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Progress Report

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**94-I Research and Development Project  
Lead Laboratory Support**

**Fiscal Year 1997**

**Technical Program Plan  
Los Alamos National Laboratory**

*Compiled by*

**Steven D. McKee**

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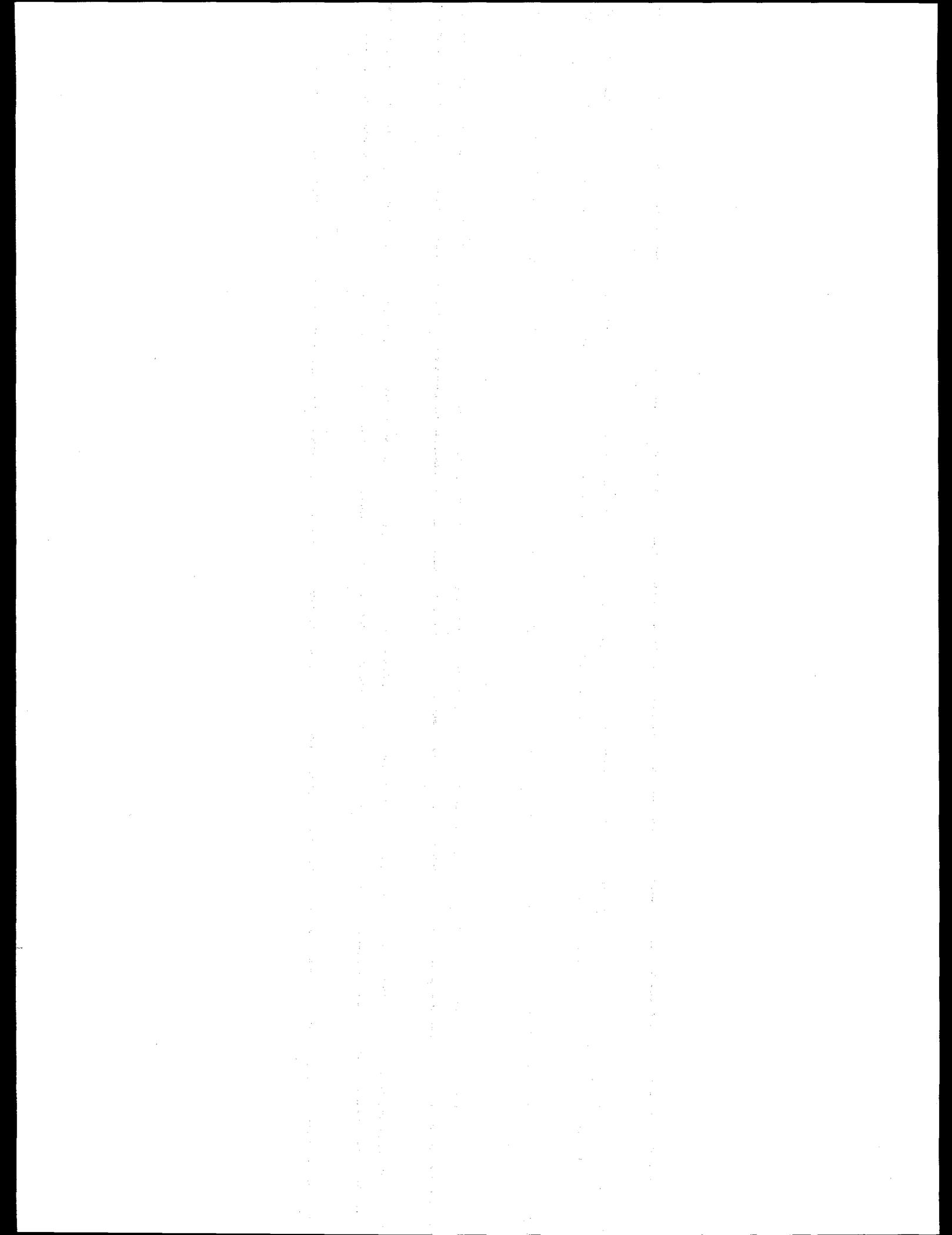
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## Table of Contents

<b>1.0.0</b>	<b>Fiscal Year 1997 Program Description</b> .....	<b>3</b>
<b>1.1.0</b>	<b>Materials Identification and Surveillance</b> .....	<b>11</b>
<b>1.2.0</b>	<b>Stabilization Process Development</b> .....	<b>21</b>
<b>1.2.1</b>	<b>Pyrochemical Salts</b>	
1.2.1.1	Pyrochemical Salt Oxidation .....	23
1.2.1.2	Pyrochemical Salt Distillation .....	26
1.2.1.3	Pyrochemical Salt Filtration .....	29
<b>1.2.2</b>	<b>Combustibles</b>	
1.2.2.1	Size Reduction/Cryogenic Crushing .....	31
1.2.2.2	Nitric Acid-Phosphoric Acid Oxidation .....	33
1.2.2.3	Catalyzed Chemical Oxidation .....	35
1.2.2.4	Pyrolysis—Polycubes .....	38
1.2.2.5	Washing .....	41
1.2.2.6	Mediated Electrochemical Oxidation .....	45
<b>1.2.3</b>	<b>Ash</b>	
1.2.3.1	Vitrification Issues with Rocky Flats Environmental Technology Site Ash and Sand, Slag, and Crucible .....	48
1.2.3.2	Vitrification of Rocky Flats Environmental Technology Site Ash .....	51
<b>1.2.4</b>	<b>Maximum Waste Loading of Particulates in the Cement Waste Form</b> .....	<b>53</b>
<b>1.3.0</b>	<b>Surveillance and Monitoring</b> .....	<b>55</b>
<b>1.3.1</b>	<b>Tomography</b> .....	<b>57</b>
<b>1.3.2</b>	<b>Moisture Probe</b> .....	<b>59</b>
<b>1.3.3</b>	<b>Acoustic Resonance Spectroscopy</b> .....	<b>61</b>
<b>1.3.4</b>	<b>Nondestructive Assay: Gamma Salts</b> .....	<b>63</b>
<b>1.3.5</b>	<b>Calorimetry</b> .....	<b>65</b>
<b>1.3.6</b>	<b>Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site</b> .....	<b>67</b>
<b>1.4.0</b>	<b>Core Technology</b> .....	<b>69</b>
<b>1.4.1</b>	<b>Actinide Solution Chemistry in Residues and in Residue Stabilization and Treatment Processes</b> .....	<b>72</b>
<b>1.4.2</b>	<b>Chemical and Physical Interactions of Actinides with Residue Substrates</b> .....	<b>75</b>
<b>1.4.3</b>	<b>Identification and Characterization of Changes in the Chemical State of Plutonium in Interim Waste Forms</b> .....	<b>78</b>
<b>1.4.4</b>	<b>Actinide-Organic Interactions</b> .....	<b>81</b>
<b>1.4.5</b>	<b>Corrosion</b> .....	<b>83</b>
<b>1.4.6</b>	<b>Plutonium Diffusion Science</b> .....	<b>87</b>

## Table of Contents (continued)

<b>1.4.0</b>	<b>Core Technology (continued)</b>	
<b>1.4.7</b>	<b>Separations</b>	
1.4.7.1	Polymer Filtration .....	89
1.4.7.2	Polymer Foams .....	93
<b>1.4.8</b>	<b>Materials Science</b>	
1.4.8.1	Thermodynamics .....	96
1.4.8.2	Mineral Waste Forms .....	98
<b>1.4.9</b>	<b>Synthesis and Structural Characterization of Plutonium(IV) and Plutonium(VI) Phosphates</b> .....	100
<b>1.4.10</b>	<b>Plutonium Phosphate Solution Chemistry</b> .....	103
<b>1.4.11</b>	<b>Molten Salt/Nonaqueous Electrochemistry</b> .....	105
<b>1.4.12</b>	<b>Improved Methods for the Detection of Alpha-Emitting Isotopes in the Environment</b> .....	107
<b>1.5.0</b>	<b>Project Management</b> .....	109
<b>1.5.1</b>	<b>Infrastructure Support</b> .....	111
<b>1.5.2</b>	<b>Administration</b> .....	113
	<b>Appendix A. Detailed Schedules</b> .....	A-1
	<b>Appendix B. Unfunded Projects</b> .....	B-1
	<b>Storage Issues</b>	
	<b>Plutonium Disposition Methodology</b> .....	B-3
	<b>Stabilization Process Development</b>	
	<b>Ceramification of RFETS Incinerator Ash</b> .....	B-5
	<b>Measurement of Moisture in Pyrochemical Salts</b> .....	B-7
	<b>Electrochemical Scrubbing of Rocky Flats Environmental Technology Site Residues</b> .....	B-8
	<b>Solubilization of Plutonium in Rocky Flats Environmental Technology Site Ash-Type Residues</b> .....	B-10
	<b>Hydrothermal Oxidation</b> .....	B-12
	<b>Catalyzed Chemical Oxidation—Radioactive Demonstration at Los Alamos</b> .....	B-14
	<b>Mediated Electrochemical Oxidation—Development Activities beyond Rocky Flats Environmental Technology Site Rebaseline Exercise</b> .....	B-17
	<b>Pyrolysis (Proposal requested/none received)</b>	
	<b>Process Analytical Chemistry</b>	
	Aqueous Stabilization Processes .....	B-22
	Pyrochemical Salt Distillation .....	B-25
	Mediated Electrochemical Oxidation .....	B-27
	Pyrochemical Salt Oxidation .....	B-30
	Washing .....	B-32

## Table of Contents (continued)

### Appendix B. Unfunded Projects (continued)

#### Surveillance and Monitoring

Pressure-Sensitive Devices (Proposal requested/none received)

Position-Sensitive Boron-Loaded Scintillating-Optical-Fiber

Neutron Counting System for Assay of Plutonium

in Lean, Highly Impure Residues ..... B-34

Advanced Tomographic Gamma Scanner Development ..... B-36

#### Packaging

Electrolytic Decontamination: activity currently funded for  
development under the Advanced Recovery and Integrated  
Extraction System (Proposal requested/none received)

#### Engineered Systems

Modular Concept (Proposal requested/none received)





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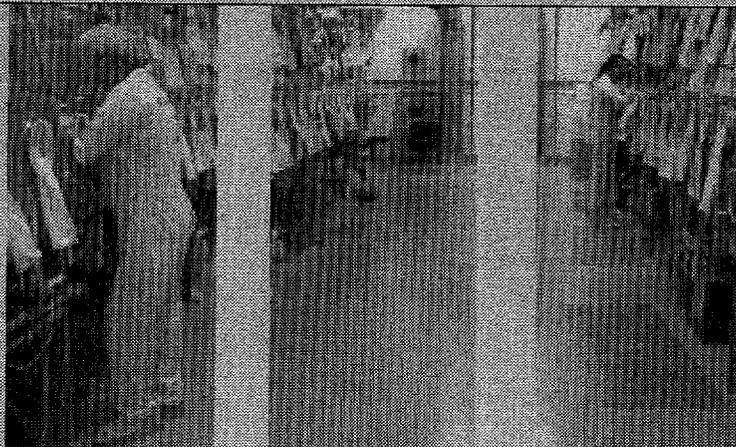
**Steven D. McKee**

**Abstract**

**The research program described in this plan details the fiscal year 1997 activities for the R&D portion of Defense Nuclear Facilities Safety Board Implementation Plan 94-I.**



## Fiscal Year 97 Program Description



On May 26, 1994, the Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 94-1,<sup>1</sup> which expressed the board's concern about nuclear materials left in the manufacturing "pipeline" after the United States halted its nuclear weapons production activities. The DNFSB emphasized the need for remediation of these materials. The Department of Energy accepted DNFSB Recommendation 94-1 on August 31, 1994. After establishing the Nuclear Materials Stabilization Task Group (NMSTG), DOE issued an implementation plan to address these concerns.<sup>2</sup>

As part of Recommendation 94-1, the DNFSB defined the research objective as follows:

**That a research program be established to fill any gaps in the information base needed for choosing among the alternate processes to be used in safe conversion of various types of fissile materials to optimal forms for safe interim storage and the longer-term disposition.**

To achieve this objective a research and technology development program with two elements is needed:

- A technology-specific program that is focused on treating and storing materials safely, with concomitant development of storage criteria and surveillance requirements, centered around 3- and 8-year targets and;
- A core technology program to augment the knowledge base about general chemical and physical processing and storage behavior and to assure safe interim material storage until disposition policies are formulated.

In responding to DNFSB Recommendation 94-1, DOE committed to complete specific nuclear materials stabilization tasks assigned to 3- and 8-year time frames. A research committee was formed to review existing technologies available and technologies currently under development in order to determine adequacy of these technologies relative to the 3-year commitments. This committee also outlined R&D requirements to address technologies needed to support the DOE 8-year commitments. The responsibility for updating the 94-1 R&D Plan<sup>3</sup> for FY97 was charged to the Technical Advisory Panel (TAP).

### **Fiscal Year 1996: A Review**

The "94-1 Research and Development Project Lead Laboratory Support, Fiscal Year 1996 Technical Program Plan for Los Alamos National Laboratory" documented recommendations for the R&D activities necessary to support stabilization projects.<sup>4</sup> Guidance and direction for supporting activities was obtained with specific input from Hanford Site, Rocky Flats Environmental Technology Site (RFETS), Savannah River Site (SRS), and the NMSTG. As the lead laboratory for plutonium stabilization, Los Alamos issued the fiscal year (FY96) technical program plan that outlines 29 funded research and development tasks with 180 milestones. At end of FY96, 156 milestones had been completed on schedule. Seven incomplete milestones are in projects that are continued in FY97.

The activities funded in FY96 included areas associated with standards development, stabilization process development, packaging, surveillance, and core technology. The level 2 work breakdown structure (WBS) for FY96 is depicted in Fig. 1. Figure 2 illustrates the funding for each level 2 activity. For FY96, no funding was directed to support transportation issues.

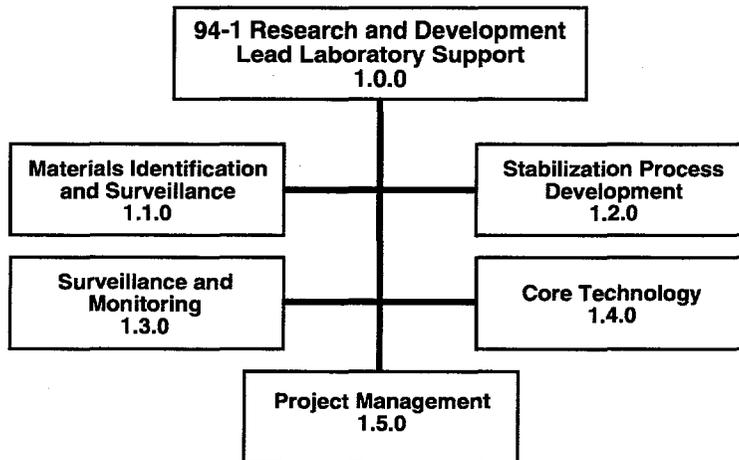


Fig. 1. FY96 work breakdown structure (WBS), level 2.

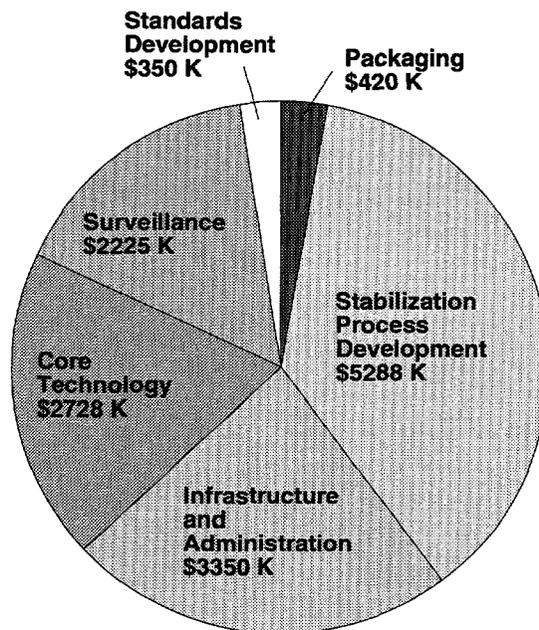


Fig. 2. FY96 funding for the lead laboratory 94-1 R&D Project at WBS, level 2.

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The technical successes for FY96 are plentiful and begin to bring a number of new technologies to bear on problems regarding plutonium stabilization and remediation. Some of the important successes include the following:

- plutonium solution stabilization (We completed experimental testing, safety analysis, procedure development, and training for RFETS.);
- successful development and testing of a prototype cryogenic crushing system for a glovebox;
- successful demonstration of electrolytic decontamination to reduce and/or to remove radioactive decontamination from storage cans and gloveboxes;
- successful demonstration of salt oxidation for the effective stabilization of pyrochemical salt residues transferred to RFETS;
- successful installation and testing of a production prototype unit for salt distillation (Some plutonium-bearing residues from this process meet low-level waste [LLW] criterion.);
- installation of a hydrothermal processing reactor in the Los Alamos National Laboratory Plutonium Facility (TA-55) (We are awaiting readiness assessment evaluation before commencing treatability studies.);
- initial development of a residue washing flow sheet for combustibles (This project will continue in FY97 in order to support the RFETS baseline.);
- development of experimental protocol for the Metal, Oxide, Residue Shelf-Life Program, with input from the various sites (i.e., members of the Materials Identification and Surveillance working group); and
- core technology activities in the development of x-ray absorption near-edge structure and extended x-ray absorption fine structure techniques for plutonium characterization.

As the 94-1 R&D Program moves forward, we expect changes in the work scope to reflect the conclusions of NMSTG trade studies on combustible residues and ash residues, as well as recent discoveries associated with the long-term stabilization of impure oxide. Building upon the successes of FY96, the program is well positioned to continue technology development in FY97.

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### Fiscal Year 1997: Activity Scope

In FY96 the NMSTG directed five trade studies, the results of which are intended to show the best solutions available for the sites to handle various types of materials. Trade studies serve to evaluate alternatives on the basis of requirements and constraints. These trade studies provided a method to analyze end-state pathways for the stabilization of various plutonium residues. This method is based upon performance and technical measures. The plutonium residues evaluated in this manner included the following categories of material types: scrub alloy and salt residues; combustible residues; metal and oxide residues; sand, slag, and crucible (SS&C) residues; and ash residues.<sup>5-9</sup> Some of the findings in these studies are as follows:

- Participants in the scrub alloy and salt residues trade study determined that an underlying uncertainty existed in the characterization of the salts.<sup>5</sup> Provision for dealing with this lack of characterization data is absent from either the R&D plan or from the reported activities funded in FY97. Given difficulties identified at RFETS, researchers concluded that the approach with the highest probability of success consisted of on-site pyrochemical oxidation followed by off-site treatment.
- The recent DOE decision for a consolidated procurement of an automated stabilization and packaging system for plutonium metal and oxides was based on a conclusion of the metal and oxide residues trade study.<sup>7</sup> The NMSTG is currently working with British Nuclear Fuels, Ltd., and a prototype is expected to be installed at RFETS in late 1997.
- The SS&C trade study produced recommendations for options that were site-specific.<sup>8</sup> For example, Hanford personnel will cement SS&C for disposal, and Los Alamos and SRS personnel will separate the plutonium. SS&C from RFETS is to be sent to SRS for plutonium recovery.
- Similarly, the combustible residues and ash residues trade studies identified site-specific alternatives.<sup>6,9</sup> For both residues, the largest inventories exist at RFETS. For RFETS ash, vitrification is the preferred alternative treatment recommended by trade study researchers. Combustibles at RFETS have a number of identified technical uncertainties, and Los Alamos personnel are currently developing several methods for dealing with these uncertainties. The RFETS baseline approach is washing.

The trade studies have serious implications for the FY97 program regarding the direction of technology development in several areas funded for FY96. Possible stabilization technologies for RFETS combustible materials include salt distillation and salt oxidation, vitrification and ceramification for the stabilization of RFETS ash, DETOX<sup>SM</sup>, hydrothermal processing, mediated electrochemical oxidation, and washing. In addition, current rebaselining efforts for the RFETS residue program will impact the direction of the FY97 program, particularly with respect to the schedules for technology development activities.

Significant redirection of effort is needed for combustibles. In FY96, DETOX, hydrothermal processing, mediated electrochemical oxidation (MEO), and washing were funded as possible stabilization technologies for RFETS combustible materials. For FY97, the preferred options under evaluation include MEO and washing as potential treatments for combustible materials stabilization. Currently, no activities funded in FY97 are associated with matrix destruction. This redirected focus in several areas is reflected in the FY97 WBS level 4 for the 94-1 R&D Project lead laboratory support technical program plan (Fig. 3).

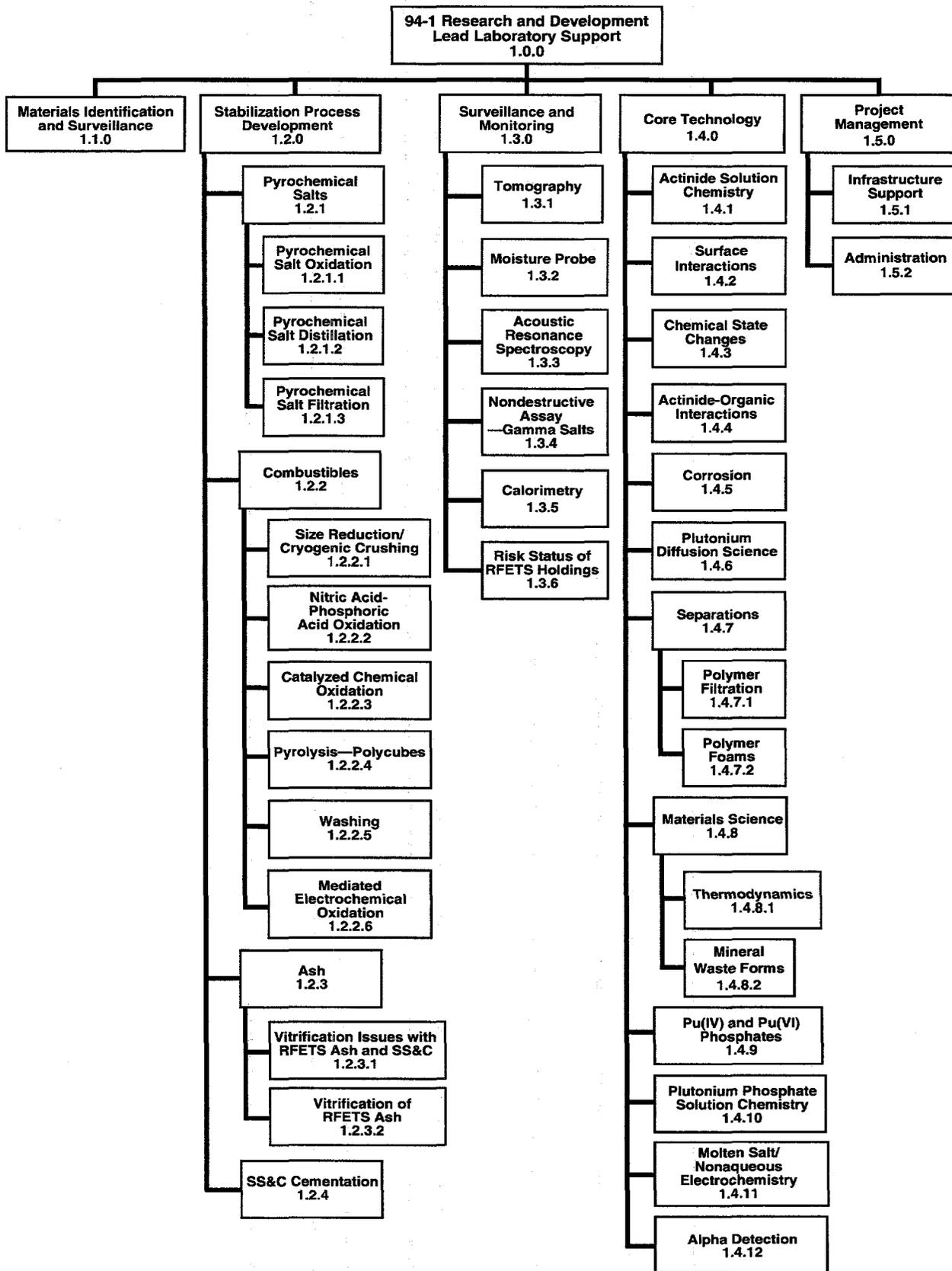
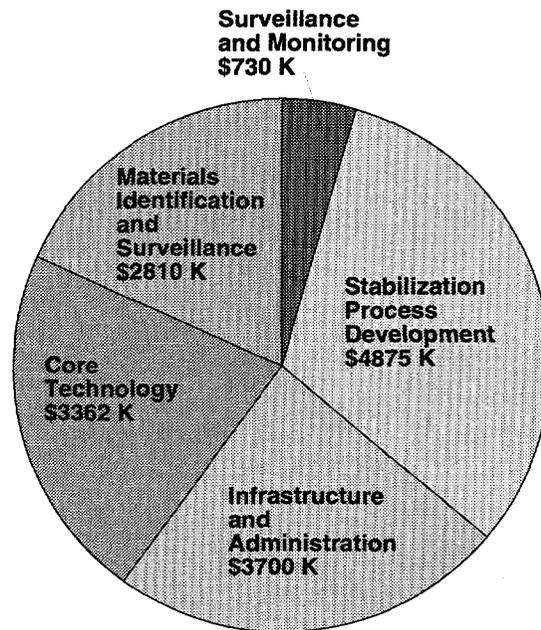


Fig. 3. WBS, level 4.

The FY97 lead laboratory technical program plan for the 94-1 R&D Project presents work scopes for 34 technical projects, including project administration. These technical projects comprise 268 tasks and 81 specific milestones that are tracked on a quarterly basis. Individually funded statements of work and schedules for the FY97 lead laboratory activities follow. Detailed schedules appear in Appendix A. Many of the activities associated with the lead laboratory 94-1 R&D Project can be monitored at the following World Wide Web site: <http://www.lanl.gov/purd94-1/>.

Some projects have been given no guidance for funding from either the sites, from NMSTG, or from the trade studies. We have removed work packages for these projects from the WBS and have transferred them to an unfunded section in Appendix B. Figure 4 shows the funding breakdown for FY97.



