LA-13161-SR
Status Report

94-1 Research and Development Project Lead Laboratory Support

Status Report

January 1 – March 31, 1996

Los Alamos
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Mark Dinehart

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EXECUTIVE SUMMARY

ELECTROLYTIC DECONTAMINATION

Electrolytic decontamination equipment is being modified for installation at the Los Alamos Plutonium Facility (TA-55), Building PF-4, for a glovebox demonstration of electrolytic decontamination of a long-term storage container. Additional staff made it possible to begin development of a semiautomatic cleaning head for glovebox decontamination. Using the existing equipment, we decontaminated a glovebox to levels that enabled the glovebox to be moved to a new location and reinstalled in PF-4. Ultrafiltration is being developed to remove hydroxide precipitates from the electrolyte before recycling the solution back to the stainless steel surface. We are evaluating filtration products from three suppliers and assembling a back-flushing apparatus. Initial batch processing of the solution eventually will be replaced by continuous flow.

COMBUSTIBLES

Cryogenic Crushing

We have fabricated a jaw crusher to crush hard materials, such as polystyrenes and we successfully demonstrated the crusher on polystyrene pellets, polycubes with iron, and leaded gloves. Liquid nitrogen (LN_2) was used to cool materials and equipment and to wash smaller particles out of the crusher during the operation. We improved the filter shredder and successfully tested it. Filters are cooled in LN_2 and are automatically fed into the shredder. Size of the materials exiting the shredder can be optimized when parameters for washing or other processing have been determined. We have demonstrated a new process using an LN_2-cooled industrial blender to reduce soft waste more quickly than in the jaw crusher, with the further advantage of producing no dust. Also, we have successfully demonstrated size reduction of rubber gloves, Tyvek™, cloth, paper, and plastic sheeting. Iron-loaded polycubes have been provided to researchers on the Pyrolysis task for their demonstration of process. We also provided ground polystyrene, polycubes with iron, glovebox leaded gloves, and a matrix of soft waste to the Hydrothermal Oxidation team for testing. Project operating funds are being converted to capital for the purchase of a Franklin Miller shredder that is suitable for use on soft wastes at Rocky Flats Environmental Technology Site (RFETS).

Hydrothermal Oxidation

We constructed and tested a small-scale hydrothermal unit for treatment of transuranic-contaminated combustible materials. A problem with leaking seals is being corrected with the vendor. A simulant of general laboratory trash was processed with varying H_2O_2:waste slurry ratios, and a maximum H_2O_2:slurry mix was determined.

Stabilization of Polycubes Using Pyrolysis

During the cold war, polystyrene matrices loaded with plutonium and/or uranium oxide were cast into cubes as large as 2 in. on a side for use in criticality experiments. The polymeric materials can be volatilized and removed from the oxides by heating to a high temperature in an inert atmosphere. We are devising a treatment to break down components of the reactor off-gas to CO_2 and H_2O. Los Alamos researchers will evaluate catalytic conversion, a silent discharge plasma, and the use of an afterburner. We are studying the rate at which off-gas leaves the reactor, and these studies will form the basis of treatment technology design. The rate tests show that most of the decomposition products leaving the reactor are liquids at ambient conditions. A small amount of residue, which is presumed to be carbon, is left. Gaseous products leaving the system are 11% of the total. We used gas chromotagraphy and mass spectroscopy to determine the composition of both the condensate and the gaseous products. Review of the literature on catalytic converters reveals the following:

- that the most appropriate catalyst for this application is platinum, palladium, and/or rhodium present on either a metal or ceramic support and
- that the temperature of the feed gases coming in contact with the catalyst and the temperature of the catalyst must be controlled to prevent sintering, coking, or other factors from adversely affecting performance.

Gas temperature of the effluent from the converter can be controlled by air-flow rate, but problems arise in glovebox operation at high flow rates. To solve heat generation and removal problems, we modified the design of the pyrolysis setup to allow for the components in the reactor off-gas to be condensed, then pumped into the catalytic converter at a more controlled rate.

We are conducting discussions with several companies to determine which vendors have the appropriate catalysts, the technical expertise, and the willingness to design a converter for the polycube process. In addition, results of the rate tests enabled us to design and build a coaxial silent discharge plasma prototype unit. The performance of this system is being evaluated in an experimental setup. We used organic liquids as surrogates for the off-gas, and we analyzed the performance of the system using a range of argon and oxygen flow rates. The setup includes in-line gas/liquid analytical capabilities, such as gas chromatography and mass spectroscopy, flame ionization detection, and nondispersive infrared spectroscopy, for measuring CO and CO_2 concentrations.

DETOX

The contract to continue development with Delphi Corporation is in place, after a delay of several months. An RFETS change-of-station employee will provide oversight to Delphi, and a technician has been selected to provide TA-55 interface with the contractor. We are proceeding with evaluation of liquid effluent disposition. The hydrolysis method of conversion of spent ferric chloride process solution to ferric oxide is 80% successful. Work continues on heater design, heating rate, reactor configuration, and solution agitation.

Residue Washing Flow-Sheet Development

This project—to evaluate a proposed process flow sheet to remove organics, solvents, and finely divided plutonium metal from combustibles—was begun in March. We prepared an experimental plan that first used a cerium surrogate and then used plutonium-loaded surrogate materials. We obtained the cerium surrogate from Safe Sites of Colorado (SSOC) at RFETS.

SAND, SLAG, AND CRUCIBLE

Magnetic Separation

Throughout the DOE complex, sand, slag, and crucible (SS&C) residues may hold as much as 10-20% plutonium. The magnetic separation process exploits differences in magnetic susceptibility, in order to concentrate the actinides in a process waste stream. The purpose of such concentration is to form a low-volume, actinide-rich stream for subsequent reprocessing and a high-volume, actinide-lean stream for disposal.

Los Alamos has had success with two dry powder separators for plutonium-contaminated residues. A small open-gradient magnetic separator, which creates the necessary magnetic energy gradient through the shape of the magnet pole pieces, has worked successfully to create a rich stream for reprocessing and a lean stream suitable for discard. However, because of low throughput, the usefulness of this separator is limited. To improve processing rates for dry powders, we have one type of rare-earth roll separator available for testing. In this process, a thin belt passes over two rollers, one of which consists of a 1- to 2-tesla magnet. A powder is fed onto the belt; and slightly magnetic particles stick to the belt in the vicinity of the magnet, causing the magnetic and nonmagnetic particles to be deflected in different directions and bringing about separation. For plutonium-contaminated graphite residues, this device created a rich fraction, in which 85% of the plutonium was concentrated in 4% of the bulk material, and a lean fraction that was suitable for discard.

Los Alamos researchers will work with personnel at Westinghouse Hanford Company (WHC) to review and characterize waste for magnetic separation tests. Los Alamos residues have been identified for testing. After magnetic separation tests, the process will be optimized; and the feasibility of using it on WHC SS&C will be evaluated. Initially, we are repairing and modifying equipment for use in a glovebox in TA-55. Several items are on order for replacement and installation. The vendor, INPROSYS, has been consulted for expertise on the operation and optimization of the roll separator.

We prepared a surrogate SS&C for vendor testing by spiking ground magnesium oxide (MgO) crucibles with copper oxide, which has approximately three-quarters of the magnetic susceptibility of PuO_2. In this experiment, attempts to high-grade the rich fraction were unsuccessful because half of the MgO gravitated to the rich fraction. Perhaps this movement was caused by a magnetic mineral component in the MgO. We are in the process of determining the magnetic susceptibility of the material, and we will address pertinent problems in the next planned experiment. An experiment to examine belt speed with SS&C residue is under way at Los Alamos.

Compaction

We are investigating the processes of compaction and sintering for stabilization of SS&C materials. We did an experiment on a lean residue item, and we plan a companion experiment using a rich residue. The crushed and blended the material is being tested with PEMCO™ frit P-25, a borosilicate material with a low melting temperature. This material, by virtue of its low melting temperature, should provide a low sintering temperature. We pressed pellets with no added binder or lubricant. Two test matrices, with varying percentages of added frit and with varying sintering temperatures and furnace gas atmospheres, were established. We measured the sintered pellets from the first test matrix for shrinkage and density calculations, but we have not yet evaluated the second test matrix. We will employ a surrogate sample, using cerium oxide to do thermogravimetric analysis to determine temperatures, heating rates, and atmospheric conditions affecting iodine release and conversion of calcium metal to oxide.

Damage to a larger oxygen-atmosphere furnace and difficulties in getting parts have delayed installation of the furnace in a glovebox. This furnace was to be used in sintering of plutonium compacts at temperatures above 1000°C. The delayed furnace installation also has caused postponement of tests with the addition of porcelain to the SS&C and tests without additives, which require higher temperatures. The compaction of the SS&C material in the form of ballinders, which require a larger furnace than is presently available; and the performance of drop-and-crush tests using these materials also have been delayed.

SURVEILLANCE

Digital/Real-Time Radiography

In February, we installed real-time radiography equipment in the Plutonium Facility. A 225-keV real-time radiography device from VJ Technologies of Bohemia, New York, was chosen to meet the requirements of the plutonium Packaging Project and to evaluate existing vault packages. Researchers from Savannah River Site (SRS) will work together with Los Alamos personnel to evaluate and optimize the capabilities of the system to monitor existing storage containers and to support the Los Alamos surveillance Shelf-Life Project. We have selected bellows developed by Miniflex of Ventura, California, for surveillance of the first containers packaged at

Los Alamos in the plutonium Packaging Project. Statistical tests so far indicate that radiographs of the bellows inside the container provide an excellent indicator of pressure. Comparison testing using the real-time system will continue. New bellows designs, including a more robust configuration and a filter to eliminate convolution exposure to plutonium oxide, will be tested at Miniflex this year.

Tomography

Researchers at Los Alamos are working with SRS personnel to construct test objects and to provide imaging data to aid in the evaluation of commercial x-ray systems and to cooperate in development of a computerized tomography (CT) system for eventual deployment in the SRS FB processing line. Savannah River researchers constructed two tomography phantoms of different nonradioactive chemical compounds in order to evaluate the efficacy of dual-energy tomography for materials identification. One of these phantoms was delivered to Los Alamos. We have identified failure mechanisms that we observed in stored nuclear materials at Los Alamos and that may be identified by CT. We are proceeding with computer modeling of stored Los Alamos materials, which will lead to design and fabrication of test objects. A tomographic gamma scanner (TGS) was installed in TA-55. We will evaluate TGS performance for measurements of historically hard-to-measure materials, such as salts.

Shelf-Life Project

We selected for study an RFETS surrogate plutonium oxide/magnesium oxide material. We characterized the material for particle size and surface area after it was calcined at 600°C and at 980°C. For each calcination temperature, we will determine moisture adsorption rates and make pressure-volume-temperature observations over an extended time period.

In collaboration with other sites, we have tentatively targeted several materials for study. Personnel from SRS, WHC, and SSOC at RFETS will meet with Los Alamos personnel to prepare detailed plans for shelf-life studies of materials at these sites. Although materials similar to those at other sites may be found in the Los Alamos inventory, Los Alamos researchers plan to establish shipping links in order to obtain materials from the entire DOE complex. Hanford has vault holdings of plutonium oxide calcined at about 500°C that indicate little or no pressure increase over the past 10–20 years. Los Alamos researchers plan to perform gas analysis and loss-on-ignition measurements on materials in these containers.

Shelf-Life Project Subtask: Optical Monitoring of Residues and Oxides in Storage Containers.

We have designed and are fabricating experimental long-term-storage-type containers with viewing ports. The containers include bellows to adjust the height of the powder in case of settling. Using gadolinium as a surrogate for plutonium, we conducted laser-induced breakdown spectroscopy experiments in order to optimize signal detection and element identification, varying parameters such as buffer-gas content and pressure.

Both temporal and spatial evolution are highly dependent on buffer gas and buffer-gas pressure. Argon enhances atomic emission in the red wavelength over emission obtained in helium. In further experiments, we tentatively identified three trace elements. We will verify these identifications by comparison with spectra of gadolinium without the elements present. Future experiments will include different gas compositions. Start-up of experimentation in TA-55 is being delayed by facility modifications to support the Advanced Recovery and Integrated Extraction System (ARIES) Project.

Acoustic Resonance Spectroscopy

Surveillance must be performed on containers of plutonium-containing materials in storage, and more sophisticated and precise noninvasive tools are needed. Gas resonances are easily detected inside an otherwise empty container. Unfortunately, when even small amounts of simulated plutonium oxide (sand) are added to the cylinder, the sand absorbs enough energy so that the gas resonances become undetectable. A simple modification to the container created an analysis chamber in which the gas resonance can be excited and monitored, even though the rest of the container is full of sand. Thus, we demonstrated the feasibility of using acoustinc resonance spectroscopy (ARS) to monitor gas composition and pressure inside a modified inner residue cylinder. The sensitivity of ARS to detect changes in gas composition based on shifts in the frequency of the gas peak by 1 Hz have been calculated for mixtures of helium, hydrogen, and argon. Using a variety of coupling geometries, we have designed a set of experimental chambers to test the ability to couple acoustic responses between an inner and outer container. We have begun theoretical modeling of the acoustical response of a gas mode interacting with a container mode. Results have been very encouraging.

CORE TECHNOLOGY

Solution Chemistry

This work seeks to measure critical thermodynamic parameters governing actinide chemistry under chemical conditions different from those carried out during the weapons era, so that separation processes can be designed and optimized quickly. The absorption capability at TA-55 was made operational, incorporating improved sample handling and mechanical stability. Glovebox services must still be connected. We prepared samples and acquired spectra on a Pu(IV) nitrate system, using approximately 100 solution samples that covered three different ionic strengths and ranged up to 22.5 molal total nitrate concentration. We will continue data analysis concurrently with additional sample preparation and data gathering. We began work on interactions of higher plutonium oxidation states, principally Pu(VI) with other inorganic anions. We collected preliminary spectroscopic and solubility data on chloride, carbonate, and perchlorate systems.

Chemical and Physical Interactions of Actinides with Surfaces

The purpose of this task is to study the interactions of plutonium and uranium species adsorbed onto solid-phase materials. Actinide species interact with surfaces by means of a number of mechanisms—surface complexation, physisorption, matrix diffusion, entrainment—to yield a wide variety of surface-bound species. From the existing TA-55 inventory, we selected a number of ash residues for characterization. We obtained Raman spectral data that show a number of vibrational bands consistent with plutonium-oxygen stretching modes that we saw previously for high-fired PuO_2. Equipment is being upgraded, and the laboratory space is being refitted.

Changes in the Chemical State of Plutonium

The goals of the project are to study and characterize the chemical state of plutonium in various residues. Twenty samples of two types—loaded resins and ash—were prepared for extended x-ray absorption fine structure (EXAFS) work at the Stanford Synchrotron Radiation Laboratory. We selected for study a series of new anion-exchange resins that have higher distribution coefficients and more rapid kinetics of absorption. In these resins, the binding site has been molecularly engineered to provide a chemically more attractive site for the plutonium hexanitrato complex, which may result in faster, more efficient separations. Results of these studies will provide a base line for evaluation of changes in resins that have been loaded for many months.

Ash residues that we studied using electron microscopy show small plutonium dioxide particles that are substoichiometric with respect to oxygen. These will be studied by EXAFS along with carefully prepared oxides of plutonium for calibration. ^{239}Plutonium and ^{242}plutonium solutions were purified by anion-exchange chromatography prior to spectrographic studies. Electrochemical synthesis of stock solutions of Pu(III), Pu(IV), Pu(V), and Pu(VI) was completed, and the samples were assayed using ultraviolet/visible absorption spectrum/near-infared spectroscopy to assure that each solution contained a single oxidation state. We examined this series of samples by x-ray absorption near-edge structure spectroscopy in order to determine the absorption-edge energy for each oxidation state. This background information is vital for comparing oxides, residues, and column-sorbed materials in order to determine oxidation states of the latter materials.

Actinide-Organic Interactions

The purpose of this task is to investigate actinide organometallic chemistry and interactions between actinides and organic substrates. The glovebox used to perform organoactinide work must be repaired. We will use the downtime to install new thermogravimetric analysis/differential scanning calorimetry equipment for characterization and kinetics studies. We will investigate the chemical interactions of plutonium with tributylphosphate (TBP) at several temperatures. Speciation of TBP is dependent on oxidation state; but chemistry associated with organic destruction of TBP is unknown.

Crystallographic Corrosion Studies

We selected nickel, titanium, and beryllium for early studies on the nature of corrosion. The goals are to determine the effect of surface structure on pitting, to gain insight into the stochastic nature of corrosion, and ultimately to improve corrosion resistance of common materials through intelligent surface processing or texturing. We examined nickel foils with three different crystallographic textures in order to obtain x-ray pole figures for each texture. Our purpose was to obtain detailed information about the predominant bulk crystallographic orientations. We prepared the foils for dc polarization experiments in order to compare the pitting tendencies of each foil. Preliminary results on randomly oriented beryllium indicate that polycrystalline beryllium is susceptible to selective attack at basal planes.

Plutonium Diffusion Science

The objective of this task is to determine the diffusion of different forms of plutonium into metal matrices at room temperature over a long period of time. We will determine diffusion coefficients for very small concentrations embedded over a few microns. We will evaluate various surface science techniques. For example, in laser ablation spectroscopy, surface layers of metals exposed to plutonium are removed by laser ablation while plutonium concentration is measured; and time-of-flight secondary-ion mass spectroscopy can be used to perform depth profiling for very low species concentrations.

Determining the depth of diffusion and knowing the time of exposure will result in determination of the diffusion coefficient. A literature search is nearly complete, and scoping studies will be performed. We are pursuing identification of existing technologies at Los Alamos that may be available for use in these studies. Finally, we are collecting, for future experiments, samples of metal that have been in contact with plutonium for long periods of time.

Nondestructive Assay

Sensitivity calculations show that the in-plant neutron multiplicity Counter may be able to detect as little as 1-2 g of plutonium oxide in 2 kg of metal, assuming a count time of 30 min and low-ambient neutron background. Determination of environmental variables in a plant setting is a goal of the project. We will measure clean unoxidized plutonium metal samples and add small amounts of oxide back into them. We have obtained two items from the vault, and we have set aside a portion of each item to be converted to oxide. Also, we will study the applicability of neutron-counting methods to detection of plutonium hydride. Because present neutron assay instruments detect only thermalized neutrons, only multiple-ring instruments may have the capability; and it is not known whether current multiple-ring instruments are sensitive enough to detect this change.

Separations: Polymer Filtration

Polymer filtration will remove actinides from solutions to very low levels. The goal of this task is to optimize solubility, filterability, binding strength, and capacity as a function of parameters such as metal-ion loading, pH, polymer concentration, metal-ion speciation, and ionic strength. We will accomplish this optimization by carefully adjusting the molecular structure of the water-soluble polymer. We have begun preparation for characterization of the polymers and have obtained a viscometer to characterize the degree of functionalization of the various polymers. We will use a high-performance liquid chromatograph for gel permeation chromatography to determine relative molecular weights for newly synthesized polymers. We have begun preperation of polymers with the synthesis of linear polyethyleneimine , which will allow us to do comparison studies with some of the commercially available linear polyamines. Experiments to optimize synthesis of various functionalized polymers are under way. Construction of the apparatus for the fluorescence studies is progressing.

Separations: Polymer Foams

The goal of this task is to develop advanced microcellular foams for recovery of radioactive species from waste streams. We have prepared eight types of polychloromethylstyrene/styrene foams, varying factors such as polymerization initiator, amount of surfactant, and water/oil ratios. We are evaluating flow properties with dyes in solution. The first experiment in functionalizing the foam with phosphonic acid groups demonstrated that the foam survived harsh conditions and has essentially the same dimensions as it did before treatment. Titration to determine the extent of functionalization is in process.

Materials Science: Thermodynamics

The objective of this task is to study the phase behavior and thermodynamic properties of plutonium oxychloride (PuOCl), a potential byproduct of the salt-oxidation step of the salt-distillation process. Experiments that we conducted about a year ago revealed that the vapor pressure of PuOCl falls between that of plutonium chloride and plutonium oxide. A comprehensive understanding of the vaporization processes and thermodynamics of PuOCl is still needed to enhance our ability to model the salt-distillation process and optimize separations. We plan further experimentation in these areas. A high-temperature mass spectrometer and vacuum system were tested, and several parts were replaced. Further studies will include calibration of the mass scale and the sensitivity of the mass spectrometer, vaporization studies with PuOCl, x-ray diffraction phase analysis, and completion of a report.

Materials Science: Vitrification

The goal of this task is to install and demonstrate a glovebox-scale vitrification process that can be used to study the application of the process as an alternative to cementation. We have identified six waste streams for demonstration. We are compiling the performance specifications for the final waste form. These specifications are based on meeting Waste Isolation Pilot Plant transportation and storage standards, nonmixed waste status, and relevant definitions of glass quality from the high-level vitrification field. We will establish equipment constraints relating to glovebox work. Major concerns are in the areas of off-gas treatment and temperature. System selection is proceeding. We will choose equipment that will allow compatibility studies to be conducted with the glass matrix on various waste streams.

94-1 RESEARCH AND DEVELOPMENT PROJECT LEAD LABORATORY SUPPORT

Status Report
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Compiled by

Mark Dinehart

ABSTRACT

This document reports status and technical progress for Los Alamos 94-1 Research and Development projects. An introduction to the project structure and an executive summary are included.

