. A total of five hours was required to complete all three sites. Since sample throughput is a high priority at field sites, a rapid (10-minute) SFE step was used for each sample. This step yielded an extract ready for GC analysis without additional preparation. Extracts were returned to the lab for GC analysis, and the 10-minute SFE extractions showed good recoveries of all of the PAHs present in the sample (based on sonication of the SFE residues in methylene chloride for 14 hours). As shown in Table 1, recoveries were typically 80%–100% using the 10-minute field extraction for lower molecular weight PAHs, and 50%–90% for higher molecular weight PAHs. Reproducibilities of the field extraction were good (relative standard deviations [RSDs] generally <15%).

TABLE 1

Analytical Extraction Efficiencies of PAHs Performed at Three Field Sites
Using a 10-Minute SFE Extraction at 150°C

| | % Recovery (%RSD)[a] | | | | | |
|---|---|---|---|---|---|---|
| | Site 1 | | Site 2 | | Site 3 | |
| Phenanthrene | 92 | (6) | 100 | (0) | 81 | (19) |
| Anthracene | 91 | (4) | 100 | (0) | 78 | (2) |
| Fluoranthene | 89 | (5) | 98 | (5) | 79 | (9) |
| Pyrene | 89 | (5) | 97 | (5) | 80 | (9) |
| Benz[a]anthracene | 83 | (4) | 97 | (7) | 71 | (16) |
| Chrysene | 85 | (4) | 98 | (4) | 71 | (13) |
| Benzo[b+k]fluoranthene | 74 | (2) | 88 | (16) | 53 | (36) |
| Benzo[a]pyrene | 87 | (10) | 94 | (6) | 65 | (8) |
| Indeno[1,2,3-cd]pyrene | 85 | (5) | 89 | (11) | 50 | (24) |
| Benzo[g,h,i]perylene | 79 | (5) | 83 | (13) | 51 | (16) |

[a] Percent recoveries were based on sequential 10-minute SFE extractions performed in the field at 150°C and 400 atm with pure $CO_2$, followed by 14 hours of sonication in methylene chloride. %RSDs are based on quadruplicate extractions at each sample site.

After arriving at a new site, the total time elapsed before beginning SFE was typically <15 minutes (including unloading and assembling the SFE unit and all related apparatus, starting the generator and equilibrating the SFE instrumentation, and digging and preparing the soil samples for SFE). The only support vehicle was a standard 1987 Bronco II (the personal vehicle of the principal investigator). The commercial SFE (ISCO, Inc.) unit also behaved well under field conditions using generator power, with the minor problem that the restrictor heater controller needed resetting if the generator "cut out" and caused an interruption in electrical power. However, momentary losses of electrical power did not affect the extraction efficiencies or cause any loss in sample throughput.

## 3.3   Optimization of SFE Conditions for Field Use

Samples from local PAH-contaminated sites and from the Manitoba Hydro PCB-contaminated site were brought to the lab for optimizing SFE conditions. Since the goal is to provide reliable and rapid extractions under field conditions, we are optimizing the extraction conditions to use pure $CO_2$ (rather than modified $CO_2$, which would require carrying additional organic solvents into the field) and to yield the highest recoveries in the shortest extraction times. As shown in Table 1 by the preliminary field extraction results (based on GC analyses with flame ionization detection [FID]), a 10-minute extraction at 150°C gave reasonable recoveries of the majority of PAHs, however, the recoveries were as low as 50% for the higher molecular weight PAHs from one of the soil samples. Therefore, extraction efficiencies versus extraction times were determined, and the results demonstrated that 30-minute extractions were sufficient to give good quantitative recoveries of all of the PAHs. As shown in Figure 1, the 30-minute SFE extractions with pure $CO_2$ at 150 °C and 400 atm yielded recoveries of all of the PAHs that compare very well with the results of a 14-hour sonication in methylene chloride. Therefore, 30-minute extractions in the field should be sufficient if true "100% recovery" is required, however, 10-minute extractions are certainly sufficient for surveying field sites to obtain "near-quantitative" results, as demonstrated in Table 1. Further comparisons of the PAH recoveries obtained using 30 minutes vs. 14 hours of liquid solvent extraction (sonication and Soxhlet) are now being performed.

Samples of PCB-contaminated soil from the Manitoba-Hydro site were extracted both at 80°C and 150°C with pure $CO_2$ at 400 atm. As shown in Figure 2 by the total PCBs extracted at different times during the SFE, extraction at 150 °C is much faster than extraction at 80°C (based on GC analysis of the extracts with electron capture detection [ECD]). Also, similarly to the PAHs discussed above, the largest quantity of the PCBs are recovered in only ca. 10 minutes; however, ca. 30 minutes is required to obtain 100% extraction efficiencies. To rigorously determine the extraction efficiencies obtained at 150 °C with pure $CO_2$, samples were extracted at 150 °C for 30 minutes, and the quantity of PCBs extracted were compared to the amounts extracted with 18 hours of Soxhlet extraction in hexane and acetone. These comparisons showed excellent recoveries for the 30-minute SFE field method compared to the 18-hour Soxhlet extractions. For example, a sample showing 65±5 ppm (total PCB as Aroclor 1260) by Soxhlet extraction (triplicate extractions) showed 65±3 ppm PCBs using the 30-minute SFE field conditions (triplicate extractions).

It is important to note that the SFE extractions yielded extracts that were immediately ready for analysis by capillary GC without further cleanup steps normally required for liquid solvent extracts. Also note that the same SFE conditions can be used for both the PAH and PCB
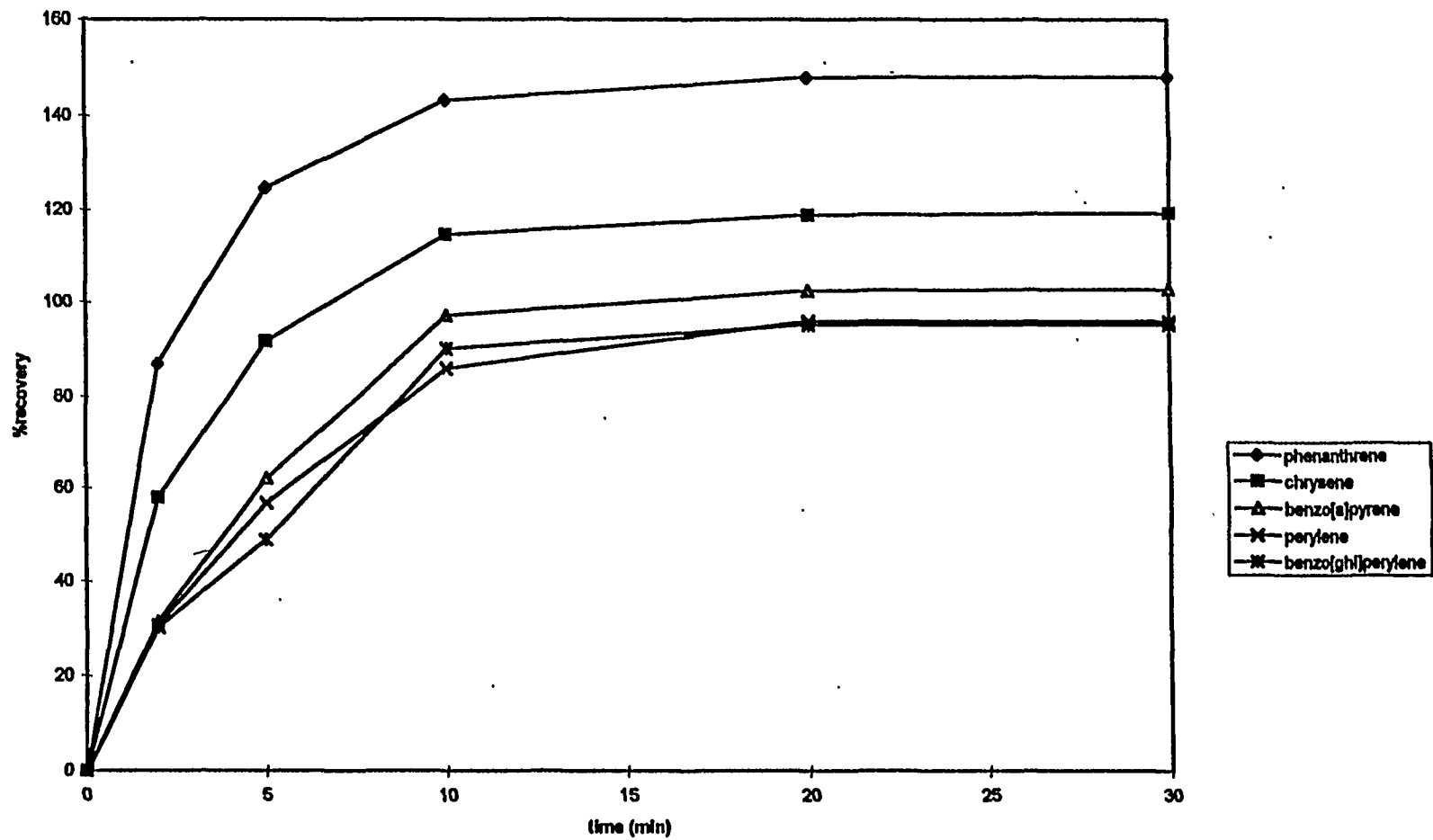
Figure 1. SFE extraction rate of PAHs from an abandoned railroad bed soil. % Recoveries are estimated compared to a 14-hour sonication extraction of replicate samples.
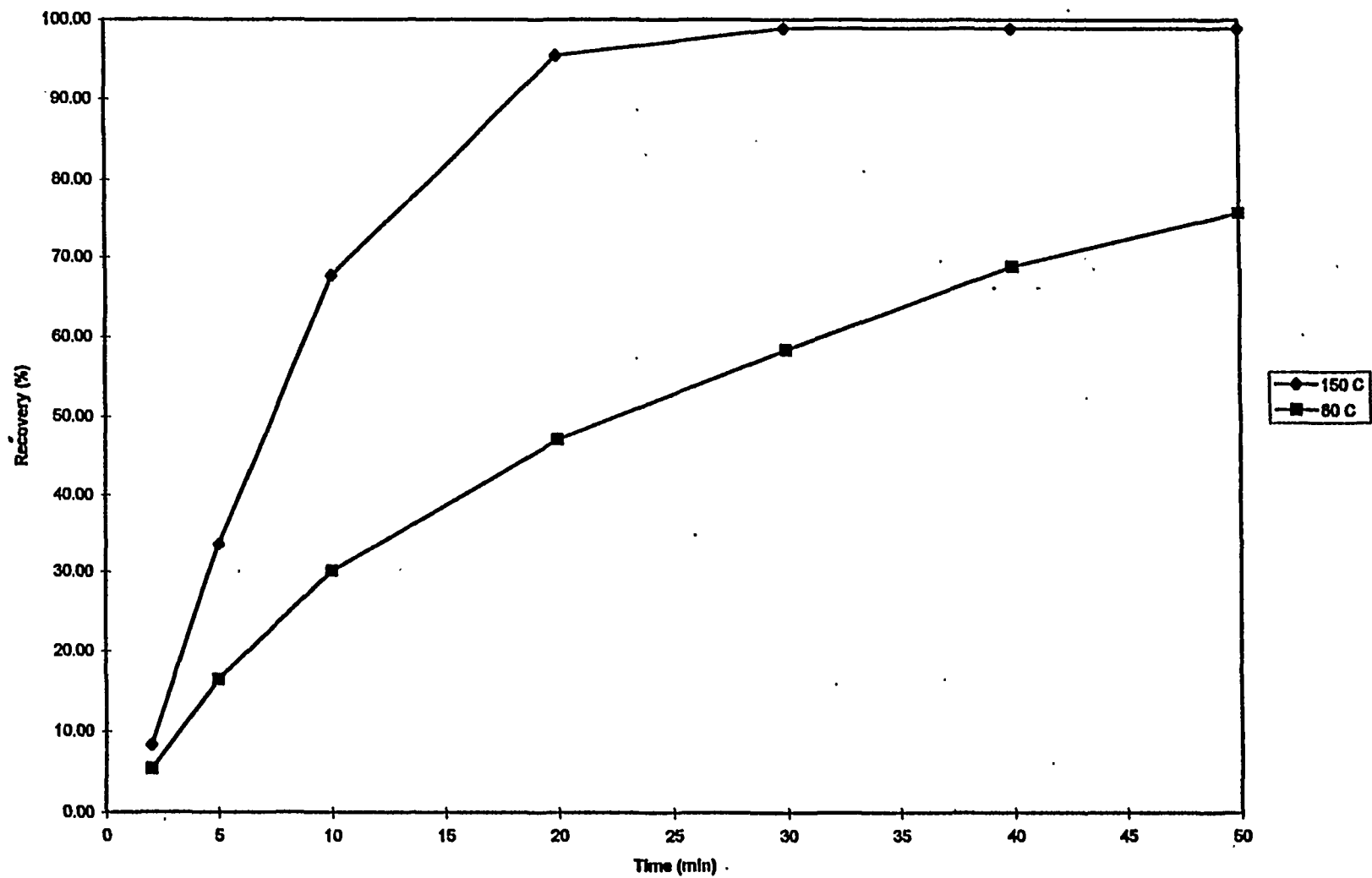
Figure 2. SFE extraction of total PCBs from soil using 400 atm $CO_2$ at 80°C (lower curve) and 150°C (upper curve). Extractions were performed on 5-gram soil samples at a $CO_2$ flow rate of ca. 1.5 mL/minute.