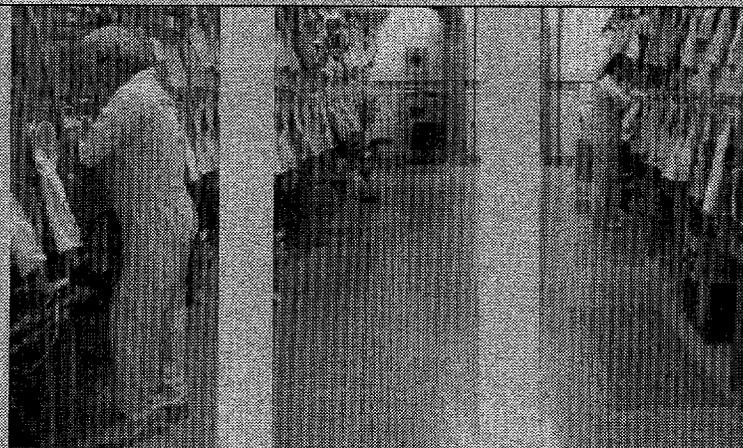
**Fig. 4. FY97 funding for the lead laboratory 94-1 R&D Project at WBS, level 2.**  
(source: NMSTG guidance letter of November 6, 1996).<sup>10</sup>

### References

1. "Defense Nuclear Facilities Safety Board Recommendation 94-1, Improved Schedule for Remediation in the Defense Nuclear Facilities Complex" (Washington, DC, May, 1994).
2. "Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan," U.S. Department of Energy report DOE/EM-0199 (February 28, 1995).
3. "Research and Development Plan," U.S. Department of Energy Idaho Operations Office Plutonium Focus Area technical report DOE/ID-10561 (November 1996).
4. Research and Development Project Lead Laboratory Support, Fiscal Year 1996 Technical Program Plan for Los Alamos National Laboratory," Los Alamos National Laboratory report LA-UR-96-991 (March 26, 1996).
5. "Department of Energy Plutonium Salts Trade Study," U.S. Department of Energy report (January 1996).
6. "Department of Energy Plutonium Combustibles Trade Study," U.S. Department of Energy report (December 1996).
7. "Department of Energy Metal and Oxide Residues Trade Study," U.S. Department of Energy report (November 1996).

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8. "Department of Energy Plutonium Sand, Slag, and Crucible Trade Study," U.S. Department of Energy report (August 1996).
  9. "Ash Residue End-State Trade Study," U.S. Department of Energy Idaho Operations Office Plutonium Focus Area technical report DOE/ID-10560 (October 1996).
  10. Letter from Martin Seitz, DOE/NMSTG, to George Werkema of U.S. Department of Energy Albuquerque Operations Office, November 6, 1996.

## 1.1.0 Materials Identification and Surveillance



The Materials Identification and Surveillance (MIS) Program, often referred to as the Metal, Oxide, and Residue Shelf-Life Program, is an effort to fill gaps in existing knowledge about the behavior of plutonium-bearing materials for long-term storage. The MIS Program will sponsor materials and packaging studies in order to confirm the suitability of materials processing methods and packaging for long-term storage under DOE standard 3013. Studies will include characterization of plutonium oxide from all sites and assessment of the adequacy of the 950°C and 2-hour stabilization process for these materials. Experimental tasks and surveillance monitoring will be carried out to determine the behavior of the oxide and packaging materials under storage conditions. Additional sponsored activities will develop alternate methods for measuring the effect of volatiles on the oxide, will determine the thermal conditions of storage, and will model the pressure generation in sealed containers. Researchers in the program will prepare a database and analyze materials from Hanford Site, Rocky Flats Environmental Technology Site, Savannah River Site, and Los Alamos National Laboratory.



## **Materials Identification and Surveillance Work Breakdown Structure No.: 1.1.0**

**Date Issued:** October 1996

**Principal Investigator:** David R. Horrell

**Budget:** Fiscal Year 1997      \$2600 K Operating/\$250 K Capital

**94-1 IP Milestone:** IP-3.2-022

**R&D Plan:** 3.1.2.3

### **Objective**

The goal of the Materials Identification and Surveillance Program is to establish parameters for safe storage of plutonium-bearing materials in accordance with DOE standard 3013 (DOE-STD-3013-96)<sup>1</sup> containers that are destined for materials disposition. Researchers from Los Alamos National Laboratory, Hanford Site, Rocky Flats Environmental Technology Site (RFETS), and Savannah River Site (SRS) will identify materials to be stored and necessary processing for materials stabilization. The primary method of stabilization will be calcination to 950°C for 2 h, according to DOE-STD-3013-96. Analytical methods will be developed to determine specificity for loss-on-ignition (LOI) measurements, separating weight changes caused by loss of water from those caused by other volatile constituents, and determining gains caused by oxidation or other mechanisms. Substitute measurements for volatiles will be developed. Safe storage of legacy plutonium materials is defined by low pressure generation and absence of corrosion.

### **Scope**

Los Alamos personnel have formed the Materials Identification and Surveillance (MIS) working group to assist in setting direction and in evaluating data generated by project researchers. The group is composed of members from Los Alamos, RFETS, Hanford, and SRS. RFETS, SRS, and Hanford researchers have requested work that greatly expands the Los Alamos Lead Laboratory 94-1 R&D Materials Identification and Surveillance Program. Over the next several years, Los Alamos personnel will characterize and analyze plutonium-containing residues (>50 mass % plutonium) from Los Alamos and from the other sites to determine suitability of materials for storage. Studies on pure oxide to verify plutonium storage standards were expanded to cover impure oxides. In addition, RFETS requires ever-increasing analytical and surveillance support for packaging and storage programs.

Los Alamos contributes to this project in the following ways:

- prepares experimental plans and oversees experimentation;
- provides facilities, space, personnel, and approved procedures needed to conduct the experimentation according to approved plans;

- 
- provides extensive analytical capabilities and develops new analytical capabilities when they are required;
  - administers a central MIS database on existing materials;
  - issues reports on experimental results; and
  - conducts the program in accordance with the Los Alamos Plutonium Facility (TA-55) Quality Assurance Management Plan.

Shelf-life study experimental containers will provide data for evaluating 50-year storage behavior of materials in DOE-STD-3013 containers.

***Hanford, RFETS, and SRS Test Items Shipped to Los Alamos.*** At TA-55 we have received from Hanford Site nine items of legacy plutonium-containing materials that will be gas-sampled before materials stabilization and shelf-life evaluation. We will evaluate the materials for their suitability for storage when they are received and after they have been calcinated at 600°C and 950°C. The Hanford samples, some of which are nearly 20 years old, will yield invaluable information on gas generation in stored materials and some data regarding corrosion over long-term storage. Personnel from other sites may also request Los Alamos gas-sampling support.

During fiscal year 1997 (FY97), RFETS personnel will be shipping 23 items of their legacy materials to Los Alamos for basic analytical evaluation, thermal stabilization, moisture reloading, and shelf-life evaluation. In addition, Los Alamos researchers are also supporting specific RFETS requests for thermal modeling, sample analysis for materials disposition, and elevated temperature kinetics studies on the formation of hydrogen gas. These activities will benefit all sites. Some RFETS items represent materials on which stabilization information is most urgently needed, i.e., high-purity oxide that is first in the queue for the plutonium stabilization and packaging system. Los Alamos researchers will fill several British Nuclear Fuels, Ltd., (BNFL) containers in accordance with DOE-STD-3013-96 and empirically determine thermal profiles. Los Alamos personnel will conduct experimentation on Hanford materials until the RFETS items arrive. After we receive the RFETS materials, we will put into effect a detailed plan that incorporates both Hanford and RFETS materials. With the RFETS prototype packaging system scheduled to be delivered to Kaiser-Hill Company in the fall of 1997 and to come on-line in January 1998, Los Alamos must respond by October 1997.

SRS will ship approximately 10 items to Los Alamos during FY97. We expect to receive them in August 1997, after receipt of RFETS items; and we will then integrate all items into the experimentation schedule. The applicability of thermal stabilization to legacy SRS materials must be determined before F-canyon processing operations cease. The SRS items are representative of metal alloy materials that are scheduled to be thermally stabilized for long-term storage.

***Characterization and Stabilization of Unique Site Holdings.*** Even with representative sampling of each site's inventory, additional questions will arise that require specific and timely answers. The MIS working group will put a high priority on evaluating specific impure oxides in order to determine suitability of these oxides for safe, long-term storage. To accomplish this goal, we will receive items for immediate analysis, establish relevant analytical techniques, compare results with the expanding database on properties of materials, and evaluate and publish results in a

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timely manner. For example, our R&D approach for oxides that yield an LOI of >0.5% will include the following:

- develop a method that assures stabilization of the material,
- at the same time, develop a method that separates volatile LOI constituents for identification (such as water),
- recommend a stabilization and packaging procedure that fulfills the intent of DOE-STD-3013 and that avoids additional in-line analytical equipment, and
- verify the results with the Metal, Oxide, Residue Shelf-Life Program.

To provide this assurance, for example in the case of oxides containing salts, Los Alamos researchers seek to understand the reactions that occur in the materials at 950°C and to determine the absolute water content after 950°C calcination by using supercritical fluid carbon dioxide (CO<sub>2</sub>) extraction. As another example, we will evaluate mixed oxides of uranium-plutonium in order to determine possible mechanisms for weight gain. Los Alamos personnel will develop discrete LOI measurements for separating water content and other volatile constituents. Researchers in the Metal, Oxide, Residue Shelf-Life Program will verify these results with time.

**Task Breakdown.** The program comprises the following tasks:

- *Oxide Characterization and Metal, Oxide, Residue Shelf-Life Studies.* We will characterize both calcined and untreated samples from the Hanford, RFETS, and SRS items and then monitor the samples in specially designed storage containers in order to determine chemical and radiolytic stability, gas generation, gas recombination, reaction rates, and corrosive effects. We will develop requirements to support stabilization and long-term storage from sample analysis (chemistry), elevated temperature experiments (calcination), monitoring of materials in confinement with time (kinetics), thermal profiles for metal and oxide, nondestructive testing (surveillance), and gas analysis of the Hanford cans. The primary method of stabilizing samples will be thermal heating to 950°C in air, as stated in DOE-STD-3013. The greatest deleterious storage effect, i.e., pressure increase, is considered to be caused by water on pure oxide. However, impure oxides bring up more complex stabilization issues than can be solved by simply removing the water.

The tasks are as follows: (1) to evaluate pure and impure oxides, including surface area and water uptake; (2) to determine parameters for shelf-life studies, including collecting empirical data on thermal profiles; (3) to contain pure and impure oxides in approved shelf-life vessels capable of pressure-volume-temperature (PVT) measurements; (4) to collect shelf-life kinetics data; (5) to coordinate material characteristics, data analysis, and reporting; (6) to perform independent measurements using thermal desorption and other analytical tools; (7) to determine parameters for shelf-life studies; (8) to calcine selected materials at elevated temperatures greater than 950°C and for more than 2 h; (9) to support basic research for mixed plutonium-uranium oxides and chloride-rich legacy materials; and (10) to support endeavors based on problems regarding stabilization and corrosion.

- 
- *Materials Preparation.* For analytical and shelf-life surveillance studies, we will calcine materials as requested; and we will conduct LOI, surface area, and moisture-uptake studies.

The tasks are as follows: (1) to support stabilization of pure and impure oxides; (2) to calcine materials; (3) to test LOI, surface area, and particle size; (4) to prepare and transport samples for other analysis; (5) to track analyses; and (6) to collect and report results.

- *Thermal Modeling.* We will establish thermal profiles of materials in long-term storage in order to support DOE-STD-3013. To support this activity, we need and will pursue oxide thermal conductivity data from the oxide characterization tasks.

The task is to use the BNFL consolidated procurement container and the Los Alamos DOE-STD-3013 container filled with metal and oxide.

- *Analytical Support.* Basic studies to support DOE complex-wide needs include small-scale kinetics studies and water-measurement methods other than LOI. These activities provide baseline information needed by all DOE sites in to support processing and to predict storage behavior. Particle size/surface area/water uptake studies may be conducted by analytical groups and by materials preparation groups. Supercritical fluid CO<sub>2</sub> is currently being evaluated for use in a water removal technique to complement the LOI measurements.

The specific tasks are as follows: (1) to standardize procedures for LOI testing, to verify the technical basis, and to issue updated procedures (if necessary) for LOI testing on pure and impure oxides, as applicable to the Metal, Oxide, Residue Shelf-Life Program; (2) to support LOI studies for RFETS; (3) to support and to expedite chemical sampling for the shelf-life program and to coordinate with processing personnel; (4) to establish a database for chemical impurities and plutonium compounds that will include basic properties in support of LOI studies and corrosion effects; (5) to conduct feasibility studies using supercritical fluid CO<sub>2</sub> for water extraction and analysis; and (6) to issue reports.

We will develop techniques in optical monitoring of residues and oxides. As the containers are monitored over time, we will use two optical techniques, laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy, to determine changes in gas composition in storage containers and changing surface chemistry of the materials. Observed changes from an established baseline will provide information on the long-term chemical behavior of actinides and related gas production. In fiscal year 1996, we designed and fabricated storage cans with optical ports, shutters to protect the optical windows, and bellows to allow adjustment of the powder in the can if settling occurs. In addition, a Raman cell that can be attached directly to a modified storage container for gas monitoring has been fabricated. We also performed extensive experiments with nonradioactive materials, using the LIBS system and the plutonium-surrogate gadolinium. The capability of the LIBS system in optically characterizing materials and in identifying the presence of trace amounts of materials in a metal matrix was demonstrated.

- *Container Testing.* RFETS personnel have requested support to determine lid deflection at 100 pounds per square inch (psi) using existing x-ray techniques, i.e., real-time radiography and film. They also request feasibility studies to determine the use of a real-time radiography system for weld quality assurance.

## Benefits

Shelf-life surveillance will provide the DOE complex with a mechanism for gathering, interpreting, and reporting experimental storage data on plutonium-bearing materials, thus supporting DOE-STD-3013-96 and site-specific materials characterization and stabilization requirements. This process will ensure safe storage of plutonium-bearing legacy materials for at least 50 years.

## Reference

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).

## Milestones

1. Complete complex-wide experimental plans ..... October 31, 1996

### Los Alamos Inventory Materials

Experimentation ..... October 31, 1996–January 15, 1997

1. Complete impure oxide characterization and stabilization ..... October 31, 1996
2. Place impure oxide in surveillance containers ..... January 15, 1997
3. Complete mixed oxide characterization and stabilization ..... January 2, 1997
4. Place mixed oxide in surveillance containers ..... January 15, 1997

### Babcock and Wilcox Hanford Company (BWHC) Shipping

1. Ship nine items to Los Alamos ..... June 25–July 15, 1996
2. Receive items at Los Alamos ..... July 16, 1996

BWHC Experimentation ..... September 2, 1996–October 31, 1997

1. Characterize and stabilize nine items ..... September 2, 1996–September 15, 1997
2. Place nine items into surveillance containers ..... January 30–September 30, 1997
3. Complete reports on nine items ..... October 31, 1997

RFETS Shipping ..... June 25, 1996–July 31, 1997

1. Ship selected items to Los Alamos ..... June 25, 1996–July 31, 1997
2. Receive 13 items at Los Alamos ..... April 30, 1997
3. Receive 10 items at Los Alamos ..... July 31, 1997

RFETS Experimentation—Phase I ..... May 1, 1996–January 30, 1998

1. Characterize and stabilize 13 items ..... May 1–September 15, 1997
2. Place 13 items into surveillance storage ..... June 2–September 30, 1997
3. Complete characterization and stabilization ..... September 30, 1997
4. Place stabilized materials into surveillance storage ..... August 1, 1997–January 30, 1998
5. Complete placement of Phase I items into surveillance storage ..... January 30, 1998
6. Complete reports on 13 items ..... February 2, 1998

### Milestones (continued)

RFETS Experimentation—Phase II .....	February 2–September 30, 1998
1. Characterize and stabilize 10 items .....	February 2–September 30, 1998
2. Place 10 items into surveillance containers .....	To Be Determined (TBD)
3. Complete characterization and stabilization .....	TBD
4. Complete placement of items into surveillance storage .....	TBD
5. Complete reports on 10 items .....	September 30, 1998
SRS Shipping .....	May 22–August 29, 1997
1. Prepare and ship selected materials to Los Alamos .....	May 22–August 29, 1997
2. Receive items at Los Alamos .....	August 29, 1997
SRS Experimentation .....	August 19, 1997–September 30, 1998
1. Characterize metal materials .....	August 29, 1997–May 28, 1998
2. Place alloys into surveillance containers .....	April 3–June 17, 1998
3. Characterize and stabilize oxide materials .....	June 15–August 31, 1998
4. Place stabilized oxide materials into surveillance storage .....	July 16–September 15, 1998
5. Complete reports on 10 SRS items .....	September 30, 1998
Oxide Studies—Thermal Profiles of BNFL Containers .....	February 3–August 1, 1997
1. Prepare and load three BNFL containers with oxide for thermal profiles .....	February 3–March 31, 1997
2. Analyze initial data from first can .....	March 3, 1997
3. Collect final data .....	August 1, 1997
Thermal Modeling .....	June 3, 1996–September 30, 1997
1. Model BNFL containers in RFETS Building 371 vault .....	June 3–December 19, 1996
2. Provide complex-wide support for storage .....	January 2–September 30, 1997
Container Testing .....	March 3–July 30, 1997
1. Test BNFL lid deflection .....	March 3–April 30, 1997
2. Evaluate BNFL container radiographic weld .....	July 30, 1997
Analytical Development .....	July 1, 1996–September 30, 1997
1. Supercritical CO <sub>2</sub> development .....	July 1, 1996–March 31, 1997
Demonstrate supercritical CO <sub>2</sub> proof of principle .....	July 1–October 31, 1996
Develop supercritical CO <sub>2</sub> for water analysis .....	December 2, 1996–March 31, 1997
2. X-ray fluorescence for materials identification .....	January 1–May 29, 1997
Demonstrate x-ray fluorescence proof of principle for elemental analysis .....	January 2–May 29, 1997

### Milestones (continued)

#### Analytical Development (continued)

3. LIBS/Raman spectroscopy ..... October 1, 1996–September 30, 1997
- Assemble LIBS system in TA-55,  
Building PF-4, fill surrogate can  
system with oxide powder ..... October 1, 1996–January 31, 1997
- Perform experiments using LIBS, vary  
backfill gas and temperature. .... January 31–September 30, 1997
- Develop Raman spectroscopy  
for water determination  
on plutonium oxide ..... October 1, 1996–March 31, 1997



## I.2.0 Stabilization Process Development



**Stabilization Process Development** involves developing methods for stabilizing plutonium residues. These residues include oxides; solutions; salts; sand, slag, and crucible (SS&C); combustibles; and incinerator ash. Holdings of plutonium solutions at Hanford Site, Rocky Flats Environmental Technology Site (RFETS), and Savannah River Site (SRS) are currently being processed at the various sites, as detailed by the site integrated stabilization management plan (SISMP). Currently, no efforts associated with plutonium solution stabilization are funded in fiscal year 1997 (FY97).

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Two residues that currently have immature technologies for stabilization are combustibles and ash. The combustibles trade study contains recommendations for plutonium separation from the residue matrix at RFETS using mediated electrochemical oxidation (MEO) and cryogenic crushing technology.<sup>1</sup> Continued development of sonication washing, catalyzed chemical oxidation or DETOX<sup>SM</sup>, and nitric acid-phosphoric acid oxidation are also recommended as promising alternatives. Of these three methods, all of which involve some type of aqueous processing capability, the latter two are matrix destruction technologies. Hydrothermal oxidation, initially developed in fiscal year 1996, is not included in the scope of work funded for FY97 (see Appendix B). Immobilization of ash, by either ceramification or vitrification, represents the alternatives identified by the ash residues trade study for the stabilization of RFETS incinerator ash.<sup>2</sup> For ash at RFETS, microwave vitrification is the baseline technology that is presently being reconstituted at the site. For FY97, Safe Sites of Colorado personnel have identified areas in which developmental work is necessary to complete their mission. Their requests are presented in this technical program plan.

A number of issues still influence proposed stabilization activities at RFETS. These issues include stakeholder perceptions, site infrastructure, necessary resources (including budget), site baseline activity for stabilization (as defined in the SISMP), and safeguard termination limits. Indecisiveness has had a major impact on technology development.

#### References

1. "Department of Energy Plutonium Combustibles Trade Study," U.S. Department of Energy report (December 1996).
2. "Ash Residues End-State Trade Study," U.S. Department of Energy Idaho Operations Office Plutonium Focus Area technical report DOE/ID-10560 (October 1996).

**Stabilization Process Development**  
**Pyrochemical Salts: Pyrochemical Salt Oxidation**  
**Work Breakdown Structure No.: 1.2.1.1**

**Date Issued:** November 19, 1996

**Principal Investigators:** James A. McNeese  
Eduardo Garcia  
William Averill (Colorado School of Mines)

**Budget:** Fiscal Year 1997 \$300 K

**94-I IP Milestone:** IP-3.3-012A

**R&D Plan:** 4.3.1.2.1

### **Objective**

The task for Los Alamos National Laboratory researchers is to demonstrate treatment methods for oxidizing wet or reactive pyrochemical salts in order to satisfy the near-term Defense Nuclear Facilities Safety Board 94-1 R&D Project schedule for reducing, within three years, the risk of potentially unstable pyrochemical salt residues. The objective of this task is to develop and to transfer to Rocky Flats Environmental Technology Site (RFETS) process technology that will stabilize reactive metals contained in these pyrochemical salts. Such stabilization will prevent dangerous levels of hydrogen-gas generation during storage and will minimize corrosion from water interactions with the salts and with their containers or drums.

### **Scope**

Researchers on this task will continue development of chemical oxidation approaches to treating spent pyrochemical salts, with the purpose of mitigating all safety concerns regarding interim on-site storage. We will focus on optimizing the oxidation process that prepares feed for the salt distillation process. For optimum performance, the salt distillation process requires oxidized salts as feed. We will perform parametric studies in order to minimize the amount of chemical oxidant necessary to ensure that the oxide heel from the distillation process has the maximum special-nuclear-material concentration and that the distilled salt has the minimum amount of actinide.

This effort is a continuation of fiscal year 1996 research, in which the chemical oxidation parameters for electrorefining (ER), molten salt extraction (MSE), and direct oxide reduction salts were developed in stabilizing pyrochemical salts with chemical oxidants in standard pyrochemical furnaces. We will verify treatment effectiveness by determining the hydrogen gas evolution of treated salts in water and by the performance of the oxidized salts in the distillation process. Recommended process parameters, process equipment, and facility needs will be identified for each salt system. Upon completion of process development efforts, personnel from RFETS will come to Los Alamos to be trained on the operation of the process. Their coming will facilitate transfer of the process to RFETS for incorporation into that site's salt stabilization activities.

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During molten salt processing of plutonium metal, we use ceramic crucibles to contain the charges of salt and metal. Because the crucibles we have used were brittle and sensitive to thermal shock, they generally lasted only for a single charge. During the cooling and breakout of the completed product metal and byproduct salt, the crucible was often reduced to a collection of shards of various sizes. Crucibles and crucible shards from pyrochemical processes exhibit the same reactive characteristics that salt residues do. We will continue investigating a molten salt treatment option for crucible shards in the salt oxidation process, with the goal of stabilization and subsequent maximum plutonium removal and recovery.

A further effort for fiscal year 1997 will be to determine the effectiveness of liquation of pyrochemical salts after oxidation. This research will determine the feasibility of using a settling technique to decrease the amount of salt feed that requires distillation. The effort involves the chemical oxidation of pyrochemical salts and allows variable times for the more dense oxides to settle to the bottom of the molten salt before the salt freezes when the temperature is reduced. Los Alamos personnel have had some success with this approach; but we have not reached the safeguards termination levels, nor have we used this chemical oxidation method. This effort will necessitate investigating the technique with the safeguards termination limit in mind.

Liquation objectives include the following:

- establish the operating limits for successful actinide separation using liquation for each of the salt categories in the RFETS inventory;
- determine the optimum set of conditions for actinide separation by means of liquation for each salt category; and
- demonstrate successful actinide separation using liquation with a set of operating parameters that will work for all salt categories. (If we cannot develop a set of parameters for all salt categories, we will determine for each salt the specific modifications required for the molten salt oxidation operating procedure.)

### **Benefits**

Successful completion of this task will fully integrate the oxidation process into a feed treatment process for salt distillation. For sodium-potassium chloride salts, the coupled process will result in a stabilized oxide product that is suitable for long-term storage and a distilled salt residue that is extremely low in actinide concentration and can be shipped to the Waste Isolation Pilot Plant (WIPP) in the least number of containers. This processing technique will be directly applicable to meeting 94-1 R&D Project concerns at Los Alamos and at RFETS. This technique will also satisfy the intent of the safeguards termination limits that are currently being applied for shipments to WIPP. The chemical oxidation process will also serve as a pretreatment to the disposition of calcium chloride-containing salts. This process will also meet the intent of the safeguards termination limits that are currently being applied for shipments to WIPP. Crucible stabilization techniques will allow for safe storage of the pyrochemical crucible residues, pending final determination of final disposition of these residues. The liquation technique could have the benefit of decreasing the amount of feed to the salt distillation process.

## Milestones

### Optimization of Process for Salts from Oxidation

- through Distillation ..... October 1, 1996–June 25, 1997
1. Optimize process for ER salts ..... October 1, 1996–March 28, 1997
  2. Optimize process for MSE salts ..... March 31–April 28, 1997
  3. Optimize process for salt-strip salts ..... April 28–June 25, 1997

### Pyrochemical Crucible Oxidation Process

- Development ..... January 1–September 30, 1997
1. Complete development of method for crucible pyrochemical oxidation ..... January 1–March 14, 1997
  2. Complete design for crucible oxidation system ..... March 17–August 15, 1997
  3. Prepare report on crucible oxidation process ..... August 15–September 30, 1997
  4. Issue report on crucible oxidation process ..... September 30, 1997

### Investigation of Feasibility of Liqation Process ..... January 1–June 30, 1997

1. Determine liqation parameters ..... January 1–February 28, 1997
2. Prepare report on feasibility of process ..... March 3–April 1, 1997
3. Issue report on feasibility of process ..... April 1, 1997
4. Complete liqation process optimization ..... April 1–June 30, 1997

**Stabilization Process Development**  
**Pyrochemical Salts: Pyrochemical Salt Distillation**  
**Work Breakdown Structure No.: 1.2.1.2**

**Date Issued:** October 1, 1996

**Principal Investigator:** Eduardo Garcia

**Budget:** Fiscal Year 1997      \$750 K

**94-I IP Milestone:** IP-3.3-012A

**R&D Plan:** 4.3.1.2.2

### **Objective**

Los Alamos National Laboratory researchers are developing this process, which will separate plutonium-containing pyrochemical salts into a very lean salt fraction (a goal of <100 parts per million [ppm] plutonium) and a plutonium oxide suitable for storage under DOE standard 3013.<sup>1</sup> The chloride component of the pyrochemical residues is converted into totally stable, slightly contaminated salt; and the plutonium component is separated into a homogeneous, well-characterized oxide material that is suitable for long-term storage.

### **Scope**

Separation of sodium chloride (NaCl)-potassium chloride (KCl) salts from plutonium using a vacuum distillation technique has been demonstrated on a pilot scale (1-kg batch size, 50 kg total) in an experimental program. Based on these results, in fiscal year 1996 (FY96) new equipment was designed, purchased, tested with nonradioactive salts, and placed into a plutonium glovebox. A full-scale demonstration is currently under way. Full-scale testing will establish the reliability of the equipment and the robustness of the process. We propose that pyrochemical salts at Los Alamos be used as feed for such a demonstration. The production-scale equipment acquired in FY96 can process a 3-kg batch size in a 24-h period.

We will use the design of this unit, Prototype I, and the data collected from the full-scale demonstration planned in fiscal year 1997 (FY97) as the basis for the design of a second unit, Prototype II. This second unit will potentially have greater throughput and will be easier to operate and to maintain in a production setting. Prototype II will be designed for installation at Rocky Flats Environmental Technology Site (RFETS). We will use the design criteria established to generate a procurement specification package with an architectural/engineering (A&E) contractor. The specification package will include a high-temperature (1000°C) vacuum chamber that is easily accessible and is sealed in a glovebox environment. The equipment must be robust and capable of almost continuous operation with minimal maintenance requirements for at least 5 years.