INTRODUCTION

This is the second status report published for the Los Alamos 94-1 Research and Development Project. Descriptions and milestones for 94-1 Research and Development subprojects are found in report LA-UR-96-991, "94-1 Research and Development Project Lead Laboratory Support Technical Program Plan," (April 1996). Figure 1 presents the Work Breakdown Structure for this effort. The first project status report, LA-13133-SR (May 1996), comprises project descriptions and progress, needs and benefits for the DOE complex, and collaborations for eight sub-projects—Cryogenic Crushing, Hydrothermal Oxidation, Mediated Electrochemical Oxidation, Catalyzed Oxidation of Organics, Electrolytic Decontamination, Oxide Pelletizing, and the Shelf-Life Project. The present document reports status and technical progress for a larger sampling of the Los Alamos 94-1 R&D project. Projects not previously reported are briefly described.

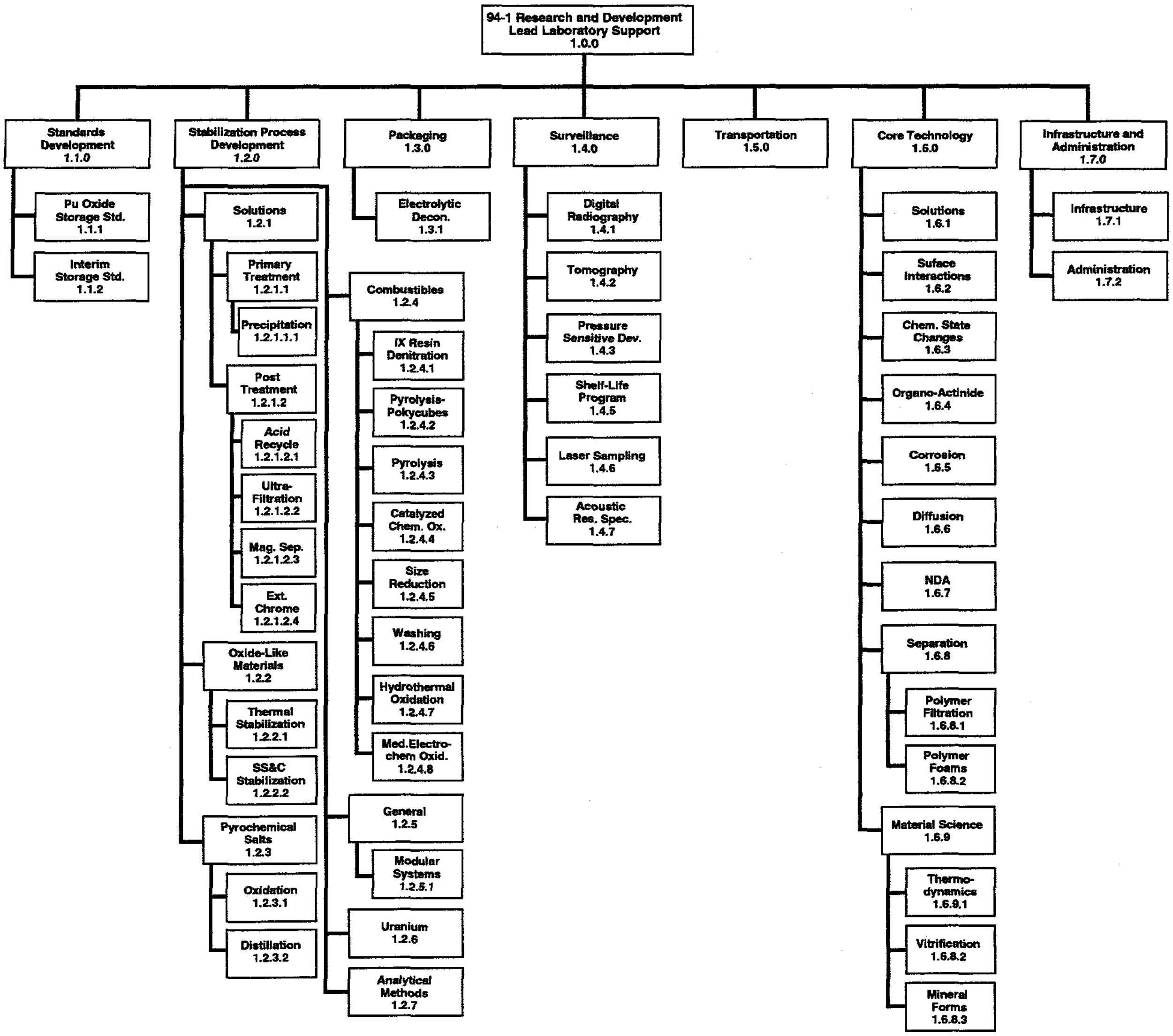

Fig. 1. Work Breakdown Structure.

Electrolytic Decontamination

Principal Investigator: Timothy O. Nelson

Introduction

With several sponsors, we are developing electrolytic decontamination for several applications. Of particular importance to the DOE complex-wide nuclear material stabilization effort is the decontamination of long-term storage containers and glovebox decontamination for site clean-up.

Container Decontamination

For the glovebox demonstration of the electrolytic decontamination process for long-term storage containers, we are evaluating a proposed design change in the material can. The new configuration eliminates one of the two welds and moves the welded area from the corner to the side of the container and to about an inch below the top surface. For electrolytic testing of this new container, a can of the modified configuration was fabricated locally. However, before this test, we will further investigate the operating parameters of electrochemical processes for decontaminating, and we will add an ultrafiltration system to the electrolytic decontamination system for radioactive materials. The delivery of more new containers supplied by a vendor should occur in the third quarter. We will perform additional testing, as more material cans arrive.

We have selected the glovebox configuration for the electrolytic decontamination demonstration in the Los Alamos National Laboratory Plutonium Facility (TA-55), Building PF-4. This glovebox incorporates a longitudinally split fixture placed vertically into an all-vertical partition. A clam-shell-type door in the partition swings open in both directions to provide access into and out of the fixture. In order to evaluate the structural integrity of the system and to develop probable fabrication schemes, we fabricated and hydrostatically tested a mock-up of an off-center longitudinally split fixture. The results proved that the split fixture should meet the needs and requirements for both the glovebox demonstration and the integrated electrolytic decontamination and automated glovebox can-out demonstration. We are pursuing plans for fabricating and incorporating this split fixture into a glovebox.

Glovebox Decontamination

This quarter, with the help of additional staff, we began development of semiautomatable cleaning heads for glovebox decontamination. A preliminary design revealed that we needed to address local control of current density. We fabricated a second head that incorporates better current density control, and testing with nonradioactive materials is under way. Using the old electrolytic decontamination apparatus for gloveboxes, we decontaminated a small glovebox to levels that enable the glovebox to be recycled. This box had previously been decontaminated, but scheduling its removal took so long that the glovebox became recontaminated. Currently, this glovebox is approved for removal and is awaiting plan-of-the-day scheduling, which should happen in April.

Electrolytic Decontamination Support Efforts: Ultrafiltration and Process Support for Electrolytic Decontamination of Stainless Steel

Support efforts for electrolytic decontamination of stainless steel include precipitate removal by ultrafiltration, some results of which are discussed below. Also, we are investigating process parameter characterization, such as the use of different electrolytes and precipitation enhancements . These efforts will be discussed in future reports.

We are developing ultrafiltration, or cross-flow filtration, as a method to remove the hydroxide precipitates from the electrolyte before recycle to the stainless steel surface. Our goal is to produce 1 gal/min of filtrate with a module that easily integrates with other system components in a glovebox.

We have evaluated products from three suppliers. Clean water filtration rates for Carbosep™ membranes from Rhone Poulenc, with effective pore sizes of 10,000 daltons to 0.14 µm, were measured. Permeate fluxes with ferric hydroxide were measured for two membranes that represent the practical range of pore sizes. At 40,000 MW, we observed little decrease in flux as the suspension increased in concentration by a factor of five. However, we did observe a decrease in flux for a pore size of 0.14 µm. Back-flushing at regular intervals would be necessary with this membrane. We are evaluating two polymeric membranes, since they promise to be less expensive and are available in more compact modules than inorganic membranes. We are assembling an automatic back-flushing for evaluation of microfiltration membranes.

We are near to completing final assembly of an ultrafiltration unit for radioactive testing in the demonstration of electrolytic decontamination of material cans. The apparatus to be integrated is the electrolytic decon unit. This initial radioactive testing of the ultrafiltration process will not produce a continuous flow of clean solution, but the ultrafiltration process will be operated in a batch mode. Future systems will incorporate continuous-flow cleaning. The flow requirements for a continuous process require a much larger ultrafiltration module than we currently have.

Combustibles: Cryogenic Crushing
Principal Investigator: Timothy O. Nelson

Introduction

Cryogrinding is reducing materials in size at a temperature low enough to keep the material below its glass transition temperature. Below this temperature, a material behaves in a brittle manner and no longer plastically deforms. In the second quarter, we accomplished the following tasks:

- Fabricated a jaw crusher and tested it to grind hard materials, such as the polycubes;
- Modified the filter shredder to improve handling in the glovebox;
- Tested a cryogenic blender and found it to quickly size-reduce glovebox gloves;
- Size-reduced and then particle-sized various materials;
- Fabricated and provided for pyrolysis-testing polycubes with and without iron;
- Prepared various matrices of sized materials for hydrothermal testing; and
- Began the procurement process for the Franklin Miller shredder.

Jaw Crusher

We fabricated a nipping machine, called a jaw crusher, to crush hard materials such as polystyrene. A photograph of the equipment is shown in Fig. 2, and a drawing is shown in Fig. 3. This jaw crusher is a modified Dodge form with double toggles used when grinding tough, hard materials. The advantage of the Dodge form is the uniform particle size. The crusher works as follows:

- The motor drives the flywheel and eccentric crankshaft;
- The crankshaft moves the pitman up and down;
- The pitman moves the toggles into a horizontal position, multiplying the force from the pitman due to mechanical leverage; and
- The toggle moves the jaw.

The material is fed into the top opening and is crushed into smaller pieces as it moves down through the jaws. The opening at the bottom of the jaw can be made variable. It is advantageous to set the opening to the largest size allowable for the next process in order to decrease the amount of time required to size-reduce the material.

The rate of throughput depends on the initial size of the feed material and final size of the output. We have processed 1/4-in. polystyrene pellets to 0.060-in. nominal size at 10 g/min at 100 rpm. However, to grind the pellets to 0.020-in. nominal size would slow the rate to 3 g/min at 100 rpm. Currently, the crusher runs only at 100 rpm; but the rate could be increased to 200 rpm if a gear is changed.

During processing, a small stream of liquid nitrogen (LN_2) is poured into the inlet to keep the material cold and to remove small particles from the jaw. The energy required to break the material appears to be dissipated as thermal energy and thus warms the material to above its glass transition temperature. Also, smaller particles stick to the side of the jaw. The crushing process generates static charge, which is large enough for particles less than ~0.015-in. in diameter to be held to the wall. The flowing LN_2 washes the smaller particles out of the jaw crusher by viscous drag.

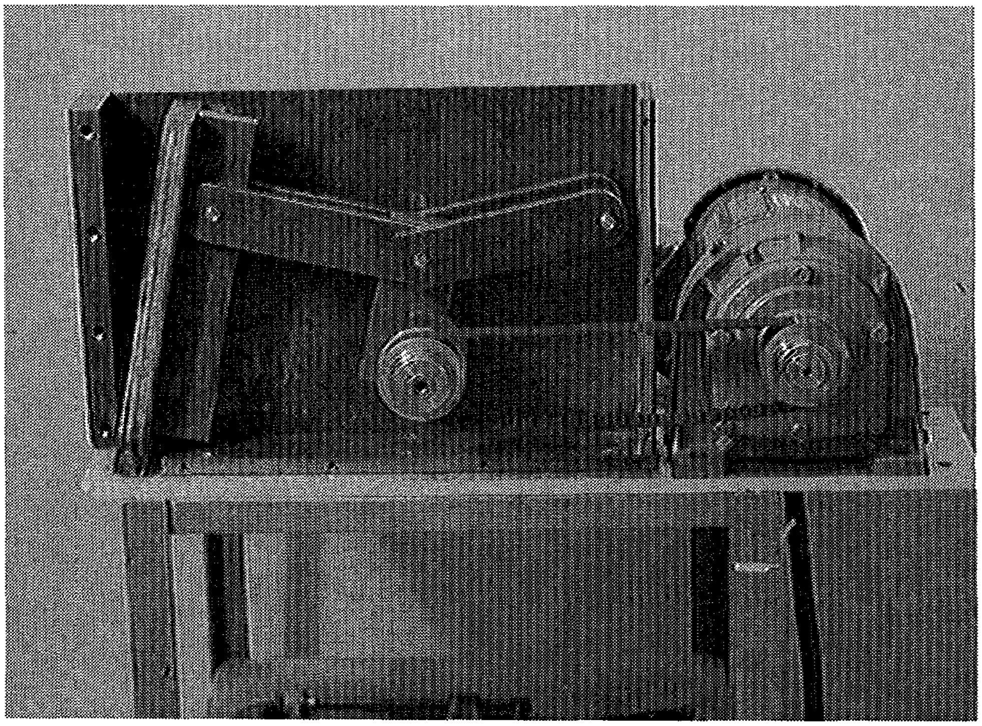

Fig. 2. The jaw crusher.

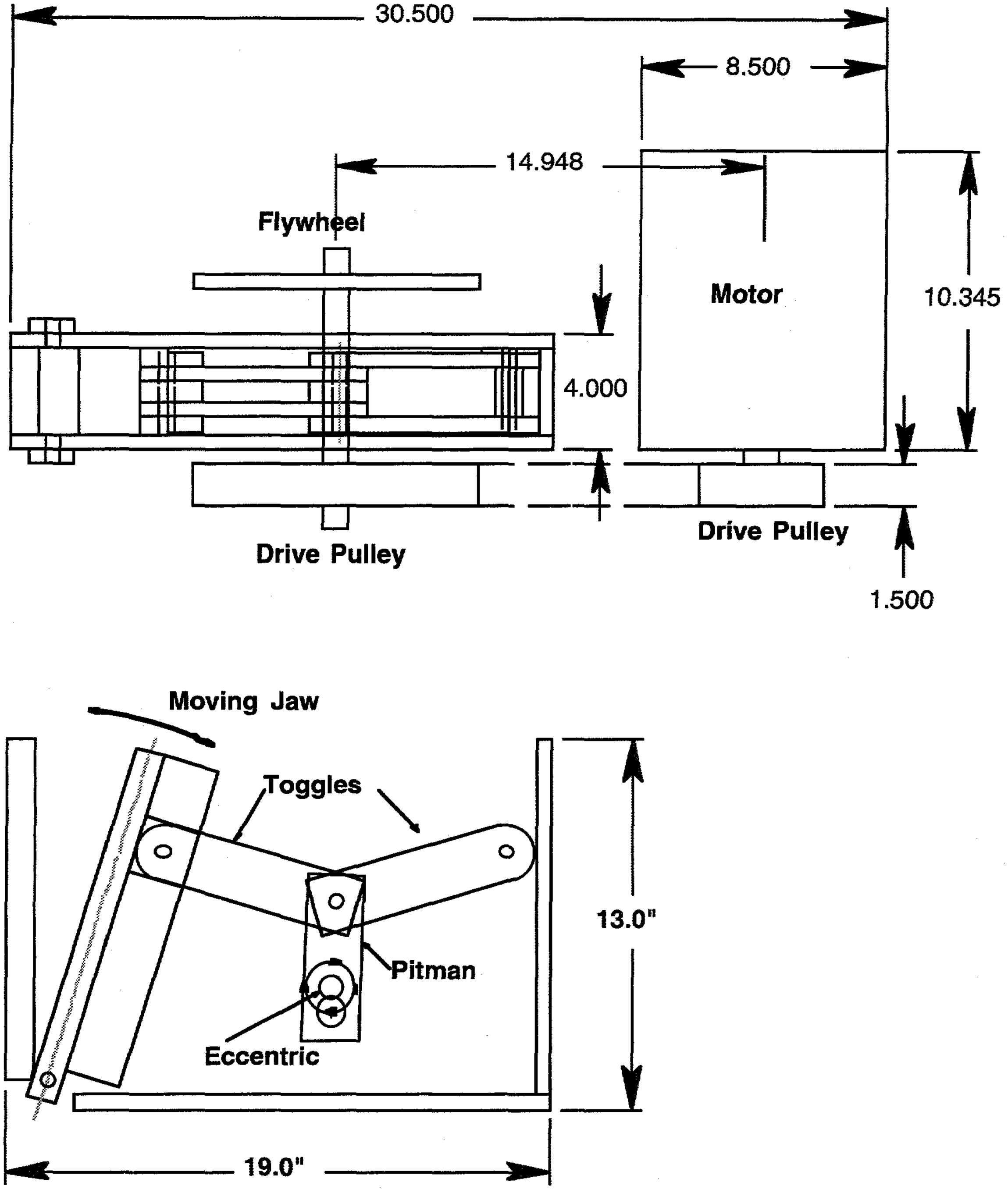

Fig. 3. Jaw crusher schematic.

We have used the jaw crusher to size-reduce polystyrene pellets, polycubes with iron, and leaded gloves. We have particle-sized the ground polycubes and polystyrene. The results are shown in Figs. 4 and 5. In Fig. 4, it can be seen that the polystyrene was ground with a 0.021-in. opening in the jaw crusher, a process that produced about 70% of the mass between the 20 mesh (0.033 in.) and the 60 mesh (0.001 in.). In Fig. 5, the size distribution of the polycubes with iron shows about 55% of the mass above 16 mesh (0.045 in.). Figure 6 shows iron-ground polycubes that were crushed using a 0.077-in. opening in the jaw crusher. The larger particles tended to be rectangular in shape, since only the minimum dimension has to be smaller than the opening of the jaw crusher.

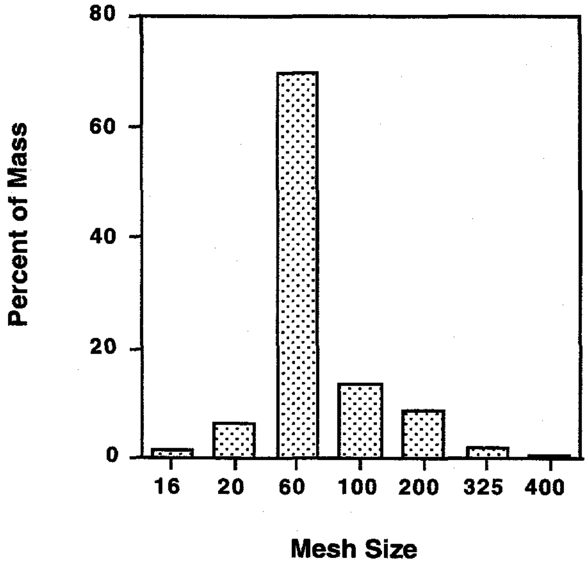

Fig. 4. Particle distribution for polystyrene ground in jaw crusher with 0.021-in. opening.

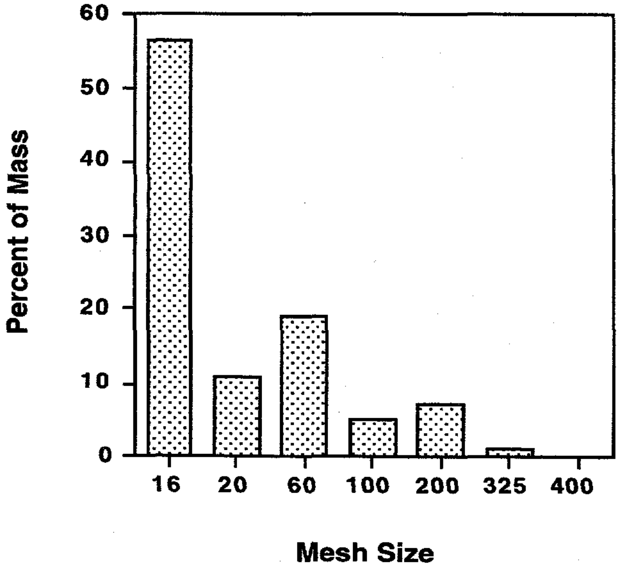

Fig. 5. Particle distribution for polycubes with iron ground in jaw crusher with 0.075-in. opening.