extractions. Therefore, one extract can be used for quantitative determination of both PAHs and PCBs (as well as several other compound classes of semivolatile pollutants).

## 3.4    Immunoassay Determination of PAHs and PCBs in SFE Extracts

Our original intention was to use capillary GC to analyze the SFE extracts in the field. However, there has recently been great interest in using immunoassay to determine organic pollutants in the field, primarily because of the simplicity and excellent field-portable capabilities of immunoassay. One major problem that immunoassays have for organic pollutant determinations is their inability to tolerate organic solvents (except dilute aqueous solutions of solvents such as acetone or methanol). Therefore, an immunoassay is an ideal match for SFE, since the only solvent required for SFE is the collection solvent. We have obtained the cooperation and necessary apparatus from the leading producer of immunoassay systems for the determination of PAHs and PCBs and are beginning the evaluations.

## 3.5    Development of SFE–IR Interfaces

Prototype SFE–IR and SFE–FT-IR (Fourier Transform IR) instruments have been constructed and tested based on a simple fiber-optic approach. A schematic of the fiber-optic interface is shown in Figure 3. Both the SFE–IR and SFE–FT-IR approaches are suitable for field use. In addition, a universal adapter that allows simple installation of the interface into most commercial FT-IR instruments has been constructed.

Both SFE–IR (at selected wavelengths) and SFE–FT-IR (yielding full spectral information) have been tested using real environmental samples. For example, the SFE–FT-IR spectrum of a soil sample contaminated with diesel fuel is shown in Figure 4 (the intense absorbance bands at ca. 2400 and 3500 cm$^{-1}$ are from the $CO_2$). Quantitative determinations with both interfaces have also begun. Preliminary tests indicate that the detection limit for total petroleum hydrocarbons (TPH) using the prototype SFE–IR instrument was ca. 5 ppm (wt TPH/wt soil) while the SFE–FT-IR interface gives detection limits <1 ppm. The prototype is now being modified in an attempt to lower detection limits.

## 3.6    Commercial Interest

A leading SFE instrument manufacturer, ISCO (a small business with ca. 450 employees), is presently evaluating the fiber-optic interface for SFE–IR and SFE–FT-IR for its commercialization potential. The developers of this interface (Dr. David Tilotta, UND Chemistry and Dr. Steven Hawthorne, EERC) visited ISCO in early April for related discussions. A second SFE instrument company (Suprex Corporation) has also expressed interest in producing commercial instrumentation based on our fiber-optic design.

Foxboro Instruments supported the development of the portable SFE–IR interface by loaning a portable IR instrument to the project for ca. ½ year.

Ohmicron (a leading supplier of immunoassay kits, including a field-portable version) has agreed to donate the kits needed for a full evaluation of the use of SFE and immunoassay for extraction and quantitation of PAHs and PCBs in the field.
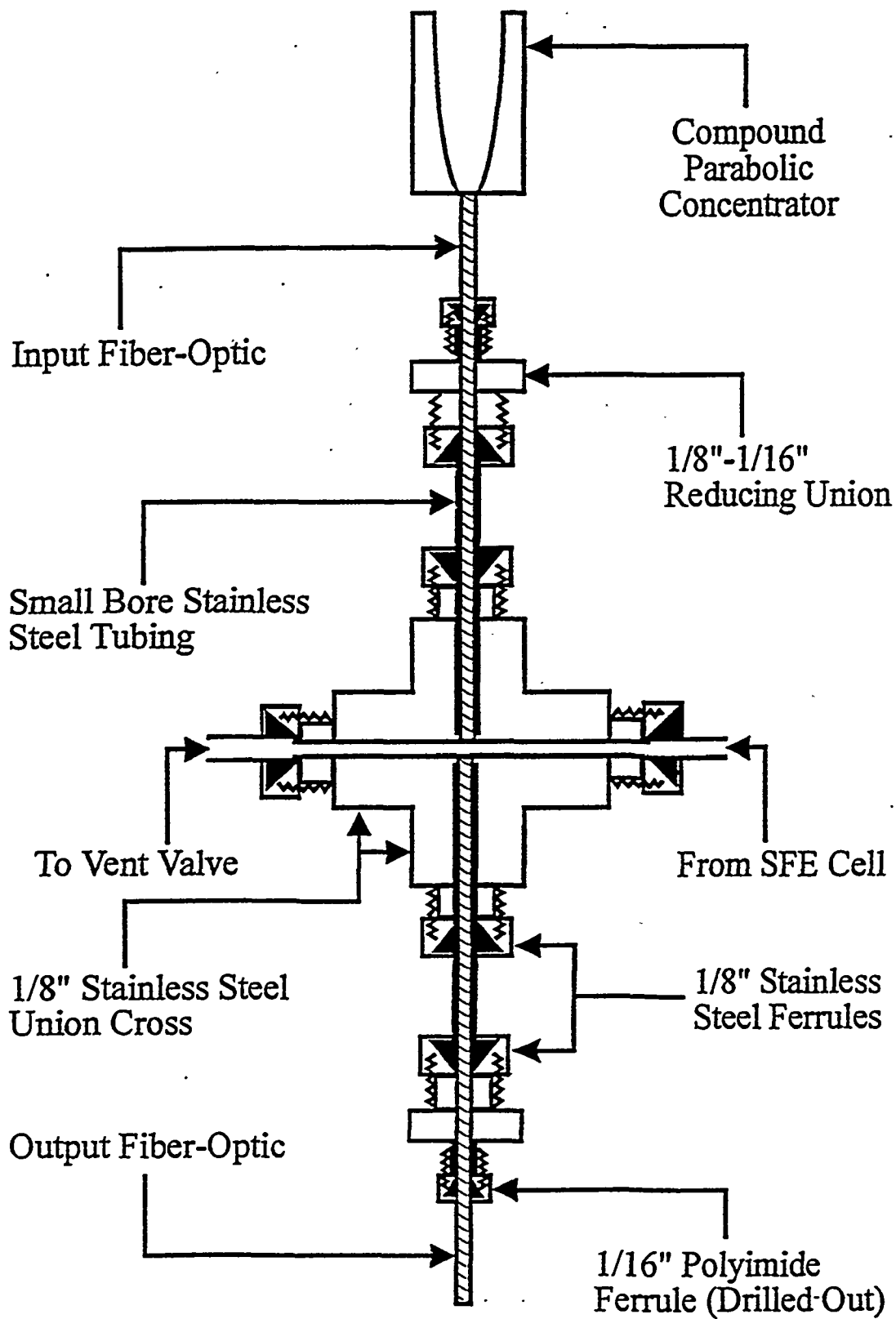
Figure 3.    Schematic diagram of the high-pressure fiber-optic interface for SFE–IR and SFE–FT-IR.
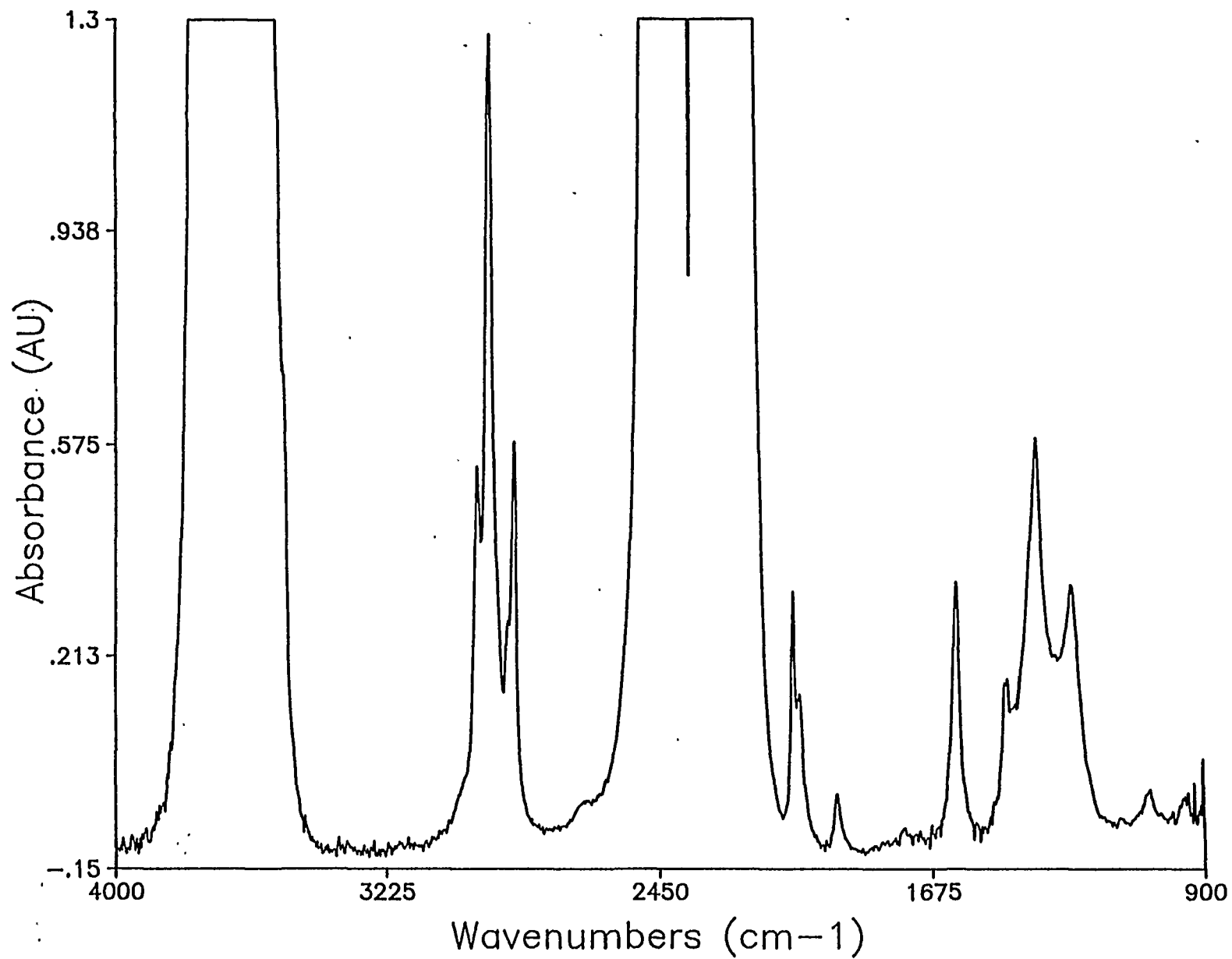
Figure 4. On-line SFE–FT-IR determination of soil contaminated with diesel fuel. The intense bands at ca. 2400 and 3500 cm$^{-1}$ are from $CO_2$.