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Calcium chloride salts can be treated by distillation. Unfortunately, distillation of calcium chloride salts requires a much higher temperature, which introduces material compatibility problems. So, it is proposed to treat calcium chloride salts by a different process. These salts will first be oxidized by sodium carbonate, and the resulting stabilized product will be subsequently dissolved in water. The salt solution will be filtered to separate the actinide oxides. The filtrate will be evaporated to dryness, and the recovered salt will be melted and cast into a convenient waste form. Then we will dry the separated actinide oxides and package them for long-term storage. Experimental work supported in FY96 demonstrated the feasibility of this process. The plutonium concentration in the recovered salts has been comparable to concentrations in distilled NaCl/KCl salts. A full-scale demonstration of the calcium chloride process is now also needed. This demonstration will test the reliability of the equipment and the robustness of the process, with emphasis on minimizing the volume of liquid waste generated.

As a pretreatment step for both the distillation and dissolution processes, we will investigate molten salt filtration. This step will be incorporated as part of the carbonate oxidation process and will be optimized to remove about 75% of the salt through the filter. The remaining 25% of the salt, containing almost all of the actinides, will then be processed through the appropriate separation process in a much shorter time. We have designed the filtration equipment, and we will fabricate and test it during FY97.

### **Benefits**

Researchers performing the pyrochemical salt trade study evaluated the benefits of several technologies and recommended salt distillation for significant portions of the inventory.<sup>2</sup> The economic and risk benefits associated with the removal of actinides to facilitate the disposal of the salt is well documented by this study. The technologies being developed in the R&D effort focus on stabilization of pyrochemical salt residues (oxidation) and on elimination of the legacy material by means of preparing another material that can be economically disposed of at the Waste Isolation Pilot Plant under existing regulations.

### **References**

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).
2. "Department of Energy Plutonium Salts Trade Study," U.S. Department of Energy report (January 1996).

## Milestones

- Prototype I Testing ..... October 1, 1996–July 30, 1997
1. Conduct production-scale processing ..... October 1, 1996–June 25, 1997
  2. Demonstrate reliability of equipment ..... October 1, 1996–June 25, 1997
  3. Optimize process for salts from oxidation  
through distillation ..... October 1, 1996–June 25, 1997
  4. Issue report on processing results ..... June 25, 1997
  5. Demonstrate salt distillation process to RFETS  
personnel ..... June 25–July 30, 1997
- Prototype II Design and Development ..... February 3, 1997–July 1, 1998
1. Select A&E firm ..... February 3–April 30, 1997
  2. Design Prototype II ..... April 30–August 1, 1997
  3. Review preliminary design ..... July 1, 1997
  4. Complete Prototype II design ..... August 1, 1997
  5. Develop procurement specifications ..... August 1–September 30, 1997
  6. Issue bid package ..... September 30, 1997
  7. Select vendor ..... October 1, 1997–January 1, 1998
  8. Construct and deliver initial Prototype II ..... January 1–April 1, 1998
  9. Test Prototype II ..... April 1–July 1, 1998
- Calcium Salt Treatment Alternatives ..... January 15, 1996–September 30, 1997
1. Evaluate salt treatment alternatives ..... January 15, 1996–September 30, 1996
  2. Decide on salt distillation as opposed  
to aqueous process ..... September 30, 1996
  3. Procure equipment for aqueous process ..... October 1–November 1, 1996
  4. Test equipment with nonradioactive  
materials ..... October 1, 1996–January 20, 1997
  5. Install equipment in glovebox ..... January 20–February 20, 1997
  6. Train operators and test equipment ..... February 20–April 1, 1997
  7. Develop and test process ..... April 1–August 1, 1997
  8. Issue report on production-scale processing  
of calcium chloride salts ..... August 1, 1997
  9. Transfer process to RFETS ..... August 1–September 30, 1997
- Salt Filtration for Distillation  
and Dissolution ..... October 1, 1996–September 30, 1997
1. Design and construct equipment ..... October 1, 1996–January 31, 1997
  2. Test with nonradioactive materials ..... January 31–March 31, 1997
  3. Modify designs ..... March 31–May 30, 1997
  4. Test filtration equipment  
with radioactive materials ..... June 2–August 1, 1997
  5. Filter heel through distillation ..... July 1–September 30, 1997

**Stabilization Process Development**  
**Pyrochemical Salts: Pyrochemical Salt Filtration**  
**Work Breakdown Structure No.: 1.2.1.3**

**Date Issued:** November 30, 1996

**Principal Investigator:** Bartley B. Ebbinghaus (Lawrence Livermore National Laboratory)

**Budget:** Fiscal Year 1997 \$239 K

**94-1 IP Milestone:** IP-3.3-012A

**R&D Plan:** 4.3.1.3.2

### **Objective**

The purpose of this task is to demonstrate molten salt filtration as a simple and low-cost conditioning process for the stabilization and volume reduction of plutonium-contaminated salt residues. Lawrence Livermore National Laboratory (LLNL) researchers intend that this process will permit improved conformance with the Defense Nuclear Facilities Safety Board (DNFSB) 94-1 Implementation Plan schedule for storage or disposal of residue salts at Rocky Flats Environmental Technology Site (RFETS).<sup>1</sup>

### **Scope**

Laboratory-scale demonstration tests will involve melt filtration tests of salt residues. We will compare the results of these tests to other proposed salt conditioning options, such as salt scrub and salt distillation. Experiments will use untreated salt residues existing on-site at LLNL and, later, residues from other laboratories. LLNL personnel will perform filtration tests using various porous ceramic filtering media.

Molten salt filtration has been used at LLNL to support the salt scrub process. We melted spent salts and filtered them through a tantalum strainer, which removed actinide oxides, oxychlorides, and metal. In the proposed molten salt filtration process, we will filter the actinide-bearing salts using a porous ceramic crucible, e.g., zirconia or the equivalent, in a standard pyrochemical furnace heated to about 1000°C. The porous crucible will be suspended over a larger ceramic or metal receiving crucible. After filtration, more residue can be added to the filter cake, remelted, and refiltered in order to collect larger quantities of concentrated actinides. The collected concentrate can ultimately be washed with water to remove any thermally stabilized occluded salt and then be packaged to the requirements of DOE standard 3013.<sup>2</sup>

The main waste stream will consist of a very large volume of salt depleted in actinides and a much smaller volume of actinide concentrates. There will also be a small fraction of filtration and receiver crucibles. We will minimize these wastes by reusing the crucibles as much as possible.

In an exploratory salt filtration test on calcium chloride (CaCl<sub>2</sub>) salt residue, the salt residue charge of 900 g containing about 60 g of actinide was filtered through a commercial porous zirconia crucible at 850°C for 2 h. We observed that 530 g of the salt passed through the filter crucible and 370 g of salt remained. The actinide concentration in the products was determined by neutron counting to measure <sup>240</sup>Pu content and then by rationing the known isotopic content to get total plutonium content. We found the filtered salt to have ~ 3 g of plutonium and the concentrate to have ~ 57 g of plutonium. The plutonium trichloride is soluble in molten CaCl<sub>2</sub> and is passed through the porous filter. As a result, oxidizing the salt before filtration in order to get better actinide removal efficiencies may be necessary. The Los Alamos method of pyro-oxidation can probably be used. Once oxidized, the particulate matter in the salt (plutonium oxide and plutonium oxychloride) should not be able to penetrate the porous ceramic filter.

### Benefits

The process is a simple operation applicable to all salt residue types. The necessary equipment exists within the DOE complex. The operation permits improved conformance with the DNFSB recommended schedule for treating salt residues. The process is applicable to salts with low actinide contents. A lean salt residue can be shipped to the Waste Isolation Pilot Plant; and, compared to pyro-oxidation, this method will require fewer waste drums and shipments. Consequently, the process is cost effective.

### References

1. "Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan," U.S. Department of Energy report DOE/EM-0199 (February 28, 1995).
2. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).

### Milestones

Salt Filtration .....	September 16, 1996–March 14, 1997
1. Evaluate viability of molten salt filtration process .....	September 16–December 6, 1996
2. Define processing parameters needed for implementation .....	November 18, 1996–February 14, 1997
3. Prepare report on salt filtration development .....	February 14–March 14, 1997
4. Issue report .....	March 14, 1997

**Stabilization Process Development**  
**Combustibles: Size Reduction/Cryogenic Crushing**  
**Work Breakdown Structure No.: 1.2.2.1**

**Date Issued:** November 30, 1996

**Principal Investigator:** Horacio E. Martinez

**Budget:** Fiscal Year 1997      \$500 K

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.9

### **Objective**

Combustible residues contaminated with plutonium and other hazards can be treated in one of several ways. These methods, which either remove the plutonium from the matrix or destroy the matrix, leave the plutonium in a form suitable for processing. The plutonium can then be processed to a stable form that is suitable for long-term storage or for disposal at the Waste Isolation Pilot Plant (WIPP). The goal of this project is to demonstrate size-reduction technologies for combustibles.

Activities of Los Alamos National Laboratory researchers in fiscal year 1996 supported the development and testing of cryogenic-based size reduction on several combustible matrices. Materials we investigated by these processes included polycubes to support pyrolysis activities at Hanford Site and filters and soft combustibles for Rocky Flats Environmental Technology Site (RFETS).

### **Scope**

At RFETS about 600 high-efficiency particulate air (HEPA) filters are being stored. These filters were exposed to nitric acid vapors during previous processing operations. The HEPA filter assemblies are constructed of plywood or of particle board frames, and the filter element is urethane-glued inside the wood frame. A potential hazard arises: when the wood is exposed to nitric acid, the wood is potentially saturated with nitrate (which is an oxidizer). The nitrate is in intimate contact with the wood (a combustible fuel). The Defense Nuclear Facilities Safety Board (DNFSB) has designated the oxidizer-fuel combination as one of the most important combustible waste problems. This problem is requiring immediate action.

Researchers on this project will evaluate and examine various methods of removing the outer wood layer from four solid sides of the filter box assembly. We will select off-the-shelf equipment that requires minimal changes and is small enough to fit inside a glovebox. After the equipment is demonstrated and the report on its performance is completed, we will upgrade the equipment with various safety and interlock features. Those features will include safety enclosures and a dust-collection system. We will prepare the equipment for installation in the

mockup glovebox at RFETS. The incorporation of the equipment will be a joint effort between Los Alamos and RFETS personnel. The details of the process will develop in equipment assembly for the RFETS mockup.

The mockup line being prepared for handling combustibles at RFETS, which includes the HEPA filter processing line, will also include a grinder from Franklin Miller. Los Alamos personnel will contribute to the process and to the operation of the overall project.

### Benefits

For many categories of combustibles, the need has been identified for either a pretreatment or size-reduction process before matrix destruction or actinide removal technologies are used. Coupling cryogenics, which embrittle many combustible materials, with size reduction produces desired particle size distributions and robust operations. Other benefits include increased worker safety and simplifying the general handling of combustible residues.

### Milestones

#### Development of HEPA Filters

- |   |                                    |
|---|------------------------------------|
| Disassembly Unit.....   | October 1, 1996–September 30, 1997 |
| 1. Present a basic design to RFETS<br>for review and recommend equipment .....                      | October 1–18, 1996                 |
| 2. Purchase equipment and perform<br>nonradioactive demonstration<br>on nonradioactive filters..... | October 18–December 20, 1996       |
| 3. Supply upgraded equipment<br>with safety and interlock features<br>to RFETS .....                | December 20, 1996–March 28, 1997   |
| 4. Install support unit at RFETS.....   | March 31–September 30, 1997        |

#### Transfer of Support Technology Regarding Cryogenic Grinding Operations

- |                |                                    |
|----------------|------------------------------------|
| to RFETS ..... | October 1, 1996–September 30, 1997 |
|----------------|------------------------------------|

**Stabilization Process Development**  
**Combustibles: Nitric Acid-Phosphoric Acid Oxidation**  
**Work Breakdown Structure No.: 1.2.2.2**

**Date Issued:** September 19, 1996

**Principal Investigator:** Robert A. Pierce (Savannah River Site)

**Budget:** Fiscal Year 1997      \$240 K

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.4

### **Objective**

In order to develop the nitric acid-phosphoric acid system for plutonium-bearing combustible residues at Rocky Flats Environmental Technology Site (RFETS), several tasks need to be undertaken that specifically target glovebox operations. This project will complete the development of a system for treating radioactive-contaminated organic materials. Savannah River Site (SRS) researchers will test and verify the applicability of the nitric acid-phosphoric acid oxidation system to combustible organic compounds that are contaminated with plutonium. Other associated tasks include developing a sensor for *in situ* monitoring of key compounds in the oxidation process, measuring plutonium fractionation during operations, measuring potential off-gas emissions, and verifying the final immobilization of the resulting acid-metal mixture.

### **Scope**

To date, SRS researchers have successfully demonstrated this technology in the laboratory on a wide range of organic compounds, including paper, plastics, resins, tributylphosphate (TBP), pump oil, and machining fluids. Preliminary oxidation rates have been established and preliminary testing of an off-gas/acid recycle system has been performed. The final phosphoric acid waste stream can be immobilized as a low-temperature ceramic or a low-temperature glass. Process flow diagrams and detailed material balances have been compiled, and energy balances are being calculated.

For fiscal year 1997, several aspects of the project will be completed, as follows:

- *Testing with Plutonium-Contaminated Combustibles.* Most of the effort will involve glovebox testing with plutonium-bearing residues. These tests will verify findings of previous nonradioactive tests, determine/verify that all plutonium remains in the liquid phase, optimize process parameters for a simulated RFETS waste, improve the system for glovebox operations, and demonstrate stabilization of the final phosphoric acid waste in a form suitable for the Waste Isolation Pilot Plant.
- *Off-Gas Testing and Verification.* Additional experiments must be conducted with off-gas monitoring. These tests will determine the expected emissions from the nitric acid-phosphoric acid process for compounds such as nitric oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>),

hydrochloric acid (HCl), carbon monoxide (CO), and dioxins/furans. The data will aid researchers in obtaining the permits necessary to certify and operate the process beyond the R&D step, i.e., implementation.

- *In Situ Monitoring Development.* The final area of development is related to process monitoring of the nitric acid-phosphoric acid system. The highly aggressive nature of the oxidation system will destroy the process monitors currently available for *in situ* monitoring. Key system parameters that dictate operating conditions and process end points include nitric acid, iron, and plutonium concentration. These parameters control process efficiency or some other variable in the overall process. Thus, monitoring these parameters during the process is necessary. This research effort will build on work begun in fiscal year 1996 to produce a spectrophotometer-based system that can perform *in situ* monitoring on all three parameters.

### Benefits

This technology involves a nonincineration process that is capable of destroying certain organic compounds at moderate temperatures and pressures. The technology uses a mixture of an oxidant (nitric acid) and phosphoric acid. When the metal-contaminated plastic is destroyed, the metals are also dissolved. The final liquid then can be converted to a stable form in a single processing step. Radioactive demonstration of the nitric acid-phosphoric acid process will complement nonradioactive pilot testing being conducted in support of the Mixed-Waste Focus Area Program (SR1-7-MW-32, Subtask A).

### Milestones

#### Nitric Acid-Phosphoric Acid Oxidation

Development.....	October 1, 1996–September 30, 1997
1. Install unit in a glovebox.....	October 1, 1996–February 28, 1997
2. Complete development of <i>in situ</i> monitoring.....	February 28–April 30, 1997
3. Complete plutonium fractionation testing.....	April 30–May 30, 1997
4. Complete off-gas analysis.....	May 30–July 31, 1997
5. Complete oxidation testing.....	May 30–July 31, 1997
6. Complete immobilization studies.....	May 30–July 31, 1997
7. Issue final report and recommendations.....	August 1–September 30, 1997

**Stabilization Process Development**  
**Combustibles: Catalyzed Chemical Oxidation**  
**Work Breakdown Structure No.: 1.2.2.3**

**Date Issued:** November 30, 1996

**Principal Investigators:** Charles Brown (Kaiser-Hill Company, Rocky Flats Environmental Technology Site)  
Wayne H. Smith

**Budget:** Fiscal Year 1997      \$500 K

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.3

### **Objective**

Catalyzed chemical oxidation will stabilize combustible residues for long-term storage or for disposal. This process is achieved by the destruction (oxidation) of all solid and liquid organic materials within the residue matrix and by dissolution of all radionuclides and active metals. The result is that no combustible material or hydrogen-generating constituents remain. The actinides can be separated and stored as a salt or an oxide, or the actinides can be disposed of with other metal salts and insoluble materials, such as polyethylene or polyvinyl chloride. Space constraints within gloveboxes and criticality requirements can be met because of the required relative small size of the reaction vessels. The chemistry of the process will deal with the multiple hazardous waste codes associated with residues at Rocky Flats Environmental Technology Site (RFETS) that fall within Resource Conservation and Recovery Act (RCRA) regulations.

### **Scope**

Development to date has focused on the Delphi Research DETOX<sup>SM</sup> process and has been highly successful. Delphi Research, Los Alamos National Laboratory, and RFETS now have 2 years experience operating this process with surrogate materials at the 4-L reactor vessel size, which is full scale for residue processing. A full-scale demonstration using actual plutonium residues is now needed. Reconfiguring and upgrading the current development system for glovebox operation will be required, followed by testing and demonstrating the system with radioactive materials. We began this effort in fiscal year 1996 (FY96) and will continue it in fiscal year 1997 (FY97).

The process uses iron with a combination of homogeneous metal catalysts, such as platinum and palladium, in a chloride solution. This process is a variation of wet chemical oxidation, in which the metals in solution play the major role in the destruction of the organic material. The process operates at 200°C and 0.7 megapascals (MPa) or 100 pounds per square inch (psi). Bench-scale testing of a variety of surrogate materials has shown that the DETOX process can produce a wide variety of residues, including those contaminated with mercury and cyanide. The average destruction rate for combustible-type material is 0.2 kg/h in 2 L of solution in a 4-L stirred reaction vessel.

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Researchers have incorporated the following into the design of the proposed pilot-plant system:

- process information on surrogate destruction;
- process information on the fate of cyanide and nitric acid in the DETOX solution; and
- perform component testing on stirrers, solid feed, condenser design, and secondary reactors.

Researchers on an independent study conducted by the Materials Department at the Colorado School of Mines identified the construction materials that offer the greatest corrosion resistance for this application. Delphi Research personnel have completed a process design and a safety review for a low-level mixed-waste pilot demonstration system that is currently being fabricated.

Funding for catalyzed chemical oxidation in FY97 includes the final procurement of the glovebox reactor from Delphi Research. A decision will have to be made regarding the continuation of this project. Los Alamos personnel made a continuation request to RFETS, and information in this request will serve as a basis for decisions regarding continued funding and scheduling. Factors necessary to reach this decision include the following:

- Which site can best handle installation and radioactive testing of the prototype unit—RFETS or Los Alamos?
- Does the site installation and test schedule meet the needs of the various sites; i.e., is the radioactive materials development and test schedule compatible with site integrated stabilization management plans (SISMPs) so that milestones can be accomplished?
- Which site or sites require this stabilization process?
- Does the process place the material in an acceptable end-state, or is additional handling required?

### **Benefits**

Although the relative hazards of combustible residues are dependent upon the type of residue, potential system safety problems with combustible residues generally include the following:

- radiolytic generation of hydrogen and other flammable and corrosive gases from hydrogenous material, plastic packaging material, and reactive metals;
- presence of reactive and pyrophoric metals;
- presence of nitrated organics and other fuel mixtures;
- presence of plutonium metal and organohalide mixtures; and
- degradation of plastic packaging material.

Because catalyzed chemical oxidation destroys the organic matrix, this research, development, and testing (RD&T) effort will aid in the stabilization and safer storage of these high-risk combustibles.

The following proposed schedule includes the final procurement and nonradioactive testing of a 2-L glovebox unit currently being fabricated. Installation and testing of the unit at Los Alamos requires prioritization in the Nuclear Materials Technology Division Integrated Project Plan. The installation and testing of the glovebox unit is currently an unfunded project in Appendix B.

### Milestones

#### Fabrication of Glovebox System

- with Delphi Research ..... May 29–November 22, 1996
- 1. Assemble equipment/test in mockup ..... May 29–November 22, 1996
- 2. Ship glovebox reactor to Los Alamos ..... November 22, 1996
- 3. Deliver operating manual/design report  
to Los Alamos ..... November 22, 1996

#### Evaluation of Final Disposition of Liquid Effluent and

- Spent Plutonium/DETOX Solution ..... March 15–December 13, 1996
- 1. Perform experimentation to evaluate liquid effluent  
and spent solution ..... March 15–December 13, 1996
- 2. Issue report ..... December 13, 1996

#### Decision point on whether to Continue Installation

- at Los Alamos or to Transfer to RFETS for Installation ..... December 31, 1996

**Stabilization Process Development**  
**Combustibles: Pyrolysis—Polycubes**  
**Work Breakdown Structure No.: 1.2.2.4**

**Date Issued:** November 15, 1996

**Principal Investigators:** Daniel J. Kathios  
John J. Coogan

**Budget:** Fiscal Year 1997      \$1200 K

**94-1 IP Milestones:** IP-3.3-028 and IP-3.3-029

**R&D Plan:** 4.3.4.2.1

### **Objective**

Hanford Site is currently storing approximately 1600 polycubes. The cubes range in size from 1/2 in. x 2 in. x 2 in. up to 2 in. x 2 in. x 2 in. and are sealed with a coating of aluminum paint and/or tape. The cubes are packaged in vented food pack cans with approximately 5–8 cubes per can. The objective of this 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 long-term storage. The polycube stabilization system will require a second technology to oxidize the pyrolysis off-gas so as to comply with environmental requirements of the facility.

### **Scope**

Pyrolysis is a pyrochemical technique that uses a high-temperature inert environment to break down and to volatilize polymeric materials. Los Alamos National Laboratory personnel designed a gas-tight pyrolysis reactor that is suitable for glovebox applications. Using one of three different technologies, we will oxidize to carbon dioxide and water the volatile polymeric components of the pyrolysis reactor off-gas.

- *Catalytic Conversion.* In this approach, the off-gas is fed with air to a catalytic converter that is maintained at an elevated temperature. The catalyst allows the oxygen to oxidize the organic constituents more effectively.
- *Secondary Combustion.* This approach uses a resistance heating element, the pyrolysis off-gas, and oxygen to oxidize the products of pyrolysis. Typically in commercial operations, a residence time of 2 s at a temperature of 1000°C is necessary to meet environmental requirements.
- *Silent Discharge Plasma (SDP).* In this approach, a plasma field is formed in cells that consist of two glass plates that are charged to a potential difference of 15–50 kV. Between the plates, microdischarges are formed that react with water and oxygen to give free radicals that readily oxidize the organic constituents.

During fiscal year 1996, Hanford personnel prepared an engineering study that included the three pyrolysis off-gas treatment technologies. Based on the results of this study, Hanford researchers selected SDP as the preferred off-gas treatment technology. The Los Alamos principal investigators and project personnel are concerned with the maturity of the SDP technology for this application and do not believe that it is prudent to completely discontinue work on the other two off-gas treatment technologies.

Los Alamos personnel propose that work continue on the secondary combustion and catalytic conversion processes until logical hold points are reached. Researchers will proceed on the secondary combustion system through final design and preparation of the procurement specifications. This work is scheduled for completion in December 1996. The catalytic conversion process will proceed through demonstration of the technology for the polycube stabilization application.

Los Alamos researchers propose that work continue on the SDP system, with the goal of delivering the system to Hanford in early fiscal year 1998. Los Alamos personnel will fabricate a full-scale SDP prototype unit and will operate it in tandem with a pyrolysis unit. Based on the information gathered from operation of the full-scale prototype system, Los Alamos personnel will fabricate a final SDP/pyrolysis unit and equip it with appropriate control systems. If the full-scale prototype SDP system is not successful, we will formulate an alternate polycube pyrolysis system. The final polycube system will be demonstrated at Los Alamos to train Hanford personnel on system operation. The system will then be shipped to Hanford for installation at the Plutonium Finishing Plant.

### Benefits

Polycubes are not suitable for long-term storage. Pyrolysis was once used at Hanford to process polycubes. The primary problem was frequent line-plugging in the solvent-scrubbing system that is used to treat off-gas. Leakage of the styrene monomer was also problematic. In addition, the only mode of off-gas treatment was to pass the reactor effluent through a carbon tetrachloride scrubber. A new process must be implemented that minimizes polycube handling and that more effectively processes the off-gas. The full-scale pyrolysis system designed and tested in this effort is expected to accomplish that end and to allow the remaining 1600 polycubes to be processed.

### Milestones

Pyrolysis of Polycubes .....	October 1, 1996–November 6, 1997
Midyear Project Review .....	April 1, 1997
Pyrolysis Reactor .....	October 1, 1996–July 1, 1997
1. Fabricate Unit 1 .....	October 1–November 28, 1996
2. Set up Unit 1 .....	December 2–10, 1996
3. Fabricate final unit.....	December 10, 1996–July 1, 1997

### Milestones (continued)

- Silent Discharge Plasma ..... October 1, 1996–July 1, 1997
1. Design and fabricate full-scale prototype ..... October 1–December 3, 1996
  2. Complete testing of existing one-cell system ..... December 3, 1996–March 3, 1997
  3. Complete testing of full-scale prototype ..... March 3–April 29, 1997
  4. Complete fabrication of final unit ..... April 29–July 1, 1997
- Secondary Combustion ..... October 1–December 20, 1996
1. Complete design and procurement specifications ..... October 1–December 20, 1996
- Catalytic Conversion ..... October 1, 1996–February 28, 1997
1. Complete fabrication of demonstration system ..... October 1, 1996–January 8, 1997
  2. Complete catalytic conversion demonstration ..... January 8–February 28, 1997
- Final Polycube System Implementation ..... March 3–November 6, 1997
1. Design and fabricate final polycube system ..... March 3–July 1, 1997
  2. Complete demonstration of final polycube system ..... July 1–October 1, 1997
  3. Conduct final demonstration at Los Alamos/train Hanford personnel ..... October 1-8, 1997
  4. Ship polycube unit to Hanford ..... October 10-31, 1997
  5. Conduct on-site setup and training ..... October 31–November 6, 1997
  6. Transfer complete ..... November 6, 1997

**Stabilization Process Development**  
**Combustibles: Washing**  
**Work Breakdown Structure No.: 1.2.2.5**

**Date Issued:** October 1996

**Principal Investigator:** Norman C. Schroeder

**Budget:** Fiscal Year 1997      \$425 K

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.7

**Objective**

The objectives of this project are for Los Alamos National Laboratory researchers to continue to develop and test two process flow sheets for residues at Rocky Flats Environmental Technology Site (RFETS). The two systems are as follows:

- We will design a flow sheet to stabilize the plutonium metal contaminants in organic combustible residues. Stabilization here means the conversion of plutonium metal to plutonium oxide. If desirable or required, the treatment process should also remove organic compounds—primarily carbon tetrachloride, cutting oils, and other solvents—from the residue. This objective is divided into two phases: (1) testing the baseline flow sheet and (2) developing and testing alternative flow sheets.
- We will design a flow sheet to remove nitric acid and nitrate salt contaminants from combustible residues that contain plutonium. We will obtain and test in the baseline flow sheet additional data regarding sonication, modifying the overall process.