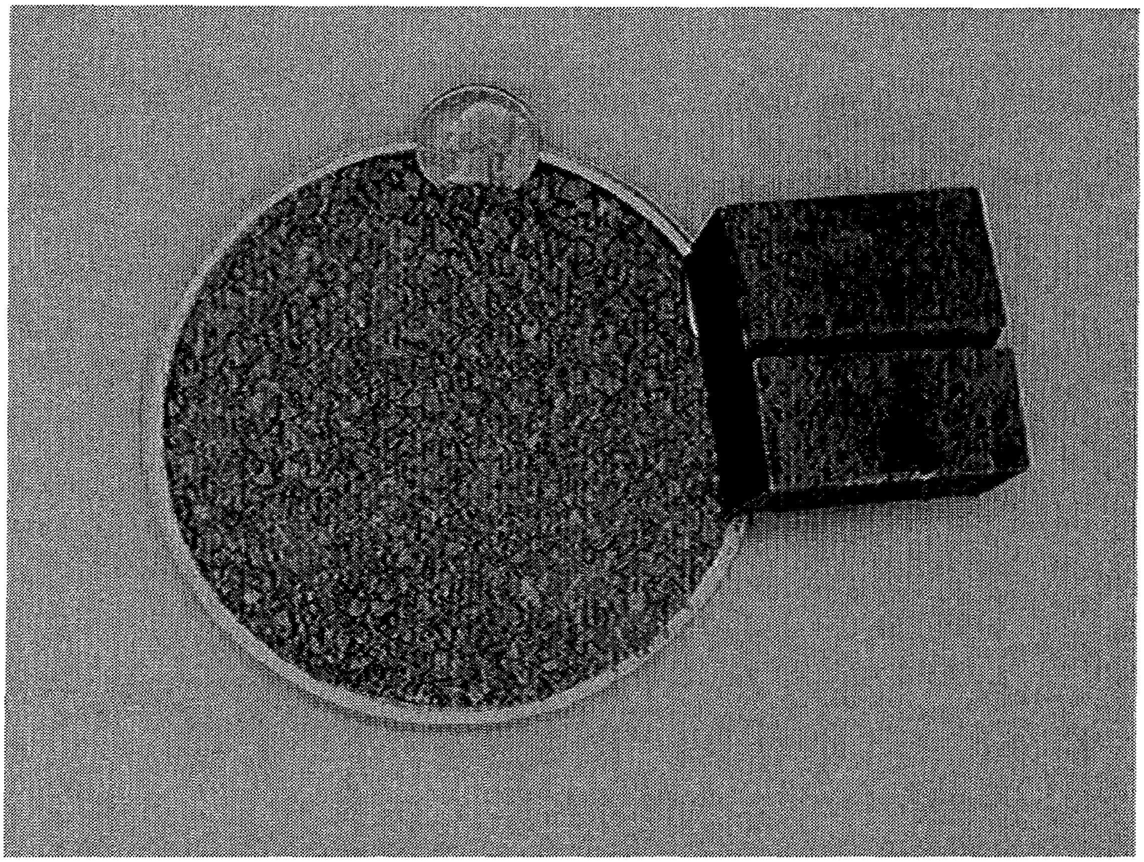

Fig. 6. Polycubes with iron ground in jaw crusher with .077-in. opening.

Filter Shredder

Since last quarter, we have improved the filter shredder. We made a stronger feed tube and blade housing in order to reduce the spacing between the cutting blades and the housing. The smaller spacing keeps filter material from going around the blades and from getting chopped finer than is desirable. We added an electric cylinder to push the filter material into the cutting blades, and this addition provided a constant feed rate of the filter into the blades. The feed rate determines the particle size.

The whole assembly is shown in Fig. 7. The filters are cooled in LN_2. If the filters are not precooled in this manner, the heat generated during cutting will melt the filter on the blades, and the process will stop. The cooled filter is placed in the feed tube, the door is shut, the motor is turned on, and the *extend* button on the electric cylinder controller is pushed. When the cylinder reaches its fully extended travel distance, the cylinder will automatically reverse and reposition itself for the next filter. The shredded filter material exits near the motor below the cutter blades into a catch pan. The catch pan can then be emptied into plastic bags for storage. Currently, the extend rate is set at 2.3 in./sec and the retract rate is set higher. The cylinder takes 1 min, 9 sec to extend and 14 sec to retract for an overall cycle time of 1 min, 23 sec. The optimum extend rate can be determined when the size of the particle required for washing is known. A filter shredder tray is being provided to catch the shredded material. This tray will allow easy removal of the shredded filter into a bag for transportation to the washing process. The outlet of the cutter housing is being increased to reduce hold-up of the shredded material. We will endurance-test the filter shredder and install safety interlocks for glovebox use. Figure 8 shows the shredded HYTREX™ filter material, and Fig. 9 presents the particle size distribution of the shredded HYTREX filters. A large portion of the material is shown to be above 16 mesh. This material is actually composed of longer micro elements and not of large solid pieces. The longer micro elements should allow easy washing.

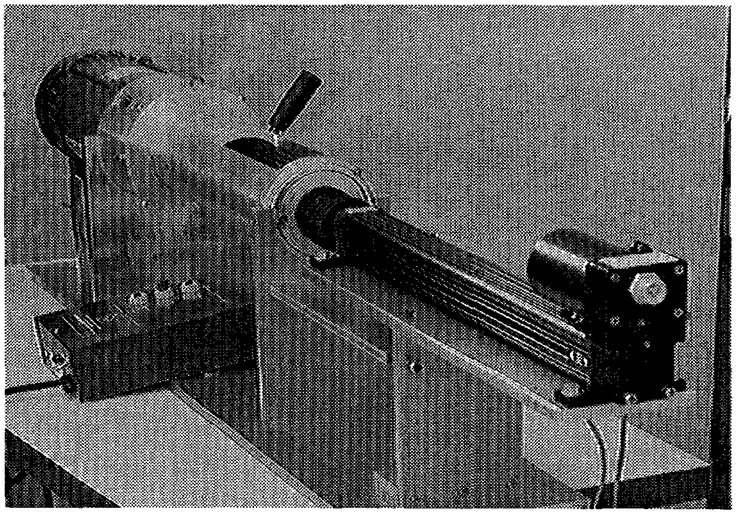

Fig. 7. Filter shredder assembly.

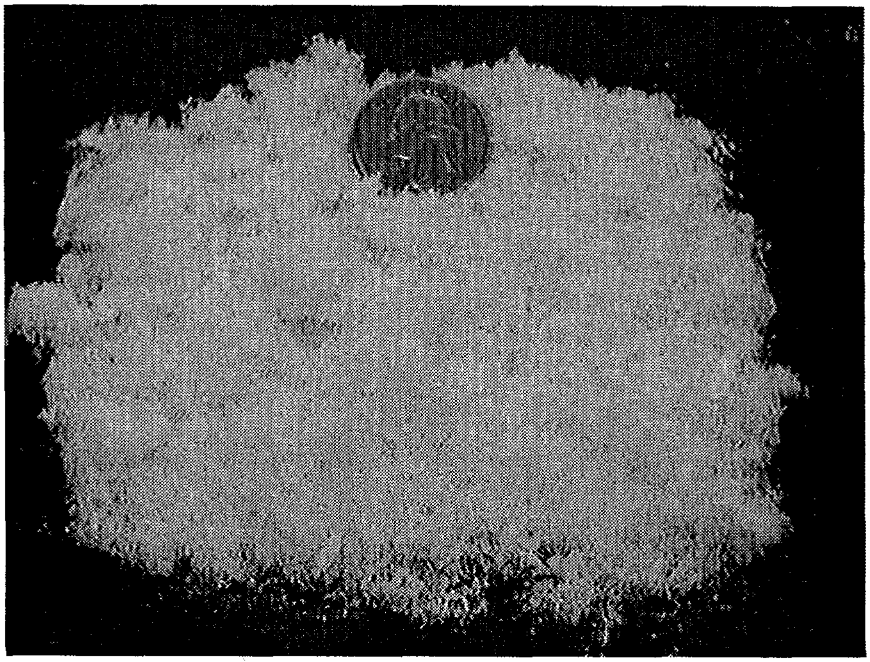

Fig. 8. Shredded HYTREX filter.

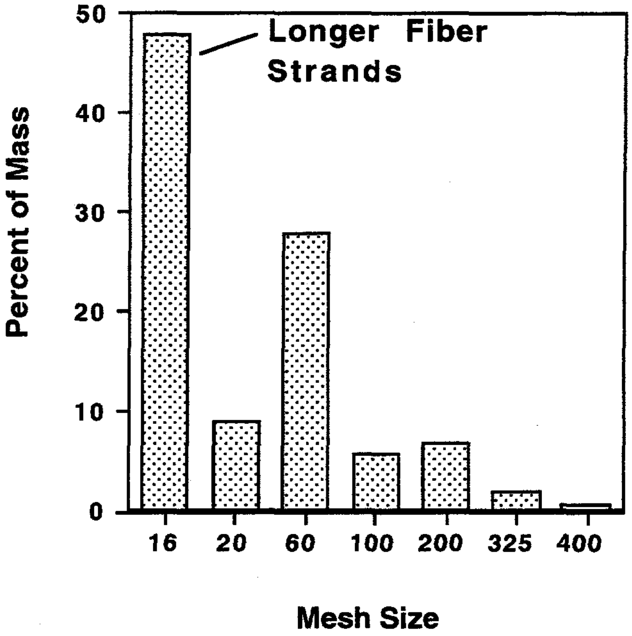

Fig. 9. Particle size distribution for HYTREX™ filters ground in the filter shredder at a rate of 0.23-in./sec.

Cryoblend Process

We developed a new process that can reduce soft waste quickly compared to the rate of the jaw crushes. It uses an industrial blender of about 1 hp and a vacuum-insulated container. The insulated container is filled with LN_2, and material is fed through the top. The longer the blender runs, the smaller the particles will be. The system can be modified for continuous flow, as shown in Fig. 10. Liquid nitrogen can be pumped from the container through a filter into a settling reservoir. The filter controls the size of the fine particles. This system has the advantage of generating no dust.

Glovebox gloves that contained lead were ground in the cryoblender. The product is shown in Fig. 11, and the particle distribution results are shown in Fig. 12. In this test, 70 g of material were ground for 3 min. This material can easily be size-reduced even more by grinding longer and by optimizing the cutter blade geometry. The cryoblender will be tried with rubber gloves, Tyvek™, cloth, paper, and plastic sheet.

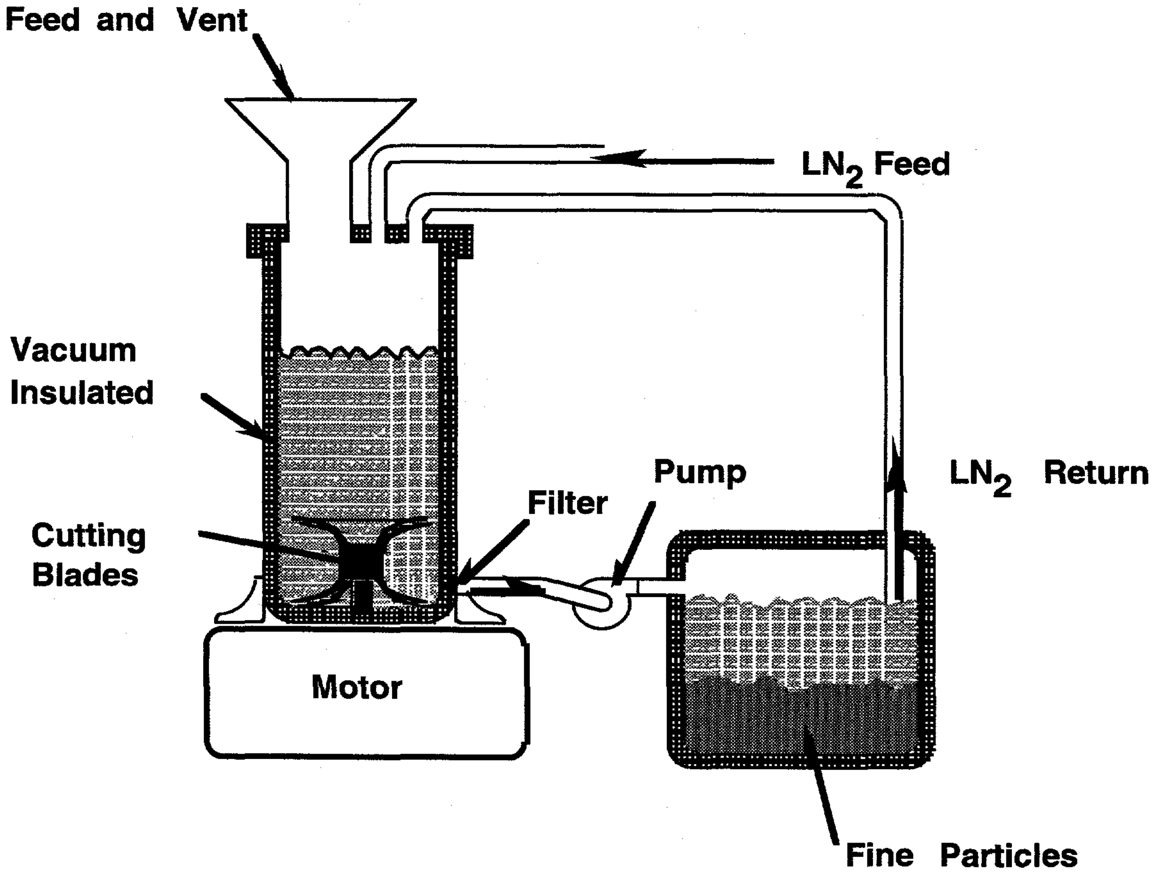

Fig. 10. Cryoblending process.

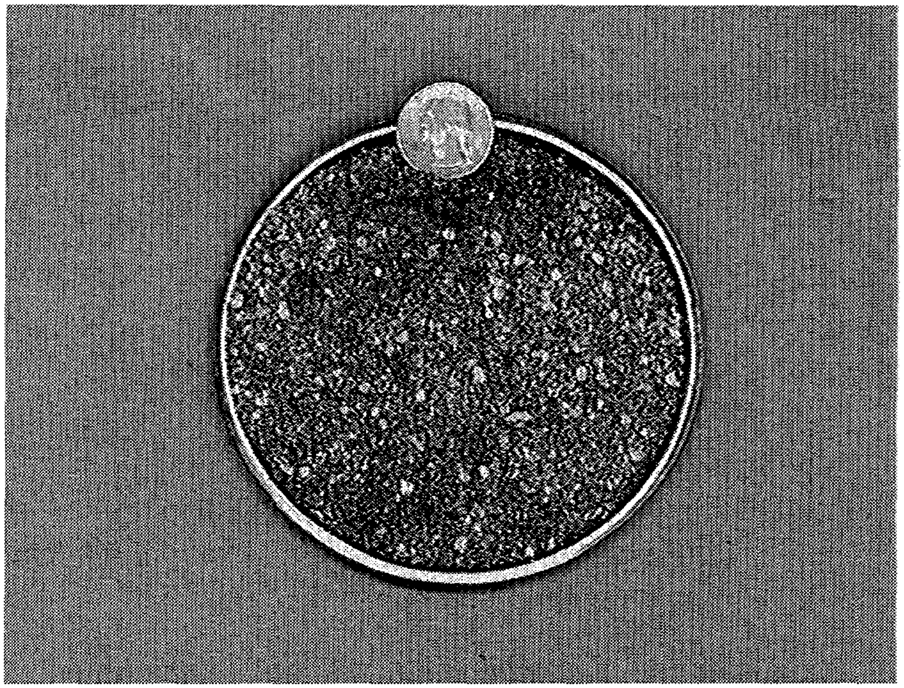

Fig. 11. Glovebox gloves ground in cryoblender.

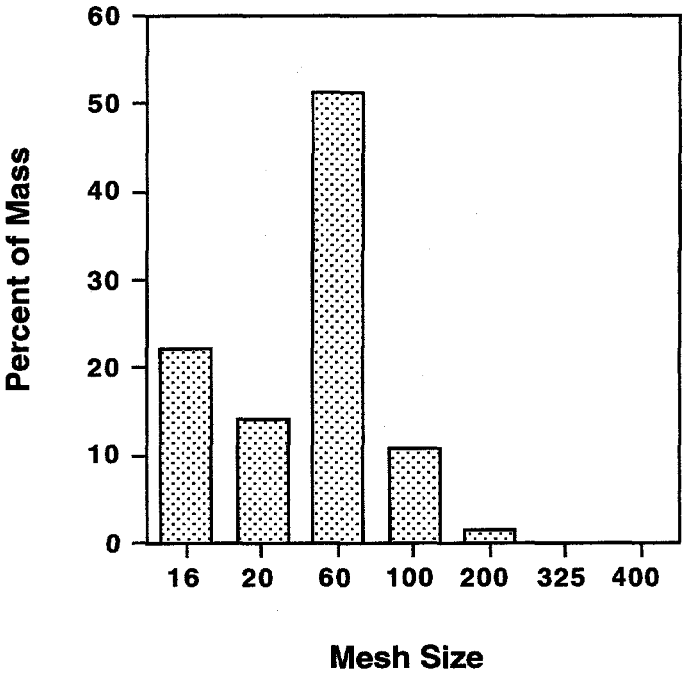

Fig. 12. Particle distribution for leaded glovebox gloves that were ground in blender.

Fabrication of Polycubes

We have fabricated polycubes of 50 wt % iron at Los Alamos. The polycubes come out of the furnace as big disks that are then machined to the same size as the Westinghouse Hanford Company polycubes (Fig. 13). These cubes are being supplied to the Pyrolysis Project. Approximately 60 polystyrene blocks with no iron were also fabricated and provided for pyrolysis-testing. Ground polycubes with iron will be provided to the Hydrothermal Oxidation Project for testing.

Test Matrices for Hydrothermal Testing

We have provided ground polystyrene, polycubes with iron, glovebox leaded gloves, and a matrix of soft waste for testing in the Hydrothermal Oxidation Project. The soft waste matrix consisted of 90 g of cotton, 90 g of rubber, 90 g of plastic, 90 g of Tyvek, and 139 g of paper. The hydrothermal process requires the soft waste to be less than 1/16-in. nominal particle size. The plastic was cut into sheets, placed on top of paper, dipped into LN_2, and then run through a paper shredder. The paper absorbs the LN_2 and keeps the plastic from melting while being shredded. Between paper, we placed Tyvek fabric that had been shredded at Nelmor to 3/8-in. nominal size, dipped the fabric in LN_2, and then ran the product through a paper shredder. The rubber, which had been previously ground at Nelmor at room temperature and melted together, we ground by hand into pieces while it was in a dewar containing LN_2.

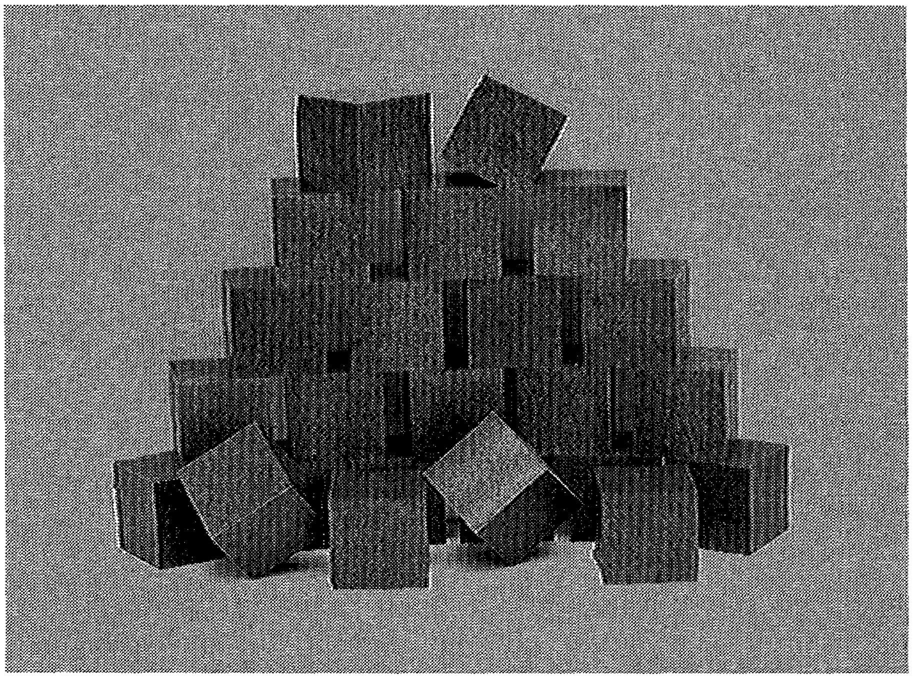

Fig. 13. Machined polycubes with 50 wt % iron.

Franklin Miller Shredder

The Franklin Miller shredder is proposed to shred soft waste of the type produced at the Rocky Flats Environmental Technology Site. This shredder is a low-rpm, small-size cutting machine. The low-rpm cutting is required because high-rpm cutting will produce cotton fluff that will become airborne. The small size is important to provide feed stock small enough for processes such as hydrothermal oxidation. A schematic of the shredder inside the glovebox is shown in Fig. 14. The purchase request has been approved, and the capital equipment money is awaiting approval at DOE-Albuquerque Operations Office. Approval is expected about April 14. We will begin testing with nonradioactive materials and glovebox modification of the Franklin Miller shredder, as soon as it is received. Typical soft wastes will be run through the shredder, and particle size will be determined. Depending on the results of the test with nonradioactive materials, we will begin installation of the shredder into a glovebox when it is appropriate to do so.