## 4.0 WORK PLANNED FOR NEXT SIX MONTHS

- Perform SFE in the field at the local PAH sites and at Manitoba Hydro (the PCB site).

- Evaluate immunoassay for total PAH and PCB determinations in SFE extracts (compared to conventional GC determinations), and perform immunoassays in conjunction with SFE field studies.

- Obtain a firm "go/no go" decision from ISCO for pursuing commercialization of the SFE–IR interface.

- Complete the construction of a field-portable SFE–IR unit and demonstrate its use at one field site for TPH determinations.

- Determine the sensitivity and quantitative abilities of the SFE–IR and SFE–FT-IR instruments.

# TASK 3

# PYROLYSIS OF PLASTIC WASTE

Semiannual Report

*for the period October 1, 1994, through March 31, 1995*

*Prepared by:*

Robert O. Ness, Jr.

May 1995

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# PYROLYSIS OF PLASTICS

## 1.0 INTRODUCTION/BACKGROUND

The chemically diverse nature of plastics has thwarted conventional chemical reprocessing of bulk waste plastic materials back to feedstock chemicals. The Energy & Environmental Research Center (EERC) is progressing rapidly toward a commercially viable plastics recycling process capable of accommodating the wide variety of plastic materials found in commercial and military waste streams.

## 2.0 OBJECTIVES

Processes to thermally depolymerize or thermally crack plastic wastes back to oils or monomers are, for the most part, new technologies. Most of these processes are limited in the types of feed materials that can be used. The EERC has developed expertise over the past two years and is progressing rapidly toward a commercially viable plastics recycling process capable of accommodating the wide variety of plastic materials found in waste streams. The EERC has both the technical background to extend this process to the separation of contaminants and the associated test equipment and analytical expertise.

The objectives of this task are the following:

- Develop a commercial process to significantly reduce the volume of mixed-plastics–paper–resin waste contaminated with low-level radioactive material.

- Concentrate contaminants in a collectable form.

- Determine the distribution and form of contaminants after pyrolysis of the mixed waste. Many contaminants should concentrate in the solid waste from the process, but some may vaporize and combine with liquid and/or gaseous products.

Activities will focus on the design of a test matrix, including the selection of surrogate contaminants based on the chemistry of substances of interest and the result from reviewing existing information on the composition of U.S. Department of Energy (DOE) waste. Actual contaminants and/or surrogates will be used in bench-scale testing later in Task Year 1, using the EERC's 1–4-lb/hr continuous fluidized-bed reactor (CFBR) test unit. A tentative list of substances of interest includes chlorinated hydrocarbons (e.g., trichloroethylene, tetrachloroethylene, chloroform, carbon tetrachloride, chlorobenzene), radionuclides (thorium, uranium, plutonium, cobalt, cesium, strontium, and tritium), metals (lead, zinc, copper, barium, mercury, chromium, and arsenic), polychlorinated biphenyls (PCBs) (i.e., Aroclor®), and various ketones and organic acids. Not all of these substances will be tested. Part of the effort in the first year will be to gather existing information on the nature and level of substances to be treated and to determine a range of contaminants, both in terms of identity of contaminants and of total volume of each contaminant to be treated. Once a clear understanding of the problem is established, a representative set of substances will be chosen. This range will be based on volatility and chemical

interaction. Since these classes of compounds sometimes occur together (e.g., metals and radionuclides), some binary and ternary sets, as well as individual components, will be examined. While surrogates will be chosen for those toxic or residual substances that are most dangerous to use, other compounds (chlorinated hydrocarbons, metals, ketones, etc.) will be used directly. Tritium is of particular interest, since the possibility for volatilization and interaction with the plastic decomposition products is likely. Deuterium will be used as a surrogate for tritium as part of the first year's testing. Elements that have nonradioactive isotopes, such as strontium, will also be used.

At the end of this task, we will have accomplished the following:

- Selected two or three representative radionuclide surrogates
- Selected two or three representative metals
- Selected two or three representative chlorinated hydrocarbons
- Selected one or two representative PCB surrogates
- Selected binary and ternary blends for evaluation

## 3.0 ACCOMPLISHMENTS/WORK PERFORMED

Bob Ness and Ted Aulich of the EERC met with Roberto Villarreal, Donald Burns, Ken Laintz, Bernard Foy, and several others from Los Alamos National Laboratory on March 21, 1995, regarding the use of radionuclide surrogates in studies of decontamination methods for mixed wastes (plastics/polymers, rubber, paper, fabrics, and resins) from weapons and energy research and production programs around the United States. Information acquired includes the following:

- Los Alamos is very interested in collaborating with the EERC on the project.

- They may be interested in performing bench-scale "surveys" of different combinations of contaminants, mixed wastes, and temperature conditions using small amounts of actual radioactive contaminants to evaluate volatility, stability, and binary combination effects at specified temperatures and processing conditions.

- Very little information is available on the compositional breakdown (e.g., how much is plastic versus rubber or what are the different types of rubbers and plastics) of mixed waste currently stored at and around Los Alamos and at other sites, most of which is contained in sealed barrels and some of which has been stored for about 40 years.

- They will soon initiate a project in which 15 barrels of heterogeneous waste will be opened and characterized for composition. Results from the project may be helpful in providing a simulated mixed-waste composition for use in preliminary pyrolysis studies.

Bob Ness and Ted Aulich of the EERC met with Charles Carter, J. Russel Stimmel, and Bob Johnson of Lockheed Environmental Systems & Technologies Company, Las Vegas, Nevada, on March 22, 1995, regarding radionuclide surrogates and the performance (at Lockheed's facility) of

pilot-scale pyrolysis studies with radioactive materials. Information acquired includes the following:

- A prepared mixture of specified concentrations of lanthanides (lighter-weight, less-radioactive elements that can be used as surrogates for the heavier, more-radioactive actinides—uranium, plutonium, etc.) can be ordered from Mountain Pass, California.

- A study is being performed in Idaho to evaluate surrogates for studies on high-temperature processing of radioactive materials. The results of the study should be available soon, which may be very helpful.

- Lockheed's "treatability facility" (which Ness and Aulich toured) appears to be workable for pilot-scale testing.

## 4.0 WORK PLANNED FOR NEXT 6 MONTHS

The first round of bench-scale testing will be devoted to individual contaminants on single polymer types and will involve 3 weeks of CFBR operation. The CFBR unit will be run for a week at a time, 24 hours a day. Six to eight test points per week are expected. The tentative test matrix is presented in Table 1. Initial determinations of contaminant distribution will consist of quantification of contaminant levels in the feed, the liquid, and the solid products. Levels in the gaseous phase will be measured and compared with values determined by difference. The assumption that material not found in the solid or liquid phase remains volatilized represents a worst case. While analytical techniques used will depend on the substances chosen, a list of analytical techniques that may be employed is given in Table 2.

After completion of single-component testing in the CFBR, a report will be prepared detailing the findings. This evaluation will address the distribution of contaminants and will determine if continuation of the test program is warranted.

## TABLE 1

### Preliminary Test Matrix

| Test | Polymer | Contaminant Type | Temperature, °C |
|---|---|---|---|
| **Week 1** | | | |
| 1 | HDPE | Metal 1 | 500 |
| 2 | HDPE | Metal 1 | 600 |
| 3 | HDPE | RNS 1 | 500 |
| 4 | HDPE | RNS 1 | 600 |
| 5 | HDPE | PCBS 1 | 500 |
| 6 | HDPE | PCBS 1 | 600 |
| 7 | HDPE | CO 1 | 500 |
| 8 | HDPE | CO 1 | 600 |
| **Week 2** | | | |
| 1 | HDPE | Metal 1 | 500 |
| 2 | HDPE | Metal 1 | 600 |
| 3 | HDPE | RNS 1 | 500 |
| 4 | HDPE | RNS 1 | 600 |
| 5 | HDPE | PCBS 1 | 500 |
| 6 | HDPE | PCBS 1 | 600 |
| 7 | HDPE | CO 1 | 500 |
| 8 | HDPE | CO 1 | 600 |
| **Week 3** | | | |
| 1 | PP | RNS 1 | 500 |
| 2 | PP | RNS 1 | 600 |
| 3 | PET | RNS 1 | 475 |
| 4 | PET | RNS 1 | 575 |
| 5 | HDPE | RNS 1 | 550 |
| 6 | HDPE | CO 1 | 550 |
| 7 | HDPE | PCBS 1 | 550 |
| 8 | HDPE | Metal 1 | 550 |

## TABLE 2

### Available Analytical Methods

| Measurement | Method |
|---|---|
| **Solid** | |
| Total Chlorine | Parr bomb digestion, ASTM[1] D808-91, with ion chromatography for chlorine quantification |
| Ash, Volatile, Fixed Carbon, Ash | Proximate analysis, ASTM D3172-89 |
| Trace Metals | Mixed-acid digestion, followed by either graphite-furnace atomic absorption spectroscopy or inductively coupled argon plasma spectroscopy, EPA Method 3051 |
| Leachability | TCLP, EPA Method 1311, and/or synthetic groundwater leaching procedure, an EERC method |
| **Liquid** | |
| Simulated Boiling-Point Distribution | GC-FID[2], based on ASTM 3710-88 |
| Total Chlorine | Parr bomb digestion, ASTM D808-91, with ion chromatography for chlorine quantification |
| Organically Associated Chlorine | GC-AED[3] |
| Tritium | GC-AED |
| Organic Acids | Esterification, followed by GC analysis |
| Component Analysis | GC-MS[4] |
| **Gas** | |
| Component Analysis | On-Line GC and/or FT-IR[5] |

[1] American Society for Testing and Materials.
[2] Gas chromatography-flame ionization detection.
[3] Atomic emission detection.
[4] Mass spectroscopy.
[5] Fourier transform-infrared detection.