**Scope**

Combustible residues are problematic for safe interim storage. Combustible residues at RFETS are plutonium-contaminated materials, which may contain nitrate, solvents, cutting oils, and other potentially hazardous materials. These mixtures could cause container corrosion, pressurization by means of hydrogen gas generation, exothermic reactions from oxidizer/fuel mixtures, and fires from pyrophoric plutonium metal. Corrosion and loss of containment, especially for materials that include free-standing liquid, are undesirable outcomes of not adequately stabilizing storage materials.

At RFETS the residues are divided into two categories: (1) organic wet combustibles contaminated with carbon tetrachloride, cutting oils, solvents, and plutonium; and (2) combustibles contaminated with nitric acid and plutonium, primarily plutonium dioxide. We will define the steps for treatment in detail, considering criteria for interim and long-term storage, ease and efficiency of treatment, safety of workers, time of processing, and other pertinent factors, such as the Waste Isolation Pilot Plant Waste Acceptance Criteria (WIPP WAC).

Safe Sites of Colorado (SSOC) at RFETS and Los Alamos are currently demonstrating and testing two flow sheets proposed by SSOC Wet/Combustible Residue Stabilization Program personnel. This program was initially limited to the feasibility of the SSOC proposed flow sheets: (1) washing or extracting cutting oils with carbon tetrachloride (CCl<sub>4</sub>), low-temperature thermal desorption of CCl<sub>4</sub>, and plutonium stabilization with a steam/air current; and (2) washing nitrates from nitric-acid-contaminated combustibles. On this task we need to support the current process flow sheets and apply other possible technologies to these problems, then select from these potential technologies for research, development, and testing (RD&T).

The scope of this project includes finishing tests of the current flow sheets and conducting studies in parallel with these experiments. These studies support the current RFETS RD&T activities in order to rebaseline the current options for treating the residues and to find alternative approaches. In effect, this project will provide a contingency plan for RFETS, given the moderate possibility that the demonstration of the current flow sheets will not be acceptable.

Three types of organic combustible residues contain plutonium: (1) wet combustibles (CCl<sub>4</sub>, trichloroethane, freon, and cutting oil), (2) high-efficiency particulate air filter frames, and (3) Full-Flo™ filters.

Table 1 shows the baseline unit operations and examples of unit operations that can be considered in the residue treatment flow sheet development.

<b>Description</b>	<b>Example</b>
Head-end processing	Sorting, size reduction, shredding (conventional or cryogenic)
Washing	Solvent, detergent wash, liquid carbon dioxide (CO <sub>2</sub> ), others
Desorption	Low-temperature thermal desorption (such as vacuum and sweep gases)
Plutonium metal oxidation	Steam, air sparge, CO <sub>2</sub> , water
Packaging preparation	Drying, compaction, absorbent addition, oxide control, others
Packaging	Containment in compliance with the WIPP WAC, TRUPACT II, safeguards, and all other appropriate regulations

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*Issues.* Formation of byproducts from radiolysis, reactivity of the nitrates, limits on treatment parameters (temperature) imposed by the characteristics of the waste, and many other variables complicate the treatment of these organic combustible residues. The new flow sheets will aid attempts to anticipate these issues.

With the current baseline process, we have identified numerous technical issues, and we will find others during the proposed investigations. These issues will require careful deliberation regarding treatment and flow-sheet design. For example, washing with  $\text{CCl}_4$  to extract cutting oils and the subsequent thermal desorption of the  $\text{CCl}_4$  is a simple solution that may mitigate container corrosion and overpressurization. However, the use of  $\text{CCl}_4$  was severely questioned during a program review; and we were subsequently advised to eliminate the washing step. Several alternatives for washing exist, including the use of nonhalogenated solvents, detergent systems, and other technologies (such as liquid  $\text{CO}_2$ ). These alternatives may solve the problem.

For the nitrate-contaminated combustibles, a simple flow sheet involving a caustic/water wash may be appropriate for removing nitrates. However, one concern that has developed is the possibility of nitrocellulose material being present in the feed material. Nitrocellulose materials may create a serious combustion problem during feed handling, head-end processes, and storage. On this project we will need to explore the potential for formation of nitrocellulose, the behavior of this potentially formed material, and, if needed, a method to neutralize the material.

Another issue is the radiolysis product of the cutting oils. For organic contaminated combustible feed, a low-temperature desorption unit operation can remove the volatile organic material (such as  $\text{CCl}_4$ ) from the combustible feed. A subsequent steam/air oxidation will stabilize plutonium metal by converting it to an oxide. However, if a radiolyzed and hardened cutting-oil coating surface is on the plutonium metal, then the oxidation attempt may be ineffective. Liquid  $\text{CO}_2$  may be capable of penetrating this barrier and, with the appropriate oxidizing modifier agent, we may be able to accomplish plutonium oxidation.

*Approach.* RFETS and Los Alamos personnel will interact to develop, test, demonstrate, and evaluate the proposed technologies. We will use data obtained from this work to recommend a process, including operating parameters and equipment required to stabilize these residues. A goal is to make the final process compatible with and able to interface with RFETS processing facilities. If, for example, certain safety features or operational steps in the proposed process are essential, but not compatible with existing facilities, we will identify the incompatible items and investigate the compatibility issues further.

We will extend our literature search for additional methods of treating the residues, and we will compile this information and prepare a report about the known hazards associated with the various possible treatments.

### **Benefits**

The major benefits of this development activity are summarized as follows:

- A contingency plan for treating the wet combustible and nitrate wastes will be available if the RFETS baseline is not suitable.
- The flow sheet may be used at other DOE sites where similar wastes are stored.

## Milestones

Flow sheets will emphasize the advantages and limitations of safety issues, process parameters, and final product criteria.

- Combustible Washing Experiments ..... October 1, 1996–December 1, 1998
  - 1. Install Parr reactor and test glovebox operations ..... October 1, 1996–January 1, 1997
  - 2. Continue plutonium experiments on baseline wet combustible flow sheet ..... October 1–December 20, 1996
  - 3. Revise work scope, as appropriate ..... October 1, 1996
  - 4. Complete review of literature/DOE complex experience for alternate and nitrate flow-sheet development ..... October 1–15, 1996
  - 5. Organize and update status of contact points ..... October 15–30, 1996
  - 6. Report on plutonium-surrogate work for baseline process ..... December 20, 1996
  - 7. Meet with RFETS contact about treatment technologies for combustible residues ..... January 15, 1997
  - 8. Complete and review flow sheet for alternate washing treatments ..... January 15–February 14, 1997
  - 9. Revise flow sheets for alternate and nitrate washing processes and obtain final approval ..... February 17–28, 1997
  - 10. Revise work scope, as appropriate ..... March 3–14, 1997
  - 11. Conduct scoping experiments for alternate and nitrate flow sheets ..... March 17–September 15, 1997
  - 12. Complete summary report on alternate and nitrate flow sheet RD&T ..... September 30, 1997
  - 13. Revise statement of work, as appropriate ..... October 1, 1997
  - 14. Continue plutonium experiments on alternate and nitrate flow-sheets ..... October 1, 1997–December 1, 1998
  - 15. Perform full-scale demonstration on radioactive materials ..... August 3, 1998
  - 16. Optimize treatment operating parameters and perform final demonstration ..... August 3–October 1, 1998
  - 17. Prepare final report on full-scale testing and Los Alamos recommendation of wet combustibles final baseline washing flow sheet ..... October 1–November 13, 1998
  - 18. Issue final report ..... November 13, 1998
  - 19. Train personnel and complete technology transfer to RFETS ..... December 1, 1998

**Stabilization Process Development**  
**Combustibles: Mediated Electrochemical Oxidation**  
**Work Breakdown Structure No.: 1.2.2.6**

**Date Issued:** October 28, 1996

**Principal Investigators:** Jeff Surma (Pacific Northwest National Laboratory)  
Dean Kurath (Pacific Northwest National Laboratory)  
Martyn G. Adamson (Lawrence Livermore National Laboratory)  
Bryan Balazs (Lawrence Livermore National Laboratory)  
Wayne H. Smith

**Budget:** Fiscal Year 1997      \$150 K

**94-1 IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.6

### **Objective**

The purpose of this work is to continue developing the mediated electrochemical oxidation (MEO) technique as a viable technology for treatment of combustible residues and for removal of surface contamination from selected matrices. Researchers have as their final goals to demonstrate the feasibility of this process, using real combustible waste as feed, and to oversee the installation of a full-production-scale unit at Rocky Flats Environmental Technology Site (RFETS). The work will take place at Pacific Northwest National Laboratory, Lawrence Livermore National Laboratory, and Los Alamos National Laboratory.

### **Scope**

MEO has been demonstrated as a technology suitable for treating selected combustible residues. However, MEO has not been demonstrated on the residues existing at RFETS. The scope of this project is threefold:

- design and test a pilot-scale MEO unit that is capable of treating RFETS residues;
- test this apparatus on radioactive or surrogate residues; and
- design, test, and install a full-production-scale unit for use at RFETS.

In selected mixed wastes, MEO can destroy the organic matrix and recover the radioactive component. For example, chlorinated hydrocarbons, such as tetrachloroethylene, carbon tetrachloride ( $\text{CCl}_4$ ), and chloroform, can be very efficiently converted to carbon dioxide ( $\text{CO}_2$ ) at room temperature; but other organic materials, such as polypropylene and polyethylene, are fairly inert. Thus MEO will be an ideal technology for the treatment of waste such as the polyethylene process-line filters (Full-Flo™), which are contaminated with  $\text{CCl}_4$  and plutonium. Treatment with the MEO process will convert  $\text{CCl}_4$  to  $\text{CO}_2$ , dissolve plutonium for subsequent recovery by standard recovery procedures, and leave filters free of both organic and radioactive

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contamination. After MEO treatment, the filters would be ready for packaging and shipment to the Waste Isolation Pilot Plant as transuranic or possibly low-level waste. A similar scenario can be envisioned for the high-efficiency particulate air filter residues. These two residues together represent approximately one-third of the total bulk combustible residues at RFETS.

The initial activity funded for fiscal year 1997 involves calculations to determine the volumes of liquid effluent generated by the MEO treatment process. An initial determination made by RFETS is questionable and will contribute to a decision regarding the subsequent funding of this activity (see Appendix B). RFETS personnel determined that a significant liquid waste volume would be produced by MEO treatment of combustibles. This determination was made as part of the RFETS rebaselining exercise for a number of residues, including combustibles. The factors necessary to reach the decision on subsequent funding include the following:

- What is the balance of materials and volume of waste generated by MEO treatment?
- Does the process place the material in an acceptable end-state, or is additional handling required?
- Does the site installation and test schedule meet the needs of the various sites; i. e., is the radioactive materials development and test schedule compatible with site integrated stabilization management plans (SISMPs) so that milestones can be accomplished?
- Which site or sites require this stabilization process?

### **Benefits**

One of the conclusions of the combustible residues trade study<sup>1</sup> is that no one technology, other than possibly incineration, is capable of treating the full suite of combustible residues. However, it is unlikely that incineration is a viable option because of the difficulty and uncertainty in obtaining a permit. Therefore, we realize that at least two technologies will be necessary to deal with the RFETS combustible residues. Currently, we think MEO can be used to remove the contamination from the surface of hard plastics, such as filter materials and plastic bottles. Another chemical oxidation technique will be necessary to treat the remaining residues.

The advantages of using MEO to treat filter media are (1) that this technology has already been demonstrated as applicable to the treatment of selected combustible residues and (2) that obtaining a permit to operate should not be difficult because MEO is an aqueous process that operates at ambient pressure and temperature. These two factors should expedite implementation at RFETS. Direct participation by site personnel during the evaluation studies will also aid implementation. If we can demonstrate that MEO will treat the majority of the remaining residues, added benefits include using a technology that has already been installed, has the appropriate permits for a waste treatment operation, and requires only minor modification.

### **Reference**

1. "Department of Energy Plutonium Combustibles Trade Study," U.S. Department of Energy report (December 1996).

### Milestones

- MEO Demonstration and Testing Activities ..... October 1, 1996–September 30, 1997
1. Determine material balance and liquid waste volume generation (PNNL) ..... October 1, 1996–September 30, 1997
  2. Issue report ..... December 2–January 15, 1997
  3. Decide status of demonstration and testing activities ..... January 1–31, 1997
  4. Report decision ..... January 31, 1997

**Stabilization Process Development**  
**Ash: Vitrification Issues with Rocky Flats**  
**Ash and Sand, Slag, and Crucible**  
**Work Breakdown Structure No.: 1.2.3.1**

**Date Issued:** November 22, 1996

**Principal Investigators:** Gerald W. Veazey  
Ronald K. Nakaoka  
Jon R. Hurd  
Mike Elliott (Pacific Northwest National Laboratory)

**Budget:** Fiscal Year 1997                      \$515 K

**94-1 IP Milestone:** IP-ES-025

**R&D Plan:** 4.3.5.3.1

### **Objective**

The objective of this project is to support the effort by Safe Sites of Colorado (SSOC) in developing a vitrified waste form for ash and for sand, slag, and crucible (SS&C) at Rocky Flats Environmental Technology Site (RFETS). SSOC personnel have identified two areas in which additional information is needed to accomplish their goal. These areas are (1) determining nondestructive assay (NDA) constraints and operating parameters for the vitrified waste form using the segmented gamma scanner (SGS) and (2) investigating a conventional furnace system for producing a glass-based waste form.

### **Scope**

The following tasks are to be performed at Los Alamos National Laboratory and/or at Pacific Northwest National Laboratory (PNNL):

- *NDA Constraints and Operating Parameters.* A series of tests will be conducted to determine whether the vitrified material can be assayed by the SGS instruments at RFETS. The tests are to be performed at Los Alamos using actinide-containing ash in a glass waste form. The waste form we produce will resemble as closely as possible the form we anticipate finding at RFETS. If we find that SGS analysis does not provide adequate accuracy, we will evaluate thermal neutron counter (TNC) instrumentation.
- *Conventional Furnace Melting.* A series of tests will be conducted to investigate the use of a conventional furnace for producing a glass-based waste form for both ash and SS&C. The waste form will be designed to meet the performance criteria for interim storage and final disposition of transuranic waste forms. PNNL personnel will conduct the development of the glass-frit formulations for both materials. The focus will be on developing a low-melting-temperature glass. Researchers will identify the primary frits for evaluation by using a PNNL computer model that predicts performance in the characteristics required to meet the standards of this study. The final frit choice will be made using crucible-size

samples with surrogate material from RFETS. Operating parameters yet to be determined include waste loading, throughput, temperature, and time-at-temperature. Los Alamos researchers will verify PNNL results. If the verification procedure is successful, Los Alamos personnel will provide a flow sheet for implementing this technology at RFETS.

### Benefits

Researchers see two benefits to pursuing this project.

- *NDA Constraints and Operating Parameters.* Generator-site and Waste Isolation Pilot Plant accountability both require accurate knowledge of the radioisotopic composition of the glass waste form. Although development of vitrified waste forms is being pursued at several sites, little data has been collected on NDA techniques for vitrified waste forms. In this study, using SGS instrumentation, we will collect data on the glass-based waste form and its associated packaging. A concern with SGS analysis is whether attenuation will prevent an accurate analysis. In addition, the accuracy of the SGS technique is highly dependent on homogeneity of the plutonium in the waste form. Results of this study will provide data on these subjects to assist in deciding whether the SGS technique can be used for this waste form. We will evaluate the TNC technique if inadequate results are obtained with the SGS.
- *Conventional Furnace Melting.* Conventional furnace melting is the baseline technology for ash at RFETS and is the backup technology to microwave melting for SS&C. However, the RFETS microwave operation is currently in a stand-down mode because of safety concerns and may not be reactivated in the near future. Researchers on this project will demonstrate the feasibility of conventional furnace melting and will identify the operating parameters that can be applied to successfully implementing this technology at RFETS. The benefit of the low-temperature glass to be developed in this project will be to minimize temperature buildup in the glovebox and to reduce volatilization in the off-gas system.

### Milestones

NDA Constraints and Operating Parameters .....	October 1, 1996–May 1, 1997
1. Obtain ash and glass frit .....	October 1, 1996–January 15, 1997
2. Generate ash/glass waste forms .....	January 15–31, 1997
3. Initiate NDA on waste forms .....	January 31–February 14, 1997
4. Prepare report on NDA constraints and operating parameters .....	February 14–May 1, 1997
5. Issue report .....	May 1, 1997
Conventional Furnace Melting .....	October 1, 1996–September 30, 1997
1. Obtain surrogate compositions .....	October 1, 1996–January 15, 1997
2. Complete computer modeling for test design .....	January 15–February 7, 1997
3. Complete development of glass frit formulation for ash .....	February 7–April 30, 1997

### Milestones (continued)

4. Complete development of glass frit formulation for SS&C ..... April 30–May 30, 1997
5. Complete variability and verification testing for ash ..... May 30–June 13, 1997
6. Complete variability and verification testing for SS&C ..... June 13–July 15, 1997
7. Complete analyses on test samples for ash ..... July 15–30, 1997
8. Complete analyses on test samples for SS&C ..... July 30–August 4, 1997
9. Complete flow-sheet development for RFETS ..... August 4–September 1, 1997
10. Prepare final report on conventional furnace melting ..... September 1–30, 1997
11. Issue final report ..... September 30, 1997

**Stabilization Process Development**  
**Ash: Vitrification of Rocky Flats Environmental Technology Site Ash**  
**Work Breakdown Structure No.: 1.2.3.2**

**Date Issued:** November 30, 1996

**Principal Investigators:** Tracy S. Rudisill (Savannah River Site)  
Don A. Burge (Savannah River Site)  
James C. Marra (Savannah River Site)  
David K. Peeler (Savannah River Site)

**Budget:** Fiscal Year 1997      \$250 K

**94-I IP Milestone:** IP-ES-025

**R&D Plan:** 4.3.5.3.1

### **Objective**

The objectives of this work are to optimize and demonstrate glass formations and processing conditions required to vitrify incinerator ash from Rocky Flats Environmental Technology Site (RFETS). Vitrification will stabilize the material and produce a stable waste form that can be discarded to the Waste Isolation Pilot Plan (WIPP). This program will build upon the vitrification of simulated ash work performed during fiscal year 1996 (FY96). In FY96 Savannah River Site (SRS) researchers successfully demonstrated vitrification of a simulated ash. They used borosilicate and soda-lime-silicate glass formulations with a simulated ash based on an average composition reported by T. C. Johnson.<sup>1</sup> Experiments performed during fiscal year 1997 will use the simulated ash (with and without the addition of plutonium oxide) and actual ash from RFETS.

### **Scope**

Using the borosilicate and soda-lime-silicate glass formulations demonstrated during FY96 as the starting point, SRS researchers will perform a statistically designed experimental program to optimize primary processing variables (liquidous temperature and viscosity) and glass durability. The program will consist of a series of 30–35 melts during which the frit and ash compositions are systematically varied to produce the most desirable processing conditions and glass durability. Key components in the ash will be varied to address the range of compositions reported for ash at RFETS. A product consistency test developed for measuring the durability of nuclear waste glasses, will be the primary measure of durability.<sup>2</sup> Initially, experiments will be performed using the simulated ash and based on the range of compositions reported by Johnson. Researchers will then repeat selected experiments, adding the simulated ash with plutonium oxide and actual ash from RFETS. The experimental results will then help establish correlation between simulated experiments and experiments with actual ash samples.

The vitrification demonstration of RFETS incinerator ash in FY96 was limited to the use of a simulated ash because of a secondary mixed-waste generation issue raised by the South Carolina Department of Health and Environmental Control (SC DHEC). This issue has been resolved; however, discussions are still ongoing between Westinghouse Savannah River Company

and SC DHEC personnel over modifications to the site treatment plan (STP), which covers disposition of the four cans of incinerator ash (approximately 2 kg) proposed for use during this study. The STP currently states the ash will be shipped back to RFETS for disposition with the site's inventory. Once the modifications to the STP are complete, the ash will be available for experimental use.

### Benefits

Incinerator ash produced at RFETS contains sufficient quantities of hydrogenous material that radiolytic generation of hydrogen is a serious concern. Calcination to oxidize combustible materials is planned to stabilize the ash for interim storage in response to Defense Nuclear Facilities Safety Board Recommendation 94-1.<sup>3</sup> However, the presence of material with a very fine particle size will require immobilization before the ash can be discarded as waste at WIPP. Waste materials must be immobilized if >1% is particulate material <10 μm in diameter or if >15% is particulate material <200 μm in diameter. These criteria will likely require additional handling and treatment at RFETS before shipment to WIPP. In contrast, the use of vitrification as a single treatment technology will produce a stable waste form that meets all WIPP waste acceptance criteria. A glass waste form is shippable and will provide resistance to chemical dissolution under repository conditions.

### References

1. T. C. Johnson, "Recovery of Plutonium from Incinerator Ash at Rocky Flats," Rocky Flats Plant report RFP-2520, (1976).
2. "Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT), Designation: C 1285-94 (American Society for Testing and Materials, West Conshohocken, Pennsylvania, February 1995).
3. "Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan," U.S. Department of Energy report DOE/EM-0199 (February 28, 1995).

### Milestones

Vitrification of RFETS Ash .....	October 1, 1996–December 31, 1997
1. Develop statistically designed experimental program .....	October 1, 1996–December 31, 1996
2. Fabricate glasses and make visual observations .....	January 1–February 14, 1997
3. Characterize microstructure of selected glasses .....	February 14–28, 1997
4. Measure viscosity/liquidous temperature of selected glasses .....	May 30–July 31, 1997
5. Assess glass performance .....	March 3–May 2, 1997
6. Perform plutonium loading tests for glass formation .....	July 1–August 1, 1997
7. Complete and issue report .....	August 4–October 1, 1997

**Stabilization Process Development**  
**Maximum Waste Loading of Particulates in the Cement Waste Form**  
**Work Breakdown Structure No.: 1.2.4**

**Date Issued:** November 30, 1996

**Principal Investigator:** Gerald W. Veazey

**Budget:** Fiscal Year 1997      \$150 K

**94-1 IP Milestones:** IP-3.3-026A

**R&D Plan:** 4.3.2.2.4

### **Objective**

The objective of this project will be to establish the waste-loading limits in a cementitious matrix for particulates in the 94-1 inventory. Wastes to be considered for evaluation will include ash; sand, slag, and crucible (SS&C); and pyrochemical salts. We will establish waste-loading limits within the confines of a waste form that meets the transuranic interim-storage and Waste Isolation Pilot Plant (WIPP) performance criteria. We will collect this information for comparative evaluations of cementation against other immobilization technologies being considered for implementation, such as vitrification and ceramification. In addition, waste-loading data may be needed to determine whether particulates that meet the safeguards termination limits should be cemented or placed in a Rocky Flats Environmental Technology Site (RFETS) pipe component because of the pipe's limited volume.

### **Scope**

Los Alamos National Laboratory researchers will determine the maximum waste loadings that produce a waste form to meet a set of performance standards designed to address WIPP, Environmental Protection Agency (EPA) toxicity characteristic leaching procedure (TCLP), and operational requirements. Operational requirements include homogeneous mixability, timely setting, and moderate hydration temperature. These requirements will impact several aspects of cementation as it applies to WIPP, including safeguard termination limits and hydrogen generation. We will work on a laboratory scale with nonactinide surrogates of the selected waste types. We will emphasize simple cementation techniques that can be readily implemented, such as in-drum mixing and using Type I/II Portland cement. Additives may be considered, if they are needed to adjust characteristics such as cement setting time and viscosity.

### **Benefits**

Cementation has always been considered a relatively simple, inexpensive, and quick immobilization technique. Although other immobilization techniques such as vitrification have been identified as the baseline for particular wastes, these benefits of cementation make it a good backup candidate, if the more exotic technologies fail to meet time and/or cost limitations. The waste-loading data collected from this study will be a major factor in a cost comparison of cementation with other technologies. This data will also be important in determining whether, from a drum-loading perspective, cementing the particulates that do not require immobilization

to meet the safeguards termination limit will be beneficial. Dry particulates can be shipped to WIPP in a 6- or 12-in. pipe component, but these containers have a relatively small capacity of ~ 12 and 48 L, respectively. Possibly, more waste can be placed in a 55-gal. drum by cementing the waste within the 210 L available in the drum than can be accomplished by placing the nonmobilized particulate in a pipe component.

### Milestones

- |  |                                    |
|--|------------------------------------|
| Cementation Development and Testing.....               | October 1, 1996–September 30, 1997 |
| 1. Determine waste form<br>performance standards ..... | October 1–December 22, 1996        |
| 2. Complete surrogate preparations.....                | December 23, 1996–January 31, 1997 |
| 3. Complete cementation work.....                      | February 3–August 1, 1997          |
| 4. Prepare report on cementation .....                 | August 4–September 30, 1997        |
| 5. Issue report.....                                   | September 30, 1997                 |

### 1.3.0 Surveillance and Monitoring



**Storage containers must be surveyed and monitored in order to ensure integrity of containers and safe storage of nuclear materials. One action necessary to surveillance is development of nonintrusive techniques that allow monitoring of long-term storage containers. Nonintrusive techniques provide adequate monitoring of storage conditions without violating the integrity of the packaging configuration or generating additional waste. The projects described in this section support technology development and testing activities associated with nonintrusive techniques. Surveillance and monitoring of storage containers is also an important aspect of the Metal and Oxide Shelf-Life program. In this program researchers will deal with numerous inventory items that represent classes of materials in storage at DOE complex sites.**



**Surveillance and Monitoring**  
**Tomography**  
**Work Breakdown Structure No.: 1.3.1**

**Date Issued:** November 15, 1996

**Principal Investigator:** Lynn A. Foster

**Budget:** Fiscal Year 1997      \$145 K

**94-I IP Milestone:** IP-3.3-022

**R&D Plan:** 7.2.2.2

**Objective**

Researchers on this project will develop a noninvasive, nondestructive method for determining the contents and the condition of the transuranic materials in containers currently being used. Researchers will investigate the feasibility of using x-ray tomography to eliminate unnecessary and unsafe handling. The DOE complex stores many containers of plutonium with poorly characterized contents and packaging. Processing for safe repackaging of plutonium-containing materials often requires opening packages in gloveboxes with noninerted atmospheres. Unexpected consequences can result. Development of more sophisticated and precise noninvasive analytical tools is needed. Initially, Los Alamos National Laboratory and Savannah River Site (SRS) personnel will use computer modeling to evaluate the feasibility of computerized tomography (CT) to quantify changes in stored vault items.

**Scope**

Researchers will investigate the feasibility of using x-ray tomography to determine discrete chemical and elemental characteristics within currently stored inventories of plutonium. Using surrogate materials, we will evaluate the ability of commercially available x-ray tomography equipment to distinguish between plutonium compounds in sealed metal containers. Identification of plutonium corrosion products, such as plutonium hydride and plutonium oxide, will be investigated. Being able to determine the existence of pyrophoric material before containment is lost will be invaluable. The specific location and amount of hydride formation within a matrix will be investigated. Los Alamos and SRS personnel will begin to investigate measurement techniques that are complementary to CT, such as gamma-ray backscattering and alpha neutron emission, including algorithms for integration of results with CT data. Los Alamos personnel will install and evaluate an existing prototype instrument, the tomographic gamma scanner (TGS), that utilizes related technology. This instrument is a large-scale tomographic system used for nondestructive assay (NDA) of nuclear materials in containers up to 55-gal.-drum size.