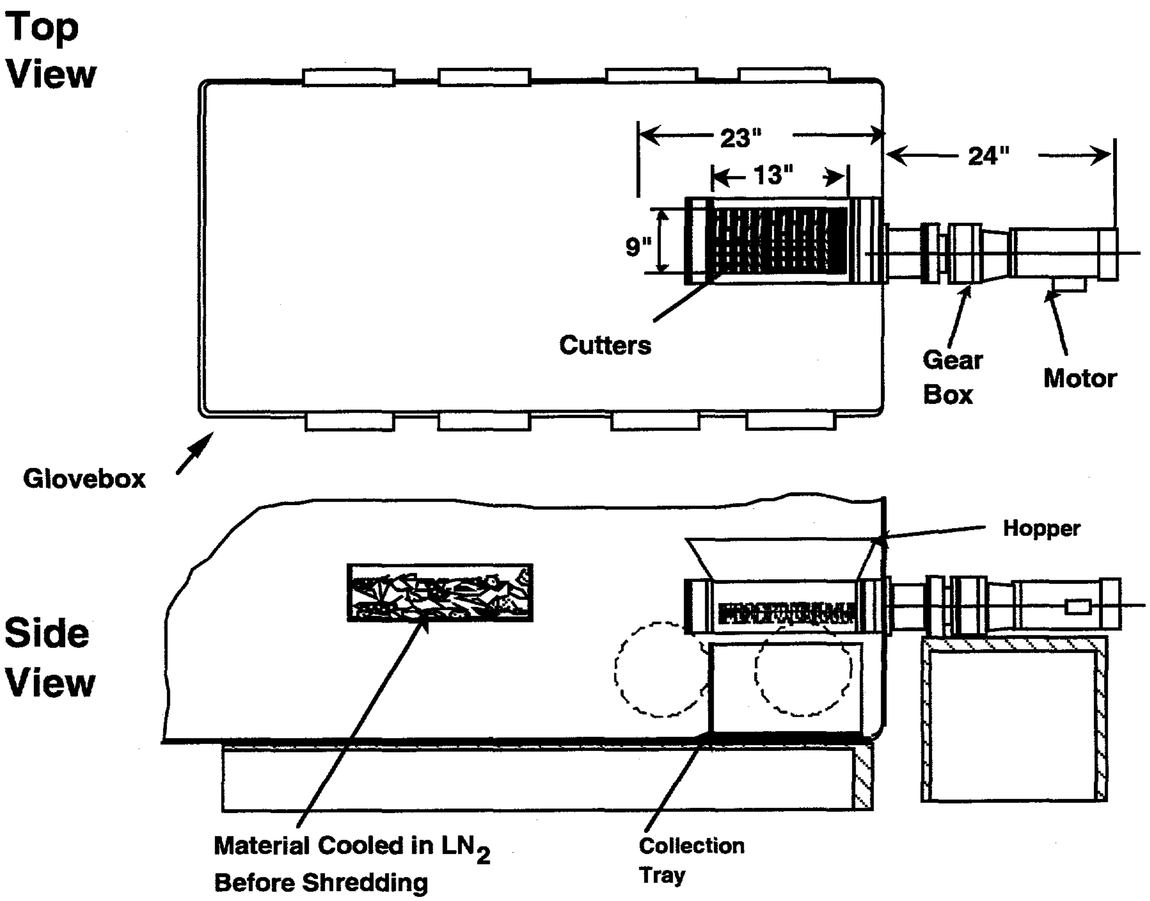

Fig. 14. Franklin Miller shredder inside a glovebox.

Combustibles: Hydrothermal Oxidation
Principal Investigator: Laura Worl and Steve Buelow

Introduction

The task is to design, build, and test a hydrothermal processing (HTP) unit for the removal and recovery of organic and hazardous substances from transuranic (TRU)-contaminated solids and liquids. Oxidation of the organic and reduction of the nitrate components of combustible waste will mitigate safety hazards, reduce waste volume, and facilitate separation of radioactive elements.

Status/Progress

During the second quarter of FY96, a small-scale hydrothermal unit for the treatment of TRU-contaminated combustible material was constructed and tested. The process flow diagram and schematics of the layout of the unit were included in the previous quarterly report. Initial testing of the unit showed that the main reactor seals leaked after one to two hours of operation. Discussion of the problem with the manufacturer of the reactor vessel revealed that creep criteria had not been included in the design. In order to fix the problem with the reactor seals, the manufacturer designed and fabricated a new reactor vessel that has unlimited seal life at the reactor's designed operating temperature and pressure of 540°C and 6700 psi. The new reactor vessel was delivered at the end of March, has been installed, and is being tested. This problem with the reactor seals has delayed equipment installation into the Los Alamos National Laboratory Plutonium Facility (TA-55) until the end of May.

Work continues on hydrothermal safety documentation and glovebox preparations for equipment installation. Hydrothermal Oxidation received a National Environmental Policy Act categorical exclusion (memos ESH-20-6124 and DOE LAN-96-9) in late March. We prepared with and submitted to the Los Alamos Area Office of DOE on March 13, 1996, the Treatability Studies (memo ESH-19:96-74) for treating nine mixed-waste streams. We completed and documented the Air Quality Compliance Review (ESH-17:96-107). The review states that HTP will not require a permit either under Title 20 of the New Mexico Administrative Code (20 NMAC) or under the Code of Federal Regulations. The final draft of the HTP safe-operating procedure has been issued for signatures to the reviewers. The Los Alamos National Materials Technology Division Facilities Group has approved the Hazards Analysis package and is completing the Unreviewed Safety Question Determination. Personnel from the Los Alamos Engineering Sciences and Applications Division Engineering Analysis Group have completed a design analysis for the secondary containment for the new reactor vessel and has concluded that the containment system designed for the original reactor can be used. The height of the containment vessel was increased four inches to accommodate the increased length of the new reactor vessel.

Glovebox modifications are nearly complete. The electrical outlets will be changed to corrosion-resistant duplex outlets in the upcoming weeks, and the vacuum header still needs to be connected to the glovebox. These services have been delayed because available craft personnel are working on projects with higher facility priority.

Testing of nonradioactive simulant mixtures continues. This quarter, we tested a simulant of general laboratory trash mixture provided by the Cryogenic Crushing Project. This mixture consisted of 18% cloth, 27.8% paper, 18% Tyvek, 18% plastic, and 18% rubber, cryogenically shredded and passed through a 1/8-in. screen. The zippers were removed from the clothing. Then we slurried the mixture with water (84.5% water, 12.1% laboratory trash, and 3.4% carboxymethyl cellulose [CMC] sodium salt by weight). The CMC is used as a viscosity-enhancing agent.

We reacted the mixture in varying ratios with 30 wt % hydrogen peroxide at 5600 psi and 540°C. The reaction times were near 69 seconds. The total organic carbon in the effluent was below our detection limits of 2 ppm. The liquid effluent pH ranged from 4.5 to 4.9. The reactor effluent contained less than 100 ppm of total inorganic carbon, chloride, sodium, or potassium, and about 120 ppm of nitrate. In the gas phase, only oxygen and carbon dioxide were detected. Figures 15–18 show the effluent pH and concentrations of oxygen, carbon dioxide, nitrate, chloride, sodium and potassium vs the H_2O_2:Slurry ratio. The oxygen vs H_2O_2:Slurry ratio indicates that the maximum loading of slurry mix is at H_2O_2:Slurry ratio value between 0.4 and 1. Ratios lower than this will not have sufficient H_2O_2 for complete oxidation of the organic.

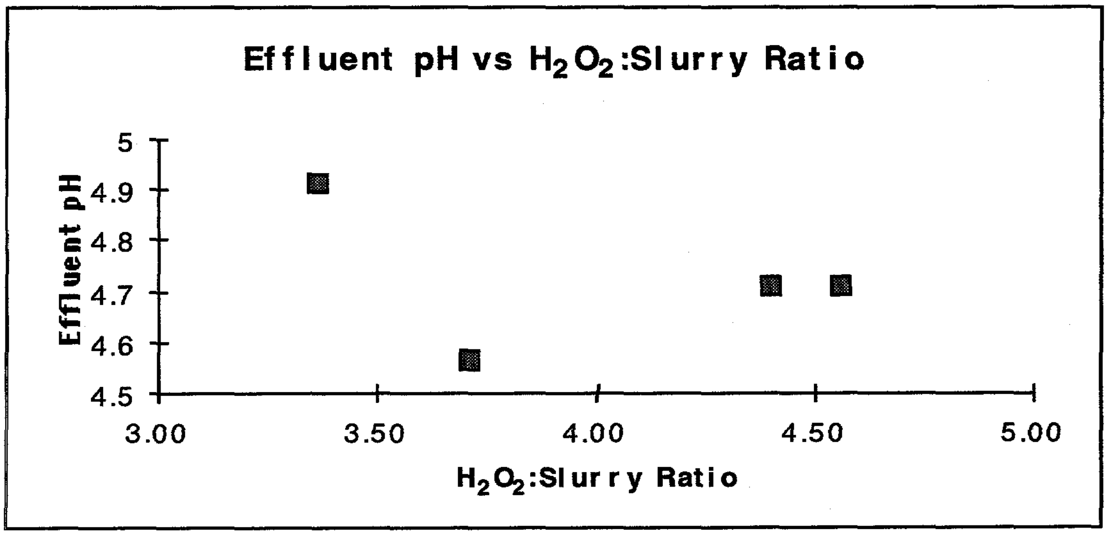

Fig. 15. Effluent pH vs H_2O_2: Slurry ratio.

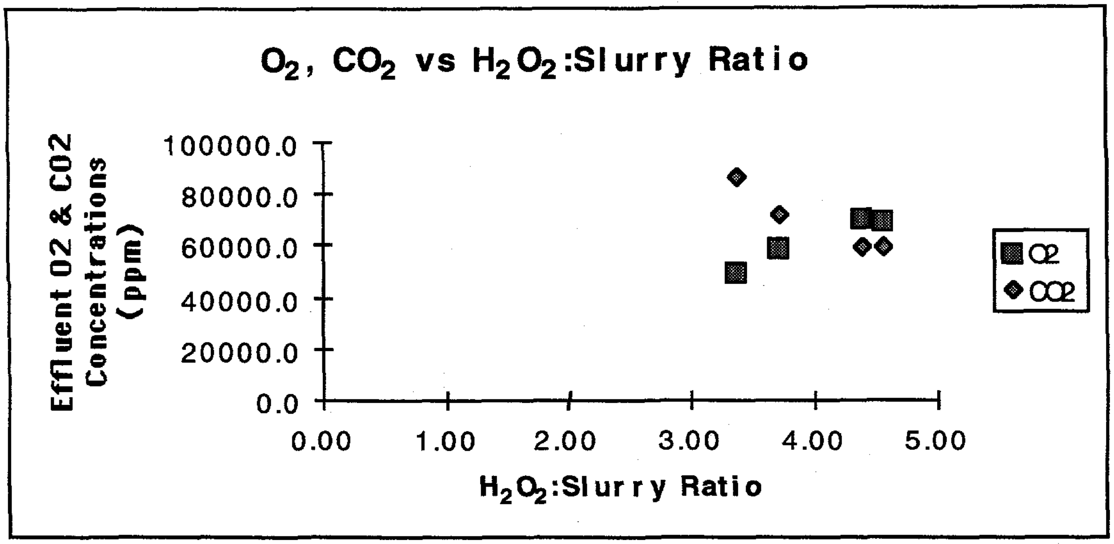

Fig. 16. Effluent oxygen and carbon dioxide concentrations vs H_2O_2: Slurry ratio.

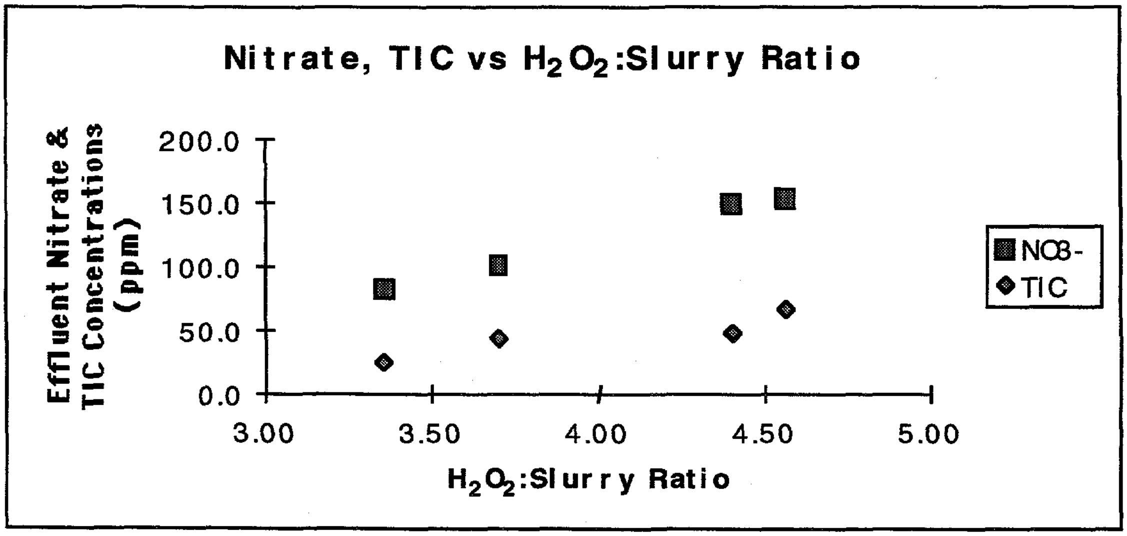

Fig. 17. Effluent nitrate and total inorganic compound concentrations vs H_2O_2: Slurry ratio.

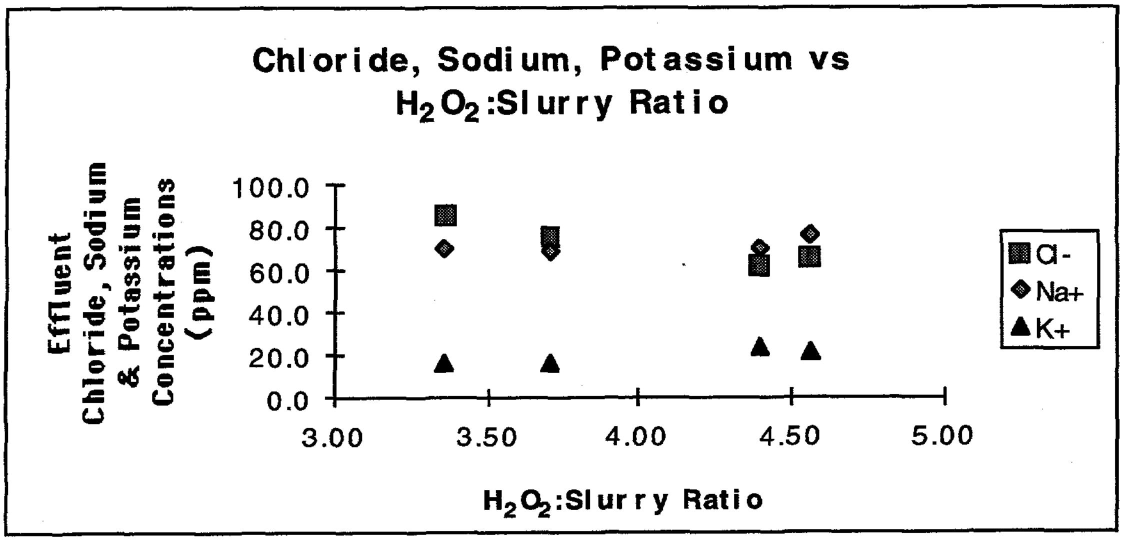

Fig. 18. Effluent chloride, sodium, and potassium concentrations versus H_2O_2: Slurry ratio.

Combustibles: Stabilization of Polycubes Using Pyrolysis
Principal Investigator: Daniel J. Kathios

Introduction

Polycubes are mixtures of plutonium and uranium oxides cast in a polystyrene matrix. To perform criticality studies, the cubes were once manufactured at various sites in the nuclear complex. The cubes now represent a waste that is not suitable for long-term storage. Approximately 1600 cubes are presently in storage at Westinghouse Hanford Company (WHC). The cubes vary in size, the largest of which is 2 in. on a side. A number of the cubes are coated with aluminum paint and/or tape.

Pyrolysis is a pyrochemical technique by which a high-temperature inert environment is used to break down and volatilize polymeric materials. The objective of our work is to design, test, and implement a pyrolysis system that will effectively destroy and remove the polystyrene matrix from the plutonium and uranium oxides, leaving the oxides as free-flowing powders that are suitable for either dissolution or long-term storage.

Los Alamos researchers have recently designed a gas-tight pyrolysis reactor that is suitable for glovebox applications. Preliminary tests with nonradioactive materials have shown that this design allows for almost 100% removal of the polystyrene without the formation of tars from other constituents that could adversely affect its operation. At this point, an off-gas treatment technology needs to be introduced to break down the components in the reactor off-gas to an environmentally benign form. This breakdown is necessary in order to allow pyrolysis to operate in compliance with both safety and environmental regulations.

The objectives of this work are as follows:

- To identify an off-gas treatment technology that will allow pyrolysis to operate in compliance with these regulations,
- To design and build a pyrolysis system complete with this off-gas treatment technology that is suitable for glovebox operations, and
- To deliver the pyrolysis system to WHC to process the remaining inventory of polycubes.

Status/Progress

Identification of Off-Gas Treatment Technologies. We identified three off-gas treatment technologies as potential candidates for this application. Each of these technologies calls for processing the reactor effluent by oxidizing the hydrocarbons in the off-gas to carbon dioxide and water. How these technologies would be configured with the pyrolysis reactor is illustrated in Fig. 19.

- **Catalytic Conversion.** In this approach, the off-gas is fed with air to a catalytic converter that is maintained at a temperature of approximately 400°C. The catalyst allows the oxygen to more effectively oxidize the hydrocarbons at this low temperature.

- **Silent Discharge Plasma.** In this approach, a plasma field is formed between two glass plates maintained at a potential difference of 15-50 kV. The off-gas is fed with O_2 into this field where microdischarges react with the O_2 to give free radicals. The free radicals then readily oxidize the hydrocarbons to carbon dioxide and water.

- **Afterburner.** In this approach, the off-gas is fed with air to an environment exceeding temperatures of 760°C. At these high temperatures, the hydrocarbons are converted, by direct thermal oxidation, to carbon dioxide and water.

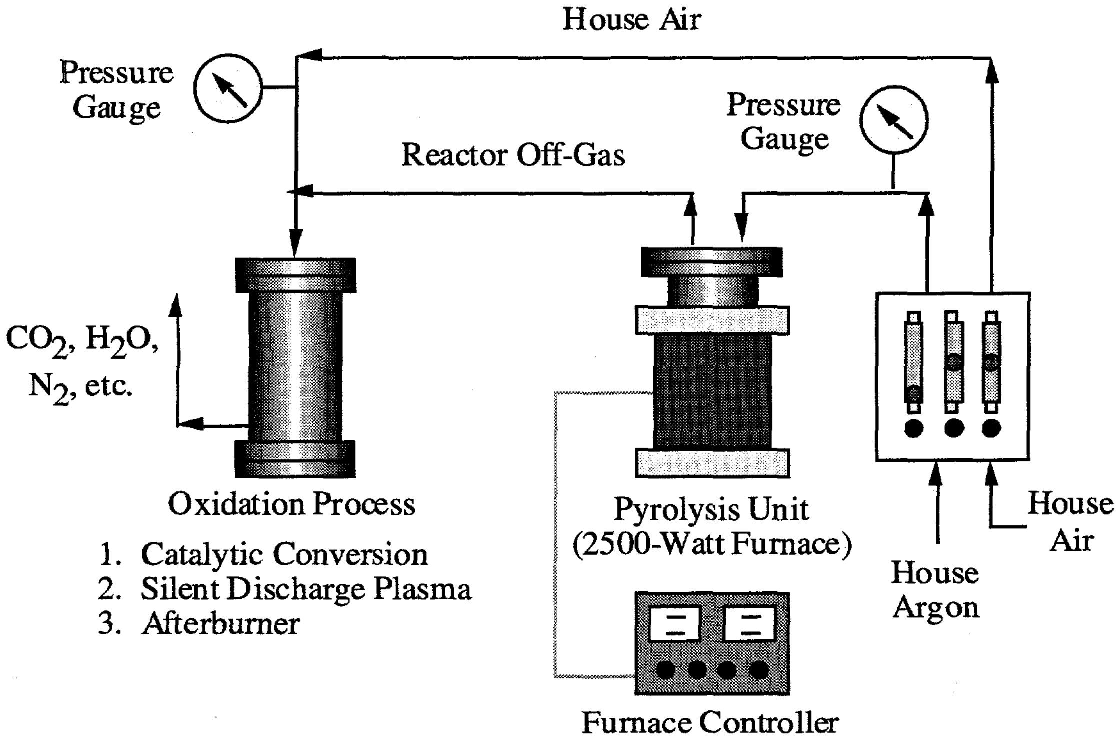

Fig. 19. Preliminary design for the pyrolysis process. A polycube is placed in the pyrolysis reactor and is brought to 700°C in an inert environment. The decomposition products exit the reactor and leave the metal oxides behind. The decomposition products then pass through an off-gas treatment technology by which they are oxidized to carbon dioxide and water.