# TASK 4

# STABILIZATION OF VITRIFIED WASTES

*Semiannual Report for the Period*
*October 1994 through March 1995*

*Prepared by:*

Jan W. Nowok
Debra Pflughoeft-Hassett
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May 1995

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# TASK 4 – STABILIZATION OF VITRIFIED WASTES

## 1.0 INTRODUCTION/OBJECTIVES

Simply vitrifying a material into a glassy slag does not necessarily produce an environmentally stable product. To make a waste material stable for disposal, the chemistry of the materials will need to be assessed and, possibly, modified with additives and nucleation agents. An assurance that toxic metals and radionuclides have been incorporated into stabilized phases will also need to be determined. The ability of a material to produce stable phases is largely dependent upon chemical composition, time, and temperature. A leaching protocol developed at the Energy & Environmental Research Center (EERC), called the synthetic groundwater leaching procedure (SGLP), and a long-term leaching (LTL) procedure will be applied to vitrified waste materials. Long-term leaching will determine the mass of leachable materials as well as predict the rate of leaching. This task will contribute to the U.S. Department of Energy's (DOE's) identified technical needs in waste characterization, low-level mixed-waste processing, disposition technology, and improved waste forms.

The specific objectives of this task are to 1) demonstrate a waste vitrification procedure for enhanced stabilization of waste materials and 2) develop a testing protocol to understand the long-term leaching behavior of the stabilized waste form.

The proposed work will proceed in the following four major steps:

- Selection and Characterization of Test Mixtures for Vitrification

- Fabrication and Characterization of Optimized Vitrified Test Wastes

- Environmental Assessment of Vitrified and Crystallized Waste Forms Using Advanced Leaching Protocols

- Refinement and Demonstration of Vitrification and Crystallization Methods Leading to Commercialization

## 2.0 ACCOMPLISHMENTS/WORK PERFORMED

### 2.1 Subtask 1 – Survey of Ex-Situ Stabilization Technologies

#### 2.1.1 Introduction

A literature review has been completed that provides an overview of low- and high-level nuclear waste immobilization. The objective of the survey was to make a concise summary of glass properties with nuclear wastes and/or hazardous elements for their effective immobilization, and to specify directions of further tests to produce durable and highly stable glasses. Emphasis is on technologies based on borosilicate glasses since this glass will be used in the United States and in Europe to immobilize radioactive high-level liquid wastes (HLLW) for ultimate geological disposal.

Radioactive wastes are produced at all stages in nuclear fuel cycles over the world. In the United States, they are stored at three DOE sites: the Hanford reservation in Richland, Washington, the Savannah River Site in South Carolina, and Idaho Chemical Processing Plant in Idaho Falls. The Hanford site was the world's first to concentrate plutonium used for atomic weapons. It holds from $3 \times 10^7$ to $6.5 \times 10^7$ gal of HLLW. To store the waste, DOE is considering enhanced waste form options for numerous sites, because the immobilization of radionuclides requires materials with long-term chemical durability, preferably more than $10^4$–$10^6$ years (1). Therefore, vitrification of nuclear wastes is considered the best alternative for radionuclide immobilization and has been a subject of interest for almost four decades (2).

Generally, the stability of any material can be characterized by its thermodynamic equilibrium with its surroundings and by the rate of structural and/or chemical changes to reach this equilibrium. As an example, glasses with their disordered structures are less stable than their crystalline forms under normal environmental conditions, so the glasses are somewhat less durable than crystalline forms. However, sufficient knowledge exists today to develop selection criteria for glass compositions based on long-term rather than short-term behavior.

The durability of glass in contact with groundwater, and its ability to retain nuclear waste within its structure, depends on bulk glass properties, hydrodynamic constraints, the groundwater composition, and the solubility and complexation behavior of nuclear wastes (3–5). The presence of low-level impurities such as iron may enhance the solubility of the glass (6). All these factors may cause the same material fabricated in two different laboratories to have different chemical durabilities. However, two major factors contribute to the suitability of immobilizing high-level nuclear wastes into glass matrices: technical performance—such as chemical durability, the ability to incorporate waste streams having small amounts of flux components, and limited requirements for purchased additives—and ease of fabrication (7, 8).

Research programs on HLLW immobilization using vitrification technologies have been mostly concentrated on either borosilicate glass or Synroc ceramic made from a reactive mixture of Al, Ba, Ca, Ti, and Zr oxides. In borosilicate glasses, hazardous elements can be immobilized by dissolving them in the glass, forming Si–O–M–O chemical bonds, and by encapsulation where bonds are not formed (9).

### 2.1.2 Characterization of nuclear waste streams

Generally, radioactive wastes are separated into two groups: 1) high-level waste (HLW), which includes transuranic constituents (elements with atomic numbers greater than uranium) generated from reprocessing spent fuel and making plutonium, and 2) low-level waste (LLW), which include medical materials and protective casings and tools used around radioactive materials. Many DOE sites have large-volume waste streams that contain a significant amount of high-level nuclear waste both from military programs or from defense reactors which are rich in plutonium and uranium along with large quantities of other contaminates.

An example of a site where high-level waste is stored are the three silos at the Fernald Environmental Management Project in Fernald, Ohio, which contain residues from the processing of pitchblende ores. Silos 1 and 2, designated collectively as K-65, contain the depleted ore, while Silo 3 contains calcined residue from processing solutions. Silos 1 and 2 also contain a bentonite clay cap that was added to the silos to reduce the random emanation from the waste. The K-65

residue totals 8.6 million kg (9500 tons). It is a siliceous material containing uranium, uranium-derived products, and thorium with high levels of radium and lead, while Silo 3 residue is lower in silica and consists largely of metal oxides and sulfates, phosphates, nitrates, carbonates along with uranium and thorium (10). The gamma radiation from the residue is sufficient to result in an average dose of about 200 mr/h outside the silo dome. The radon concentration of the silo headspace is around 30 million pCi/L.

At another site, the Savannah River Site (SRS) in Aiken, South Carolina, HLW is stored as a concentrated liquid radioactive waste by-product of plutonium processing, consisting of a strongly caustic solution of nitrate salts. Also, insoluble and highly radioactive metal oxide sludge is present in some of the materials. These waste streams are pumped from the separations facilities (Canuon buildings) to the liquid radioactive waste handling facilities (called the waste tank farms) located in F-Area and H-Area. The tank farm facilities consist of 51 underground waste tanks with a nominal capacity of one million gallons each. The sludge of highly radioactive metal oxide undergoes aging and several chemical processes prior to vitrification in borosilicate glass (11).

Examples of other materials in waste streams are the following:

- Scrap metals, e.g., 22 wt% of the buried wastes at the Idaho National Engineering Laboratory Radioactive Waste Management Complex

- Metal oxides, e.g., the K-25 pond sludge/soil of over 16 million kg at the DOE Oak Ridge site, which contains 25 wt% iron oxide, 20 wt% aluminum oxide, and 20 wt% calcium oxide (8, 12). Other wastes contain chromium and nickel oxides. Because the maximum solubilities of iron, chromium, and nickel oxides in borosilicate glass are 20 wt%, 3 wt% and 3 wt%, respectively, a large amount of glass will be necessary to fix these materials (8).

Analytical results have shown that nuclear wastes may also contain organochloride pesticides, ketones, and other volatile and semivolatile components. As this waste is heated, volatiles are released, and organics are either pyrolyzed in an oxygen-poor atmosphere or oxidized in an oxygen-rich atmosphere. Offgas treatment is required to minimize air emissions (13).

### 2.1.3 Borosilicate Glass Use in the Vitrification of High-Level Nuclear Wastes

Borosilicate glass was selected in 1982 as the reference waste matrix for solidifying high-level radioactive wastes stored in tanks at Savannah River and West Valley. The vitrified waste produced by the Defense Waste Processing Facility (DWPF) at the Savannah River Site will be in the form of glass logs contained in 2-ft × 10-ft Type 304L stainless steel canisters. This disposal system is designed to provide a safe and permanent storage form.

Borosilicate glasses have been shown to be a good solid matrix for immobilization of the radioactive wastes. Its success stems from its:

- Amorphous structure and strong interatomic bonding;

- Ability to be processed at lower temperatures than other glasses;

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- Higher durability than that of other most glasses; and

- Boron remaining in the residual glass phase upon crystallization of other phases (14).

### 2.1.4 Glass Structure

Oxides that form glasses when melted and cooled are called glass-forming or network-forming oxides. They include $SiO_2$, $GeO_2$, $P_2O_5$ and $As_2O_5$ because of their ability to build continuous three-dimensional (amorphous) random networks. On the other hand, modifying oxides such as $Na_2O$, $K_2O$, $CaO$, $MgO$ are incapable of building a continuous network, and the effect of such oxides is usually to weaken the glass network. The addition of the modifiers to the network-forming oxides invariably lowers the viscosity of the glass melt.

The nature of the bonding between the cations and oxygen plays a critical role in the immobilization of nuclear waste. The bonding behavior is described by the model validity constraints. Generally, those oxides with highly covalent bonds to oxygen are more likely to assume the role of network formers than oxides in which the bonding is predominantly ionic. One measure of the power of a cation to attract electrons, and therefore, a description of the covalent or ionic nature of the bonds it will form, is the ionic field strength, given by (15)

$$F = Z/r^2 \hspace{4cm} \text{[Eq. 1]}$$

where Z is the valency and r the ionic radius. Table 1 lists the ionic radius and the ionic field strength for some cations. The data show that some ions such as $U^{4+}$ and $Pu^{4+}$ may occupy either network-forming positions because of their high charge, or network-modifying positions because of their low F values.

Generally, the maximum concentration of either network formers or modifiers in a glass depends on structural limits. In Table 2, the approximate measured solubilities of elements in silicate waste glass are listed.