**Benefits**

For safety and processing efficiency, we need to be able to recognize specific identifiable characteristics within sealed containers. Unprocessed materials, currently stored throughout the several DOE sites, often require extensive handling to determine their condition. Such handling increases worker exposures, contamination incidents, and inhalation risks. Development of

noninvasive analytical tomography equipment for remote handling will vastly improve our current knowledge of stored inventories. X-ray tomography may reveal potential hazards that other analytical tools miss, improving worker safety and reducing environmental contamination.

### Milestones

- |   |                                  |
|---|----------------------------------|
| Evaluation of TGS .....   | January 1, 1996–January 31, 1997 |
| 1. Install existing TGS .....   | January 1–23, 1996               |
| 2. Review failure mechanisms for stored plutonium materials .....   | February 23–March 1, 1996        |
| 3. Use computer modeling to evaluate the ability of CT to detect and quantify changes in stored items ..... | March 1–April 1, 1996            |
| 4. Complete development of CT test objects using surrogate materials .....                                  | April 1–30, 1996                 |
| 5. Implement test plan for experimental evaluation .....  | April 30–May 21, 1996            |
| 6. Evaluate TGS in comparison to current NDA technology .....   | May 21–31, 1996                  |
| 7. Modify existing CT software to detect changes in stored items .....                                      | May 31–July 31, 1996             |
| 8. Complete report documenting TGS evaluation .....   | July 31–August 14, 1996          |
| 9. Evaluate requirements for facility integration .....   | August 14–30, 1996               |
| 10. Complete functional specification for the digital radiography (DR)/CT system .....                      | August 30, 1996–January 31, 1997 |
| 11. Prepare draft version of Los Alamos report documenting DR/CT experimental evaluation .....              | August 14, 1996–January 31, 1997 |
| 12. Decide whether to proceed and fund project .....  | January 31, 1997                 |
| Installation of DR/CT Capability .....  | February 3–September 30, 1997    |
| 1. Complete procurement specification of DR/CT system .....   | February 3–28, 1997              |
| 2. Initiate procurement specification of DR/CT system .....   | February 28, 1997                |
| 3. Initiate facility safety review/modifications for the DR/CT system integration (SRS) .....               | February 28–March 31, 1997       |
| 4. Complete facility integration requirements (SRS) .....   | March 31–August 15, 1997         |
| 5. Install the DR/CT system at SRS .....  | August 15–29, 1997               |
| 6. Report on complementary measurement techniques for stored-item monitoring .....                          | September 1–30, 1997             |
| 7. Complete field test and evaluation of DR/CT on nuclear materials in storage containers .....             | September 30, 1997               |

**Surveillance and Monitoring**  
**Moisture Probe**  
**Work Breakdown Structure No.: 1.3.2**

**Date Issued:** November 15, 1996

**Principal Investigators:** Lynn A. Foster  
Daniel Holslin (Science Applications International Corporation)  
Jerry L. Stakebake (Department of Energy, Rocky Flats  
Field Office)

**Budget:** Fiscal Year 1997                      \$200 K

**94-I IP Milestone:** IP-3.3-022

**R&D Plan:** 7.2.2.7

**Objective**

A neutron-based moisture probe will be field tested at the Los Alamos National Laboratory Plutonium Facility. Science Applications International Corporation (SAIC) is currently developing a bench-top model for nondestructive assay of moisture content in plutonium oxide ( $\text{PuO}_2$ ). This bench-top model will be delivered to Los Alamos and will be tested using  $\text{PuO}_2$ , with known moisture content, that has been sealed in long-term storage containers. Los Alamos personnel will produce and characterize the  $\text{PuO}_2$  "standards" for this study. These Los Alamos-produced "standards" will contain moisture contents that bracket the 0.5 wt % required for long-term storage of  $\text{PuO}_2$ . The applicability of neutron-moderation techniques for quantification of moisture content in  $\text{PuO}_2$  at or below the 0.5 wt % level will be evaluated in this project.

**Scope**

The large quantity of fissile and radioactive material present complicates the analysis of moisture content in  $\text{PuO}_2$  using neutron moderation. The technique needs to be carefully investigated. First, both the spontaneous fission of plutonium and  $\alpha, n$  reactions produce a large, intrinsic neutron background signal that can dampen the signal that the moisture probe is trying to measure. Second, neutron multiplication complicates the neutron signature. The interrogating neutrons will interact with the fissile  $^{239}\text{Pu}$  atoms to induce fissions, creating an additional source of neutrons. We must field-test this technique on actual plutonium standards that are typical of long-term storage conditions so that we can carefully evaluate neutron moderation for measuring moisture content for long-term storage of plutonium oxides.

To aid in the evaluation, Los Alamos researchers will produce a set of  $\text{PuO}_2$  "standards" to be used for this application only. The standards will cover a range of moisture content from less than 0.1 to >1.0 wt % water. We will produce the set of standards by processing several 3- to 4-kg lots of  $\text{PuO}_2$  at a series of different bakeout temperatures. The result will be a set of standards with graded moisture content. The final moisture content will be quantified by loss-on-ignition (LOI) measurements. The set of standards will then be packaged in long-term

storage containers. Then this set of standards will be used to evaluate the applicability of neutron moderation for analysis of moisture contents at and below the 0.5-wt % level.

On successful demonstration of the neutron moderation technique for analysis of moisture content in PuO<sub>2</sub> canisters, SAIC will be contracted to design and produce a prototype model. On completion of this system, the prototype model will be installed and field tested at the Rocky Flats Environmental Technology Site (RFETS) in conjunction with the packaging of PuO<sub>2</sub> materials in the British Nuclear Fuels, Ltd., system.

### Benefits

Detecting and quantifying moisture through neutron moderation will provide a nondestructive and noninvasive technique for evaluating sealed PuO<sub>2</sub> materials. Neutron measurements of moisture content can be performed quickly and cheaply on materials in the configuration chosen for long-term storage. An instrument of this nature can be useful throughout the DOE complex as a complementary technique to LOI measurements or as a replacement technique when LOI is not feasible.

### Milestones

Moisture Probe Development .....	October 1, 1996–September 30, 1998
1. Complete bench-top model (SAIC) .....	October 1, 1996–April 18, 1997
2. Deliver bench-top model to Los Alamos (SAIC) .....	January 31–May 16, 1997
3. Complete standard fabrication (Los Alamos Nuclear Materials Technology Division Nitrate Systems Group) .....	January 31–April 28, 1997
4. Complete measurements for field test at Los Alamos .....	February 28–June 30, 1997
5. Document/evaluate field test results (conditional upon satisfactory test results and funding) .....	April 30–August 31, 1997
6. Initiate procurement of prototype moisture probe .....	September 1, 1997
7. Fabricate and deliver prototype moisture probe to RFETS .....	September 1, 1997–June 3, 1998
8. Test and evaluate prototype system at RFETS .....	April 1–September 30, 1998
9. Complete testing and evaluation of prototype system at RFETS .....	September 30, 1998

**Surveillance and Monitoring**  
**Acoustic Resonance Spectroscopy**  
**Work Breakdown Structure No.: 1.3.3**

**Date Issued:** November 15, 1996

**Principal Investigator:** D. Kirk Veirs

**Budget:** Fiscal Year 1997      \$100 K

**94-I IP Milestone:** IP-3.3-022

**R&D Plan:** 7.2.2.4

**Objective**

Los Alamos National Laboratory researchers are investigating the feasibility of using acoustic resonance spectroscopy (ARS) to detect pressure increase and gaseous components, specifically hydrogen. Researchers on this project will continue to develop a noninvasive, nondestructive method for determining the gas composition and pressure buildup in long-term storage containers. Surveillance must be performed on containers of plutonium-containing materials in storage. Development of more sophisticated and precise noninvasive analytical tools is needed. ARS has been sufficiently well developed at this point so that determining its viability for this application is possible.

**Scope**

We will continue with studies that use surrogate materials in cans to represent plutonium metal, oxide, and residues. Measurement of partial pressures for hydrogen, oxygen, and helium components has been researched. We are conducting experiments to elucidate the effects of such factors as temperature, data acquisition rate, frequency range, and step size on the ability to detect changes within a can. Further areas that need investigation are changes in pressure and composition of the gas and changes in the can itself. Observing changes in a can within a second can has been successful. We are monitoring changes and trying to determine whether the technique will detect changes within the can-in-a-can configuration. The ARS technology will continue to be investigated for application as a tool for support of the Metal, Oxide, Residue Shelf-Life Program and in future storage sites.

**Benefits**

For storage safety, recognition of specific identifiable characteristics within sealed containers is significant. Development of ARS for application to storage will vastly improve our current capabilities to detect changes in the containers. ARS can detect the changes in pressure and composition of the gas within the container. Because ARS can detect changes, detecting a defective weld in a container is theoretically possible.

### Milestones

- Acoustic Resonance Spectroscopy ..... January 15, 1996–September 30, 1997
1. Evaluate feasibility of detecting  
gas pressure in a sealed container ..... January 15–March 1, 1996
  2. Issue feasibility report ..... March 1, 1996
  3. Evaluate feasibility of gas recognition  
of hydrogen and helium mixtures ..... March 1–September 30, 1996  
Complete design, fabricate containers,  
set up experiment ..... March 1–May 14, 1996  
Conduct experiments ..... May 14–September 30, 1996
  4. Evaluate feasibility of ARS measurements  
of gases in double-sealed long-term  
storage containers ..... March 1–September 30, 1996  
Complete design, fabricate  
containers, and set up experiment ..... March 1–May 14, 1996  
Conduct experiments ..... May 14–September 30, 1996
  5. Evaluate gas pressure measurements  
on long-term storage containers,  
using argon, helium, and surrogate  
materials ..... March 1–September 30, 1996  
Complete design, fabricate containers,  
and set up experiment ..... March 1–May 14, 1996  
Conduct experiments ..... May 14–September 30, 1996  
Decide on conceptual feasibility of ARS  
techniques for detecting changes  
in materials in long-term storage ..... September 30, 1996
  6. Continue testing and obtain  
measurement techniques ..... October 1, 1996–September 30, 1997
  7. Continue testing and obtain  
measurement systems ..... October 1, 1996–September 30, 1997
  8. Continue testing and obtain  
measurement fixtures ..... October 1, 1996–September 30, 1997
  9. Continue evaluation and development  
of ARS for application  
to shelf-life containers ..... October 1, 1996–September 30, 1997
  10. Continue software development ..... October 1, 1996–September 30, 1997

**Surveillance and Monitoring**  
**Nondestructive Assay: Gamma Salts**  
**Work Breakdown Structure No.: 1.3.4**

**Date Issued:** November 30, 1996

**Principal Investigators:** Teresa L. Cremers  
Thomas E. Sampson

**Budget:** Fiscal Year 1997      \$150 K

**94-I IP Milestone:** IP-3.3-012A

**R&D Plan:** 7.2.2.4

**Objective**

The capability to accurately determine plutonium isotopics is necessary in order to support neutron and calorimetry measurements of plutonium-bearing salts. This activity will provide a means to analyze heterogeneous plutonium- and americium-bearing salts for plutonium isotopic distribution and americium concentration. Los Alamos National Laboratory researchers propose to build on existing technology and enhance the personal computer (PC) Fixed energy Response function Analysis with Multiple efficiency (FRAM) gamma-ray isotopic distribution code already in use at the Los Alamos Plutonium Facility (TA-55).

**Scope**

Pyrochemical processing produces residues in which americium is present in a low-density salt matrix that has imbedded plutonium metal residues. In this situation plutonium gamma rays suffer attenuation that may be dominated by self-absorption in the plutonium metal, whereas americium gamma rays are primarily absorbed by the salt matrix. These circumstances give rise to different absorption characteristics, depending on whether the emitted gamma rays arise from the plutonium or the americium. Thus, the relative detector efficiencies are different for plutonium and americium.

The FRAM plutonium isotopic code was initially developed during the late 1980s and has been used to assay nearly 10,000 items at TA-55. The data acquisition and computer hardware are now obsolete, and the code has been rewritten in the C programming language and has been transferred to a PC platform.

The PC platform has enhanced the functionality and flexibility of the code and has allowed the quick acquisition of spectra by using either a single coaxial detector or a single planar detector. Analysis with a coaxial detector permits measurement of the isotopic distribution of plutonium inside lead-lined storage containers. Calorimetric assay technicians will not have to open and unpack items to accomplish gamma-ray isotopic analysis. Eliminating the opening and the unpacking will significantly reduce operator radiation exposure and improve safety.

The first part of our proposal outlines the development of parameter files that are essential for determining plutonium isotopic distribution and americium concentration in plutonium-bearing salt residues stored in lead-lined containers. We will develop and test parameter sets for the analysis of heterogeneous materials and of high americium concentrations, and we will address the issue of various interfering contaminants such as neptunium ( $^{237}\text{Np}$ ) and americium ( $^{243}\text{Am}$ ).

One of the strengths of the FRAM code is that qualified users can reconfigure it to each specific measurement problem without the need for lengthy, expensive software modifications. However, this versatility presents problems to less skilled operators when they are presented with measurement options.

In the second part of our project, we will streamline the measurement type selection process by building into the code automatic selection of the appropriate analysis parameter set. We will design the automated selection process to choose among parameter sets appropriate for shielded or unshielded samples, samples with high  $^{243}\text{Am}$  or  $^{237}\text{Np}$ , or samples in which the americium and plutonium are heterogeneously distributed.

### Benefits

A large inventory of residue salts is awaiting processing and disposal throughout the DOE complex. Nondestructive assay will provide a means to analyze heterogeneous plutonium- and americium-bearing salts for plutonium isotopic distribution and americium concentration and to support neutron and calorimetry measurements.

### Milestones

Nondestructive Assay—Gamma Salts .....	October 1, 1996–September 30, 1997
1. Develop and test heterogeneous material parameter sets .....	October 1, 1996–January 20, 1997
2. Complete heterogeneous parameter testing .....	January 20, 1997
3. Develop and test automated parameter sets .....	October 1, 1996–September 1, 1997
4. Deploy automated parameter set .....	September 1, 1997
5. Continue testing of additional parameter sets .....	May 1–September 30, 1997

**Surveillance and Monitoring**  
**Calorimetry**  
**Work Breakdown Structure No.: 1.3.5**

**Date Issued:** November 15, 1996

**Principal Investigators:** Teresa L. Cremers  
Jerry R. Wetzel  
Francisco M. Guerra

**Budget:** Fiscal Year 1997      \$100 K

**94-I IP Milestone:** IP-3.2-022

**R&D Plan:** 7.2.2.7

**Objective**

Los Alamos National Laboratory researchers propose to apply finite element analysis to obtain a model that will predict calorimeter performance and will make possible the design of smaller, faster calorimeters. Calorimetric assay is often the most precise and accurate method of nondestructive assay (NDA). It is insensitive to chemical matrix and thus is an excellent choice for measurement of many difficult materials, such as pyrochemical processing residues. However, calorimetric measurements take a long time and calorimeters are bulky, large instruments. Putting a large calorimeter in a glovebox line is difficult because the instrument is so large as to not conveniently fit under a glovebox.

**Scope**

Calorimetry has many advantages over other destructive and NDA methods. Sampling problems are eliminated because the whole item is analyzed and chemical interferences are few. In general, calorimetric assay minimizes handling and reduces operator exposure to radiation. We propose to develop a finite element model that will help predict calorimeter performance and guide calorimeter design. We will build on work already performed at EG&G Mound Applied Technologies. In this effort researchers proved the value of and demonstrated the feasibility of finite element analysis as applied to calorimetry. Our project will be divided into logical steps in order to allow for analysis and redirection as the work continues. Our long-term goal is to set up independent finite-element modeling capability for our calorimeter designers, while maintaining close contact with Los Alamos thermal analysis experts for help with difficult projects.

The first part of our project will be to evaluate the EG&G work and to identify the necessary hardware and software. We believe that our groups have the necessary computer hardware and that we will not need much new equipment. We will optimize and integrate our software purchases to avoid duplication and redundancies.

The second part of our project will be to create the finite element model. We will use the model to predict the radial temperature distribution through the calorimeter. The model will also be used to predict the sensitivity and measurement times of the calorimeter. We will verify the

performance of the model with actual data taken from an operating calorimeter. Our results will be used to guide our future work.

Finally, we will use our finite element model to assist in the design of new calorimeters. Our model will enable us to design calorimeters that will make faster measurements, are easier to put under gloveboxes, and can be fielded as transportable instruments.

### Benefits

The disadvantages of calorimetry are the long assay times and the bulky nature of the equipment. The liabilities of calorimeter response time and size have been difficult to address because calorimeter design has been an intuitive process based on past experience and on expertise of calorimeter designers. Better understanding of the steady-state temperature distribution can be used to reduce size and improve sensitivity of calorimeters. This better understanding can be accomplished by using a finite element model to predict the temperature distribution and the response time of calorimeters.

### Milestones

- |   |                                    |
|---|------------------------------------|
| Calorimetry.....  | October 1, 1996–September 30, 1997 |
| 1. Evaluate Mound work and<br>evaluate existing hardware and software ..... | October 1–December 31, 1996        |
| 2. Develop finite element model .....                                       | January 1–September 30, 1997       |
| 3. Identify operating calorimeter to be used<br>to test model .....         | January 1–20, 1997                 |
| 4. Construct finite element model .....                                     | January 1–February 28, 1997        |
| 5. Create drawings or data about test calorimeter .....                     | January 1–February 28, 1997        |
| 6. Complete testing and evaluate model .....                                | March 3–June 1, 1997               |
| 7. Compare model and experiment .....                                       | June 2–August 1, 1997              |
| 8. Make recommendations for calorimeter design .....                        | August 1–September 30, 1997        |
| 9. Make recommendations for future work .....                               | September 30, 1997                 |

## **Surveillance and Monitoring**

### **Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site Work Breakdown Structure No.: 1.3.6**

**Date Issued:** November 30, 1996

**Principal Investigators:** Thomas L. Rising  
Nelson S. DeMuth

**Budget:** Fiscal Year 1997      \$180 K

**94-1 IP Milestone:** IP-3.3-034

**R&D Plan:** 7.2.2.6

### **Objective**

Los Alamos National Laboratory Technology Modeling and Analysis Group (TSA-7) will assess the risk status of residue holdings at Rocky Flats Environmental Technology Site (RFETS) that come under the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 94-1.<sup>1</sup> At issue is the change in risk status that results from aging effects and from mitigation efforts, such as drum venting and repackaging. The analysis should address the risk status before DNFSB Recommendation 94-1 remediation efforts, the current risk status, and possibly, future behavior that will be predicted on the basis of various program scenarios.

### **Scope**

This task is complicated by the fact that currently no validated methodologies exist for assessing time-dependent risk status, either unremediated or mitigated. Application of the risk methodology developed by TSA-7 and used to assess the risk for processing Los Alamos vault holdings will require acquisition of a large amount of surveillance data, which may not be available at RFETS. Acquisition of these data is beyond the scope and schedule of this proposal.

We propose to investigate, along with the Rocky Flats Field Office (RFFO), precisely what information is needed to determine the risk status. We will then review the available RFETS data, along with available risk assessment methodologies, with the aim of satisfying the requirements that we developed with RFFO. By the end of the project, we will provide a preliminary assessment of the risk status and a scope and estimate for the remaining work.

Initially, we will need to coordinate the project requirements, approach, and expected results with RFFO and the Nuclear Materials Stabilization Task Group (NMSTG). We will evaluate the risk management program and information on residue holdings developed at RFETS for the DNFSB 94-1 Implementation Plan.<sup>2</sup> An approach to assessing the risk status will be defined. Along with other techniques, we will evaluate the applicability of the methodology developed by TSA-7 for the Recommendation 94-1 holdings at Los Alamos. Preliminary assessments of the risk status from January 1994 through the present will be developed and reported to requesters, along with a description of the inspection and analysis information required for in-depth assessments and risk tracking.

In order to carry out this project, we will need from RFETS information on residue characteristics, container degradation, and potential personnel hazards.

### Benefits

Researchers on this proposed task will be better able to evaluate the current risk at RFETS and will provide information regarding whether progress is being made to reduce the risk.

### References

1. "Defense Nuclear Facilities Safety Board Recommendation 94-1, Improved Schedule for Remediation in the Defense Nuclear Facilities Complex" (Washington, DC, May, 1994).
2. "Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan," U.S. Department of Energy report DOE/EM-0199 (February 28, 1995).

### Milestones

- Risk Status of Residue Holdings at RFETS ..... October 1, 1996–May 1, 1997
1. Coordinate project requirements, approach, and expected results with the RFFO and the NMSTG ..... October 1, 1996–January 1, 1997
  2. Evaluate information on status of stored residues and determine applicability of candidate methodologies ..... January 2–15, 1997
  3. Conduct workshop at DOE headquarters describing risk-based analysis for Los Alamos 94-1 R&D Project implementation ..... January 15–31, 1997
  4. Develop an approach and brief project principles on scope and expected results ..... January 15–31, 1997
  5. Perform preliminary assessments of risk status using available information on residue characteristics, on container degradation, on potential hazards, and on degradation processes observed at other sites ..... February 3–April 1, 1997
  6. Develop plan containing resource and information requirements for in-depth assessments of risk status at RFETS ..... April 1–May 1, 1997

## 1.4.0 Core Technology



In its acceptance of the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 94-1,<sup>1</sup> the DOE developed an implementation plan that included a core technology program. The objectives of this program are as follows: (1) to augment the knowledge base about general chemical and physical processing and about storage behavior of actinide-containing materials and (2) to assure safe interim storage until disposition policies are in place.

As such, the program is needed (1) to develop a detailed understanding of the processes that affect stabilization, (2) to provide technology for predicting the long-term behavior of nuclear materials in storage, and (3) to develop and maintain capabilities to address unforeseen problems associated with managing these materials over time. Further, the development of a strong effort in fundamental actinide science will also enhance DOE's ability to ensure the success of other DOE programmatic missions.

The initial core technology program was formulated in late 1995 and early 1996 for the fiscal year 1996 technical program. In August and September of 1996, the fiscal year 1997 (FY97) technical program was formulated based on the latest input from the Technical Advisory Panel, guidance from DOE headquarters, and the rationale contained in the DNFSB 94-1 Implementation Plan.<sup>1</sup> Based on this information, Los Alamos National Laboratory personnel developed a weighting scheme against which ongoing work and new starts were evaluated. Factors that were considered in the evaluation process were the following:

- The core technology program mission is to support the five 94-1 R&D Project research, development, and testing (RD&T) areas (stabilization, standards, packaging, transportation, and surveillance). This support is accomplished (1) by developing the scientific basis underlying critical problems, (2) by ensuring continued competency in the most important technical disciplines for these five RD&T areas, and (3) by providing a pool of technical talent that can rapidly respond to unforeseen problems as the 94-1 R&D Project mission is executed. All core technology activities must address at least one core competency area and/or underlying science issue. These core competencies are identified in Table 2.
- Core technology activities should reflect the urgency of technological gaps in the five RD&T areas. Accordingly, in the initial program (and in the FY97 program), planners emphasized stabilization questions that had the greatest uncertainty and need. As the 94-1 R&D Project matures, this emphasis should shift toward packaging and surveillance issues. For core technology, the technical needs in standards and transportation, as currently understood, are judged to be less compelling.
- In the core technology program, the level of support of the various competency areas should be balanced with the 94-1 R&D Project mission in mind. Thus, it was considered better to support a number of critical competency areas at least at a minimal level than to concentrate the funding in only a few areas.
- By definition, all core technology components must have a strong basic RD&T aspect. Otherwise, they should be supported in the directed RD&T portfolio.
- As a target, the core technology fraction of the total 94-1 R&D Project budget was set at 25%.
- Continuity is important in order to ensure that the highest-quality researchers are readily available. In general, project lifetimes of at least a few years are desirable as long as the activities are progressing and remain responsive to the core technology mission. To ensure the vitality and responsiveness of the program, a target rate of about 25% new starts was set.
- As core technology activities mature, they will either be terminated or transferred to the applied part of the 94-1 R&D Project. An example of the latter is the movement of nondestructive assay activities in FY97 from core technology to the applied part of the RD&T program.

Table 2 summarizes the 14 core technology activities that will be supported in FY97. The core competency, underlying science, and RD&T area being supported are listed for each activity.

#### Reference

1. "Defense Nuclear Facilities Safety Board Recommendation 94-1 Implementation Plan," U.S. Department of Energy report DOE/EM-0199 (February 28, 1995).

**Table 2. Core Technologies Supported in Fiscal Year 1997**

<b>Activity</b>	<b>Core Competency*</b>	<b>Underlying Actinide Science</b>	<b>94-I R&amp;D Project Area Supported**</b>
<b>Continuing Work</b>			
Actinide solutions	A, B, C	Solution speciation	SA
Surface interactions	A, B	Surface interactions	SA
Chemical state changes	A	Valence/structure changes in stored materials	SA, SU
Actinide-organic	A, B, D	Actinide-organic interactions	SA
Polymer filtration	B	Soluble polymer chelators	SA
Polymer foams	B, E	Foam chelators	SA, SU
Thermodynamics	B, C, E	Oxychloride thermodynamics	SA, P
Corrosion	E	Actinide-materials interactions	SA, P, SU
Diffusion	E	Plutonium migration in metals	P, SU
<b>New Starts</b>			
Mineral waste forms	C, D, E, G	actinide silicate synthesis	SA
Pu(IV)/(VI) phosphates	B, C, D	Actinide phosphate synthesis	SA
Phosphate solutions	B, C, D	Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )/nitric acid (HNO <sub>3</sub> ) chemistry	SA
Molten salt electrochemistry	B, C, F, G	Actinide low-temperature melt properties	SA
Alpha scintillometry	B, H	Extractive scintillators	SA

\* Core competency designations are as follows: A is Characterization, B is Separations, C is Thermodynamics, D is Synthesis, E is Materials Science, F is Electrochemistry, G is Pyrochemistry, and H is Analytical Development.

\*\* 94-I R&D Project area designations are as follows: SA is Stabilization, P is Packaging, and SU is Surveillance.

**Core Technology**  
**Actinide Solution Chemistry in Residues**  
**and in Residue Stabilization and Treatment Processes**  
**Work Breakdown Structure No.: 1.4.1**

**Date Issued:** October 30, 1996

**Principal Investigator:** John M. Berg

**Budget:** Fiscal Year 1997      \$400 K

**94-1 IP Milestone:** Core Technology

**R&D Plan:** 9.2.1.1

**Objective**

Los Alamos National Laboratory researchers working on this project seek to describe aspects of the chemistry of plutonium in legacy solutions and in proposed residue treatment processes. They intend to provide sufficiently detailed descriptions that will guide stabilization and disposition decisions and enable efficient optimization of treatment processes.