Rate Tests. Properly designing each of the off-gas treatment technologies depends on knowing the rate at which the off-gas leaves the pyrolysis reactor, the composition of the off-gas, and the manner of rate and composition change with time. To determine these parameters, we constructed an experimental setup to capture and sample the off-gas emitted from the reactor during an actual pyrolysis run. A diagram of this setup is illustrated in Fig. 20. As shown in the diagram, the off-gas from the reactor first passes through a chilled water condenser and then through a cold finger trap present in a dry ice/acetone bath. These two cooling media condense virtually all of the organic constituents present in the off-gas. A syringe is used to remove liquid samples from the collection flask at 5-min intervals over the 2-h time frame of the pyrolysis run. The mass of each sample is subsequently measured with an analytical balance, and the data is used to calculate the rate at which condensate collected in the flask during the course of the experiment. A gas-sampling pump and collection bag are also included to continuously collect a fraction of the gas leaving the process. The composition of this gas sample, along with the liquid samples removed from the cold finger trap and the collection flask, are later determined using gas chromatography/mass spectroscopy.

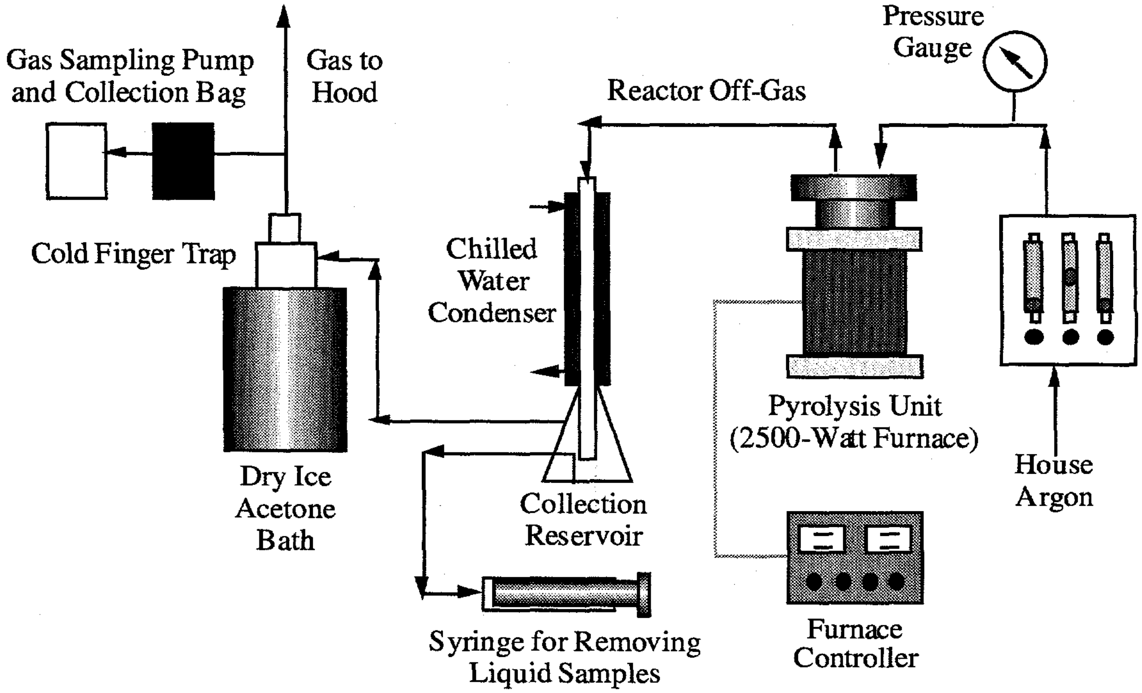

Fig. 20. Experimental setup used to determine the rate at which the off-gas leaves the reactor during the pyrolysis of a polycube. The setup also allows for sample removal for subsequent determination of off-gas constituent composition.

The rate tests show that most of the decomposition products leaving the reactor are liquids at ambient conditions. Only a small amount of dry, black, residue (presumed to be a form of carbon) is left in the reactor. Less than 11% of the decomposition products escapes the system as a gas.

Because most of the decomposition products are condensable liquids, the rate at which condensate accumulates in the collection flask is a good estimate of the rate at which the off-gas leaves the reactor during a pyrolysis run. As shown on the graph in Fig. 21, the maximum rate at which this occurs for a single cube is 4.6–5.2 g/min.

This rate is not significantly affected by the form of polystyrene (i.e., cube or pellets) or by the presence of aluminum paint, polyvinyl chloride (PVC) tape, or Shurtape™.

As shown on the graphs in Figs. 21 and 22, approximately 1 h elapses before any condensate is observed in the collection flask. This is the time required for the reactor and its contents to reach the temperature for pyrolysis to occur. The temperature in the reactor at this time is in excess of 500°C. This is far above the crystalline melting point of polystyrene (238°C) and thus indicates that the polystyrene melts and becomes a liquid long before the bulk of its decomposition products leaves the reactor.

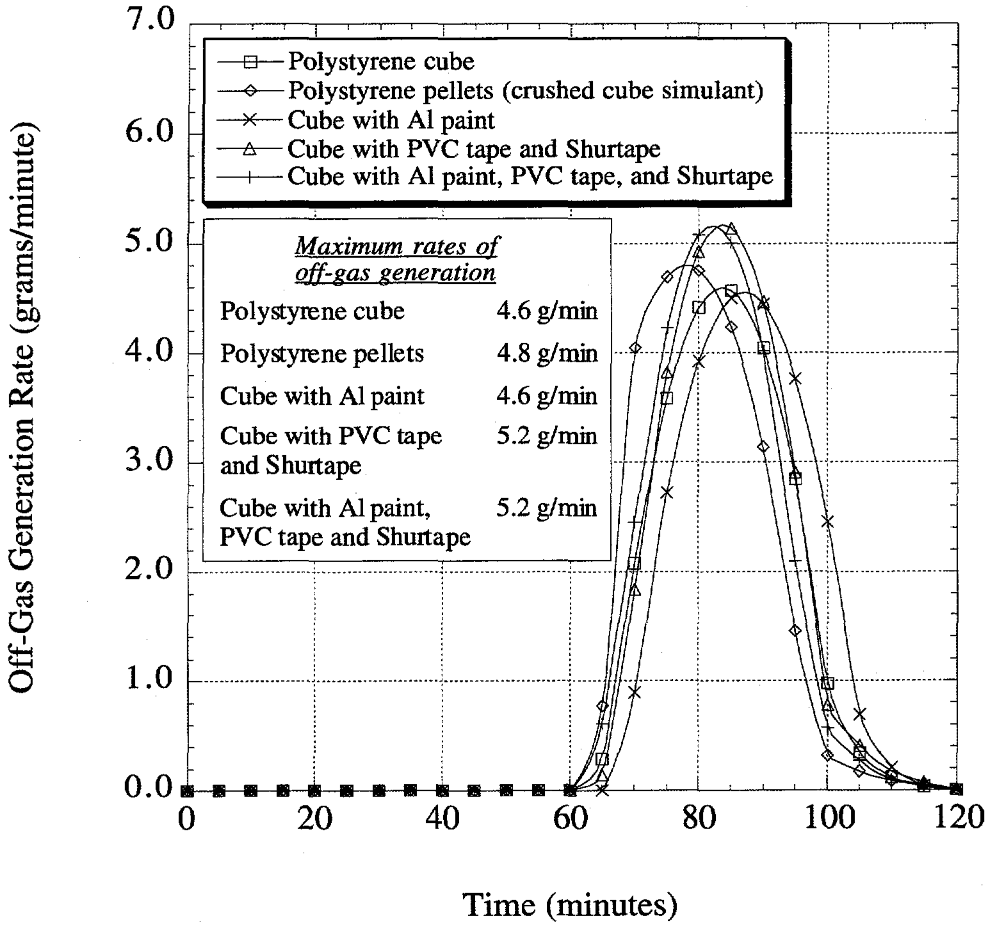

Fig. 21. Rate at which off-gas is generated from a single a 2-in. polystyrene cube. The maximum rate of off-gas generation is 4.8-5.2 g/min. This rate is not significantly affected by the form of polystyrene (whole or crushed cube) or by the presence of aluminum paint, polyvinyl chloride (PVC) tape, or Shurtape™.

As shown on the graph in Fig. 22, the rate at which off-gas is generated from the pyrolysis of multiple cubes is greater than that generated from a single cube. However, the maximum rate of off-gas generation does not scale directly to the number of cubes placed in the reactor. With a total of three cubes in the reactor (the maximum number that can fit in the given reactor design), the maximum rate of off-gas generation is 9.1 g/min.

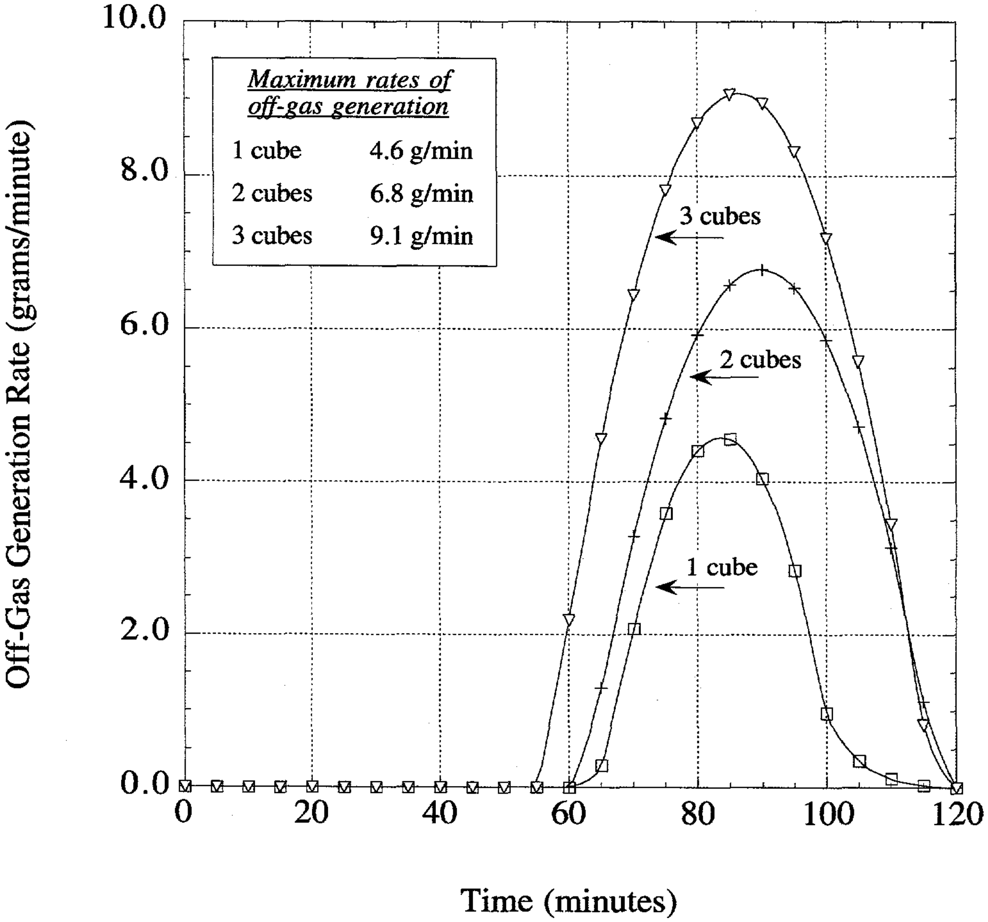

Fig. 22. The rate of off-gas generation for the pyrolysis of multiple polycubes. With a total of three cubes in the reactor (the maximum number that can fit in the given reactor design) the maximum rate of off-gas generation is 9.1 g/min.

Gas chromatography/mass spectroscopy showed that the condensate is composed primarily of styrene, toluene, and ethylbenzene, with an appreciable amount of constituents with higher molecular weight. The composition of the liquid phase is not significantly affected by the form of polystyrene or by the presence of PVC tape or Shurtape. The gases leaving the reactor are also composed primarily of styrene, toluene, and ethylbenzene. However, the gases coming from the cubes coated with

PVC tape do give off vinyl chloride, chloroethane, and 1,2-dichloroethane. All three gases contain chlorine.

Designing and Testing the Catalytic Converter. We reviewed a number of journal articles and brochures provided by catalyst companies in order to better understand catalytic conversion as a mode of off-gas treatment. We used the information obtained from this review to determine the type of catalysts that would best meet the needs for this application and to establish the design parameters (operating temperatures, flow rates) required for these catalysts to be tested. The following information was obtained:

- The most appropriate catalyst for this application would be a precious metal catalyst (i.e., platinum/palladium/rhodium used together or seperately) present on either a metal or a ceramic support.

- The temperature of the feed gases must be at least 450°C before they come in contact with the catalyst. This temperature is necessary to ensure virtually complete oxidation of the more stable hydrocarbons (e.g., aliphatic hydrocarbons) entering the process.

- The temperature of the catalyst (and thus the gas leaving the converter) must not exceed 600°C. This temperature keeps sintering, coking, and other factors from adversely affecting catalyst performance and decreasing catalyst longevity.

We used these criteria with the rate data to conduct an energy balance around the catalytic converter, in order to determine the temperature of the effluent gas leaving the converter during the pyrolysis of a single polycube. As shown on the graph in Fig. 23, the temperature of the effluent gas for the first 65 min of the run is identical to the feed temperature of 450°C. The temperature then increases as hydrocarbons in the reactor off-gas are introduced and are oxidized to carbon dioxide and water. If an air-flow rate of 109 standard cubic feet per hour (scfh) is fed to the converter (i.e., the stoichiometric amount of air required to fully oxidize 5 g/min of styrene), the temperature of the gas leaving the converter increases dramatically. The resulting temperature is much higher than that which could be tolerated by either the catalyst or by the materials from which the converter would be fabricated. One way to reduce this temperature is to provide excess air to the process. This would dilute the heat generated into a larger volume of gas, thus allowing the effluent gas to exit at a lower temperature. As shown on the graph, air-feed rates greater than 2000 at scfh would be required to keep this temperature from exceeding the maximum operating catalyst temperature of 600°C.

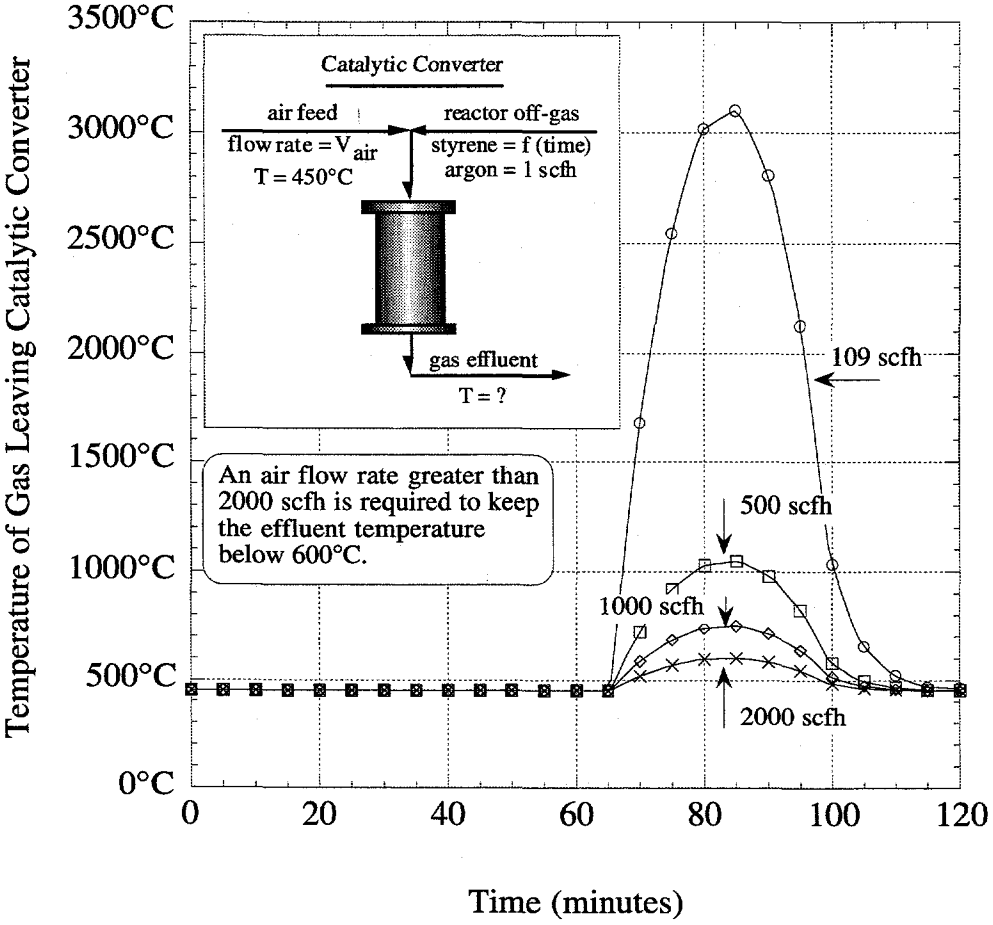

Fig. 23. Temperature of the gas leaving the catalytic converter vs time for different air-flow rates. Very high air-flow rates are required to keep temperature of the gas from becoming excessively high.

An air-flow rate of 2000 scfh could pose the following problems for glovebox operations:

- If such a high flow rate is introduced to the glovebox, an equally high flow rate must exit the glovebox. This condition is necessary to ensure that glovebox internal pressure remains lower than that of the outside environment.
- Preheating 2000 scfh of air from room temperature to 450°C would require 8000 W—a heating requirement much greater than that which could be provided by the 5000-W furnace commonly used in glovebox operations.
- Heat introduced into the glovebox by the furnace and by oxidation process must be effectively removed in order to keep the temperature of the glovebox from exceeding its upper operating limit.

In an attempt to solve these heat-generation and heat-removal problems, we modified the design of the pyrolysis setup to allow for the components in the reactor off-gas first to be condensed and then to be pumped into the catalytic converter at a slower and more controlled rate. The modified setup is illustrated in Fig. 24. Although these modifications would increase the amount of time required to process a polycube, the changes would allow the process to be run with a lower, and thus more reasonable, air-feed rate.

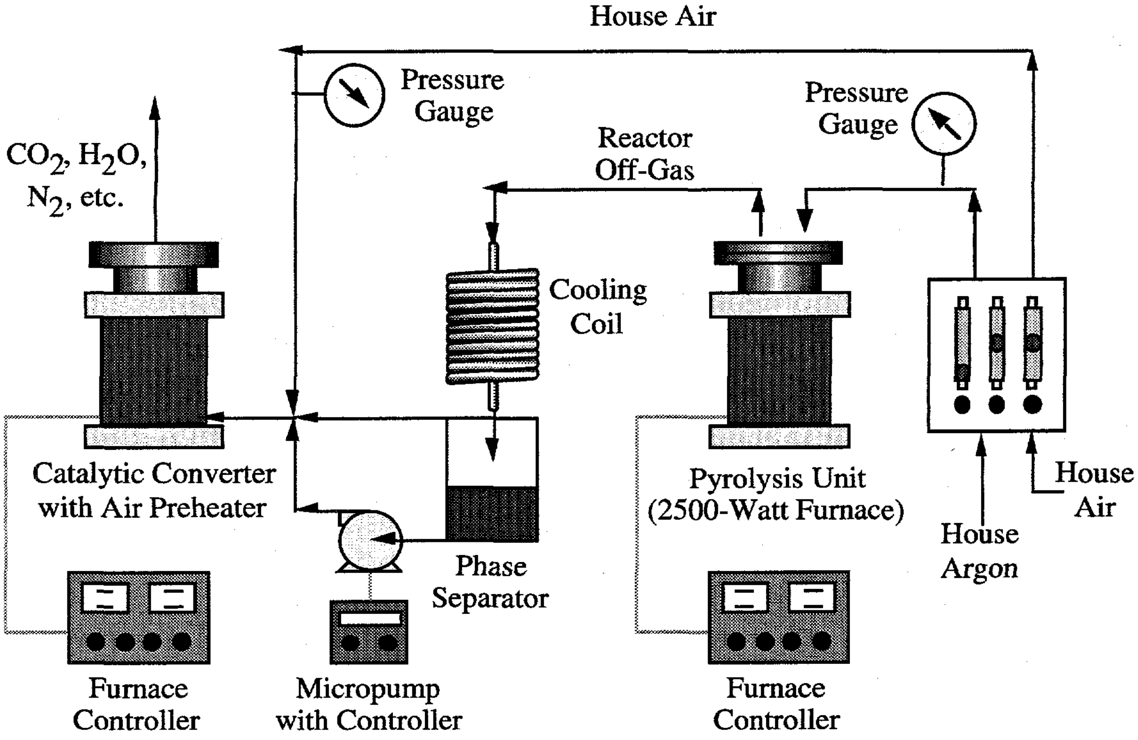

Fig. 24. Conceptual design of the modified pyrolysis process. Condensing the components in the reactor off-gas and pumping these components into the catalytic converter at a slower rate allows the process to be run without generating an excessive amount of heat in the glovebox.

We conducted a series of calculations to determine a rate at which the condensate could be pumped into the converter and could avoid the excessive heating and cooling requirements. The calculations showed that pumping the condensate at a rate of 1 g/min would require an air-flow rate of approximately 400 scfh to keep the temperature of the gas leaving the converter from exceeding 600°C. Preheating this air stream to 450°C would require less than 2000 W—a heating requirement that easily can be provided by conventional furnaces commonly used in glovebox operations. This flow rate is also low enough that the heat generated by the process can be removed by the air exiting the glovebox. Construction of the modified pyrolysis setup is now under way, and this setup will be used to evaluate the performance of a number of catalysts.