Since some oxides have limited solubility in glass, it is important to obtain information on the solubility properties from the Handbook of Glass Manufacture prior to vitrification (16). An example of target composition determined for the DWPF is shown in Table 3 (17).

The composition of nuclear wastes are often unknown which makes it difficult to predict glass properties such as liquidus and softening temperatures, and even the probable level of radioactivity of the waste. For example, only 1–3 wt% plutonium in a vitrified waste is enough to create a chain reaction which will dramatically increase the radioactivity of the material. The presence of water, which is an excellent neutron moderator, around the glass can substantially increase the probability of a chain reaction (18). In addition, technology constraints related to viscosity of the molten glass can be difficult to predict (19, 20).

### 2.1.5 Glass Processing

The most important technological property for glass processing is its viscosity. The viscosity determines the working, annealing, and fining (removal of bubbles from the melt) temperatures,

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## TABLE 1

### Ionic Field Strength of Cations Present in Silicate Glasses

| Ion | Ionic Radius, Å | Field Strength ($Z/r^2$) | Structural Role in Glass |
|-----|-----------------|--------------------------|--------------------------|
| $B^{3+}$ | 0.23 | 56.7 | Network- |
| $Si^{4+}$ | 0.42 | 22.6 | Forming |
| $As^{5+}$ | 0.46 | 23.6 | Ions |
| $Al^{3+}$ | 0.51 | 11.5 | Intermediate Ions |
| $Ti^{4+}$ | 0.68 | 8.7 | |
| $Mg^{2+}$ | 0.66 | 4.6 | Network- |
| $Ca^{2+}$ | 0.99 | 2.04 | Modifying Ions |
| $Na^+$ | 0.97 | 1.06 | |
| $K^+$ | 1.33 | 0.57 | |
| $U^{4+}$ | 0.97 | 4.2 | |
| $Pu^{4+}$ | 0.93 | 4.6 | |
| $Cs^+$ | 1.67 | 0.35 | |
| $Sr^{2+}$ | 1.12 | 0.79 | |

## TABLE 2

### Approximate Solubilities of Elements in Silicate Glasses[1]

| | |
|---|---|
| Less than 0.1 wt% | Ag, Au, Br, H, Hg, I, Pd, Pt, Rh, and Ru |
| Between 1 and 3 wt% | As, C, Cl, Cr, S, Sb, Se, Sn, Tc, and Te |
| Between 3 and 5 wt% | Bi, Co, Cu, Mn, Mo, Ni, and Ti |
| Between 5 and 15 wt% | Ca, F, Gd, La, Nd, Pr, Th, B,and Ge |
| Between 15 and 25 wt% | Al, B, Ba, Ca, Cs, Fe, Fr, K, Li, Mg, Na, Ra, Rb, Sr, U, and Zn |
| Greater than 25 wt% | P, Pb, and Si |

[1] Taken from Reference 13.

upper temperatures of use, and devitrification rate. These properties are often defined in terms of the viscosity ($\eta$) as follows (21):

- Glass melting temperature: $\log \eta = 2.0$ poise
- Working temperature: $\log \eta = 4.0$ poise
- Flow point: $\log \eta = 5.0$ poise
- Softening point: $\log \eta = 7.6$ poise
- Annealing point (upper annealing temperature): $\log \eta = 13.0$ poise
- Transition temperature ($T_g$): $\log \eta = 13.3$ poise
- Strain point (lower annealing temperature): $\log \eta = 14.6$ poise

Typical acceptable viscosity values for melt processing should range between 2 and 10 Pa · s (20–100 poise) (22), because these lower viscosities ease homogenization of the constituents. The addition of 14% waste to the melt can lower the viscosity by a factor of two. Depending on the vitrification process, glass-forming constituents should be added as a premelted ground glass frit to the precalcined radioactive waste.

## TABLE 3

### Target Composition Range for DWPF Waste Glass

| Component | Minimum Range, wt% | Maximum Range, wt% |
|---|---|---|
| $SiO_2$ | 44.6 | 54.4 |
| $Al_2O_3$ | 2.9 | 7.1 |
| $B_2O_3$ | 6.9 | 10.2 |
| CaO | 0.8 | 1.2 |
| MgO | 1.3 | 1.5 |
| $Na_2O$ | 8.2 | 12.1 |
| $K_2O$ | 2.1 | 4.6 |
| $Li_2O$ | 3.1 | 4.6 |
| $Fe_2O_3$ | 7.4 | 12.7 |
| MnO | 1.6 | 3.1 |
| $TiO_2$ | 0.6 | 1.0 |
| $U_3O_8$ | 0.5 | 3.2 |
| $ThO_2$ | 0.01 | 0.8 |
| Group A[1] | 0.08 | 0.2 |
| Group B[2] | 0.08 | 0.9 |

[1] Isotopes: Tc, Se, Te, Rb, and Mo
[2] Isotopes: Ag, Cd, Cr, Pd, Ti, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Co, Zr, Nb, Eu, Am, and Cm

In addition to viscosity, the temperature of glass transition, $T_g$, is a very important glass property. Below it, glass loses its ductility and becomes brittle, and its volume significantly decreases. If a quenched glass is reheated above the $T_g$, it speeds devitrification. It is desirable, therefore, that a glass containing radioactive material is not subjected to temperatures higher than the $T_g$ so that the radioactive material does not segregate into crystals where the radioactive elements are highly concentrated. Also, atmosphere plays important role in glass processing, reduced glasses tend to be less durable than oxidized glasses (23). However, to avoid precipitation of metals and metal sulfides such as NiS and CaS from the glass-forming solution, processing should occur under reducing conditions at which the $Fe^{2+}/Fe^{3+}$ ratio is higher than 0.5.

In addition to glass properties, several properties of the feed materials will also limit the effectiveness of vitrification, including the following (13):

- Feed moisture content (lower than 20 wt% for many processes)

- Feed material composition

- Feed compatibility (ability of the process to handle all the sizes and types of materials)

- Presence of combustible material (organics)

- Presence of process-limiting materials (halogens, reducing agents, and metals)

- Potential volatilization of contaminants and metals with low partial pressures (e.g., Hg, Pb, and Cd)

- Potential shorting of electrodes in Joule-heating caused by metals

### 2.1.6 Devitrification

Devitrification implies the growth of crystalline material in the glass. It can occur as a result of the selection of an unsuitable glass composition or prolonged contact and reaction with the furnace refractories in stagnant regions of the melting furnace. The addition of nucleating agents to the glass may promote devitrification. Usually, the nucleating agents are soluble in the molten glass.

Devitrification of borosilicate glass occurs to a certain extent between 900° and 500°C (24). Usually, the crystalline phase will be a maximum of 3.6 vol% of the canisters filled with glass (25). The size and number of crystalline phases depend on the rate of cooling. Thus, to avoid generation of internal stresses (mainly tensile stresses around the temperature of glass transformation that lead to cracking and void formation), the cooling rate should be carefully controlled. Stresses in glass can be relieved above the glass transition temperature, 430°–450°C, so cracking usually occurs as the temperature drops below 450°C (26). At room temperature, the rate of crystallization of borosilicate glass is very slow and is not expected to occur for $10^6$–$10^{13}$ years (27).

Borosilicate glasses are also susceptible to phase separation into two or more noncrystalline phases. If the phase separation takes place in the melt at a temperature above the liquidus temperature, it is described as stable immiscibility, whereas phase separation occurring below the liquidus is described as metastable immiscibility (28). The presence of stable immiscibility is important in glass manufacturing. Two mixed glassy phases often have quite different properties than a single phase of the same average composition. Devitrification rates and leachability are higher in phase-separated glasses. Phase separation occurs only if the waste compositions are modified to contain much higher levels of $B_2O_3$ (29). Generally, there is no evidence of phase separation in properly formulated borosilicate glasses (30–32).

Decay of radionulcides in nuclear waste glasses, self-irradiation, and internal and external stresses generate heat, and the temperature of the material may rise to the glass transition temperature, which can lead to devitrification. The temperature can subsequently increase exponentially with the cumulative irradiation dose (33).

Devitrification of glass may have a number of deleterious effects on the integrity of the glass waste form (14). They include the following:

- Depletion of silica leaves the residual glass phase with a lowered chemical durability.

- Problems with draining of the melt occurs if it crystallizes at the bottom drain tube.

- Crystalline materials are more susceptible to radiation damage than glasses, and chemical durability may decrease even more than it does for a glass.

## 2.1.7 Durability of Nuclear Waste Glass

Long-term glass stability is related to the maintenance of silica saturation in the surrounding environment. Generally, glass dissolution in an aqueous solution is controlled by the orthosilicic acid activity in solution (34). Glasses with more alkali than metals total boron and aluminum tend to yield alkaline leach solutions in which the increase of pH is faster than the accumulation of silica. The exchange of hydronium ions in solution for the alkalis in the glasses is the main rate-determining step, and the rate of the glass reaction depends on the concentration of the hydronium ions (35). The main glass reaction process can be presented as

$$Glass\text{-}O^-R^+ + H_3O^+(solution) \rightarrow Glass\text{-}OH + R^+(solution) + H_2O \qquad [Eq.\ 2]$$
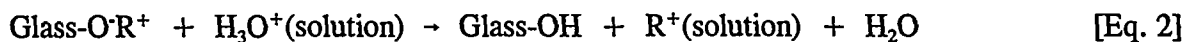
where $R^+$ represents an alkali metal.

It has been shown that waste glass durability also depends on 1) the amount of water contacting the glass waste, 2) temperature, 3) the ratio of glass surface area to solution volume, 4) radionuclide decay effects, 5) glass composition, and 6) alteration phases resulting from glass hydration (36). The chemical behavior of individual radionuclides in glass depends on the glass homogeneity and the reaction conditions such as pH, temperature, flow rate of water, and pressure. Also, glass dissolution is enhanced by the presence of clay (37).

Usually, radiation influences glass stability through the formation of corrosive daughter products and by physically altering the glass structure through atomic displacements. Radioactivity can also make the surrounding aqueous solution more reactive through the ionization of water molecules, mostly from gamma and alpha radiation, which creates very reactive radicals. Also, nitrogen and carbon dioxide dissolved in the water undergo radiolytic decomposition to form nitric and carboxylic acids, respectively (38, 39). These processes can change the leachate pH and glass dissolution rates. Under batch test conditions, glass corrosion has been shown to increase up to three- to fivefold in irradiated tests relative to nonirradiated tests (40).

Many studies have shown that the $Al_2O_3$ (alumina) reduces borosilicate glass leachability because of the stronger interconnection of alkali and alkaline-earth elements within the network structure of glass containing alumina (41). There is, however, an anomalous increase of the dissolution rate at 150°C (42).