Residue stabilization and treatment processes must be efficient and targeted at the present-day issues of safety, stability, and economics of disposal. Aqueous chemical separations will be needed for primary treatment and post-treatment during stabilization of many legacy materials. These aqueous separations will have to be carried out under chemical conditions that differ considerably from those used in production of materials for weapons. Researchers propose to measure critical thermodynamic parameters that govern plutonium chemistry under these chemical conditions. We believe this work will enable researchers to more accurately predict the behavior of plutonium in residues and during treatment processes.

**Scope**

Separation of plutonium from other elements and bulk substrates generally depends on partitioning the actinide into a different phase (solid-liquid, liquid-liquid). The chemical information important in plutonium separations and stabilization processes includes (1) plutonium oxidation state, (2) thermodynamic formation constants for species likely to form, (3) solubility of limiting phases, and (4) sorption properties. Our work focuses on measuring thermodynamic parameters and molecular structure information for the complexation of Pu(IV) in aqueous solution by nitrate, chloride, fluoride, carbonate, and oxalate ligands and for the complexation of Pu(VI) by carbonate, nitrate, and oxalate ligands. Each of these systems are, or will be, important in legacy material chemical behavior or in residue processing chemistry.

The Pu(IV) nitrate chemical system has long been central to plutonium processing, and it continues to be important in the ion-exchange separation of plutonium from other metals. However, despite this long history and central importance, we do not understand in sufficient detail at a molecular level either Pu(IV) nitrate solution complexes or resin-adsorbed species. This lack of understanding makes difficult the prediction of the effects of chemical perturbations on these

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processes or on future behavior of these processes, when different feeds may be used during stabilization efforts. Our work will make such predictions possible (1) by identifying major nitrate and mixed halide/nitrate complexes under a wide range of conditions, (2) by investigating the structures of these complexes, (3) by identifying the spectral signatures of these complexes, and (4) by determining the thermodynamic parameters for formation of these complexes so that we can predict the abundance of them under most expected solution conditions.

Plutonium carbonate chemistry is another focus of this effort. Stabilization and separations processes based on plutonium carbonate precipitation, sorption, or selective solubilization will have the inherent advantage of using an environmentally benign ligand. Initially, we will study Pu(VI) carbonates because of their potential importance under oxidizing conditions. We will synthesize a series of Pu(VI) carbonate species. We will also optimize the preparation of the compounds and characterize each solid and corresponding solution species. The methods used will include a combination of optical absorbance spectroscopy, diffuse reflectance, x-ray absorption fine structure, and powder x-ray diffraction. We will study the solution thermodynamics of Pu(VI) carbonate species at low and high ionic strengths.

The carbonate chemistry of Pu(V) will also be important under particular solution conditions that are achievable during residue processing, roughly less than  $10^{-3}$  molar plutonium concentrations of low-to-moderate ionic strengths (below 3 M) and of near-neutral pH (5.5–9.5). Because the solubility of these concentrations is very low in the presence of  $\text{Na}^+$  and  $\text{K}^+$ , the species,  $\text{PuO}_2(\text{CO}_3)_2^{3-}$  and  $\text{PuO}_2(\text{CO}_3)_3^{5-}$ , have never been identified in solution. We will attempt to synthesize and structurally characterize these solution species. After fiscal year 1997, we will conduct similar studies of Pu(IV) carbonate chemistry and of Pu(VI) and Pu(IV) oxalate chemistry.

### **Benefits**

Information gained on this project will enhance competency in actinide characterization, separations, and thermodynamics and will aid development in the underlying science of actinide solution behavior.

Separations of plutonium from other elements and from bulk substrates generally rely on partitioning the actinide into a different phase (solid-liquid, liquid-liquid). Molecular-level chemical information potentially can predict more accurately the chemical stabilities of residues and speed optimizing of stabilization and separations strategies. This task is targeted at developing such a fundamental chemical understanding of centrally important solution systems for plutonium-containing residues and residue processing. This understanding will enable researchers to more accurately assess unknown residue chemistry and predict the effects of proposed treatment processes on the plutonium component in residues.

### Milestones

- Actinide Solution Chemistry ..... October 1, 1996–September 30, 1997
1. Complete acquisition of data  
on Pu(IV) nitrate system ..... October 1–November 15, 1996
  2. Complete analysis of Pu(IV)  
nitrate solution speciation ..... November 15–December 31, 1996
  3. Complete analysis of Pu(IV)  
chloride solution speciation ..... January 1–March 31, 1997
  4. Synthesize Pu(VI) carbonate solids ..... October 1, 1996–March 31, 1997
  5. Synthesize limiting Pu(IV) carbonate ..... October 1, 1996–March 31, 1997
  6. Publish Pu(IV) nitrate results ..... May 1, 1997
  7. Determine structures of Pu(VI) carbonate solids ..... April 1–June 30, 1997
  8. Publish Pu(IV) chloride results ..... July 31, 1997
  9. Complete characterization of limiting Pu(IV)  
carbonate species ..... April 1–August 1, 1997
  10. Complete Pu(IV) nitrate/chloride competition ..... July 1–September 30, 1997
  11. Report on solution thermodynamics of Pu(VI)  
carbonate solution species ..... September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
Chemical and Physical Interactions  
of Actinides with Residue Substrates  
**Work Breakdown Structure No.: 1.4.2**

**Date Issued:** October 30, 1996

**Principal Investigators:** David E. Morris  
John M. Berg  
C. Drew Tait  
George J. Havrilla

**Budget:** Fiscal Year 1997      \$400 K

**94-1 IP Milestone:** Core Technology  
**R&D Plan:** 9.2.1.2

**Objective**

Los Alamos National Laboratory researchers on this project will study the chemical interactions and the surface structural characteristics of plutonium and uranium species that are adsorbed onto solid-phase substrates found in the processing residues throughout the DOE complex. Actinide species can interact with these residue substrates by means of a number of mechanisms (surface complexation, physisorption, matrix diffusion, and entrainment) to yield a wide range of surface-bound species.

Efficient stabilization of these residues by removing the actinide species from the matrix, while minimizing secondary waste volumes, is a goal not yet achieved. In many instances, developing and implementing strategies have been thwarted by the failure to understand and incorporate fundamental surface chemistry of the actinides in the design of the treatment process. We propose to employ macroscopic and microscopic molecular spectroscopic probes in conjunction with microscopic elemental imaging on several prototypical actinide/substrate systems. By using this process, we hope to obtain detailed characterization and imaging about the nature and the extent of surface interaction between the actinide species and the substrate.

The advantage of this approach relative to more commonly used surface characterization tools (e.g., scanning electron microscope [SEM], transmission electron microscope [TEM], and Auger electron spectroscopy) is that molecular speciation information is provided directly for any type of actinide phase (crystalline or amorphous, ion-exchanged or surface-complexed) without the frequently perturbative sample preparation requirements (e.g., thin-sectioning) or extreme conditions (e.g., ultrahigh vacuum). This information will provide a basic framework for surface interactions of actinides with processing residues, a framework that can be incorporated into future stabilization activities.

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## Scope

We will focus our efforts on three large-volume components in the residue inventory: ion-exchange resins, cellulosic materials, and incinerator ash. The ion-exchange resins are an interesting class of residues because they represent several potential stabilization challenges. In addition to the residual plutonium in these resins, the chemical conditions to which they have been subjected in use and storage (high nitric-acid concentrations) may lead to the formation of new binding sites for metals and to nitro-organics that pose an explosive hazard. Cellulosic materials (rags, clothing, packaging, and containers) represent an enormous volume in the residue inventory, and the materials have likely oxidized (chemically and radiolytically) over time, leading to new and potentially stronger interaction with plutonium. The incinerator ash was generated using resins, cellulosic material, and other processing waste as feed stock. The plutonium in the ash may be associated with a wide range of mineralized substrates, and the stoichiometry and speciation may vary widely within and between ash batches.

These characterization and stabilization issues will be addressed in the following tasks:

**Task 1. Spectroscopic investigations of the chemical and physical degradation of ion-exchange resins under high-nitric-acid conditions.** These studies will use Fourier transform infrared (FTIR), Raman, and luminescence spectroscopies to assess the nature and extent of degradation of typical ion-exchange resins as a result of contact with concentrated nitric acid solutions typical of those used for plutonium processing. We will assess any nitration effects that could lead to potentially explosive nitro-organic species, and we will identify new sites on the resins for binding of actinide species.

**Task 2. Chemical and spectroscopic studies of the surface interactions between actinide species and ion-exchange resins.** The focus of these studies is to derive a detailed description of the chemical and/or physical interaction between actinide species and exchange resins under process-like conditions. Studies will be done on virgin resins, on degraded resins characterized in Task 1, and on residue resins currently in the inventory. We will specifically investigate the number and strength of the different binding sites on the resins and determine the speciation of the actinide species in these binding sites. To accomplish these investigations, we will use electronic (absorption, photoacoustic, and luminescence) and vibrational (Raman and FTIR) spectroscopies. Our current understanding of Pu(IV) adsorption on anion-exchange resins from nitric acid is that nitrate adsorbed by the resin may play a crucial role in binding plutonium from solution. We will determine the role of bound nitrate by studying the kinetics of Pu(IV) adsorption as a function of nitrate concentration and as a function of the direction from which ideal conditions are approached.

**Task 3. Chemical and spectroscopic studies of the surface interactions between actinide species and cellulosic materials.** These studies will parallel those in Task 2, but we will be using virgin cellulosic material and material that has been chemically oxidized to mimic the aged material in the inventory. The scientific issues (i.e., number and strength of the different binding sites and speciation of the actinides) and the methods will be the same as in Task 2.

**Task 4. Development and implementation of a mesoscale imaging system for elemental and molecular characterization of plutonium.** In this effort, we will use microprobe x-ray fluorescence and vibrational (Raman and FTIR) spectroscopies for spatially resolved analyses and

imaging of residue materials. The data provided by each method will be integrated in order to provide a comprehensive analysis that will address both elemental composition and phase, oxidation state, and molecular form and structure. The ultimate aim of this work is to provide nondestructive elemental and molecular level images of materials. The initial focus of this effort will be to investigate the heterogeneity and the scale of heterogeneity of plutonium speciation in incinerator ash.

### Benefits

Work on this task will support competency in actinide characterization and separations and will help develop the underlying science of actinide surface interactions in residues.

A common theme in the stabilization of most residues is the extent to which the actinide species can be mobilized. In general, if readily implementable schemes can be devised to mobilize the actinide, then residue processing to remove the actinide is a viable strategy for stabilization. Conversely, some actinide-substrate interactions may be of such a tenacious nature that residue processing is intractable. We propose to provide (1) necessary fundamental information to assess the probability for successful actinide mobilization and (2) sufficiently detailed chemical and physical characterization data to devise the most appropriate mobilization strategies. Also, all proposed spectroscopic probes can be implemented on challenging samples, such as heterogeneous and mixed-phase residues with no sample preparation; and most of these spectroscopies can be implemented in the microscopic imaging mode. This approach has been demonstrated successfully on a range of samples, including uranium-contaminated soils from Fernald Environmental Management Project and high-level tank wastes from Hanford Site. Thus, we can be certain of the integrity of both the samples themselves and the surface characterization data.

### Milestones

Surface Interactions .....	October 1, 1996–September 30, 1998
1. Procure residue samples for investigation from the Los Alamos Plutonium Facility (TA-55) .....	October 1, 1996–January 31, 1997
2. Complete resin kinetic studies .....	February 3–July 31, 1997
3. Complete resin degradation studies .....	August 1–September 30, 1997
4. Present results at national topical meeting .....	September 30, 1997
5. Report resin kinetic and degradation studies .....	October 30, 1997
6. Complete development of integrated imaging system .....	October 1, 1996–September 30, 1997
7. Complete spectroscopic studies of plutonium-resin interactions .....	October 1, 1997–March 31, 1998
8. Demonstrate integrated imaging capabilities on plutonium residues .....	April 1–September 30, 1998

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Identification and Characterization of Changes**  
**in the Chemical State of Plutonium in Interim Waste Forms**  
**Work Breakdown Structure No.: 1.4.3**

**Date Issued:** November 8, 1996

**Principal Investigators:** D. Kirk Veirs  
Steven D. Conradson  
David L. Clark  
Mary P. Neu  
Coleman A. Smith

**Budget:** Fiscal Year 1997      \$ 422 K

**94-1 IP Milestone:** Core Technology  
**R&D Plan:** 9.2.1.3

**Objective**

The purpose of this work is to identify and characterize changes in the physicochemical state of the myriad of plutonium compounds found in residues. Los Alamos National Laboratory researchers will study plutonium-containing materials other than metal and pure oxide. We will use both powder and single-crystal x-ray diffraction (XRD), x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy (XPS), and optical spectroscopies (reflectance absorption and Raman). Using these technologies, we hope to identify changes in the local chemical environment of the plutonium metal center. Changes in local chemical environment can indicate the onset in the waste form of deleterious transformations that may lead to unsafe storage conditions.

**Scope**

Plutonium-containing materials that are not pure oxide or metal are being considered for interim storage. We anticipate storage times of decades, and the chemical behavior of plutonium-containing materials over this long a time is not known. These materials may contain constituents that may lead to generation of gas and corrosion. The chemical behavior of this material, especially the material intimately in contact with plutonium, needs to be studied over time to ensure that any chemical changes that do occur do not adversely affect the waste form.

The oxidation state of plutonium is especially vulnerable to aging effects, and we have shown that x-ray techniques are successful in determining plutonium valence. XAS is sensitive to the local chemical environment of a metal, in this case plutonium, and thus is an outstanding analytical technique for studying changes in the materials that are directly bonded to plutonium. We have used XAS, which includes the extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) regions, and optical spectroscopies in our research. We have studied the following: (1) the speciation of plutonium in nitric acid, (2) the local structure of plutonium alloys, (3) the chemical form of plutonium and neptunium in

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carbonate ground water at the Yucca Mountain Project, and (4) the form of uranium in soils at the Fernald Environmental Management Project. XAS has high sensitivity to plutonium embedded into or sorbed onto other material. Los Alamos maintains facilities at the Stanford Synchrotron Radiation Laboratory (SSRL) for XAS studies of radioactive materials. We will use this unique expertise to carry out the experimental plan.

In this work we will concentrate on problem plutonium residues such as salts, ash, alloys, and carbides. We will identify samples of pertinent residues from the inventories of the Los Alamos Plutonium Facility (TA-55) and, if possible, from other sites within the DOE complex. We will study these samples, along with samples of pure compounds, over the length of the project, using diffuse reflectance, XRD, XAS, and XPS techniques. Initially, our focus will be on determining the oxidation state of plutonium. XANES spectroscopy and XPS are established techniques for determining oxidation state and local chemical environment. Actinide oxidation states can also be determined by binding energy shifts, relative to the actinide metal, that are in the XPS photoemission spectra. We will prepare and characterize pure samples of appropriate plutonium salts, carbides, and alloys. X-ray powder diffraction, reflectance absorption spectroscopy, vibrational spectroscopy (when appropriate), and XAS will be used. Analysis of the XRD and XAS data will yield the necessary database of plutonium solid structures. Absorption spectra of plutonium compounds vary considerably and are very sensitive to the structure and orientation of the ligands that surround the plutonium. Correlation may be possible between the structure obtained by XRD and XAS data and the optical spectra of the pure compounds. Such information will be useful in identifying when chemical changes take place in residues or in other plutonium-containing materials.

Sample preparation will take place within facilities at TA-55 and at the Los Alamos Chemistry and Metallurgy Research (CMR) Building. We will obtain absorption spectra, x-ray powder, and single-crystal diffraction data using existing equipment at TA-55, at the CMR building, and at Los Alamos Radiochemistry Site (TA-48). XAS experiments will be conducted at SSRL, and the data will be analyzed at existing computing facilities at Los Alamos.

### **Benefits**

Work performed on this task will support competency in actinide residue characterization and will help develop the underlying science of valence and structure changes in stored actinide materials.

For meeting safe storage objectives, early identification of chemical changes in residues in interim storage is necessary. Such early identification also may be used to guide future disposition technologies. A comprehensive understanding of the chemical changes that occur in stored residues will enhance safety of the storage media and assessment of sites that are storing the materials. Early identification of problematic chemical changes will allow sufficient lead time to assess options on disposition of the materials.

### Milestones

- Changes in the Chemical State of Plutonium ..... July 1, 1996–April 30, 1999
1. Synthesize pure plutonium compounds ..... July 1, 1996
  2. Complete optical spectroscopic characterization ..... July 1–31, 1996
  3. Complete first XAS experiment ..... August 1–30, 1996
  4. Complete first XAS data analysis ..... September 2, 1996–January 1, 1997
  5. Complete initial plutonium structural database ..... January 1–April 30, 1997
  6. Prepare second set of plutonium samples ..... May 1–June 30, 1997
  7. Complete second XAS experiment ..... July 1–September 1, 1997
  8. Complete second XAS data analysis ..... September 1, 1997–January 1, 1998
  9. Incorporate results into plutonium structural database ..... January 1–May 1, 1998
  10. Prepare third set of plutonium samples ..... May 1–July 1, 1998
  11. Complete third XAS experiment ..... July 1–September 1, 1998
  12. Complete third XAS data analysis ..... September 1, 1998–January 1, 1999
  13. Incorporate results into plutonium structural database ..... January 1–April 30, 1999

In addition to these milestones, we will submit quarterly progress reports to the project office, make research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national or international meeting.

**Core Technology**  
**Actinide-Organic Interactions**  
**Work Breakdown Structure No.: 1.4.4**

**Date Issued:** November 8, 1996

**Principal Investigators:** Carol J. Burns  
Steven D. McKee

**Budget:** Fiscal Year 1997      \$250 K

**94-I IP Milestone:** Core Technology  
**R&D Plan:** 9.2.1.4

**Objective**

On this project Los Alamos National Laboratory researchers propose to provide a basic understanding of the interaction between actinide ions (primarily plutonium) and organic materials. Organic materials are defined as organic matrices (such as polymers and rubber) or soluble organic species (such as carboxylic acids). These materials are representative intermediates produced in several of the organic matrix destruction technologies that are under development for the 94-1 R&D Project. Knowledge about the nature of plutonium interactions with organic materials can aid in evaluating washing, matrix destruction, or other treatment technologies associated with combustibles.

**Scope**

A number of problems associated with combustible-type materials involve actinide residues in contact with an organic matrix. These problems result in questions about the effective treatment, storage, stabilization, and disposition of these residues. Efforts proposed to stabilize combustible-type materials include washing, immobilization, and matrix destruction. In this effort for fiscal year 1997 (FY97), we will focus on understanding the fundamental interactions between (1) plutonium and solid organic matrices and (2) the solution chemistry and complexation of plutonium with organic materials in aqueous solution.

In studies associated with plutonium residues and solid organic matrices, we initially will investigate three types of organic materials: plastics, filter-type materials, and cellulose-type materials. For FY97, the proposed schedule includes experiments involving surface characterization of organic matrices that are contaminated with actinides. Each matrix will be characterized according to chemical form of plutonium residue entrained, particle sizes and distribution, and possibility of plutonium residue removal by washing or some other process. We will explore speciation variation of the plutonium solution (for example, chloride, nitrate, or plutonium polymer). In addition, we will characterize matrices that are exposed to actinide solutions in order to determine the actinide uptake in the matrix. Porous materials, such as flow-through filters, are expected to have greater uptake. We expect such variables as solution pH, plutonium oxidation state, and contact time to affect actinide uptake. In addition, filter material, porous

size, and actinide species will be compared with each other; and correlations will be determined. These experiments will answer some fundamental questions about the mechanism of surface and matrix contamination.

Also scheduled to begin in FY97 are several solution studies on the complexation of plutonium with organic materials in aqueous solution. Two primary organic materials that we will explore are carboxylic acids and cellulose monomers. Carboxylic acids are proposed intermediates in a number of matrix-destruction technologies. Complexation of cellulose monomer could provide some additional information as it applies to the adsorption of plutonium solutions on a cellulose matrix (such as cheesecloth or Kimwipes®). The presence of plutonium and the process of complexation may inhibit organic destruction, especially under the nonequilibrium conditions found in a number of the matrix-destruction methods. Furthermore, we expect the oxidation state of plutonium to play a significant role in the complexation chemistry, and we will investigate this possibility. We propose to focus these initial solution experiments as they might evolve in mediated electrochemical oxidation. Investigating solution oxidation processes of the complexed organic group will be a supplement of this work.

### Benefits

Information gained on this task will support competency in actinide characterization, separation, and synthesis and will help develop the underlying science of actinide-organic interactions. This work has a direct bearing on the proposed solution treatment technologies under development to solve problems associated with combustible residues.

### Milestones

Actinide-Organic Interactions .....	October 1, 1996–September 30, 1997
1. Retrofit glovebox optical well .....	October 1–December 20, 1996
2. Install glovebox according to configuration management .....	October 1, 1996–September 30, 1997
3. Conduct surface characterization experiments .....	October 1, 1996–September 30, 1997
4. Complete plastics characterization .....	June 30, 1997
5. Complete cellulose characterization .....	September 30, 1997
6. Complete rubber characterization .....	September 30, 1997
7. Conduct actinide-uptake experiments of organic matrices .....	October 1, 1996–September 30, 1997
8. Conduct aqueous-solution actinide-organic oxidation experiments .....	March 3–September 30, 1997
9. Conduct aqueous-solution radiolytic-degradation and hydrolysis experiments .....	March 3–September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Corrosion**  
**Work Breakdown Structure No.: 1.4.5**

**Date Issued:** October 30, 1996

**Principal Investigator:** Darryl P. Butt

**Budget:** Fiscal Year 1997      \$350 K

**94-1 IP Milestone:** Core Technology

**R&D Plan:** 9.2.3.2

**Objective**

The objective of this proposed 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 site-specific corrosion (e.g., pitting and crack initiation). Los Alamos National Laboratory researchers hope to gain insight into the stochastic nature of corrosion and ultimately to improve the corrosion resistance of common materials through effective surface processing or through texturing.

**Scope**

We propose to examine the effects of crystallography on localized corrosion (pitting) and general corrosion (dissolution of surfaces) by coupling the scanning reference electrode technique with orientation imaging microscopy (OIM). These capabilities are unique to Los Alamos. Previous studies have focused on the corrosion behavior of single crystals with exposed low index planes. Our proposed study will make possible examination of real, polycrystalline engineering materials instead of the model single crystals that we examined previously. Also, we will examine all crystallographic orientations instead of a few chosen orientations. Depending on the results, subsequent tests could incorporate electrochemical studies on single crystals in order to further detail the electrochemical behavior of individual orientations of interest. Although this work is fundamental in nature, it has direct application to the 94-1 R&D Project initiative for, in particular, the storage of residues in containers. The studies are particularly relevant to the storage and processing of waste in stainless steel containers. In fiscal year 1996 (FY96), we focused much of our efforts on environments that simulate nitric acid/hydrofluoric acid waste-processing systems at Savannah River Site (SRS).

Our research will include the following activities:

- We will fabricate or modify the surfaces of polycrystalline materials in order to achieve desired microtexturing. Microtexturing will be accomplished using bulk processing methods, such as hot extrusion and hot pilgering, or surface modifications, such as laser surface treatments and high-energy particle deposition.

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- We will map the microtexture of these materials using our automated OIM, which provides two-dimensional maps of individual crystal orientations (including grain boundaries and defects) from automatic analysis of electron backscatter Kikuchi diffraction patterns.
  - We will subject specimens to environments that lead to selective attack, such as halide-rich aqueous solutions and residues relevant to the 94-1 R&D Project initiative.
  - We will characterize the pitting processes using ac and dc electrochemical spectroscopy and scanning reference electrode technology (SRET). The Los Alamos Materials Corrosion and Environmental Effects Laboratory has two SRET systems. With SRET we will map microgalvanic potentials on the surface of the metals (i.e., local corrosion phenomena).
  - We will superimpose maps of texture on maps of corrosion. Correlations will be made among texture and initiation and propagation of pits. These studies will show trends in the microstructure that either enhance corrosion resistance or trends that maximize the corrosion process. The trends that minimize corrosion can then be accentuated in the processing to minimize corrosion, or the trends that accentuate the corrosion process can be minimized during processing.

In FY96, we focused on characterizing the bulk effects of texture on selective attack. In fiscal year 1997 (FY97), we will focus on characterizing the effect of local grain orientation on initiation and propagation of surface pitting (including textured polycrystalline materials and single crystals in our study) and on environmentally assisted crack propagation. In the final year of this study, we will focus on optimizing materials texture for corrosion prevention.

Our research into the effects of crystallographic orientation on the electrochemical behavior of materials began in March 1996. The milestones described later were all completed by or before the specified dates, and a report summarizing the year's progress was completed by October 30, 1996. Initial efforts included a thorough literature review, materials selection (beryllium, nickel, and 304 stainless steel), and preparation of textured materials. We selected beryllium as a model material because of its high degree of anisotropy (hexagonal structure), nickel because of lack of evidence in the literature to suggest that texture affects the corrosion behavior of nickel, and 304 stainless steel because of its technological importance, specifically to processing plutonium-bearing solutions at SRS.

We prepared samples of each material. In the case of beryllium and 304 stainless steel, the samples were randomly oriented. In the case of nickel, we fabricated five foils that had varying predominant orientations.

We have performed preliminary electrochemical tests on all three materials. In each case, we observed a significant relationship between texture and selective attack (i.e., pitting morphology, etch pit formation, or repassivation potential). In the case of beryllium, we observed pronounced attack along basal planes. Upon completion of two beryllium specimens by OIM, we mapped out the microstructures. These samples will be carefully subjected to environments that induce pitting, and we will directly correlate sites of selective attack with grain orientation and mismatch. We have demonstrated in preliminary electrochemical experiments on nickel

exposed to chloride solutions that the repassivation potential, in particular, is strongly influenced by texture. These studies have progressed to a stage that warrants performing OIM, and samples are being prepared. In addition, we have recently discovered a narrow set of conditions in sodium chloride-nitric acid environments (representative of the solution processing chemistry at SRS) in which faceted corrosion pitting occurs in stainless steel. Studies are currently under way to assess the mechanism of this preferential attack.

### Benefits

Engineering materials have a variety of crystallographic orientations that often vary in susceptibility to localized corrosion. Our research will identify those varying susceptibilities and may lead to corrosion inhibition through preferential texturing of materials. More generally, the results would enhance the understanding of the stochastic nature of localized corrosion. These studies also could lead to mitigation of localized corrosion through reprocessing or surface treatments of materials in order to obtain specific textures. Corrosion inhibition will play an important role in the effective long-term storage of plutonium and other actinide residues.

### Milestones

Corrosion .....	October 1, 1996–September 30, 1998
1. Conduct scanning reference electrode tests coupled with orientation image analyses of common polycrystalline engineering materials .....	October 1, 1996–September 30, 1998
2. Conduct scanning reference electrode tests on single-crystal orientations of interest .....	January 30, 1997–September 30, 1998
3. Superimpose maps of texture onto maps of corrosion .....	July 30, 1997–September 30, 1998
4. Conduct surface-enhanced Raman spectroscopy of oxides on textured substrates .....	September 1, 1997–September 30, 1998
5. Set up and begin stress corrosion cracking studies .....	February 28, 1997–September 30, 1998
6. Report on second-year results .....	September 30, 1997
7. Correlate stress corrosion cracking propagation with orientation .....	August 31–September 30, 1998

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

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### **Program Leveraging and Collaborations**

This project has developed into a strong collaboration with researchers at SRS, who have technological interest in the effects of crystallographic orientation on the corrosion of piping systems that handle hazardous waste. Consequently, in FY96, SRS provided a portion of the funding for our research to the Los Alamos Nuclear Materials Division Advanced Technology Group and Materials Science and Technology Division Metallurgy Group. The project has also generated interest from universities such as Carnegie Mellon University and the University of California at Berkeley (UC Berkeley). Consequently, in FY97 and in fiscal year 1998, approximately \$35 K of this money will be sent to UC Berkeley for surface-enhanced Raman spectroscopy of single crystals. This small amount of money will strongly leverage the technical capabilities of Los Alamos and will fund one student's advanced degree.