We provided a number of companies that produce catalysts with the information we have so far acquired, in order to help them better understand and address the specifications for this application. Follow-up conversations with the sales and technical representatives of these companies determined the firms that possess the appropriate types of catalysts, the technical expertise, and the willingness to assist us in designing a converter for the polycube pyrolysis process. These companies are Johnson Matthey of Wayne, Pennsylvania; Prototech Company of Needham, Massachusetts; and Catalytic Products International of Lake Zurich, Illinois. Each of these companies will be sending catalysts to be evaluated for this application.

Designing and Testing the Silent Discharge Plasma Unit. We used the results of the rate tests to design and build a coaxial silent discharge plasma prototype unit. We also constructed an experimental setup (shown in Fig. 25) to evaluate the performance of this unit, using styrene and other organic liquids as surrogates for the reactor off-gas. The setup is designed to analyze the performance of the unit over a range of argon and O_2 flow rates. The syringe pump allows hydrocarbons to be fed at various rates in order to more effectively simulate the off-gas generation rates from the pyrolysis reactor. The setup also includes in-line gas/liquid analytical capabilities (such as gas chromatography/mass spectroscopy, flame ionization detection, and nondispersive infrared spectroscopy) for measuring carbon monoxide and carbon dioxide concentrations. We are now conducting preliminary tests. Once the unit is optimized, we will configure it with the pyrolysis reactor setup for actual pilot-scale testing and evaluation.

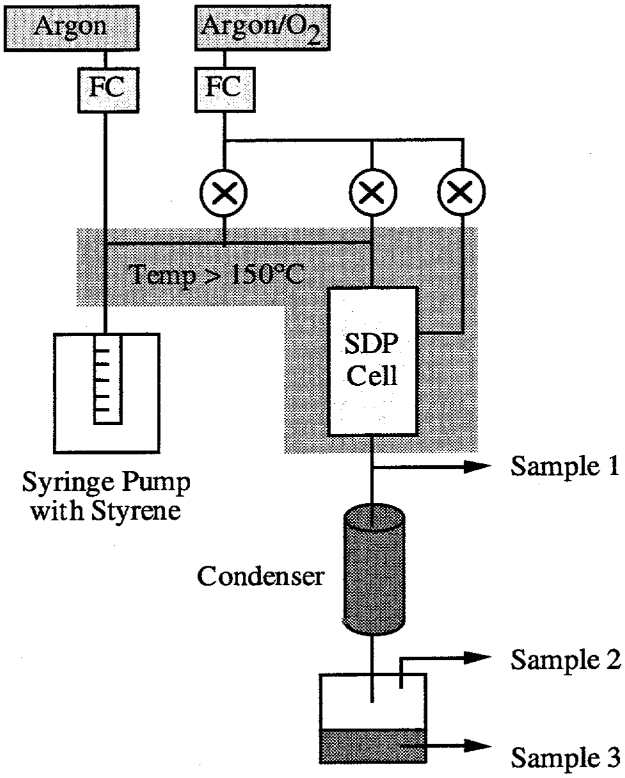

Fig. 25. Experimental setup constructed to test and optimize the silent discharge plasma prototype unit.

Combustibles: DETOX

Principal Investigators: Guy Lussiez and Charles Brown

Introduction

The DETOX project at this point consists of the following two major activities: (1) establishment of a contract with Delphi Research, Inc., to design and construct a glovebox-size DETOX reactor, and (2) a continuing development effort to evaluate the final disposition of liquid effluent and spent DETOX reaction solution.

Status/Progress

The contract negotiation was to have been completed by mid-March, but it was put on hold pending further guidance from the Nuclear Materials Stabilization Task Group. This instruction will come out of the ongoing combustibles trade study concerning whether to proceed with the project. However, since this study will continue until the end of July, we decided to proceed without further delay. The contract involving Delphi's contribution has been submitted to the Los Alamos National Laboratory Business Division. A Rocky Flats Enviromental Technology Site–Kaiser-Hill employee will provide technical guidance directly to Delphi. We are currently approximately six weeks behind our original milestone date. What is needed at this time to bring the project back on schedule is a technician who is knowledgeable in the workings of the Los Alamos National Laboratory Plutonium Facility (TA-55). This technician could interface with Delphi, initiating and following the progress of facility equipment installation and start-up. We are currently trying to find the appropriate person for this responsibility.

Work is proceeding on schedule in the effort to evaluate disposition of liquid effluent and spent solutions. Personnel from the Los Alamos National Laboratory Chemical Science and Technology Inorganic Elemental Analysis Group (CST-8) have been investigating conversion of the spent ferric chloride process solution to ferric oxide prior to disposal of the substance. A complete hydrolysis using a safe and reliable method that can be carried out in a glovebox is required. Thus far, CST-8 personnel have been able to carry out this conversion to the 80% level. Several hydrolysis tests have been run to determine the effects of heater design, heating rate, reactor configuration, and agitation on the rate and extent of hydrolysis. Work is continuing on this facet of the project. In addition, we have initiated the paperwork necessary to provide CST personnel with standard TA-55 training, so that they will be able to conduct experiments with radioactive materials when the equipment is available for use.

Combustibles: Residue Washing Flow-Sheet Development
Principal Investigators: Norman C. Schroeder and Moses Attrep

Introduction

Researchers on this project will test a proposed process flow sheet designed to direct the removal of organics (cutting oil), solvents (carbon tetrachloride), and finely divided plutonium metal contaminants from combustible residues. We will evaluate the advantages and limitations of the technology. Combustible residues are problematic for safe interim storage for a number of reasons that are exemplified by Rocky Flats Environmental Technology Site materials contaminated with plutonium. Major concerns are container corrosion and pressurization, reactive materials resulting from oxidizer/fuel mixtures, and pyrophoric plutonium metal. Corrosion and loss of containment, especially for materials that are wet or that contain free-standing liquid, are undesirable outcomes of extended storage of materials that have not been stabilized adequately. The focus of this task will be to demonstrate the base-line process proposed by Safe Sites of Colorado for the simple washing, desorption, and plutonium stabilization-unit operations for combustibles contaminated with organics, solvents, and plutonium. We are testing the batch-contact extraction (washing), filtration/decantation, thermal desorption, and stabilization steps of the base-line flow sheet.

Status/Progress

This project began in March. We completed an experimental plan including surrogate residue material that contains cerium metal, for the initial scoping studies. We then conducted tests with a plutonium-loaded surrogate. We began accumulating the equipment and the chemical for the project, including the Texaco Transultex A and H cutting oils and the surrogate containing cerium metal. A letter dated March 29, 1996, from D. F. Dustin of SSOC to S. M. Dinehart of Los Alamos, documented the agreed-upon work scope.

Sand, Slag, and Crucible: Magnetic Separation
Principal Investigator: Laura Worl

Introduction

Task Description. Sand, slag, and crucible (SS&C) residues stored throughout the DOE complex may contain as much as 10–20% plutonium. Westinghouse Hanford Company (WHC) has 4300 kg of SS&C residues that have been targeted for treatment and disposal by dry processing. Magnetic separation is a physical separation process that takes advantage of differences in magnetic susceptibility. The actinides in process waste streams are concentrated to form a low-volume, actinide-rich stream for subsequent processing and a high-volume, actinide-lean stream for disposal. Almost all actinide compounds are paramagnetic and, in a nonuniform magnetic field, move in the direction in which the field intensity increases. Diamagnetic particles, such as calcium fluoride or magnesium oxide (MgO), move in the opposite direction. This movement serves as a basis for separation. Physical separation processes are particularly attractive because no additional waste is generated during processing. In addition, because of the potential volume reduction, the size and costs of downstream processing units can be drastically decreased. Prior to disposal, concentrating the plutonium into a rich fraction will reduce the inventory of cans for disposal to sites such as the Waste Isolation Pilot Plant and the recovery of plutonium for long-term storage.

Background. Los Alamos has expertise with two forms of dry-powder separators for plutonium-contaminated residues. A small open-gradient magnetic separator (OGMS) has been tested on plutonium-contaminated SS&C, bomb reduction sand, graphite, electrorefining salt, direct-oxide-reduction salt, and incinerator ash. This separator creates the necessary magnetic energy gradient through the shape of the magnet pole pieces. Experiments on graphite, SS&C, and bomb reduction residues resulted in a plutonium-rich fraction and a plutonium-lean fraction. The plutonium concentrations in the plutonium-lean fractions were low enough to meet the economic discard limits and be discarded without further processing. Yet, because of the low throughput of the OGMS, its usefulness is limited. To improve processing rates for dry powders, one type of rare-earth roll separator (RE Roll) is available for testing with plutonium-contaminated SS&C materials at Los Alamos. In the magnetic roll unit, the separator consists of a thin belt that passes over two rollers. One of the rollers consists of a 1- to 2-tesla permanent magnet. As a powder is fed onto the belt, slightly magnetic plutonium particles stick to the belt in the vicinity of the magnet. This process causes the magnetic and nonmagnetic particles to be deflected in different directions, effecting the separation.

Several Los Alamos lots of graphite powder, bomb reduction sand, and SS&C residues have been processed with variable results. The best results were obtained with graphite in which particles were sized greater than 125 µm. In these cases, ~85% of the plutonium was concentrated into ~4% of the bulk material. The plutonium content of the lean fraction was sufficiently low in that it could be discarded without further processing.

Approach. Our efforts will be closely coordinated with WHC for their SS&C treatment development plan. The work scope initially focuses on laboratory-scale feasibility tests. Working with WHC, we will review and characterize SS&C waste for magnetic separation tests. Such characterization includes particle-size analysis, scanning-electron and back-scattering microscopies for particle speciation, and magnetic susceptibility measurements. This information establishes whether pretreatment steps (such as grinding and sieving) are necessary prior to testing. In addition to waste characterization, the newly installed roll separator from International Process Systems, Inc., will be optimized for routine testing.

In order to efficiently use time and cost constraints, we will test Los Alamos SS&C residues. Three forms of the Los Alamos SS&C have been identified:

- The same residue that was previously tested with OGMS,
- Residue that is treated with thermal stabilization, and
- Residue that is high in plutonium content.

After performing magnetic separation tests and assaying the results, we will be able to define optimization parameters for effective magnetic separation tests. We will then perform optimized tests.

After optimization tests have been conducted, we can evaluate the feasibility of using magnetic separation for SS&C treatment at WHC. If results are favorable, we will work with WHC to design a prototype unit and to prepare a suitable flow sheet for waste processing. After prototype testing on actual residue samples, the unit will be transferred to WHC for field installation.

Status/Progress

Initial work involved repair and optimization of the roll separator from INPROSYS Company had been installed in a glovebox but had never been tested. Several items were ordered for replacement or installation. The control panel and electrostatic bar were replaced because they were not operational. In addition, a third catch pan and splitter bar were installed for refined separations.

During the time the glovebox separator was being upgraded, we went to meet with the vendor in order to obtain expertise and advice from company personnel on optimization of the separator. Specifically, appropriate belt speeds, splitter plate settings, feeder setting, ionization-bar position, desirable plume characteristics and flow-sheet design were discussed with INPROSYS. In addition, we prepared and tested a surrogate SS&C and tested it at INPROSYS by spiking ground MgO crucibles with copper oxide (CuO). Copper oxide has approximately three-quarters of the magnetic susceptibility of PuO_2.

The flow sheet for the CuO surrogate experiment was rather complex and contained eight passes, not all of which were sampled. The results are shown in Fig. 26. In summary, most of the CuO shifted to the rich magnetic fraction. A minor complication was that half of the MgO shifted to the magnetic fraction. Because of this movement, which may be attributed to a magnetic mineral component in the MgO, attempts to high-grade the rich fraction were unsuccessful. The magnetic susceptibility of the material is being determined. The problem will be dealt with in the next planned experiment.

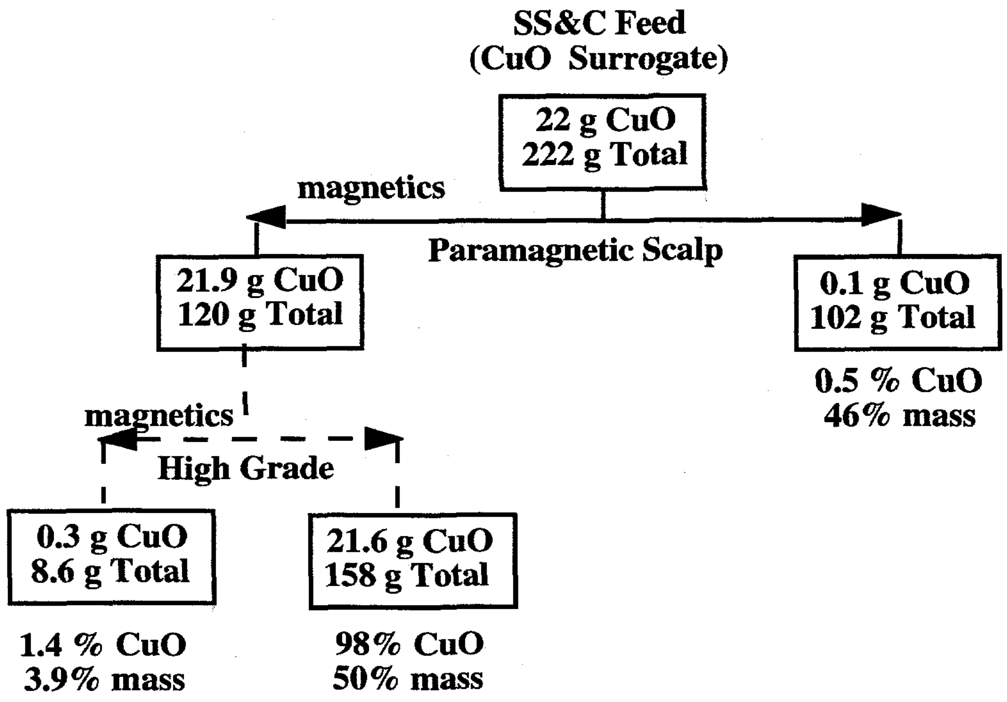

Fig. 26. Experiments at INPROSYS using spiked samples of MgO.

One experiment is underway with a Los Alamos SS&C residue. The results from the first phase of the test are shown in Fig. 27. The feed contained a particle size range of 120–850 microns. The experiments begin with a scalping pass executed at high speed to remove any magnetic material present. The variable examined was the belt speed. Following the scalping pass, further experiments are planned to reduce the plutonium-containing fraction in mass and yet to retain the plutonium content.

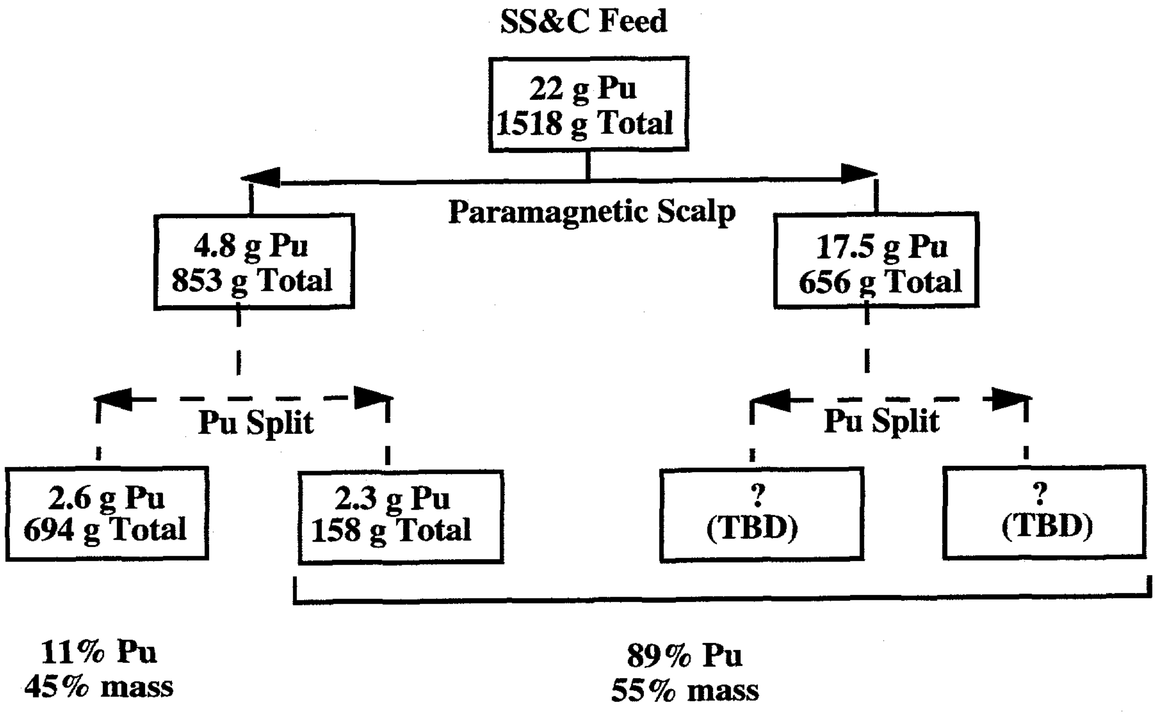

Fig. 27. Roll separator results for MAG26R.

Sand, Slag, and Crucible: Compaction
Principal Investigator: Tom Blair

Introduction

We are investigating compaction and sintering as a means of stabilizing sand, slag, and crucible (SS&C) materials that exist throughout the DOE complex.

Status/Progress

We obtained from the vault at Los Alamos an SS&C lean-residue item containing only 0.99 wt % plutonium and are in the process of identifying for evaluation another example that represents the other extreme, i.e., a material with much more plutonium and iodine in it.

The material was crushed and ground to pass it through a 20-mesh sieve. We obtained some PEMCO^{TM} frit P-25 for performing glass-sintering tests with the SS&C. This is a zinc/borosilicate glass that was selected for its low melting temperature, which means that it should have a lower sintering temperature. Six batches were prepared by mixing the SS&C and frit for compaction and sintering tests. The first three batches were prepared with 10 wt %, 20 wt %, and 30 wt % frit additions to the SS&C material. These blends could be pressed into pellets without the addition of either a lubricant or a binder. We established a test matrix in which pellets were sintered at 500°C, 700°C, 800°C, or 900°C for 1 h in flowing oxygen. We sintered one pellet from each batch at each temperature. We then measured the sintered pellets for shrinkage and density calculations. Fired shrinkage ranged from 17.0% to 18.8%. The pellets containing 10 wt % frit and sintered at 900°C had the highest density of 2.18 g/cm^3. The pellets sintered at 500°C fell apart, and those sintered at 700°C were cracked. We submitted samples of the pellets sintered at 900°C for microstructural examination, but we do not yet have the results.

The next test matrix included three batches prepared with 4 wt %, 6 wt %, and 8 wt % frit additions, with one pellet from each being sintered at 700°C, 800°C, or 900°C for 1 h in flowing oxygen. We do not yet have any analytical results for the processing of these pellets. The pellets have not been measured for shrinkage and density.

We ordered chemicals that will be used to prepare a surrogate SS&C sample using cerium oxide as a substitute for plutonium oxide. The composition of the surrogate is based on the Westinghouse Hanford Company flow sheet. We will use this surrogate to do thermogravimetric analysis in order to determine the temperatures, heating rates, and atmospheric conditions affecting the iodine release and the conversion of any calcium metal to an oxide.

We had planned to install an oxygen-atmosphere, high-temperature sintering furnace in a glovebox so that compacts made of real SS&C can be sintered at temperatures above 1000°C in air. However, damage to the furnace during shipment and numerous difficulties in obtaining replacement parts have delayed this installation for more than two months. The maximum operating temperature of the furnace currently in use to sinter the pellets made with the frit additions is 1050°C. As a result, the tests planned to evaluate the addition of porcelain to the SS&C, have not been performed as originally scheduled, because such evaluation requires sintering temperatures higher than 1300°C. Also, we have been unable to do sintering tests without any additives. And finally, the compaction of SS&C material in the form of ballinders and the performance of drop-and-crush tests also have not yet been done because the available furnace is so small that compacts greater than 0.25-in. long by 0.25-in. in diameter will not fit into it. The schedule for this task was revised to show new milestones based on the assumption that the new furnace will be operational sometime in May 1996.

Surveillance: Digital/Real-Time Radiography
Principal Investigator: David Horrell

Introduction

Researchers on the Digital/Real-Time Radiography task will evaluate radiographic systems in use at Los Alamos and elsewhere. We have established collaboration with Savannah River Site (SRS) to evaluate and optimize the capabilities of existing systems at each site.