Some controversial techniques are used in measuring the chemical durability of the glasses, such as the Savannah River product consistency test (PCT) procedure (43). The test uses washed, crushed glass powder (100–200 mesh) and a glass surface-area-to-solution-volume ratio of 2000 $m^{-1}$. It is performed with deionized water (100 mL) at 90°C. This test provides only information on the maximum solubility of glasses and wastes in deionized water and no real solubility of vitrified nuclear wastes. Also, it was acknowledged in some studies that dissolution is affected by the surface area and the volume of leachate (SA/V) (25, 31). The lack of a standardized test to determine leachability makes the results difficult to compare.

## 2.1.8 Application of Glass-Ceramics for Radionuclide Immobilization

The study of glass-ceramics for immobilizing nuclear wastes stems from pioneering work at the Hahn-Meitner Institut in Berlin on the crystallization of borosilicate-based waste glasses to

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improve the thermal stabilities and mechanical properties of the products. The compositions investigated included those that produced celsian ($BaAl_2Si_2O_8$), perovskite ($CaTiO_3$), diopside ($CaMgSi_2O_6$), or eucryptite ($LiAlSi_2O_6$) and residual glass (44).

Practically any inorganic glass can crystallize above the softening temperature. The crystals may deplete the residual glass of ions, such as $Al^{+3}$, $Zn^{2+}$, etc., that confer durability on the glass, such that the vitreous matrix becomes more susceptible to aqueous dissolution than the original glass. However, these glasses have considerably higher mechanical and impact strengths and are more resistant to cracking than their parent glass. Therefore, they may be used for radioactive waste immobilization in a low flow rate environment if crystalline phases are thermodynamically stable (45).

Also, sphene-based glass-ceramics have been considered as an alternative for HLLW immobilization in Canada. These materials consist of discrete crystals of the major crystalline phase, sphene ($CaTiSiO_5$), within a matrix of aluminosilicate glass, and the waste ions are either incorporated in the sphene structure as solid solution replacements for Ca and Ti or dissolved in the glass matrix. The aluminosilicate glass matrix that remains after sphene crystallization is a highly durable material for immobilizing those waste ions that do not partition into the sphene phase. Generally, sphene is a common accessory mineral in many types of rocks and is resistant to chemical alteration.

The glass-ceramics usually have compositions in the following ranges: $Na_2O$ (5.1–9.0 wt%), $Al_2O_3$ (5.9–11.5 wt%), CaO (9.2–17.1 wt%), $TiO_2$ (10.7–26.7 wt%), and $SiO_2$ (40.1–59.2 wt%) and can include waste oxides of Ce, La, U, Sr, Cs, and U (0–25 wt%). The melting temperature is between 1250° and 1450°C. Crystallization is accomplished by controlled reheating of the glass between 900° and 1050°C and holding for 1–3 hours before cooling to room temperature. Typically, crystalline phases that occur in the glass consist of sphene, pyrochlore, fluorite, wollastonite, anorthite, and other minor phases.

### 2.1.9 Natural Glasses in High-Level Nuclear Waste Immobilization

The common observation of natural glasses persisting in nature for long periods of time provides evidence that natural glasses can be kinetically stable in a variety of environments. Natural glasses are classified according to their silica content from silica-rich rhyolitic glasses and tektites to silica-poor basalt glasses (Table 4) (46). Tektites are glasses of excellent durability with approximately 74 wt% $SiO_2$. They are resistant to water diffusion similarly to that for nuclear glasses, which have diffusion coefficients of approximately $2 \times 10^{-24}$ m²/s at 25°C (47). The results of a series of experiments with tektite glass in water between 150° and 225°C for up for 400 days have shown that a reaction resulted in the formation of a birefringent hydration layer, that increased in thickness up to 4.8 $\mu$m as a function of the square root of time.

A series of basalt-based glass-ceramics for immobilization of nuclear wastes was developed at Battelle Pacific Northwest Laboratory (44). The suggested composition was given as 52 wt% $SiO_2$, 1.6 wt% $TiO_2$, 2.7 wt% $Na_2O$, 10 wt% CaO, 6.8 wt% MgO, 11.9 wt% $Fe_2O_3$, 14.1 wt% $Al_2O_3$, and 0.2 wt% $MnO_2$. This particular basaltic melt is able to incorporate up to 20 wt% defense and commercial wastes. The melting temperature is 1300°–1400°C with nucleation and crystallization of 670°–700°C for 0.5 hour. The final products are 35–45 vol% crystalline material with major phases of augite (a Ca,Mg,Fe pyroxene), powellite ([Ca,Sr]$MoO_4$), and a $NiFe_2O_3$ spinel.

TABLE 4

Typical Compositions (wt%) of Natural Glasses and Representative Waste Glass SRL 165[1]

| | Basalt Glass | Rhyolitic Glass | Roman Bottle Glass | Tiffany Window Glass | SRL 165 Glass |
|---|---|---|---|---|---|
| $SiO_2$ | 50.7 | 74.9 | 68.48 | 43.3 | 52.86 |
| $Al_2O_3$ | 11.7 | 14.2 | 2.61 | 2.0 | 4.08 |
| $B_2O_3$ | -- | -- | -- | 11.5 | 6.76 |
| $Na_2O$ | 4.5 | 4.68 | 19.73 | 0.2 | 10.85 |
| $K_2O$ | 0.7 | 4.59 | 0.77 | 2.7 | 0.19 |
| CaO | 10.6 | 0.53 | 6.74 | 0.35 | 1.62 |
| MgO | 6.7 | 0.02 | 0.68 | 0.03 | 0.72 |
| FeO | -- | 0.49 | 0.29 | 0.09 | -- |
| $Fe_2O_3$ | 13.1 | 0.29 | -- | -- | 11.74 |
| $TiO_2$ | 1.9 | 0.04 | -- | 0.1 | 0.14 |
| MnO | 0.4 | 0.03 | 0.65 | -- | 2.79 |
| $P_2O_5$ | -- | -- | -- | 0.26 | 0.02 |
| $Li_2O$ | -- | -- | -- | -- | 4.18 |
| NiO | -- | -- | -- | -- | 0.85 |
| $ZrO_2$ | -- | -- | -- | -- | 0.66 |
| PbO | -- | -- | -- | 38.93 | -- |
| CuO | -- | -- | 0.06 | 0.06 | -- |
| $H_2O$ | 0.1 | 0.3 | -- | -- | 0.1 |

[1] Compositions are taken from Reference 46.

Iron-enriched basalt glasses were developed at the Idaho National Engineering Laboratory, with melting temperatures of $1400°-1500°C$. Devitrification takes place during controlled cooling with an optional holding period of 16-24 hours at $1000°-1100°C$. This particular glass may incorporate transuranic defense waste. The leaching resistance, mechanical properties and degrees of crystallinity depend on the quantity of radionuclides.

Beginning in the late fifties, an alternative to high-temperature vitrification of soda-alumina-silicate glasses, a sol-gel process producing phosphate glasses was also suggested. The basic building block in phosphate glasses and crystals is the phosphorus-oxygen tetrahedron. However, in contrast to the tetravalent glass formers (such as $Si^{4+}$ in silicates), the pentavalent phosphorus is double bonded to one of its surrounding oxygen atoms. Apparently, this bonding increases the solubility of the phosphate-related glasses, so they cannot be recommended for use in immobilizing HLLW material.

### 2.1.10 Application of Synrocs for Radionuclide Immobilization

Synrocs consist of an assemblage of four main titanate minerals: zirconolite ($CaZrTi_2O_7$), hollandite ($Ba_{12}[(Al,Ti]_8O_{16})$, perovskite ($CaTiO_3$), and titanium oxide ($Ti_nO_{2n-1}$) (48). Synrocs are capable of dissolving the transuranic waste ions such as $U^{+4}$, $Np^{+3,+4}$, $Pu^{+3,+4}$, $Am^{+3,+4}$, and $Cm^{+3}$

by substituting waste ions for host ions. The creation of synrocs requires temperatures of 1250°–1400°C, and a relatively high pressure of at least 20 MPa. Since HLW contains a wide range of components, some of which are readily reduced to the elemental state and others which are readily oxidized to higher valence states, it is important to provide careful control of the atmosphere.

Zirconolite is considered to be the most durable of the synrocs and can immobilize waste actinides at levels up to 30 wt% (49). Excess uranium would react with $TiO_2$ to form very stable $CaUTi_2O_7$ crystalline phase. Cesium would react with trivalent titanium plus additional $TiO_2$ to form a cesium hollandite component, $CsTi_x^{3+}Ti_{8-x}^{4+}O_{16}$. The primary concern in synroc minerals is their excess porosity. To date, samples have been made by solid-state sintering for extended periods (about 100 hours) at 1450°C, and/or at 1250°C and 20 MPa pressure for 2 hours, and the density of the sintered materials was only about 90% (50, 51). This porosity can increase the leachability of the material.

The leachability rate of synrocs sharply decreases with time. The decrease is attributed to the depletion of monovalent and divalent cations in the surface layer leaving it enriched in $TiO_2$ and, to lesser extent, $ZrO_2$ (Figure 1) (52, 53). The chemical durabilty of synrocs is higher than that of borosilicate glasses. Also, crystalline phases formed in synrocs such as $Ca_2Nd_8(SiO_4)_6O_2$, $Gd_2Ti_2O_7$, and $CaZrTi_2O_7$, are less leachable than that of borosilicates after irradiating at doses as high as $10^{25}$ $\alpha$-decay events/m$^3$.
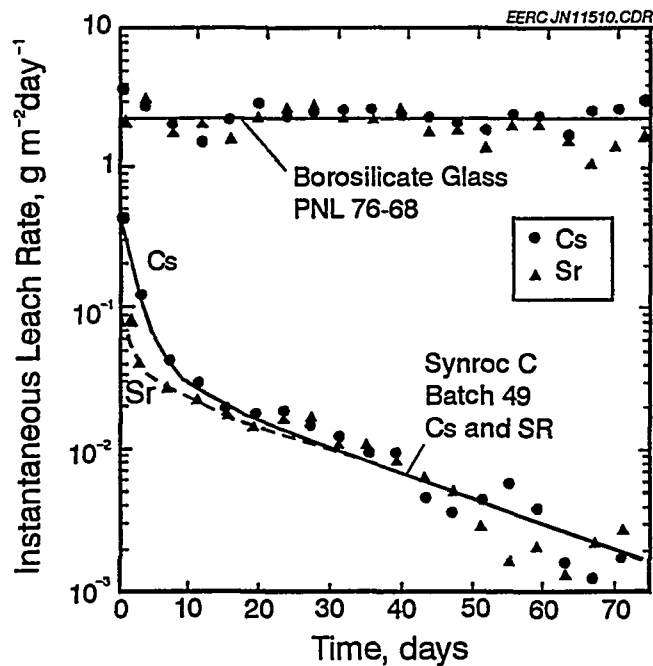


Figure 1.  Leach results for cesium and strontium from Synroc-C (10 wt% simulated HLLW) and waste glass (PNL 76-68) at 100°C; leachant: deionized water, replaced daily.