**Core Technology**  
**Plutonium Diffusion Science**  
**Work Breakdown Structure: No. 1.4.6**

**Date Issued:** November 30, 1996

**Principal Investigator:** Pamela K. Benicewicz

**Budget:** Fiscal Year 1997      \$150 K

**94-1 IP Milestone:** Core Technology

**R&D Plan:** 9.2.3.3

### **Objective**

Los Alamos National Laboratory researchers on this project are seeking to measure and understand the diffusion of plutonium into materials such as stainless steel at room temperature over long time periods. Diffusion of plutonium into construction and storage materials may be a limiting factor in stabilization issues such as long-term storage and decontamination. The diffusion coefficient, the amount of material moving across a unit area per unit time, coupled with diffusion models, can be used to predict the diffusion of plutonium through materials.

Although plutonium diffusion coefficients have been measured at high temperatures for some materials, these results have not been verified experimentally for, for example, stainless steel at near room temperature. Extrapolation of diffusion coefficients obtained at high temperatures to ambient temperatures can lead to modeling errors of many orders of magnitude. Using experimental techniques that can measure small plutonium concentrations (less than parts per million) in small material thicknesses (less than a micron), we will determine plutonium diffusion coefficients in various metals. This work will result in much more accurate predicting of plutonium diffusion for specified time periods at near room temperature in materials relevant to issues of importance to long-term storage plans.

### **Scope**

In this project, we will determine the diffusion of plutonium through materials such as stainless steel, aluminum, and uranium. Plutonium diffusion coefficients will be determined by the use of both model systems and actual container systems that have housed plutonium for extended periods of time.

In fiscal year 1996, we performed scoping studies to identify appropriate surface-science techniques for determining room-temperature plutonium diffusion coefficients, and we completed a thorough literature search. The standard methodology for measuring diffusion coefficients is to cut away layers of material and analyze the layers for diffusing species by quantitative destructive analysis. This methodology works well for substantial material penetration in cases with large diffusion coefficients, as can be found at high temperatures. However, this methodology is not applicable for the small diffusion coefficients that will be determined by this study. The reason is that very small plutonium concentrations imbedded over a few microns must be

measured because of short time frames and low temperatures. Since model predictions at low temperatures over very long time periods are desired, accurate room temperature diffusion coefficients are needed.

We will use laser ablation spectroscopy as one depth-profiling technique to determine plutonium diffusion coefficients. With this technique, metal surface layers are removed as plutonium concentrations are measured. Similarly, secondary ion mass spectrometry (SIMS) will be used for depth profiling while measuring very low species concentrations.

### Benefits

With knowledge of plutonium diffusion depths and exposure times under appropriate conditions, we will determine diffusion coefficients that are directly applicable to container storage and decontamination issues. Our efforts will maintain readily accessible core actinide competency in materials science and will develop the underlying science for understanding actinide diffusion in relevant materials.

### Milestones

Plutonium Diffusion Science .....	October 1, 1996–September 30, 1997
1. Complete quarterly report .....	January 15, 1997
2. Complete analysis of initial samples using SIMS .....	October 1, 1996–January 31, 1997
3. Complete optimization of depth-profiling technique using laser-induced breakdown spectroscopy (LIBS) .....	October 1, 1996–February 28, 1997
4. Complete quarterly report .....	April 15, 1997
5. Complete analysis of initial samples using LIBS.....	March 3–July 31, 1997
6. Complete quarterly report .....	July 15, 1997
7. Make interim comparison of results obtained by the two techniques.....	January 31–September 30, 1997
8. Issue fiscal year 1998 experimental plan .....	September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Separations: Polymer Filtration**  
**Work Breakdown Structure No.: 1.4.7.1**

**Date Issued:** October 30, 1996

**Principal Investigators:** Barbara F. Smith  
Gordon D. Jarvinen

**Budget:** Fiscal Year 1997      \$300 K

**94-1 IP Milestone:** Core Technology—Efficient Separations  
**R&D Plan:** 9.2.2.1

### **Objective**

The polymer filtration process will remove actinides from solutions produced by recovery operations. The actinide levels in the treated solutions will be low enough to meet site-specific liquid discharge requirements. The objective of this core technology work to be done at Los Alamos National Laboratory is to further optimize the polymer filtration process by understanding key properties of the polymer. Properties to be studied include solubility, filterability, binding strength, and capacity—all at a molecular level and as functions of important parameters. Such important parameters include metal-ion loading, pH, concentration of polymer, speciation of the metal ion, and ionic strength.

### **Scope**

The technology baseline requirements of the 94-1 R&D implementation plan<sup>1</sup> include actinide removal from aqueous solutions in several areas of process development, including plutonium solutions (baseline requirement 4.3.3), plutonium-contaminated combustibles (4.3.4.4), and uranium (4.3.6). Robust actinide removal processes are needed for a variety of aqueous streams from low to high pH and from very dilute to high salt concentrations.

Polymer Filtration (PF) is a technology under development to selectively recover actinide metal ions from process or waste waters. The technology uses water-soluble metal-binding polymers that are specially designed to selectively bind with actinides in aqueous solutions. The polymers have a sufficiently large molecular weight so that they can be separated and concentrated using commercial ultrafiltration technology. Water and smaller unbound components of the solution pass freely through the ultrafiltration membrane. The polymers can then be reused by changing the solution conditions to release the actinide ions that are recovered in concentrated form for recycle or disposal. Some of the advantages of polymer filtration relative to technology now in use for actinide separations are rapid metal-binding kinetics, single aqueous phase, high throughput, high selectivity and capacity, low energy and capital costs, and small equipment footprint.

Because the metal-binding polymer is the key to the process, understanding the properties of the polymer is of utmost importance. Factors that affect polymer size, structure, stability, solubility, capacity, and binding constants need to be understood, controlled, and optimized.

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New approaches that directly characterize and probe the structure and binding sites of the polymers are necessary. New and cheaper synthetic approaches, along with simple quality assurance/quality control (QA/QC) methods, are required to help the materials become commercially available for use at nuclear facilities.

The scope of this project will include both short- and long-term goals, including fundamental studies directed toward application development over a time frame of more than 3 years.

The main applications include the following:

- plutonium/ameridium-containing streams,
- uranium-containing streams,
- neptunium-containing streams,
- mixed-waste streams, and
- preconcentration for on-line or at-line analysis.

The fundamental studies include the following:

- development of direct probing techniques to characterize metal-binding polymers;
- correlation of direct structural results with physical and chemical properties of the polymer for rapid QA/QC;
- rapid survey approach to evaluate many structural effects in order to obtain a structure-function relationship in the polymers;
- improved synthetic procedures for optimized polymers; and
- evaluation of polymers for designed application, including selectivity studies.

Polymer structural issues will have general application for all aqueous streams and waste-stream-specific issues. First we will evaluate polymer properties that are not waste-stream specific. For example, europium luminescence can be used to provide details on how the chemical functionalities present on these polymers coordinate to the trivalent actinide and lanthanide ions. This data will be pertinent to understanding the complex solution behavior exhibited by these materials and will provide fundamental mechanistic data that is critical to developing new polymers with enhanced metal-ion specificity and selectivity. We will also use Raman, infrared, laser scattering, and multinuclear magnetic resonance spectroscopy (multinuclear NMR) to directly probe the structure of the polymers and to provide information on the following:

- degree of functionalization of synthesized water-soluble polymers;
- rates of metal binding;

- number of different types of coordination environments present on the polymer;
- details of coordination geometry of various metal ions in different environments; and
- shape and size of these macromolecules in solution, as a function of factors such as ionic strength, metal-ion loading, pH, and temperature.

Developing a spectroscopic method that exploits the hypersensitive properties of the trivalent europium ion could provide a probe to characterize the performance of the polymers with actinides under actual process conditions. The divalent uranyl ion ( $\text{UO}_2^{2+}$ ) is also fluorescent and can give similar information about the binding of hexavalent actinides ( $\text{AnO}_2^{+2}$ ) to the polymers. Development may be possible for on-line, real-time measurements that simultaneously furnish information about metal-ion extraction, degree of polymer loading, and physical changes in the polymer as loading proceeds.

### Benefits

Work on this task will support competency and will develop the underlying science of advanced liquid-phase actinide separations. Polymer filtration technology can provide a cost-effective treatment for aqueous solutions that result from 94-1 stabilization program work and can yield effluents that meet increasingly stringent discharge requirements. For example, at Los Alamos, we are working to save millions of dollars in capital and operating costs for renovations to the Radioactive Liquid Waste Treatment Facility by using improved extraction technology to greatly reduce the transuranic content of waste streams from the Los Alamos Plutonium Facility. The polymer filtration technology is one of the advanced extraction technologies under evaluation in this effort. Our work will greatly accelerate the development of this technology and its application to the stabilization operations of the 94-1 implementation plan.

### Reference

1. "Research and Development Plan," U.S. Department of Energy Idaho Operations Office Plutonium Focus Area technical report DOE/ID-10561 (November 1996).

### Milestones

- |  |                                 |
|--|---------------------------------|
| Polymer Filtration .....   | June 3, 1996–September 30, 1997 |
| 1. Complete preparation of first systematic series of linear, as compared with branched, polyamine polymers having a range of molecular weights and functionalized at various levels ..... | June 3–28, 1996                 |
| 2. Initiate testing of appropriate water-soluble polymer for testing with larger-scale equipment for developing engineering model .....  | July 1–September 13, 1996       |
| 3. Complete characterization of the first series of polymers .....   | September 16–30, 1996           |
| 4. Complete preliminary size determinations, and conduct initial americium and plutonium binding studies .....   | September 16–30, 1996           |

### Milestones (continued)

5. Complete construction of apparatus for fluorescence studies ..... June 3–September 30, 1996
6. Initiate fluorescence spectroscopic evaluation of polymers ..... October 1, 1996
7. Complete initial evaluation of fluorescence spectroscopy for polymers ..... October 1, 1996–January 15, 1997
8. Complete initial evaluation of a series of polymers with Raman spectroscopy to determine usefulness of this technique as a direct probe of the polymer structure in solution ..... October 1, 1996–January 15, 1997
9. Complete development of improved synthetic methods for a series of polymers optimized for actinide bonding ..... January 15–June 30, 1997
10. Complete initial evaluation of multinuclear NMR as a direct probe of polymer structure and complexation reactions in solution ..... January 15–June 30, 1997
11. Initiate uranium and neptunium separation studies ..... August 1, 1997
12. Complete study to validate the use of polymer filtration as a preconcentration technique for analysis of ultralow actinide levels ..... September 30, 1997
13. Report actinide separation results ..... September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Separations: Polymer Foams**  
**Work Breakdown Structure No.: 1.4.7.2**

**Date Issued:** October 30, 1996

**Principal Investigators:** Gordon D. Jarvinen  
Betty S. Jorgensen  
Daniel J. Kathios  
Brian C. Benicewicz

**Budget:** Fiscal Year 1997      \$300 K

**94-I IP Milestone:** Core Technology—Efficient Separations  
**R&D Plan:** 9.2.2.2

### **Objective**

For recovery of radioactive species from DOE waste streams, technologies that are faster, more efficient, and less productive of waste are needed. The polymer foam materials to be developed in this research represent a dual-use technology that can reduce costs of separations, and reducing costs are important both to DOE sites and to industry. Specific sites of the DOE complex where these new technologies are needed include Los Alamos National Laboratory, Rocky Flats Environmental Technology Site, Idaho National Engineering Laboratory, Savannah River Site, and Hanford Site. 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 that tend to lower their efficiencies, including packing instability, liquid channeling through the bed, slow sorption or desorption kinetics, and less usable surface area. Our goal in this research at Los Alamos is to overcome these problems by developing advanced microcellular polymeric foams that will be beneficial to the Defense Nuclear Facilities Safety Board 94-1 stabilization effort.

### **Scope**

**Graft-Polymerization of Ligands.** We will functionalize the foams using a variety of actinide-selective groups. One of the most promising approaches for increasing the capacities of the foams to levels much greater than can be found in beads is to graft-polymerize ligands to the surface of the foam. A free-radical initiation site that is capable of initiating polymerization of vinyl type monomers is placed on the chloromethylstyrene. Monomers that will be grafted include vinylpyridine, vinylphosphonic acid, and chloroethylvinylphosphonate. In addition, in collaboration with Dr. Spiro Alexandratos at the University of Tennessee, we will attempt graft-polymerization of diphosphonic acid monomers. We will also perform copolymerizations of monomers, such as vinylpyridine and vinylphosphonic acid, for dual functionality; or we may use the comonomers as spacer groups to provide optimum metal-ion binding.

**Polyvinylpyridine Foams.** Quaternized polyvinylpyridine resins (Reillex<sup>HPQ</sup>) are currently used in plutonium processing. They have superior separation properties, resistance to nitration, and

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high radiation stability.<sup>1</sup> It may be possible to make quaternized polyvinylpyridine foams similar to the Reillex resins. A potential problem to overcome is that the vinylpyridine monomer is hydrophilic and tends to destabilize the foam emulsion.

**Plutonium Uptake Experiment.** We will use the functionalized foams for plutonium uptake studies. The study will include sorption and desorption kinetics and plutonium uptake in solutions with varying pH.

**University Collaboration.** Dr. Alexandratos and his group have prepared resin beads containing diphosphonic acid functionalities. They will prepare foams that contain a similar functionality and compare them with the beads. In addition, the group will perform studies involving graft-polymerization of the diphosphonic acid monomer prepared by Dr. Alexandratos. Studies involving phosphonic acid esters will also be initiated. Previous work showed that phosphonic acid esters, when used on resin beads, are too hydrophobic for aqueous solutions, but the open structure of foams allows better access and metal-ion binding. However, phosphonic acid esters have the advantage of providing higher selectivity than phosphonic acids.

**Deliverables.** We plan to carry out the following activities within the scope of this research:

- produce styrene/chloromethylstyrene foams with grafted ligands for actinide uptake;
- study plutonium uptake using foams;
- investigate feasibility of preparing polyvinylpyridine foams;
- participate in 1997 Core Technology Review by the technical advisory panel;
- make presentation at the Methods and Applications of Radioanalytical Chemistry MARC IV Conference in April 1997 or at another such conference; and
- provide input for quarterly reports.

### **Benefits**

Work on this task will support competency in actinide separations and materials science and help develop the underlying science of advanced actinide liquid separations.

Microcellular polymer foam technology can potentially revolutionize the way most column separations are performed with organic solid sorbents. Specific application to process and waste streams that result from plutonium operation will provide a very useful demonstration of this technology, which has very broad industrial potential. The polymer foam material can provide a cost-effective treatment for aqueous solutions that result from 94-1 stabilization work and can yield effluents that meet increasingly stringent discharge requirements. The work proposed in this effort will greatly accelerate development of this technology and its application to the 94-1 R&D Project mission.

### **Reference**

1. S. F. Marsh, "Evaluation of a New Macroporous Polyvinylpyridine Resin for Processing Plutonium Using Nitrate Anion Exchange," Los Alamos National Laboratory report LA-11490 (April 1989.)

### Milestones

- Polymer Foams ..... October 1, 1996–September 30, 1998
1. Complete first set of actinide removal experiments ..... October 1–December 13, 1996
  2. Prepare and characterize polystyrene/chloromethylstyrene foams ..... January 1–March 31, 1997
  3. React foams and characterize resulting materials ..... April 1–July 31, 1997
  4. Complete second set of actinide uptake experiments ..... July 31, 1997
  5. Prepare and characterize polyvinylpyridine foams ..... August 1–September 30, 1997
  6. Prepare and characterize polyfunctional foams ..... August 1–September 30, 1997
  7. Select industrial partner ..... September 30, 1997
  8. Optimize actinide-selective foams ..... October 1, 1997–March 31, 1998
  9. Functionalize chloromethylstyrene foams ..... October 1, 1997–March 31, 1998
  10. React foams and characterize resulting materials ..... April 1–September 30, 1998
  11. Complete third set of actinide uptake experiments ..... September 30, 1998

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Materials Science: Thermodynamics**  
**Work Breakdown Structure No.: 1.4.8.1**

**Date Issued:** October 15, 1996

**Principal Investigators:** Mark A. Williamson  
John Y. Huang

**Budget:** Fiscal Year 1997      \$200 K

**94-1 IP Milestone:** Core Technology—Thermodynamics

**R&D Plan:** 9.2.3.1

**Objective**

The Los Alamos National Laboratory thermodynamics project has two major objectives in fiscal year 1997 (FY97). The first objective is to obtain data on vaporization thermochemistry for species of interest to researchers on the salt distillation project, including alkali halides and actinide oxyhalides, and to apply the results collected both in fiscal year 1996 (FY96) and FY97 to model and understand the distillation process. The second primary objective is to obtain thermodynamic data, including vaporization data, for materials of interest relative to plutonium stabilization and disposition and to apply the results to developing efficient fabrication and processing techniques.

**Scope**

We will use results from the experimental studies to model and to understand the salt distillation process used to separate plutonium dioxide from select chloride salt mixtures. We will conduct experiments on the vaporization behavior of actinide (i.e., plutonium and americium) oxychlorides, using high-temperature mass spectrometry; and we will report on the thermochemistry of these two compounds. Actinide oxychloride/mixed alkali chloride mixtures will be similarly studied. Such studies will enable us to do detailed modeling of the distillation process.

In order to model material processing, we will use experimentally determined phase stability data for plutonium-doped zirconium silicate. High-temperature mass spectrometry and other thermal analysis techniques will be used to establish the phase behavior and stability of plutonium-doped zirconium silicate.

Support also will be provided as needed for other 94-1 R&D Project tasks, such as oxide storage and thermal modeling of storage containers.

**Benefits**

Work on this task supports competency in actinide separations, thermodynamics, and materials science and develops the underlying science of high-temperature actinide chemistry. For example, researchers in current salt distillation technology have shown excellent separation of

plutonium dioxide from chloride salt mixtures. Researchers have done some modeling of the process, although the validation experiments were at a rather crude, integrated level and did not take all the vapor species into account. High-temperature mass spectrometry experiments initiated in FY96 will provide data on the stabilities and vaporization processes for plutonium oxychloride (PuOCl) and mixed alkali halides. Experiments completed in FY97 will provide similar data for americium oxychloride (AmOCl). These data should enable us to do detailed modeling of the vaporization process and should point the way toward process optimization.

Central to the optimization of fabrication and processing techniques used for plutonium stabilization, or disposition, is an understanding of the thermodynamic stability and phase equilibria of the material that contains the plutonium. We will investigate plutonium-doped zirconium silicate by high-temperature mass spectrometry and complementary techniques (e.g., differential thermal analysis and differential scanning calorimetry). The thermodynamic data from these studies, combined with the results of materials science studies (i.e., mineral waste forms), should enable us to perform detailed process modeling and optimizing.

### Milestones

Thermodynamics .....	October 1, 1996–September 30, 1997
1. Complete experimental studies on vaporization behavior of PuOCl .....	October 1, 1996–January 3, 1997
2. Prepare and issue report on thermochemistry of PuOCl .....	January 3–February 14, 1997
3. Complete experimental studies on vaporization behavior of AmOCl .....	January 3–March 28, 1997
4. Prepare report on thermochemistry of AmOCl .....	March 28–May 9, 1997
5. Issue AmOCl report .....	May 9, 1997
6. Complete experimental studies on vaporization of mixed halides .....	April 1–June 13, 1997
7. Prepare report on modeling of salt distillation process .....	June 13–July 10, 1997
8. Issue report on modeling of salt distillation process .....	July 10, 1997
9. Complete experimental studies on vaporization of plutonium-zirconium silicate solid solutions .....	June 13–September 1, 1997
10. Prepare report on phase stabilities of zircon materials .....	September 1–30, 1997
11. Issue report on phase stabilities of zircon materials .....	September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Materials Science: Mineral Waste Forms**  
**Work Breakdown Structure No.: 1.4.8.2**

**Date Issued:** November 5, 1996

**Principal Investigator:** John Y. Huang

**Budget:** Fiscal Year 1997      \$150 K

**94-1 IP Milestone:** Core Technology

**R&D Plan:** 9.2.3.5

### **Objective**

The actinide elements thorium and uranium are found in orthosilicate neutral minerals. Thorium orthosilicate forms tetragonal thorite and monoclinic huttonite; uranium orthosilicates form tetragonal coffinite. These tetragonal orthosilicates are isostructural with zircon ( $ZrSiO_4$ ). Zircon, because of its durability ( $\sim 10^9$  years) in geologic environments, has been proposed as a host mineral for deep borehole burial of high-grade plutonium that has been recovered from dismantled nuclear weapons. Because other tetravalent actinides, including neptunium, plutonium, and americium, have slightly smaller ionic radii than thorium and uranium do, these actinides can be substituted for zirconium in the zircon structure. Indeed, in small-scale syntheses, zircon has been doped successfully with up to 10 wt % plutonium; and plutonium silicate with zircon structure has been synthesized on a laboratory scale. The objective of Los Alamos National Laboratory researchers is to develop a material containment system for processing plutonium-bearing zircon under high-temperature and high-pressure conditions and to determine optimal parameters for processing 100-g batches of plutonium-zircon.

### **Scope**

Researchers at Los Alamos will investigate container systems that can withstand temperatures near  $1500^\circ\text{C}$ , that can be compressed isostatically at pressures near 10,000 psi, and that are inert to reaction mixtures. The reaction mixtures will initially consist of stoichiometric amounts of zirconium oxide ( $ZrO_2$ ) and silicon dioxide ( $SiO_2$ ) powders for the synthesis of zircon. For the processing, we will use the Hot Isostatic Press (HIP) at the Los Alamos Plutonium Facility (TA-55). The reaction products will be characterized by x-ray powder diffraction and other chemical analytical tools in order to determine phase and chemical compositions. We will examine the container systems for potential causes of problems. Once a suitable container system is found, reaction mixtures containing plutonium oxide ( $PuO_2$ ) and  $SiO_2$  powders will be used to synthesize plutonium silicate ( $PuSiO_4$ ) under similar conditions. After successful syntheses, we will mix zircon and  $SiO_2$  powders in different proportions in order to determine the solubility limit of plutonium in zircon.

## Benefits

This task supports actinide competency in thermodynamics, synthesis, materials science, and pyrochemistry. We will develop the underlying science of actinide silicate synthesis. The results of this work should (1) allow an estimate of the solubility limit, and, therefore, the optimum loading of plutonium in zircon; and (2) provide parameters for safe preparation of a very stable waste form for short- and long-term disposition of excess plutonium from weapons.

## Milestones

Mineral Waste Forms .....	October 1, 1996–September 30, 1997
1. Complete development of material containment system .....	October 1, 1996–February 14, 1997
2. Complete preparation and characterization of zircon .....	February 17–March 14, 1997
3. Complete initial preparation and characterization of plutonium silicate .....	March 17–June 13, 1997
4. Determine solubility limit of plutonium in zircon .....	June 16–September 12, 1997
5. Issue report on plutonium-zircon process parameters .....	September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
Synthesis and Structural Characterization  
of Plutonium(IV) and Plutonium(VI) Phosphates  
**Work Breakdown Structure No.: I.4.9**

**Date Issued:** November 30, 1996

**Principal Investigators:** Wolfgang H. Runde  
D. Kirk Veirs

**Academic Collaborators:** Bryan W. Eichhorn (University of Maryland at College Park)  
Barry Scheetz (Pennsylvania State University)

**Budget:** Fiscal Year 1997      \$125 K

**94-1 IP Milestone:** Core Technology  
**R&D Plan:** 9.3.1

**Objective**

Phosphate coordination plays a significant role in actinide chemistry and can be used to stabilize plutonium. For example, in underground storage of high-level radioactive waste, phosphate minerals are considered as potential secondary barriers or backfill materials to reduce actinide solubility and to enhance adsorption of radionuclides. These conditions are believed to be true because of the high affinity of these materials for actinides and the low solubility of actinide phosphate minerals in ground water. The same properties offer potential benefit in 94-1 stabilization efforts.

Despite the importance of actinide phosphate compounds, surprisingly little is known about structure, bonding, stability, and spectroscopic properties of these compounds. Compounds studied to date have been obtained by precipitation, under atmospheric conditions, of actinide ions from aqueous solution. The compounds can be grouped into two general categories: (1) binary phases described by varying ratios of actinide (or actinyl) and phosphate, and (2) ternary phases described by varying ratios of actinide (or actinyl) phosphate and *M*, in which *M* is an alkali or alkaline-earth ion. Although only two plutonium phosphate structures have been fully characterized, the structural and chemical diversity within these compounds is quite remarkable. This chemical diversity is because of the various actinide coordination numbers (6 to 9) and oxidation states (+III to +VI) and because of the  $\eta^1$  and  $\eta^2$  binding modes of the phosphate ligands that occupy lattice sites to generate one-, two-, and three-dimensional frameworks. These varying structural properties will influence a wide range of physical properties such as solubility, leachability, and radiation resistance.

The objective of Los Alamos National Laboratory researchers is to develop a better understanding of plutonium phosphate chemistry through synthesizing and characterizing plutonium phosphate compounds and through investigating the chemical behavior of these compounds under radiolysis and aqueous conditions. Well-characterized plutonium phosphate compounds

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produced in this work can be used to support plutonium solubility studies in the Savannah River Technology Center (SRTC) core technology task directed at nitric/phosphoric acid treatment of organics.

### **Scope**

Los Alamos personnel will focus their initial efforts on synthesis and structural characterization of solid Pu(VI) and Pu(IV) phosphates. We will perform scoping experiments using uranium in the +IV and +VI oxidation state to establish a synthesis baseline and stability range of binary and ternary Pu(IV) and Pu(VI) phosphates. We will employ conventional processes, such as precipitation from aqueous solutions, solution-based sol-gel preparation, and hydrothermal reactions of solids to prepare binary and ternary solid uranium and plutonium phosphate compounds. All solids will be characterized by powder x-ray diffraction, infrared, diffuse reflectance, Raman, and x-ray absorption spectroscopies. The spectroscopic signatures of solid phosphate compounds can be used to assist in the characterization of uranium and plutonium complexes that are formed in solution. We will use single-crystal x-ray diffraction as is appropriate. Rietveld powder x-ray diffraction analysis will be applied to the characterization of structural isotopes of plutonium phosphate compounds.

The characterization and determination of structure and composition of the plutonium compounds that are prepared as described will support the nitric acid-phosphoric acid work being performed at SRTC. We observed naturally occurring binary phosphates that contain large fractions of uranium dioxide ( $\text{UO}_2$ ) and thorium dioxide ( $\text{ThO}_2$ ) to be highly crystalline and resistant to geochemical and geophysical alteration. Consequently, we will study the radiation damage resistance of the synthetic binary and ternary phosphates with x-ray diffraction after these materials have been subjected to ion-beam irradiation. The dissolution characteristics of the radiation-damaged matrices will be evaluated with a continuous flow-through reactor.