Installation and Initial Evaluation of Radiographic Equipment at Los Alamos

Real-Time Radiographic equipment from VJ Technologies, Bohemia, New York, was installed in the Los Alamos National Laboratory Plutonium Facility (TA-55) in February 1996. This equipment is contained within a cabinet on wheels and can be moved to other locations. At its current location, it can effectively serve vault needs with minimal personnel exposure and material handling. Machine specifications were chosen by the Los Alamos Plutonium Packaging Project personnel, whose project funded the procurement, for surveillance of long-term metal and oxide storage containers and for more general vault use. Vault containers require some observations to be made through lead shielding. The Phillips x-ray tube supplies from 10-225 keV at 10 mA. This energy is more than adequate for the Los Alamos DOE-STD-3013 containers but is necessary for penetration and evaluation of many vault containers. A vault container with a potential problem was successfully evaluated with power set at 118 keV. The VJ equipment will be used extensively to evaluate existing vault containers, and we will incorporate the resulting database into our radiographic standards development technology transfer. Substantial vault holdings are stored as residues throughout the DOE complex, and the use of radiography to determine what the container and material conditions are will add greatly to our knowledge of vault materials. Conversely, materials in the TA-55 vault are often a sample of materials existing at other sites. Therefore, some extrapolation from the existing condition of containers at Los Alamos may be made to support the Surveillance Shelf-Life Project at several facilities.

Representatives from SRS and Westinghouse Hanford Company (WHC) were present for the April 2 one-day meeting to discuss the Shelf-Life Project and other surveillance activities. Among other items of business, we spent several hours evaluating and comparing recent radiographs taken of vault holdings. At Los Alamos, we have begun to evaluate items such as lifted lids that reflect off-normal configuration. Personnel at other sites are finding that radiography is an extremely useful tool in determining container condition. Savannah River personnel are developing digital radiography, and WHC has radiographic capability. The various sites are seeing many similarities in potential problems with using this tool for noninvasive evaluation.

Bellows

A bellows developed with Mini-Flex Corporation of Ventura, California, has been selected for surveillance of the first cans packaged at Los Alamos in accordance with DOE-STD-3013. We have completed extensive design development of this aneroid (evacuated) bellows and have statistically evaluated the performance of our designed bellows. The Los Alamos National Laboratory Technology and Safety Assessment Division Statistics Group (TSA-1) will issue a report in April on the performance of this bellows. In the report, researchers compare the bellows shadowgraph measurements at Mini-Flex to radiographic measurements made through a mock-up 3013 container. The conclusion is that the bellows provides an excellent indication of pressure changes.

The next series of tests will compare the previous performance of the bellows with measurements made with the new VJ Technologies real-time radiographic equipment. We have initiated a series of tests and have formulated a formal testing approach. This testing program is connected to the collaborative joint radiographic research and devopment endeavor with SRS. Results will be shared to optimized radiographic performance and procedures for use.

New bellows designs are to be tested at Mini-Flex in May 1996. These new bellows will have a more robust configuration and will include a filter to eliminate convolution exposure to plutonium oxide and a stainless steel metal sheath to add structural integrity. Bellows will also be fabricated from materials other than 304 stainless steel and will be tested for improved linearity. A more robust bellows, shorter in height and larger in diameter, is being fabricated for operation over a wider range of pressure. In August, a report on bellows development will be issued by TSA-1.

Surveillance: Tomography
Principal Investigator: Lynn Foster

Introduction

Researchers on this project will investigate the feasibility of using x-ray tomography to determine the physical and chemical characteristics of stored materials. We will evaluate the sensitivity of x-ray computed tomography (CT) to detect the onset of physical and chemical changes in stored materials, using computer modeling techniques developed by researchers at Los Alamos. Test objects using surrogate materials will be constructed, and objects will be imaged to evaluate the applicability of commercial x-ray tomography systems for the characterization of stored nuclear materials. We will also evaluate another tomographic technique that is used for nondestructive assay (NDA) of nuclear materials. A prototype Tomographic Gamma Scanner (TGS) will be evaluated and compared to the current NDA technology in use at the Los Alamos National Laboratory Plutonium Facility (TA-55).

Status/Progress

Researchers from several groups at Los Alamos are working closely with the Digital Radiography team at Savannah River Site (SRS) on this project. Savannah River will assist in the construction of test objects and will provide imaging data to aid in the evaluation of commercial x-ray tomographic systems. Los Alamos and SRS personnel have held several meetings to discuss system development and eventual deployment of an x-ray tomography system at the SRS FB processing line. Workers at SRS have constructed two x-ray tomography phantoms that contain different nonradioactive chemical compounds. These phantoms will be used to evaluate the efficacy of dual-energy tomography for material identification. One of the test objects was delivered to Los Alamos for imaging at Los Alamos facilities.

A study of the failure mechanisms observed in the stored nuclear material inventory at Los Alamos has been completed. Mechanisms that may be identified by CT have been determined and computer modeling studies for typical storage configurations for nuclear materials have been initiated. Based on the computer models, we have designed a set of high-density test objects and have ordered the fabrication of the test objects. These objects will be used to evaluate the ability of CT systems to image packaged plutonium and uranium metals and to observe small chemical and physical changes in these materials.

The TGS has been installed in TA-55. Setup and calibration of the instrument are complete. Measurements to evaluate the performance of the TGS are under way. Of particular interest in this study are materials that have been historically difficult to measure by other NDA techniques, such as salts from plutonium-processing operations.

Surveillance: Shelf-Life Project
Principal Investigator: David Horrell

Surveillance: Shelf-Life Project Subtask: Optical Monitoring of Residues and Oxides in Storage Containers
Principal Investigators: Pamela K. Benicewicz, John M. Berg, and Laura A. Worl

Introduction

The purpose of the Shelf-Life Project is to evaluate the behavior of plutonium metal, oxide, and residues in storage.

Hardware and Material Preparation for Impure Oxide Tests

We have assembled hardware for several pressure-volume-temperature (PVT) sampling systems for metals, oxide, and residues; have selected legacy plutonium materials; and have begun analysis and characterization of treated and untreated materials. Personnel to support the Shelf-Life Project are being hired and placed. About 2000 g of material currently in the the Los Alamos National Laboratory Plutonium Facility (TA-55) inventory is the initial material chosen for testing. This material was generated by oxalic acid precipitation from nitric acid solution, then was diluted with magnesium oxide (MgO) to simulate substantial existing Rocky Flats Technology Site (RFETS) legacy holdings. The plutonium oxalate and diluent MgO were then heated to about 500°C, forming impure plutonium oxide. Initially, the material was a light yellow color. We sampled this material for particle size, surface area, loss on ignition (LOI), isotopic, and chemical analysis. The 2 kg of material was heated to 600°C for 12 h and again was sampled for particle size, surface area, and LOI. In addition, moisture adsorption rates in a glovebox atmosphere will be done. The adsorption test will be monitored for at least one week. Note that, after the preliminary heating to 600°C, the material was a light gray color. Half of the original 2-kg lot will be heated to 980°C for 2 h and will be analyzed for particle size, surface area, and LOI. Again, weight gain due to atmospheric adsorption will be determined. The adsorption will take place within a glovebox atmosphere over the period of at least one week. The material calcined at 980°C will be analyzed for total plutonium, isotopic content, americium, and chemical constituents in order to determine the effect from thermal stabilization. Note that after calcination to 980°C, the material color is black.

The materials, after the 600°C treatment and after the 980°C calcination, will be placed in the long-term shelf-life storage containers to be monitored for gas generation and corrosion. Samples will be placed in air and helium atmospheres for these storage tests. The PVT containers are fabricated from 304 stainless steel and are cleaned using an aqueous surfactant. Gas samples of less than 0.5 cm^3 are taken at regular intervals. All of the analytical equipment for performing these tests is in place and has been operational for the previous pure oxide studies. Further tests on appropriate materials will follow this procedure when applicable. Materials shipped from other sites will be prepared and treated in a similar way.

Collaboration With Other Sites

Savannah River Site (SRS) has vault holdings that require identification and specification for processing or thermal stabilization. Several residue forms have been selected as candidates for the Los Alamos Shelf-Life Project, including materials of less than 50 wt % plutonium that are primarily matrixes with uranium oxide. Using SRS materials, we are working out details of a cooperative experimental plan in support of the Shelf-Life Project. Savannah River personnel face a quandary in that they are scheduled to package metal and oxide after the processing lines are inoperable. The only treatment remaining will be thermal stabilization. If thermal stabilization is not successful for some materials, workers need to know about the lack of success before their processing lines are shut down. The Los Alamos Shelf-Life Project will support the SRS endeavor to make these determinations.

Rocky Flats has several concerns to which the Shelf-Life Project could serve to add significant support. Initial contact in early February with their management and subsequent interaction indicate that researchers on the plutonium metal and oxide repackaging project conducted by Safe Sites of Colorado (SSOC) at RFETS are most receptive for a collaborative effort at this time. One reason for this desire for collaboration is their immediate need to verify LOI measurements. A meeting will be held at RFETS on April 18 with Kaiser-Hill, SSOC, and DOE-Rocky Flats Operations Office to discuss the shipment of a representative sample of their oxide to Los Alamos for analysis, LOI measurements, stabilization characteristics, and surveillance. It is hoped that Los Alamos can obtain and evaluate both pure and impure oxides from RFETS and that a more extensive collaborative effort will grow from this initial interaction.

Hanford has substantial vault holdings of plutonium oxide that have been calcined at about 500°C and that indicate little or no pressure increase over the past 10–20 years. Personnel are preparing to ship several cans of this material to Los Alamos for gas analysis and LOI measurements to confirm oxide stability, and they are hoping to eliminate a need for reprocessing. Los Alamos vault holdings include items from Westinghouse Hanford Company (WHC) that may represent identical holdings presently at the site, and these materials may be used for analysis should transportation prove to be an insurmountable obstacle. It is widely thought, however, that establishing a mechanism for shipping materials from the several sites to Los Alamos is an imperative part of several interactive programs. Los Alamos and WHC will prepare a shipper-receiver agreement no later than May 1996.

SUBTASK: OPTICAL MONITORING OF RESIDUES AND OXIDES IN STORAGE CONTAINERS

Introduction

The optical analytical techniques of laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy (RS) will be used to noninvasively monitor sealed cans that contain radioactive residues and/or oxide powders. The pressurization of sealed storage containers over time, owing to the production of gases, is known to occur. The gases can be produced by various mechanisms, such as

- Alpha decay of radioactive elements that produces helium gas,
- Radiolytic decomposition of residue materials that can generate hydrogen gas, and
- Chemical reactions between the actinides and the residue components that can produce carbon monoxide, carbon dioxide, and other gases.

Optical techniques can be used to determine changing gas composition in the storage containers and changing surface chemistry of the material in the containers. This task includes designing and fabricating cans that will permit optical sampling of the material within, setting up the LIBS apparatus at (TA-55), and conducting initial experiments to demonstrate the effectiveness of the techniques. After these initial demonstrations, we will use LIBS and RS to monitor changes within sealed containers filled with storage materials.

With LIBS, a laser beam is focused onto a sample (a solid, liquid, or gas), the sample is vaporized, and a high-temperature plasma is formed. Analysis of the plasma light provides information on the elemental content of the sample. Thus, LIBS will reveal the elemental content of the gases in the container and on the surfaces of solids inside the container.

With RS, a laser beam is directed onto a sample. Changes in the frequency of the scattered light correspond uniquely to the molecular content of the sample. Thus, RS can determine both the molecular characteristics and changes in the gases and surface chemistry changes of solids inside the container.

Using both techniques, we will monitor the sealed storage containers over time. Observed changes from an established base line will provide information on the long-term chemical behavior of actinides and related gas production—knowledge that we do not currently possess.

Status/Progress

This quarter, we completed design of the storage cans for optical monitoring studies. These cans are of identical size to standard storage cans; but they include optical ports, shutters to protect the optical windows, and bellows to allow adjustment of the height of the powder in the can if settling occurs. We expect to complete fabrication of the cans by the end of April. In addition, we have also designed a Raman cell for gas monitoring, and it is near completion. This cell can be attached directly to the storage container.

We have continued experiments, using a LIBS system setup in a nonradioactive area. We used a sample of gadolinium for these experiments. Gadolinium was selected because many of its physical properties that are important to the processes of laser ablation, and formation and evolution of plasma are similar to those of plutonium. The objective of these experiments was to optimize signal detection and element identification through the variation of system parameters, such as buffer gas and buffer gas pressure. We have obtained detailed profiles of the temporal and spatial evolution of the gadolinium optical emissions in various buffer gases (argon, neon, and helium) at different pressures (100-500 torr). The results show that both temporal and spatial evolution are highly dependent on buffer gas and buffer-gas pressure. Argon buffer gas enhances atomic emission in the red wavelength range over that obtained when helium is used.

Using the LIBS apparatus, we performed further experiments in order to determine whether any of the trace elements present in the gadolinium sample could be detected. The sample contains the following known quantities of trace elements:

- 200 ppm of terbium;
- 50 ppm of zirconium;
- 20 ppm of copper;
- 20 ppm of chromium;
- 10 ppm of calcium; and
- 1–3 ppm each of aluminum, iron, silicon, manganese, and magnesium.

The strongest atomic emission lines of these elements were identified, and those that did not overlap with known gadolinium emission lines were selected as markers of several of the trace elements (terbium, copper, and chromium). Buffer gas and buffer-gas pressure were again varied to determine the optimum conditions for trace-element detection. All three elements (terbium, copper, and chromium) have been tentatively identified. Although the spectroscopic evidence indicating the presence of these trace elements is strong, a comparison of the spectra of gadolinium without these elements present is needed before we can absolutely make their identification through spectroscopic signals.

Experiments using the nonradioactive LIBS system planned for next quarter include filling one of the fabricated storage cans with different gas compositions in order to optimize detection of changes in the gas composition and detection of trace amounts of gas. The start-up of experiments at TA-55 depends heavily on the relocation/modification schedule of the Advanced Recovery and Integrated Extraction System (ARIES). Currently, the glovebox to be used for the LIBS experiments is scheduled to be moved in July; and it cannot be used while being moved, so experiments on oxide powders/residues will be delayed until after that time.

Our first formal milestone, demonstration of the LIBS and RS capabilities, occurs July 1, 1996. However, the design and fabrication of the experimental storage container was an informal milestone that almost has been met: can fabrication will be completed by the end of April. The extensive experiments with nonradioactive materials that have been performed using the plutonium surrogate gadolinium also represent completion of another informal milestone. These experiments also demonstrate the capability of the LIBS system in optically characterizing materials and in identifying the presence of trace amounts of materials in a metal matrix. Experiments with radioactive materials at TA-55 using the LIBS and RS systems may be delayed by the planned ARIES relocation/modification effort.

Surveillance: Acoustic Resonance Spectroscopy

Principal Investigators: Kirk Veirs and Clinton Heiple

Introduction

The objective of this task is to determine the feasibility of using acoustic resonance spectroscopy (ARS) to detect pressure increase and gaseous components in sealed storage containers.

Status/Progress

We prepared a technical report that details findings from previous experiments[1]. In the report, we summarize a set of experiments designed to use ARS to evaluate the feasibility of measuring gas pressure and gas composition inside the proposed container. Gas resonances are easily detected inside an otherwise empty container. The amplitude of the gas resonances varies with gas pressure and the frequency varies with gas composition, both conditions having been predicted by theory. In addition, we observed that the frequencies of the shell resonances vary with gas pressure as well, providing a potential second measure of pressure. Unfortunately, when even small amounts of simulated plutonium oxide (sand) are added to the cylinder, the sand absorbs enough energy so that the gas resonances become undetectable. A simple modification to the container created an analysis chamber in which the gas resonance can be excited and monitored, even though the rest of the container is full of sand. Thus, we demonstrated the feasibility of using ARS to monitor gas composition and pressure inside a modified inner residue cylinder. The sensitivity of ARS to detect changes in gas composition based on shifts in the frequency of the gas peak by 1 Hz have been calculated for mixtures of helium, hydrogen, and argon. Although helium and hydrogen are similar in mass, the frequency shift when hydrogen is mixed with helium is nevertheless easily detectable. The calculations predict that an increase of less than 0.5 torr hydrogen in a local atmosphere of helium (590 torr) would be detectable.

Future work will address the following issues:

- Demonstration of a capability to observe inner-container gas modes with transducers mounted on an outer container and
- Demonstration of the ability to deconvolute acoustic resonances caused by the container and those caused by gas modes.

Using a variety of coupling geometries, we have designed a set of experimental chambers to test the ability to couple acoustic responses between an inner and outer

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[1] Kirk Viers, Clinton Heiple, and Joe Baiardo, "Feasibility Study of Measuring Gas Composition and Pressure Inside a Sealed Residue Container with Acoustic Resonance Spectroscopy," Los Alamos National Laboratory Report LA-13139-MS (In Press).

container. We will use these chambers to test for the optimum geometry of a container-to-container coupler, for the optimum thickness of lids for storage containers, and for other container parameters that will affect the successful application of ARS to storage-container surveillance. We have begun theoretical modeling of the acoustical response of a gas mode interacting with a container mode. Results have been very encouraging; i.e., the theoretical response curve reproduces many of the characteristics of experimentally observed response curves. We will begin quantitative comparison of experiment and theory, and we will begin mathematical approaches to deconvolute experimental data in order to obtain quantitative information about the gas modes.

Core Technology: Solution Chemistry
Principal Investigator: John M. Berg

Introduction

The goal of this work is to understand aspects of the solution chemistry of actinide elements in legacy residues and in proposed residue treatment processes. We hope to gain an understanding that is extensive enough to guide stabilization and disposition decisions and to enable efficient optimization of treatment processes.

Plutonium residue stabilization and treatment processes will need to be efficient and to be targeted at the present-day issues of safety, stability, and economics of disposal. Aqueous chemical separations will be required for primary treatment and post-treatment following stabilization of many of the residues. These aqueous separations will have to be carried out under chemical conditions that differ considerably from those used in production of material for weapons. We propose to measure critical thermodynamic parameters governing actinide chemistry under these chemical conditions so that treatment and separation processes can be designed and optimized quickly.

Status/Progress

The absorption spectroscopy capability required for much of the proposed work in the Los Alamos National Laboratory Plutonium Facility (TA-55), Building PF-4, was made operational in early February. This capability was made possible through a provisional approval by the Los Alamos Nuclear Materials Technology Division Facilities Group, for the operation of our glovebox at TA-55. The new system incorporates improved sample handling and mechanical stability. The only task remaining is to complete the reconfiguration is pipe-fitter work to reconnect glovebox services. This work has been cleared for scheduling and has been scoped by the pipe fitters. The reconfiguration will probably be completed by the end of April, as scheduled.

Sample preparation and acquisition of spectra on the Pu(IV) nitrate system began in mid-February. During the balance of the second quarter, we prepared and scanned approximately 100 solution samples that covered three different ionic strengths and ranged up to 22.5 molal total nitrate concentration. Analysis of that data began at the end of the quarter and will proceed concurrently with preparation of additional samples and acquisition of more data. We are on schedule to complete this stage of data acquisition by the end of May.

During this second quarter, work also began in the Los Alamos National Laboratory Chemistry and Metallurgy Research Building to study the interactions of higher plutonium oxidation states, principally Pu(VI), with other inorganic anions. Under this subtask, we collected preliminary spectroscopic and solubility data on chloride, carbonate, and perchlorate systems.

Core Technology: Chemical and Physical Interactions of Actinides with Surfaces
Principal Investigator: David Morris

Introduction

Researchers on this project study the chemical interactions and surface structure characteristics of plutonium and uranium species adsorbed onto solid-phase materials found in processing residues throughout the DOE complex. Actinide species interact with residue substrate surfaces by means of a number of mechanisms (i.e., surface complexation, physisoption, matrix diffusion, entrainment) to yield a wide range of surface-bound species. Stabilization of these residues by removal of the actinide species from the matrix while minimizing secondary waste volumes is a goal not yet achieved. In many instances, the development and implementation of treatment strategies have been thwarted because of the failure to understand and incorporate fundamental surface actinide chemistry into the design of the treatment process. We propose to employ molecular spectroscopic probes of small spot size on several prototypical actinides and substrates in order to obtain detailed characterization and imaging of the nature and extent of the surface interactions. This information can be incorporated into future stabilization activities.

Progress

Funding for this project was initiated during this quarter. Numerous planning meetings were conducted with project investigators and Los Alamos National Laboratory stakeholders, particularly investigators in the Nuclear Materials Recovery and Processing Project, to identify the highest priority and/or most relevant residue characterization issues that will be addressed in this project. We have made significant progress in winnowing the list of potential targets to a manageable number for investigation during the remainder of this fiscal year. The final list of residues and surrogate residues for which we will obtain characterization data will be provided in a milestone report at the end of April. Progress toward this milestone is currently on schedule.

From the existing archived material at the Los Alamos National Laboratory Plutonium Facility (TA-55), we have already selected a number of ash residue samples for characterization. These materials have been transferred to the Chemistry and Metallurgy Research (CMR) Building at South Mesa Site, where many of our characterization tools are housed. We have begun data collection on one of these samples. Raman spectral data have been obtained that show a number of vibrational bands consistent with plutonium-oxygen stretching modes that we saw previously for high-fired PuO_2.

We have also spent considerable effort this quarter in identifying and upgrading our facilities in the CMR Building to support this effort. We acquired a new laboratory and are presently outfitting it for new work using red-Raman and Fourier transform infrared spectroscopies. Current plans call for this laboratory to be operational by the end of April.

Core Technology: Changes in the Chemical State of Plutonium

Principal Investigator: Kirk Veirs

Introduction

We began this project in January of the second quarter. The goals of the project are to study and characterize the chemical state of plutonium in various residues.