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## 2.1.11  Cements and Bentonites

Two other groups of materials capable of immobilizing radioactive wastes include cements and bentonite.  Bentonites are weathering products of volcanic ash.  Their essential component is the clay mineral montmorillonite, present in proportions of 65%–99%.  However, their durability is less than that of borosilicate glasses and synrocs ceramics.

Cement can be used for immobilization of low- and intermediate-level radioactive wastes (48).  For use in encapsulation of radioactive wastes, cement blends have to meet a number of requirements:  they should make a stable monolith heat generation must be avoided since temperatures exceeding 100°C will result in steam generation and creation of cracks; and water should not be segregated since this complicates the encapsulation process.

Cements are chemically reactive, and after hydration, they have a mineralogy capable of incorporating a range of radionuclides.  They are also slightly water soluble and give rise to waters with high pHs.  Cement is also susceptible to failure as a result of the action of stress, its environment, and naturally occurring microorganisms (54).  However, a great deal of information exists on working with cements in natural environments.  A thermodynamic model of major crystalline phases, such as hydrogarnet ($Ca_3Al_2O_6 \cdot 6H_2O$), ettringite ($Ca_6Al_2Si_3O_{21}[OH]_{12}$), hydrotalcite ($4MgO \cdot Al_2O_3 \cdot 10H_2O$), and gehlenite hydrate ($Ca_2Al_2SiO_7 \cdot 8H_2O$), has been developed to predict the composition of solid and aqueous phases in blended cements as a function of the bulk composition (55).  Departures from the predicted model occur in cements with alkali-bearing components.

Utilization of bentonites for immobilization radioactive waste is frequently identified as a worst-case scenario.  However in Switzerland, montmorillonite will be utilized as a natural safety barrier to seal construction-caused joints and rock fractures around containers holding vitrified waste because the clay swells in the presence of water.  The solidified waste is a borosilicate glass matrix that will be encapsulated in a 25-cm-thick steel canister with a minimum life expectancy of 1,000 years.  The canisters will be placed in horizontal tunnels 3.7 m in diameter at a depth of around 1,000 m (56).

## 2.1.12  Vitrification Technologies

Two major, well-recognized types of vitrification technologies are differentiated by their heating methods, either electrical heating or heating by firing a fossil fuel.  Usually, electric heating is subdivided into Joule heating, plasma heating, and microwave heating.  These types of heating are potentially applicable in vitrification of nuclear wastes (13).

Electric heating, also called ex situ Joule heating, is an efficient method of transferring energy to a waste since no combustion air needs be heated with the waste as is necessary when firing a fossil fuel.  The method is readily applied to glasses since glass resistivity decreases by a factor of $10^{13}$–$10^{14}$ as temperature increases from ambient to 1300°–1400°C.  Since the conductivity of molten glass is a result of its ionic character, an alternating current must be used to avoid the risk of electrolysis, anodization of the electrode, and the depletion of charge carriers.  Electrodes must withstand corrosion from the molten glass bath, offer adequate mechanical strength at high temperatures, and possess low resistivity.  These limitations imply that the maximum temperatures of the melt should be ranged between 1000° and 1600°C (57).  The

commercial glass industry uses graphite and molybdenum for electrodes. Figure 2 illustrates the typical glass melter used in the glass industry.

For a Joule-heated ceramic melter, the variation in resistivity of a glass with temperature is a very important parameter, and it is highly correlated with liquidus temperature and glass viscosity. The glass liquidus temperature constraint for the Hanford melters (Hanford Waste Vitrification Plant, Westinghouse Hanford Company, WA) has been $T_L < T_M - 100°C$, where $T_L$ and $T_M$ are the liquidus and melter temperatures, respectively (58). In this type of melting, the ability to predict the electrical resistivity of a glass from its composition has the same importance as prediction of viscosity from composition (59). The electrical conductivity requirement at $T_M$, 10–100 S/m, is usually satisfied for any glasses with viscosity within 2–10 Pa · s (20–100 poise) at $T_M$ (60).

Electric furnaces may encounter several of the following processing problems:

- Foaming leading to unstable operations and pressure surges

- Cold-cap bridging occurring when liquid flows under the cold cap

- High electrical conductivity in the melt causing the current to exceed the recommended maximum

- Low electrical conductivity in the melt resulting in a high voltage potential causing conduction within the refractory material

- High viscosity slowing the processing rate

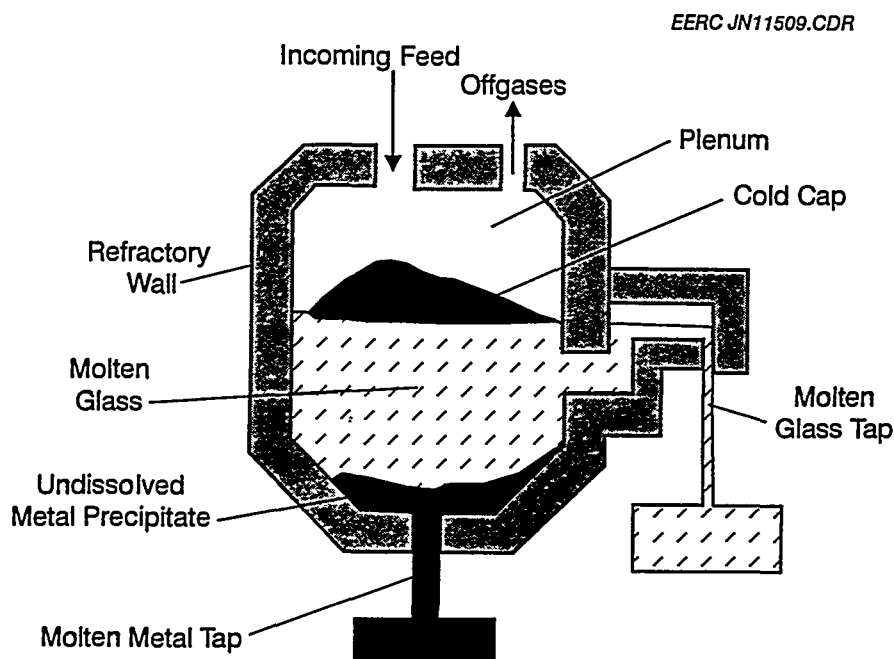- Low viscosity (<100 poise) increasing refractory corrosion



EERC JN11509.CDR

Figure 2. Scheme of a Joule-heated ceramic melter (JHCM).

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At the Savannah River Site (SRS) in Aiken, South Carolina, the vitrification of HLLW is accomplished in a Joule-heated melter. The nominal glass temperature beneath the cold cap is 1150°C, the nominal glass weight is 6500 kg, and the average residence time in the melter is about 65 hours (61). It has been suggested that the HLLW will be mixed with glass frit and vitrified to form a durable, solid borosilicate glass. A small amount of sodium titanate will be added to adsorb the traces of soluble strontium and plutonium in sludge (62).

Another Joule-heating process is induction heating developed in France and known as the AVM process (Atelier de Vitrification Marcoule). This process is accomplished by inducing currents in the material using a solenoid which subsequently create a variable magnetic field inside the coil and around it.

Plasma heating relies on the conversion of surrounding gas into a plasma (an ionized gas) by an electric arc. The technique offers high operating temperatures and high power densities. An argon plasma may theoretically offer temperatures as high as 19,000°C, but in the partially ionized plasmas that occur in industrial applications, the temperature varies between 2,000° and 5,000°C. Retech, Inc., of Ukiah, California, has developed a plasma heating furnace called the plasma centrifugal reactor (PCR) that allows the material to exceed a temperature of 10,000°C (Figure 3). The rotating reactor helps to transfer heat evenly throughout the molten phase. Periodically, the melted material is allowed to fall in to a slag chamber where it is collected in waste containers. Electro-Pyrolysis Incorporated (EPI) of Wayne, Pennsylvania, employs a similar direct-current plasma arc technology in its vitrification process. The technology was developed in cooperation with the Massachusetts Institute of Technology and Pacific Northwest Laboratories.
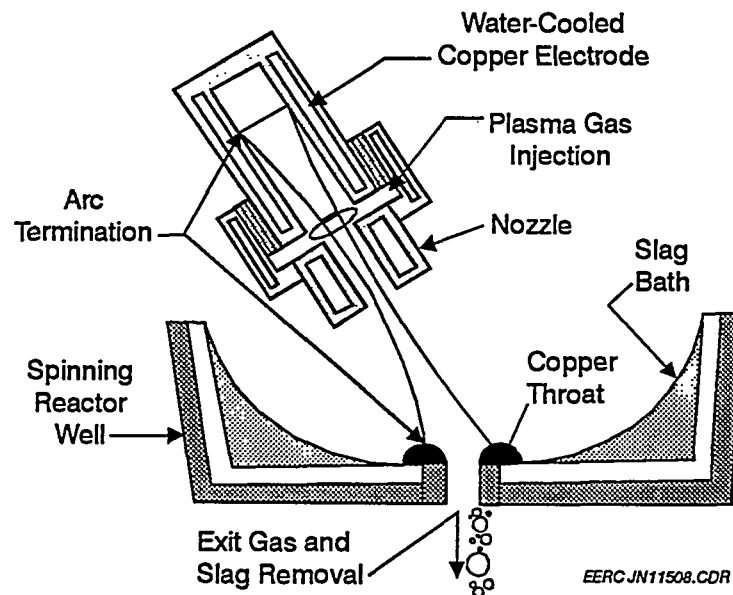
Figure 3. Schematic of the plasma centrifugal reactor (PCR).

In microwave heating, a form of dielectric heating is introduced to the body through the absorption of electromagnetic radiation. A microwave installation consists of a microwave generator, a waveguide, an applicator, and ancillary monitoring devices. The main disadvantage is its relatively high energy consumption.

The next group of thermal process heating is based on burning of fossil fuels in a rotary kiln incinerator. These methods are inherently less efficient at transferring the energy to the waste material since a large mass of combustion air must also be heated. However, the fuel is cheap and is used directly for heating the waste unlike electrical heating, where the fuel must first be converted to electricity, a process that is approximately 35% efficient. Inorganic Recycling Inc. (IRI) has developed a vitrification process using only incineration, while Marine Shale Processors has developed a vitrification process in which only a portion of the incineration products is vitrified. Figure 4 shows a scheme of the IRI process. Vortec Corporation has developed a portable system that can fire natural gas or coal. The gas flow within the combustor is forced into a strong cyclonic motion causing the molten waste to separate efficiently from the gas for casting into ingots.

### 2.1.13 Summary and Recommendations

A literature review has been completed that provides an overview of low- and high-level nuclear waste immobilization. Emphasis is on vitrification technologies based on borosilicate glasses since this glass will be used in the United States and in Europe to immobilize radioactive HLLW for ultimate geological disposal. Vitrification of aqueous radioactive wastes will achieve large volume reductions (86–97 vol%) and will ensure their stabilization. Borosilicate waste glasses are the most studied and probably best understood waste form that has been developed. Also, the application of synrocs, cements, and bentonites for radionuclide immobilization is discussed.
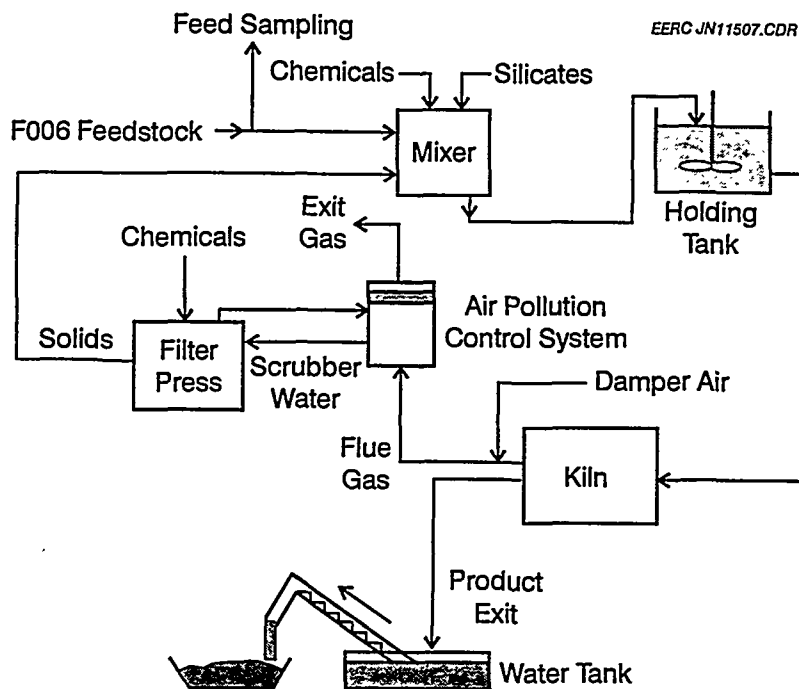


Figure 4. Scheme of IRI process (13).

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This survey indicates that a lack of information exists in the following areas:

- Vaporization of heavy or radioactive metals from the melts, and whether vaporization behavior could be controlled by modifying the heating environment in order to separate the hazardous materials from the bulk waste.

- How to avoid the formation molten sodium sulfate on the cold cap.

- Catalytic activity of radionuclides at the surface of the glass and glass corrosion in water.

- The effect of glass cooling rate on generation of residual stresses below the temperature of glass transformation and its effect on the leachability of nuclear waste glass.

- The effect of foaming of the melt on the homogenization of nuclear waste during vitrification using plasma technology.

## 2.2    Subtask 4.2 – Survey of Cleanup Sites

A two-pronged literature survey of cleanup sites has begun.  It is focusing on studies of the leaching of vitrified wastes at the sites as well as a general survey of existing hazardous DOE waste sites and waste stabilization technologies (other than vitrification) currently in use at the sites.

A preliminary assessment of leaching studies indicates that the testing procedures currently in use to determine the leachability of the waste materials is geared to short-term procedures that are directed toward regulatory compliance rather than realistic or predictive testing.  This survey is scheduled for completion in June 1995.

The survey of DOE waste sites is a part of this larger survey.  The information already reviewed indicates the existence of a wide variety of mixed wastes containing low-level nuclear material or radionuclides.  Some of the wastes are suited for vitrification.  Others would be better stabilized with alternative technologies because of the nature of some of the constituents.  These include mixed wastes with chlorinated hydrocarbons, explosives, and pesticides.  These types of wastes will not be considered in this task.

## 3.0    WORK PLANNED FOR NEXT 6 MONTHS

The survey of vitrification technologies indicates that the size and momentum of existing technologies for vitrification of radioactive waste are too great for meaningful contributions by this project.  Therefore, future work for Task 4 in the area of vitrification technologies will focus on the cleanup of heavy metal waste sites, each of which may require flexible and specific remedies.

The literature survey on waste sites and leaching procedures will continue.

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# TASK 8

# MANAGEMENT AND REPORTING

Semiannual Report

*for the period October 1, 1994, through March 31, 1995*

*Prepared by:*

Edward N. Steadman

May 1995

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# TASK 8 – MANAGEMENT AND REPORTING

## 1.0 INTRODUCTION/OBJECTIVES

The objective of the Environmental Management program at the Energy & Environmental Research Center (EERC) is to develop, demonstrate, and commercialize technologies that address the environmental management needs of contaminated sites, including characterization, sensors, and monitoring; low-level mixed waste processing; material disposition technology; improved waste forms; in situ containment and remediation; and efficient separation technologies for radioactive wastes.

Research being conducted in this program includes extraction and analysis of pollutant organics from contaminated solids, pyrolysis of plastics wastes, stabilization of vitrified wastes, extraction of hazardous metals from mixed-solid wastes, extraction of organic pollutants, and demonstration of a low-temperature plasma remediation technology.

The strategic involvement of industry in planning and implementing field demonstrations and commercialization is an important component of this program. The EERC will establish joint ventures with small businesses to advance environmental management technologies and provide coordination and technical support to resolve barriers and shorten the path to commercial implementation of novel new technologies.

The primary objective of this task is coordination of this project with other programs and opportunities such as 1) the Environmental Protection Agency-sponsored Center for Excellence on Air Toxic Metals, 2) the Department of Energy (DOE)-sponsored Jointly Sponsored Research Program, and 3) other opportunities to advance the commercialization of enhanced environmental management technologies. In addition, management oversight will be maintained to ensure that tasks are completed and coordinated as planned and that deliverables are submitted in a timely manner.

The managers of this program will actively involve and educate themselves with respect to DOE's Environmental Restoration and Waste Management Program by visiting selected DOE weapons complex sites, by attending conferences and meetings pertaining to this program, and by fostering contacts, both government and industry, with others involved in implementing and managing this program. They will especially focus on building the government–industry teams which EERC has successfully built in its DOE Fossil Energy-sponsored Jointly Sponsored Research Program.

## 2.0 BACKGROUND

The EERC has a multidisciplinary staff of 260 scientists, engineers, and support personnel dedicated to full-time work on a wide variety of energy and environmental technologies. The Center, since its defederalization as a former DOE coal laboratory in 1983, has developed unique scientific and technological assets, including patented, proprietary, and other specialized technologies applicable to characterizing, preventing, containing, and remediating hazardous mixed

wastes comprising organic, inorganic, and radionuclide contaminants. In addition, the EERC has a proven track record for accelerating and integrating the commercialization of technology through joint venture partnerships with other organizations offering complementary environmental management methods. Sustained integration of fundamental research and technology development is considered to be essential to achieving success.

The special contributions that the EERC offers in addressing DOE's environmental management problems are rooted in a multidisciplinary core of scientists and engineers devoted to the commercial development of practical solutions to real-world problems. We believe that quality of life depends upon energy security and environmental quality and that they are fundamentally inseparable. We further believe that genuine progress in resolving intractable problems in environmental management can only be made by combining in-depth scientific understanding of relevant properties and processes with innovative business practices that bring together and integrate complementary technologies. The EERC has its own patented or proprietary technologies and world-class experience and expertise in the following areas:

- Geological, physical, chemical, mineralogical, and biological site characterization
- Groundwater occurrence, flow, and quality
- Physical, chemical, mineralogical, and biological contaminant characterization
- Contaminant–site interactions
- Geochemistry
- Organic analytical chemistry using supercritical fluid extraction
- Trace metal inorganic analytical chemistry
- Waste disposal site characterization, selection, and design
- Chemical, physical, and mineralogical materials characterization
- Environmental leaching protocols
- Low-temperature plasma reactions
- High-temperature combustion systems
- Phase fractionation chemistry and predictive methods
- Reductive energy conversion processes
- Atmospheric emission control
- Air toxics release and control mechanisms
- Waste utilization and recycling
- Waste prevention and disposal
- Advanced fixation methods: cementitious, pozzolanic, and vitreous
- Mine land reclamation
- Trace element transport and attenuation
- Agricultural chemical impacts on groundwater quality

These capabilities offer important opportunities for resolving environmental management problems identified by DOE in the following categories:

- Characterization, sensors, and monitoring
- Low-level mixed-waste processing
- Material disposition technology
- Improved waste forms
- In situ containment and remediation

- Efficient separation technologies for radioactive wastes
- Technology demonstration and commercialization

The management task for this project is designed to capitalize on the technical and partnership-building experience present in the EERC management in order to meet the overall program objectives.

## 3.0 ACCOMPLISHMENTS/WORK PERFORMED

In addition to overall management of the program and reporting, significant resources in Task 8 have been expended on attending technical meetings and developing a sense of direction for the program. Specific accomplishments for this reporting period are as follows:

- Internal planning meetings were held on a regular basis with Gerald Groenewold, the Program Manager, and the Principal Investigators for each of the Cooperative Agreement tasks to discuss project objectives, deliverables, and the management philosophy for this agreement.

- Michael Jones, Everett Sondreal, Frank Beaver, Ed Steadman, and John Hendrikson from the EERC attended a 2-day conference November 16–17 at the Morgantown Energy Technology Center (METC) entitled "Opportunity '95 – Environmental Technology Through Small Business."

- A kickoff meeting was held at METC on November 18 to outline the EERC's plans for work under the Cooperative Agreement entitled "Environmental Management Technology Demonstration and Commercialization." METC personnel gave presentations about METC's role within DOE's Environmental Management program and how the EERC fits into that role.

- Follow-up meetings were held at the EERC to discuss contacts made at the METC small business conference. Opportunities were discussed, and plans were formulated for following up on those contacts where significant opportunities exist.

- A meeting was held for EERC personnel involved in the Environmental Management project, informing them about reporting requirements. Requirements were discussed and procedures established to ensure timely reporting.

- A proposal outlining a project designed to demonstrate the utility of a novel membrane technology for EM applications was submitted to METC. SpinTek has developed a centrifugal membrane technology that may have broad applications in the cleanup of DOE sites. A meeting with individuals from SpinTek was held at the EERC on January 31 – February 1. The result of the meeting was the proposal to partner with SpinTek and METC to demonstrate the new system's utility as a cleanup technology.

- A database cataloging EM-related documents and publications available at the EERC was initiated.

- Michael Jones attended the Sixth Annual Applied Research and Technology Colloquium: Waste Management and Cleanup, April 18–20 in Phoenix, Arizona. The meeting was attended by approximately 300 people representing national labs, the U.S. DOE, various contractors, and other interested parties. This meeting provided an efficient forum for the EERC to keep abreast of the latest activities and trends in the national Environmental Management program.

- Efforts in pursuing contacts and opportunities available are continuing.


## 4.0 WORK PLANNED FOR NEXT 6 MONTHS

Efforts over the next 6 months in Task 8 will continue to focus on three key areas: 1) coordination and overall management of the in-house research efforts, 2) identification of key environmental management needs and technologies by assessing current literature and attending technical meetings, and 3) the establishment of private sector partnerships that will result in the commercialization of new technologies. The EERC is also seeking commercial parties to help take its own extraction, vitrification, pyrolysis, and plasma remediation technologies to the marketplace.