Status/Progress

The Los Alamos National Laboratory Nuclear Materials Technology Division Actinide Materials Chemistry Group prepared 20 samples for extended x-ray absorption fine structure (EXAFS) experimental work at Stanford Synchrotron Radiation Laboratory (SSRL). These experiments are scheduled for March 28–April 8, 1996. The EXAFS experimental technique requires calibration by known samples, therefore some of the samples were of well-known composition and structure. There were two sample types—loaded resins and ash. The sample list is as follows:

Loaded Resins:

1.	HPQ	HPQ Resin
2.	HP25	HP Resin
3.	402	402 Resin
4.	JSK-4	Modified 402 $(CH_2)_2N(Me)_3$
5.	JSK-5	Modified 402 $(CH_2)_5N(Me)_3$
6.	JWN-25	Modified 402 $(CH_2)_5$-Nitrobenzyl
7.	JWN-29	Modified 402 $(CH_2)_5P(Me)_3$
8.	JWN-10	Modified 402 $(CH_2)_2O(CH_2)_2N(Me)_3$
9.	JWN-12	Modified 402 (CH_2)-nitrobenzyl
10.	ZY-106	Modified HP18 $(CH_2)_5N(Me)_3$
11.	LRAS3	Crystalline Diammoniumhexanitrato plutonium
12.	LRAS2	Crystalline plutonium tetranitrato
13.	LRA-S1	Pu(IV) in 8 M of nitric acid
14.	LRA-S4	Pu(IV) in 13 M of nitric acid

Ash:

1.	BASH1B-S1	Los Alamos ash
2.	RBBASH5-S1	Los Alamos virgin ash
3.	BARF3A-S1	Rocky Flats ash
4.	PuO2-x (x=0.02)	Substoichiometric plutonium dioxide
5.	PuO2+x (x=0.02)	Superstoichiometric plutonium dioxide
6.	OXPHS1-S1	Stoichiometric plutonium dioxide

Plutonium in the +4 oxidation state usually binds to anion-exchange resins as the hexanitrato complex. New anion-exchange resins have been developed based on the structure of the plutonium hexanitrato complex, as determined in previous work. These new resins have higher distribution coefficients and more rapid kinetics of absorption than did previous ones. In the new resins, the binding site has been molecularly engineered to provide a chemically more attractive site for the plutonium hexanitrato complex. We selected a series of these resins for study, in order to elucidate the structure of the bound plutonium complex and the effect on the complex by the different binding sites. The new resins may result in faster, more efficient, separations, if future processing is required. These results will also provide a base line for evaluation of changes in resins that have been loaded for many months. The nitric acid solutions and crystalline solids are to be used for calibration of the resin EXAFS data.

Ash residues from both Rocky Flats Environmental Technology Site and Los Alamos that were previously studied using electron microscopy show small plutonium dioxide particles that are substoichiometric with respect to oxygen. We selected these samples for study using EXAFS, because EXAFS is more sensitive to the local conditions surrounding the plutonium. We included carefully prepared oxides of plutonium for calibration. The calibration samples included both sub- and superstoichiometric amounts of oxygen. Production of superstoichiometric oxide by reaction of oxide with adsorbed water may have a significant impact on storage criteria. These ash samples have been stored for years and may have reacted with surface water to form superstoichiometric oxides.

Los Alamos Chemical Science and Technology Division researchers purified 1-g aliquots of ^{239}Pu and ^{242}Pu solutions, using anion-exchange chromatography. We set up the electrochemical system for preparation of pure oxidation states and completed electrochemical synthesis of oxidation-state pure-stock solutions of Pu(III), Pu(IV), Pu(V), and Pu(VI). These samples were assayed using ultraviolet/visible absorption spectrum/near infrared spectroscopy in order to assure that each solution contained a single-oxidation state of plutonium. Aliquots of each oxidation-state solution were examined by x-ray absorption near-edge structure spectroscopy in order to determine the absorption-edge energy for each oxidation state. This information will provide vital background data for comparison with oxides, residues, and column-sorbed material in order to determine oxidation-state information for these samples.

We designed and fabricated sample holders for use with the EXAFS samples. Sample loading took place in Los Alamos Chemistry and Metallurgy Research labs equipped with an EXAFS sample press for solid samples. Shipping of the EXAFS samples took additional time, in order to comply with all necessary safety precautions for working with transuranic samples at SSRL.

Core Technology: Actinide-Organic Interactions
Principal Investigators: Carol Burns, Steve McKee, and Ann Schake

Introduction

The purpose of this task is to explore the interaction of plutonium and other actinides with organic substrates. The actinide-organic interactions that will constitute the research include interactions between actinide residues and organic substrates (chemical speciation) and actinide organometallic chemistry (organoactinide chemistry).

Status/Progress

The inert glovebox, located in the Los Alamos National Laboratory Plutonium Facility, Building PF-4, Room 208, and used to perform the organoactinide part of this project, must be repaired. While the repair is being done, we are proceeding on the National Environmental Policy Act requirements for this work that are not covered under existing safe operating procedures. We will also use the box repair time to install a new thermogravimetric analysis/differential scanning calorimeter for characterization and kinetics studies. To assist in mitigating the possible schedule slippage due to the glovebox repairs, we will hold off on hiring a postdoctural staff member, but instead we will use a Chemical Science and Technology Division postdoc already working at Los Alamos and add one visiting professor for the summer. This maneuvering will allow us to make progress in obtaining additional postdoc support from the Nuclear Materials and Stockpile Management Office.

As this project contains two major subprojects, we are currently working on the actinide-organic interactions aspect, which will allow us to investigate the chemistry of plutonium with tributylphosphate (TBP) at several temperatures. Speciation of TBP is very interesting and is dependent on oxidation state. Furthermore, sufficient knowledge about this chemistry relates to processing, but the chemistry associated with organic destruction of TBP is unknown.

Core Technology: Crystallographic Corrosion Studies
Principal Investigator: Darryl P. Butt

Introduction

The objective of this study is to examine the effects of crystallographic orientation on the electrochemical behavior of engineering materials in order to discern the effect of surface structure on pitting. We hope to gain insight into the stochastic nature of corrosion and, ultimately, to improve the corrosion resistance of common materials through intelligent surface processing or texturing.

Progress

To date, we have completed an initial literature survey and have selected three materials on which to focus our early studies—nickel, titanium, and beryllium. We have processed three nickel foils with three different crystallographic textures, and we have obtained x-ray pole figures for each of these foils. These measurements give us detailed information about the predominant bulk crystallographic orientations. The foils are currently being prepared for dc polarization experiments, in which we will compare the pitting tendencies of each foil. We have also prepared specimens of randomly oriented beryllium. We have performed some preliminary polarization experiments that indicate that polycrystalline beryllium is susceptible to selective attack at grains oriented with their (0001) basal planes near perpendicular to the surface. In other words, attack occurs along basal planes. These results are only preliminary. We are currently preparing new specimens of beryllium for orientation imaging analysis (OIM). The samples will then be polarized in salt water, and we will compare OIM images that show microcrystalline orientations to sites of selective attack.

Core Technology: Plutonium Diffusion Science
Principal Investigator: Pamela K. Benicewicz

Introduction

The objective of this work is to determine the diffusion of different forms of plutonium into different metal matrices (for example, stainless steel, aluminum, and uranium) at room temperature and over long time periods. Various surface science techniques will be evaluated to identify the best method(s) to quantify plutonium diffusion at near room temperatures. We will experimentally determine the diffusion coefficients, which are highly dependent upon temperature, concentration of the diffusing metal, and phase of the metals involved. We will use thee coefficients to model the diffusion of plutonium into specific materials over long periods of time.

Diffusion of plutonium into storage materials may limit the usefulness of these materials for long-term storage. Additionally, to evaluate the effectiveness of decontamination methods, the diffusion coefficient of the contaminant (plutonium) must be known. Although diffusion coefficients for plutonium have been measured at high temperatures for some materials, extrapolation of these measured diffusion coefficients to the lower temperature relevant to long-term storage has not been experimentally verified. Use of extrapolated diffusion coefficients (when available) in models can lead to errors of many orders of magnitude. Therefore, experimental measurements of diffusion coefficients near room temperature are necessary.

The diffusion coefficient for these studies will be determined using various surface science techniques. These techniques that will first be evaluated to identify the best method(s) for measuring the plutonium diffusion into metal lattices for near room temperatures and short times.

The standard methodology for measuring diffusion coefficients is to cut away layers of material and analyze these layers for the diffusing species by quantitative destructive analysis. This methodology works well for penetration of materials with large diffusion coefficients that can be found at high temperatures. However, the diffusion coefficients that will be determined by this study will be for very small concentrations of plutonium that are imbedded over just a few microns. These diffusion coefficients are small because the temperatures are low and the lengths of time for the species to diffuse are short. However, the time periods for the model predictions are very long, requiring very accurate diffusion coefficients to be calculated at room temperature.

One surface science technique that will be evaluated for its ability to accurately determine diffusion coefficients is laser ablation spectroscopy. With this technique, surface layers of metal materials that have been exposed to plutonium are removed by laser ablation, while plutonium concentration is also being measured. Another very sensitive technique that will be evaluated is time-of-flight secondary-ion mass spectrometry (TOF SIMS). This technique can be used to perform depth-profiling for very low species concentrations. Determining the depth of plutonium diffusion into the metal and knowing the time of exposure will result in the determination of the diffusion coefficient.

Status/Progress

In FY96, the major emphasis is to perform scoping studies in order to identify the appropriate surface science techniques for determining the Plutonium diffusion coefficients. Additionally, we will complete a thorough literature search. This literature search is ~90% complete. Data on depth-profiling of coatings using laser ablation spectroscopy has been published[2], indicating a depth resolution of ~1 μm. Although this compares unfavorably with the resolution obtained by some other techniques (e.g., ~0.1 μm with glow-discharge mass spectrometry [GD MS] and ~50Å with TOF SIMS, we were using very large laser energies that produce deep craters in the material being sampled. We will investigate improving this depth resolution by varying the system parameters of laser energy, focal length of the focusing lens, and buffer gas and buffer-gas pressure.

We have made an initial evaluation of what surface science techniques, other than laser ablation spectroscopy, might be suitable for determining plutonium diffusion into various metal matrices. Existing technologies at Los Alamos have been identified (TOF SIMS, GD MS, and Scanning Auger), and contacts have been made with the personnel who own these systems. The TOF SIMS is extremely sensitive, but currently it resides in a nonradioactive area. It might be possible to move the equipment to a radioactive area, but this would require several months. The Scanning Auger is not particularly sensitive, but it is available for use at the Los Alamos National Laboratory Chemistry and Metallurgy Research Building. Currently, we are collecting samples of metal that have been in contact with plutonium for a known period of time, and we will analyze these samples for bulk plutonium content before the appropriate surface science techniques are chosen. Preliminary experiments should begin this summer.

The literature search is almost complete, although literature review will be an ongoing effort. We have begun work toward the next milestone, issuing the experimental plan. We also have begun material selection, have identified surface science techniques available at Los Alamos, and are planning experiments.

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[2] David R. Anderson et al., "Depth Profile Studies Using Laser-Induced Plasma Emission Spectrometry," *Appl. Spectrosc.* **49**, 691-701 (1995).

Core Technology: Nondestructive Assay
Principal Investigator: Teresa Cremers

Introduction

The focus of this task is the empirical evaluation of neutron generation resulting from plutonium metal transformation into compounds and the resultant alpha-n interaction. This nondestructive assay (NDA) method will be very useful in determining changes in storage containers.

Status/Progress

Our efforts during this quarter have been aimed at assessing the applicability of an existing neutron detector to the monitoring of metal samples for oxidation. We have selected several candidate metal samples and have measured them in the in-plant neutron multiplicity counter. Gamma-ray isotopic and calorimeter measurements have also been performed. We have made sensitivity calculations that show that this high-efficiency neutron multiplicity counter may be able to detect as little as 1-2 g of plutonium oxide in the presence of 2000 g of metal. This sensitivity assumes a count time of about 30 min and a low-ambient neutron background. Measurements made in an actual plant environment may be somewhat less sensitive if the neutron background cannot be well controlled. A determination of the actual effects of environmental variables is a future goal of this project. We have also begun exploring the application of neutron methods to the detection of plutonium hydride. As plutonium metal combines with hydrogen, the mean energy of the emitted neutrons will decrease. However, because present neutron assay instruments detect thermalized neutrons, only multiple-ring instruments have even a chance of detecting this change. It is not known whether current instruments are sensitive enough to detect this effect.

The experimental path we have chosen is to obtain clean, unoxidized, plutonium metal samples and to add small portions of oxide to them. We will measure the plutonium metal/oxide items to determine the effect on neutron counting of oxidation. We have discussed our procedure with plutonium processing personnel, and they have informed us that this plan will adequately model stored plutonium metal that has been oxidized. We have identified and obtained two samples of plutonium metal suitable for this study. The metal samples have been retrieved from the vault, and we have completed our first round of NDA measurements. A portion of each item has been set aside for conversion to the oxide.

In the coming weeks, we will return the plutonium metal samples to the process line for the addition of the first portion of plutonium oxide, and we will send samples for chemical analysis and NDA measurements. We will also continue our investigation into the feasibility of hydride detection.

Core Technology: Separations—Polymer Filtration
Principal Investigator: Gordon Jarvinen

Introduction

In order to meet site-specific liquid-discharge requirements, the polymer filtration process will remove actinides to very low levels from solutions produced by stabilization operations. The objective of this task is to further optimize the solubility, filterability, binding strength, and capacity at a molecular level as a function of important parameters, including metal-ion loading, pH, concentration of polymer, speciation of the metal ion, and ionic strength.

Status/Progress

We have begun characterization of the polymers and have obtained a viscometer to allow us to characterize the degree of functionalization of the various polymers. In addition, we have set up high-performance liquid chromatography equipment for gel permeation chromatography analysis. This equipment will allow us to determine relative molecular weights for the newly synthesized polymers.

We have begun preparations of the polymers, and we are in the process of synthesizing linear polyethyleneimine, which will allow us to do comparison studies with some of the commercially available polyamines. Experiments are also under way for optimizing the synthesis of various polymer-bearing functional groups that will be used in the studies.

Construction of the apparatus for the fluorescence studies is progressing. The laser and all optical components have been set in place, and the optics are being aligned. Procedures for safe operation are being written.

Core Technology: Separations:—Polymer Foams
Principal Investigator: Gordon Jarvinen

Introduction

Advanced technologies for recovery of radioactive species from waste streams is a major need for the DOE complex. Ion-exchange and chelating resins, typically in bead form, are currently used to remove nuclear materials and other solutes from processing and waste streams. However, the bead materials have problems, including packing instability, liquid channeling through the bed, slow sorption or desorption kinetics, and low usable surface areas, that tend to lower efficiencies of these materials. The goal of this task is to develop advanced microcellular foams to overcome these problems.

Status/Progress

Eight types of polychloromethylstyrene/styrene foams have been prepared. We varied such factors such as polymerization initiator, amount of surfactant, and water/oil ratios.

We developed a method for quick evaluation of flow properties, including dyes in flow solution to determine that channeling was not occurring. Evaluation of flow properties of various forms is in progress.

We have conducted the first experiment in functionalizing the foam with phosphonic acid. The foam survived harsh conditions, such as refluxing concentrated hydrochloric acid, without damage. After treatment, the foam had essentially the same dimensions as before treatment. Titration of the foam to determine the extent of functionalization is in progress.

Core Technology: Materials Science—Thermodynamics
Principal Investigator: Mark A. Williamson

Introduction

The objective of the Thermodynamics task is to study, by both experiment and theory, the phase behavior and thermodynamic properties of plutonium oxychloride (PuOCl), a potential by-product of the plutonium oxidation step of the salt distillation process.

Status/Progress

Preliminary vaporization experiments revealed that the vapor pressure of PuOCl falls between that of plutonium chloride and plutonium oxide. A comprehensive understanding of the vaporization processes and thermodynamics of PuOCl was not obtained from the preliminary studies. Understanding the vaporization behavior of PuOCl and its interaction with the salt matrix will enhance our ability to model the distillation process and could lead to optimized separations. This project was initiated on March 4.

About one year ago, we completed the preliminary vaporization studies. Because of the time span between the completion of those studies and the beginning of this project, we reviewed the experimental results of those studies and summarized them in a report. We formulated experiment plans based on the results of the previous studies. In addition, we completed a literature search on the properties of PuOCl. No new thermodynamic or vaporization data were found in the current literature.

We tested the high-temperature mass spectrometer and vacuum system, and we replaced several components in the mass spectrometer and in the system's electron energy circuit. The vacuum system achieved an ultimate pressure of 1.0^{-8} torr. The system was outgassed to approximately 1100°C and was prepared for calibration experiments. We obtained several background mass-spectrum scans.

Experiments for the third quarter of FY96 will include calibration of the mass scale of the mass spectrometer with perfluorotributylamine, calibration of the sensitivity of the mass spectrometer by vaporization of uranium tetrafluoride, vaporization studies with PuOCl, x-ray diffraction-phase analysis studies, and completion of a report on the phase behavior of PuOCl.

Core Technology: Materials Science—Vitrification
Principal Investigator: Gerald Veazey

Introduction

The primary objective of this project is to install and demonstrate a glovebox-scale vitrification process that can be used to study the application of vitrification as an alternative to cementation.

Status/Progress

We identified six waste streams for demonstration and ranked them in the order of anticipated focus. We identified high-fired ash, evaporator bottoms solution (EV), and americium dioxide (AmO_2) as the wastes in the primary focus group. Ash was chosen as the first waste stream to be evaluated because of its significant existing data and known compatibility with the glass matrix. The major selection criterion for the other waste streams was significant benefit to solution of the Los Alamos National Laboratory Plutonium Facility (TA-55) waste management problems, such as throughput, waste loading, and residue storage.

High-fired Ash. Ash was chosen as the first waste stream in order to allow quick demonstration of the vitrification equipment before more difficult waste streams are attempted. Glass-frit development for high-fired ash had already been completed as part of the effort to develop a vitrified waste form for the ash from the Los Alamos Controlled Air Incinerator (CAI). The characterization data for the ash in the TA-55 inventory is similar enough to the CAI ash to allow use of the CAI ash frit formulation.

Evaporator bottoms. Vitrification of EV waste is the process that would have the greatest benefit for TA-55 operations. EV is the largest transuranic waste stream, and cementation waste loading is kept low because of its elevated americium content and the low-wattage limit imposed on cement waste forms. Presently, the wattage from the ^{241}Am content of EV waste alone exceeds the limit of 0.16 W/drum of cemented waste, resulting in no allowance for ^{239}Pu. A vitrified waste form would have the highest wattage limit of 40 W/drum. This would shift the controlling factor to the 200 g/drum criticality limit because 40 W represents a loading of significantly more than 200 g.

The formulation development for vitrification of the EV waste stream will be conducted by Pacific Northwest National Laboratory. The Chemical Engineering Department at New Mexico State University will assist in verification of the formulation during the nonactinide phase of the project. The high-nitrate content of the EV waste stream will require an off-gas scrubber system to handle the nitrous oxide fumes.

Americium Dioxide. The next waste stream to be evaluated will be AmO_2. This is because the americium is likely to be removed from the EV waste stream to allow greater amounts of ^{239}Pu to be placed in the cement drum before the wattage limit is reached. The AmO_2 could then be placed in the 40-W limit glass matrix. This work is likely to be conducted in conjunction with Savanah River Site (SRS) because of the previous experience that SRS personnel have had with vitrification of AmO_2.

Other waste streams for consideration after the first three are sand, slag, and crucible (SS&C), graphite, and uranium oxide (U_3O_8). These waste streams do not often require cementation at TA-55, so they are ranked lower than the others.

Sand, Slag, and Crucible. Sand, slag, and crucible should be a good candidate for vitrification because the magnesium oxide component of SS&C is very soluble in glass.

Graphite. Graphite is not soluble or combustible at the 1150°C temperatures typical for vitrification. It will, therefore, not exhibit the problems of typical organics. Because of its insolubility, though, graphite will be encapsulated instead of vitrified by the glass.

Uranium Oxide. Uranium oxide (U_3O_8) is reported to have good solubility in glass.

Organics will not be investigated in this project. Examples of organics are plastic fines, cellulose-based wastes, and organic solutions. The following three problems with organics make them unsuitable for vitrification in the short term:

- Their combustivity would present a fire-hazard;
- Off-gas systems are not well developed for volatile organics; and
- Soluble carbon can cause the metals to precipitate and cause short-circuiting in joule-heated systems.

We have also begun work on the next three milestones. The performance specifications for the final waste form will be based on meeting the standards for the Waste Isolation Pilot Plant (WIPP), the shipping container for the WIPP (TRUPACT II), non-mixed-waste status, and relevant definitions of glass quality from the high-level vitrification field (for example, viscosity and electrical conductivity). These standards are being compiled.

We will establish equipment constraints imposed by TA-55 glovebox safety requirements. The major glovebox concerns will be in the area of off-gas treatment and temperature. We are currently acquiring an understanding of the TA-55 restraints in these areas.

System selection is proceeding. Deciding on the optimum system for production-scale vitrification operations will not be a goal of this project. Instead, we will choose equipment that will allow compatibility studies to be conducted with the glass matrix on various waste streams. It is the consensus of the project members at Los Alamos that focus should be on a simple melter design in order to expedite the start-up of work.