### **Benefits**

Work on this project will support actinide core competency in separations, thermodynamics, and synthesis. Researchers in this program will develop understanding of plutonium phosphate chemistry in solution and in solid state. Our academic collaborators, Prof. Bryan Eichhorn of the University of Maryland at College Park, and Prof. Barry Scheetz of Pennsylvania State University, are internationally recognized for their work in synthesis and structural characterization of multicomponent transition metal phases. The results and methodology of this study will support development of methods to separate plutonium from concentrated phosphoric acid solutions.

### Milestones

- Plutonium (IV)/(VI) Phosphates ..... October 1, 1996–September 30, 1998
1. Complete synthesis and characterization  
of binary U(VI) phosphates ..... October 1, 1996–March 28, 1997
  2. Complete synthesis and characterization  
of binary Pu(VI) phosphates ..... April 1–July 31, 1997
  3. Complete structural and compositional  
characterization of ternary U(VI) and  
Pu(VI) phosphates ..... August 1–September 30, 1997
  4. Complete synthesis and characterization  
of binary U(IV) phosphates ..... September 30, 1997–March 30, 1998
  5. Complete synthesis and characterization  
of binary Pu(IV) phosphates ..... March 31–July 30, 1998
  6. Complete structural and compositional  
characterization of ternary U(IV) and  
Pu(IV) phosphates ..... August 3–September 30, 1998

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
**Plutonium Phosphate Solution Chemistry**  
**Work Breakdown Structure No.: 1.4.10**

**Date Issued:** November 30, 1996

**Principal Investigator:** David G. Karraker (Savannah River Site)

**Budget:** Fiscal Year 1997      \$100 K

**94-1 IP Milestone:** Core Technology

**R&D Plan:** 9.3.6

**Objective**

Savannah River Site (SRS) researchers will study the chemistry of plutonium in concentrated phosphoric acid ( $H_3PO_4$ ) with the goal of developing a process for the recovery of plutonium from these solutions. The physical properties of these solutions will also be investigated. Researchers will also explore synthesis of ternary phosphates from solution and synthesis of organic acid-phosphoric acid complexes of plutonium. Phosphoric-nitric acid solutions are the basis of a process being investigated in a separate 94-1 R&D Project stabilization process development task for destroying organic-based glovebox waste. Our investigations are aimed at developing the fundamental knowledge of plutonium behavior to support process applications.

**Scope**

Previously researchers have investigated relatively dilute solutions in studying the chemistry of plutonium in  $H_3PO_4$  solutions. The focus of our work is on the properties of plutonium in concentrated (85 wt %, 14.7 M)  $H_3PO_4$ . The solubility of Pu(IV) and Pu(III) in these solutions is on the order of 0.6–1.0 M and the solutions are quite viscous. One of our goals is the exact measurement of solubility and viscosity properties.

Researchers will study methods of precipitating plutonium from 85%  $H_3PO_4$ . Two methods in particular appear attractive. These methods are (1) precipitation of a mixed plutonium phosphate-organic ligand, such as Pu(IV) oxalato-phosphate, and (2) precipitation of a ternary phosphate, such as a calcium-plutonium phosphate.

A practical goal of this work is to develop a method for recovering plutonium from the  $H_3PO_4$  waste solutions generated by phosphoric acid-nitric acid solutions that are used to destroy glovebox waste. This process, in essence "wet-ashing," shows promise for oxidizing such materials as paper, plastics, and rubber that are generated during the glovebox production operations. The solubility of plutonium in the presence of organic oxidation products (such as oxalic acid, formic acid, and acetic acid) may limit the process, and a method for recovery of the plutonium from the  $H_3PO_4$  solution is desirable in order to reduce the volume of waste.

In this program researchers will also investigate the effects of organic acids on plutonium solubility.

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### Benefits

The destruction of contaminated organic matter by wet-ashing in  $H_3PO_4$  is a promising method for reducing glovebox waste. The benefit of this study is to explore chemical and physical parameters that are important to the wet-ashing process and specifically to examine plutonium recoverability.

### Milestones

- Plutonium Phosphate Solution Chemistry ..... October 1, 1996–September 30, 1997
1. Complete studies on the precipitation of plutonium by organic precipitants from concentrated  $H_3PO_4$  solutions and characterize solid phases produced ..... October 1, 1996–August 29, 1997
  2. Complete investigation of plutonium coprecipitation with inorganic phosphates ..... October 1, 1996–August 29, 1997
  3. Characterize physical properties of plutonium phosphate solutions at elevated temperatures ..... October 1, 1996–September 30, 1997
  4. Develop process for recovery of plutonium from concentrated  $H_3PO_4$  solutions ..... September 30, 1997

Progress will be reported quarterly (January, April, July, and October). The goal is to complete the major part of the program during 1997. Significant results will also be reported at technical meetings and in technical publications.

**Core Technology**  
**Molten Salt/Nonaqueous Electrochemistry**  
**Work Breakdown Structure No.: 1.4.11**

**Date Issued:** October 20, 1996

**Principal Investigator:** Wayne H. Smith

**Budget:** Fiscal Year 1997                      \$ 125 K

**94-1 IP Milestone:** Core Technology

**R&D Plan:** 9.3.2

**Objective**

The purpose of this Los Alamos National Laboratory work is to fully characterize the chemical behavior of actinide elements in room-temperature molten-salt solvent systems. Such characterization will accomplish the following:

- develop a deeper understanding of the fundamental properties of selected actinide elements, e.g., uranium, plutonium, americium, thorium, and neptunium; and
- develop advanced actinide purification and separation schemes.

Many of the current actinide recovery and purification processes are based on redox chemistry carried out in high-temperature (600°C–700°C) molten-salt systems. However, very little is known about the kinetics and mechanisms of the chemical reactions involved, mainly because of the difficulty in making accurate measurements under these high-temperature conditions.

Room-temperature molten salts (RTMSs), comprised of a mixture of aluminum trichloride and selected organic chloride salts, are liquid at or slightly above room temperature. These solvents are highly conducting and have a very wide potential window, ~ 4.5 V (compared to ~ 1.2 V potential window in aqueous solutions), which makes them ideal for investigating the electrochemical behavior of metal ions and complexes. The solvents are also moisture and oxygen free, conditions that eliminate hydrolysis and oxide formation and allow for the stabilization of very high oxidation states. In addition, these solvents have a very wide spectroscopic window, from the ultraviolet through the near infrared. This wide window allows for spectral characterization of elements in various oxidation states and in varying degrees of complexation. We expected that measurable chemical behavior of actinide elements in the room-temperature chloride-based molten-salt systems would be exactly analogous to the behavior in the elevated temperature systems currently in use.

**Scope**

The first system to be investigated will be uranium in an aluminum trichloride/methyl-ethylimidazolium chloride (MEIC) melt. Uranium has been studied previously in other RTMS systems. We will compare results between those obtained in the MEIC system studies to those obtained in the previous research that has been reported in the literature.

Our research will serve as a basis for comparison to all other actinide elements under investigation. In the uranium study, we will characterize in a variety of melt conditions, from acidic to alkaline, the electron transfer reactions of all accessible oxidation states. Information obtained in this part of the study will be used to calculate the degree of complexation between the free chloride ion in the melt and the actinide element.

Also included in this research will be the synthesis and electrochemical and spectroscopic characterization of the mono-oxo and di-oxo uranium complexes. The oxo- complexes have never been completely characterized principally because of the instability of the mono-oxo complex in other solvent systems. With fully characterized uranium as a baseline, we will address other actinide elements chosen for this research, beginning with plutonium.

Because this project is a new Los Alamos research thrust, initially we will give some effort to the procurement of chemicals and supplies that are necessary to establish an RTMS capability. Also, two people, the principal investigator and a postdoctoral fellow, will work on this project. The postdoctoral position will be filled at the earliest possible date.

### Benefits

The RTMS solvent system for the complete electrochemical and spectroscopic characterization of actinide elements in an oxygen- and moisture-free environment. The results of this study will significantly enhance our understanding of the chemical behavior of actinides and may lead to next-generation recovery and purification processes. We will expand our knowledge of the science underlying the pyrochemical separation processes that use molten salts as solvent systems and in electrochemical technology.

### Milestones

Molten Salt/Nonaqueous Electrochemistry .....	October 1, 1996–September 30, 1997
1. Recruit and hire a postdoctoral fellow .....	October 1, 1996–January 2, 1997
2. Set up RTMS capability .....	October 1–December 30, 1996
3. Issue quarterly report .....	January 2, 1997
4. Study chemical behavior of uranium in RTMS system .....	January 2–July 1, 1997
5. Issue quarterly report .....	March 31, 1997
6. Publish results of uranium study in refereed journal .....	July 1, 1997
7. Issue quarterly report .....	July 1, 1997
8. Present results of uranium study at American Nuclear Society meeting .....	August 25, 1997
9. Study chemical behavior of near actinides in RTMS .....	July 1, 1997–September 30, 1997
10. Issue quarterly report .....	September 30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make our research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

**Core Technology**  
Improved Methods for the Detection of  
Alpha-Emitting Isotopes in the Environment  
**Work Breakdown Structure No.: 1.4.12**

**Date Issued:** November 30, 1996

**Principal Investigator:** Dale D. Ensor (Tennessee Technological University)

**Budget:** Fiscal Year 1997      \$40 K

**94-I IP Milestone:** Core Technology

**R&D Plan:** 9.3.4

### **Objective**

Current DOE activities for stabilization of fissile materials require a fundamental knowledge of the separation and the analytical chemistry of actinides. The traditional method for determining alpha emitters relies on alpha spectroscopy using surface barrier detectors. This method offers excellent energy resolution but requires time-consuming sample preparation to eliminate interfering radiological and chemical components. Tennessee Technological University researchers on this project will utilize a Photon Electron Rejecting Alpha Liquid Scintillation (PERALS®) spectrophotometer in combination with extractive scintillators. Their purpose is to develop faster, more sensitive procedures for determining alpha emitters in process waters and waste waters associated with the stabilization project.

### **Scope**

The PERALS spectrometer offers a number of advantages for determining alpha emitters. The system is a commercially available instrument designed specifically for alpha liquid scintillation. Using electronic pulse-shaped discrimination, the PERALS system can reject beta and gamma pulses with 99.9% efficiency. The system offers a very low background (0.001 becquerels [Bq]), thus providing the sensitivity necessary for the low activity found in treated waste water (0.04 Bq) and for the discharge requirements of process water (1.85 Bq) at Rocky Flats Environmental Technology Site. The liquid scintillation system is configured to yield a 99.7% counting efficiency. The energy resolution, although not as good as a surface barrier detector used for alpha spectrometry, is sufficient to quantify isotopes such as  $^{238}\text{U}$  and  $^{234}\text{U}$ . Further analysis of the spectra with curve-fitting procedures can improve the isotopic information available from the liquid scintillation spectra.

The currently available procedures for preparing extractive scintillators is based on traditional methods. For example, ALPHAEX® effectively extracts actinides from slightly acidic media. This product efficiently extracts uranium, thorium, plutonium, and americium; but it is not selective. The presence of any organic material also greatly inhibits the extraction. Developing a selective extractant scintillator that functions in nitrate media and offers good separation of various actinides, by control of pH, will intensify interest in the use of the PERALS system. This scintillator would simplify sample preparation for determining alpha emitters in process and treated

waste streams. A second area of interest is the application of solid exchangers to developing better and more efficient separation procedures before counting. Initial studies will include the use of chromatographic material in concentrating and separating the alpha emitters of interest. Materials such as Tru-SPEC™ and U-SPEC™ that are available from EICHROM Industries would be studied.

### Benefits

Using PERALS to determine alpha-emitting isotopes promises to be faster, more efficient, and more sensitive than current methods. The results of this work will add to the analytical and separation knowledge base of actinide solution chemistry. This project will support the training of at least two undergraduate and/or graduate students in actinide research. This project will provide new techniques to measure actinides at low concentrations, give training for students, and reduce the overall time and cost of measuring alpha emitters.

### Milestones

Alpha Isotope Monitoring .....	March 3–September 30, 1997
1. Complete evaluation of more selective extractants for the PERALS system .....	March 3–April 1, 1997
2. Complete testing of curve-fitting procedures in order to improve isotopic information .....	April 1–May 30, 1997
3. Complete testing of commercially available resins in order to concentrate and separate isotopes .....	June 2–August 1, 1997
4. Complete studies on applying PERALS to plutonium process waste .....	August 1–September 1, 1997
5. Issue report on applying PERALS to aqueous low-level alpha waste .....	September 1–30, 1997

In addition to these milestones, we will submit quarterly progress reports to the project office, make research results available for the Core Technology Review, and complete at least one peer-reviewed publication and/or presentation for a national meeting.

## I.5.0 Project Management

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**Project Management  
Infrastructure Support  
Work Breakdown Structure No.: 1.5.1**

**Date Issued:** October 1, 1996

**Principal Investigator:** Steven D. McKee

**Budget:** Fiscal Year 1997      \$2200 K

**94-1 IP Milestone:** Not Applicable (NA)

**R&D Plan:** NA

**Objective**

The objectives of this work are as follows:

- to provide the resources and systems required to support the 94-1 R&D Project-related technical operations at the Los Alamos National Laboratory Plutonium Facility (TA-55), including materials control and accountability, vault operations, training, access control, and waste management;
- to provide health and safety oversight for all TA-55 safety activities;
- to furnish radiological control technicians for all research, demonstration, and testing (RD&T) activities;
- to provide industrial hygiene, industrial safety, criticality safety, emergency response, and medical services to TA-55 personnel;
- to provide physical security for the nuclear materials facilities at TA-55; and
- to provide the infrastructure, integrated project planning and tracking, authorization basis, and support activities.

**Scope**

We will manage the special nuclear materials (SNMs) at TA-55 in compliance with DOE orders and with state and federal regulations. We will provide the training required to conduct RD&T activities at TA-55. Another part of the project will be to design and develop training programs for health and safety, safeguards and security, emergency procedures, and conduct of operations to ensure that these programs meet the appropriate regulations. We will also have the responsibility to handle hazardous and radioactive waste at TA-55 in an environmentally responsible manner, ensuring the safety of workers and of the public. We will maintain TA-55 compliance with applicable DOE waste management orders; federal, state, and local regulations; and Laboratory policies and procedures for waste handling and disposal. Finally, we will provide guidance on waste minimization, identification, preparation, and documentation, as well as on certifying, handling, packaging, documenting, and preparing wastes for shipment.

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### **Benefits**

The scope of work outlined in infrastructure support provides the 94-1 R&D Project with access to a fully functioning Category I facility that can handle RD&T activities essential in meeting the 94-1 R&D Project commitments.

**Project Management  
Administration  
Work Breakdown Structure No.: 1.5.2**

**Date Issued:** October 1, 1996

**Principal Investigator:** Steven D. McKee

**Budget:** Fiscal Year 1997      \$1500 K

**94-1 IP Milestone:** Not Applicable (NA)

**R&D Plan:** NA

**Objective**

The objectives of this work are as follows:

- project management,
- program office support, and
- off-site personnel support.

**Scope**

**Project Management.** The project managers will establish an effective project management system for this program. They will develop the program tracking and reporting system based on the work breakdown structure. Responsibilities include, but are not limited to, the following:

- plan all tasks necessary to meet program requirements;
- establish project teams and develop work packages with technical objectives, scope, benefits, schedules, and budgets;
- monitor all project activities, identifying any deficiencies and deviations from the plan and ensuring that actions are taken to resolve them;
- provide periodic status reports to the program manager;
- design review reports, interim technical reports, and a final technical report at the completion of a project; and
- coordinate activities to meet customer needs.

**Program Office Support.** Support will come from the Nuclear Materials and Stockpile Management Program director, deputy director, and their staff, including the program manager for nuclear materials stabilization and disposition. Financial support, secretarial support, and specialized financial and accounting assistance and information needed to forecast and control costs for the program also will be provided.

**Off-Site Personnel Support.** Los Alamos National Laboratory will provide support directly to the Nuclear Materials Stabilization Task Group (NMSTG) by funding technical staff in the NMSTG office at DOE Headquarters. These personnel are under the direct supervision of the NMSTG office during their stay in Washington.

### Benefits

A successful program must have successful project management. Communication is an essential component.

### Milestones

#### Administration of Fiscal Year 1997 (FY97)

- |  |                                  |
|--|----------------------------------|
| 94-1 R&D Project .....   | October 1, 1996–November 3, 1997 |
| 1. Complete FY97 technical program plan .....  | October 1–December 31, 1996      |
| 2. Issue FY97 first quarterly report.....  | February 1, 1997                 |
| 3. Conduct technical advisory panel (TAP)<br>core technology review .....                    | February 13, 1997*               |
| 4. Issue FY97 second quarterly report.....   | May 1, 1997                      |
| 5. Conduct mid-year program review .....   | April 1–May 30, 1997**           |
| 6. Assist TAP/Plutonium Focus Area<br>in R&D plan revisions for fiscal year 1998 (FY98)..... | June 2–August 29, 1997           |
| 7. Solicit proposals for FY98<br>technical program plan.....                                 | June 2–August 29, 1997           |
| 8. Draft FY98 technical program plan.....  | September 1–30, 1997             |
| 10. Issue FY97 third quarterly report .....  | August 1, 1997                   |
| 11. Issue FY97 fourth quarterly report .....   | October 15, 1997                 |
| 12. Issue FY98 technical program plan .....  | November 3, 1997                 |

\* Tentative schedule based on best available information

\*\* Los Alamos internal project review of FY97 program to begin FY98 draft of technical program plan

## Appendix A



### Detailed Schedules

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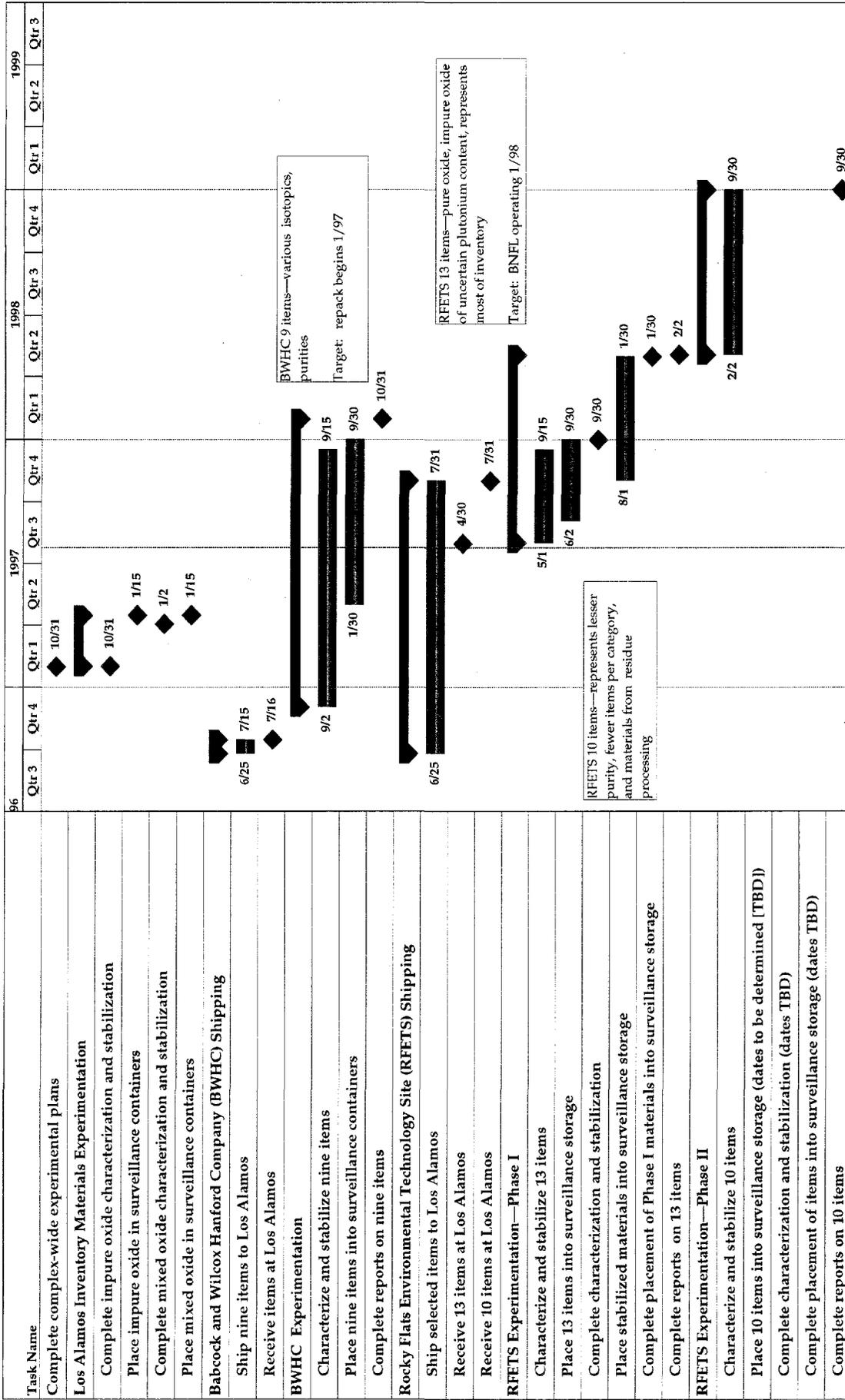
## TEXT COLORS

Black = Task

Blue = Activity

Orange = Milestone

# Materials Identification and Surveillance



Task  
Progress

Baseline Milestone

Baseline Milestone Summary

Baseline Summary

# Materials Identification and Surveillance (Continued)

Task Name	96				1997				1998			
	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	
Savannah River Site (SRS) Shipping												
Prepare and ship selected materials to Los Alamos												
Receive items at Los Alamos												
SRS Experimentation												
Characterize metal materials												
Place alloys into surveillance containers												
Characterize and stabilize oxide materials												
Place stabilized oxide materials into surveillance storage												
Complete reports on 10 SRS items												
Oxide Studies—Thermal Profiles of BNFL Containers												
Prepare and load three BNFL containers with oxide for thermal profiles												
Analyze initial data from first can												
Collect final data												
Thermal Modeling												
Place BNFL containers in Building 371 vault												
Provide complex-wide support for storage												
Container Testing												
Test BNFL lid deflection												
Evaluate BNFL container radiographic weld												
Analytical Development												
Supercritical carbon dioxide development												
Test supercritical fluid carbon dioxide proof of principle												
Develop supercritical carbon dioxide for water analysis												
X-ray fluorescence for materials identification												
Provide x-ray fluorescence proof of principle for elemental analysis												
Laser-Induced Breakdown Spectroscopy (LIBS)/Raman Spectroscopy												
Assemble LIBS system in TA-55; Building PF-4; fill surrogate can system with oxide powder												
Perform experiments using LIBS; vary backfill gas and temperature												
Develop Raman spectroscopy for water determination on plutonium oxide												

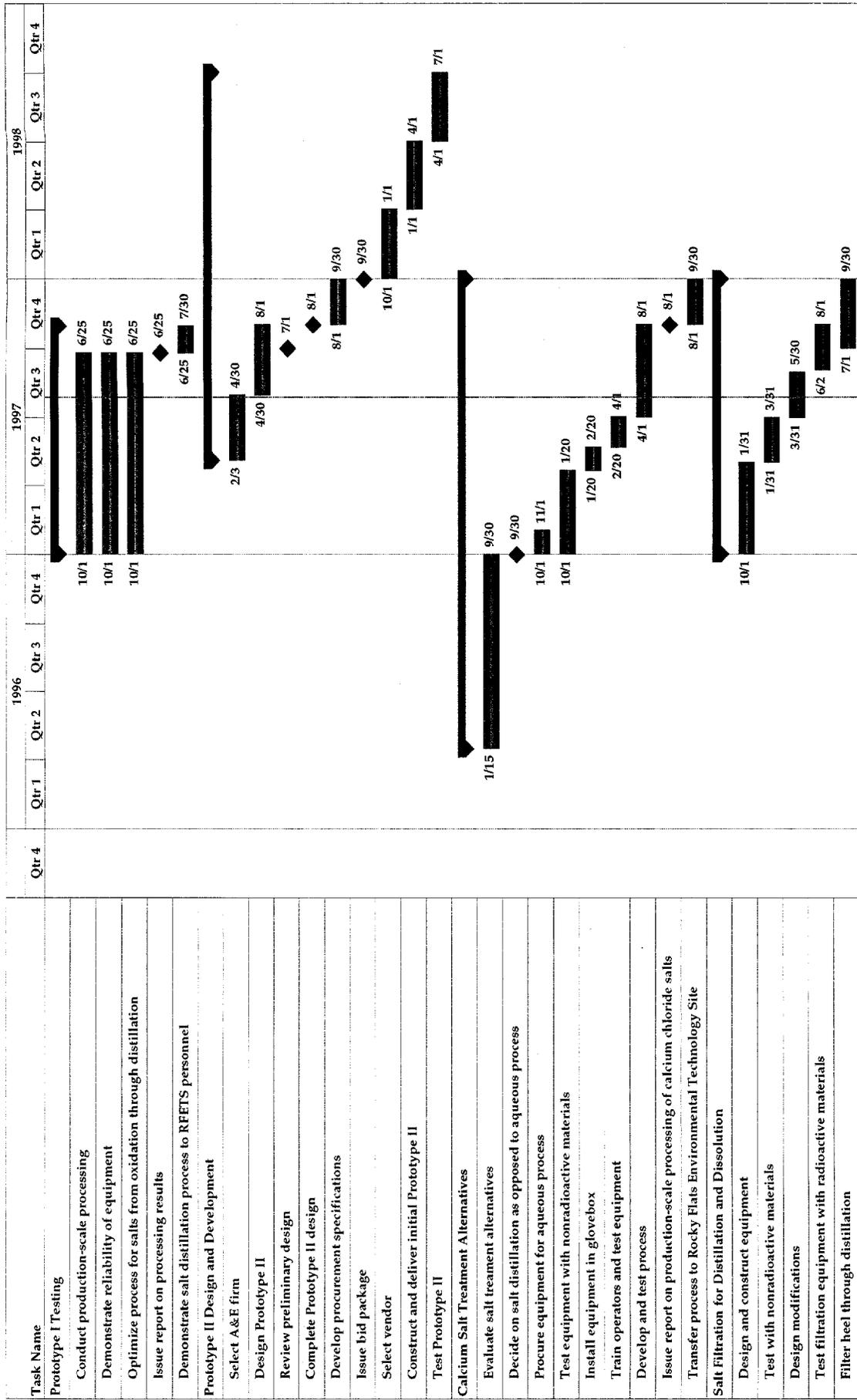


## Pyrochemical Salt Oxidation

Task Name	1997					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Optimization of Process for Salts from Oxidation through Distillation						
Optimize process for electrorefining salts	10/1	3/28				
Optimize process for molten salt extraction salts		3/31	4/28			
Optimize process for salt-strip salts		4/28	6/25			
Pyrochemical Crucible Oxidation Process Development						
Complete development of method for crucible pyrochemical oxidation		1/1	3/14			
Complete design for crucible oxidation system			3/17		8/15	9/30
Prepare report on crucible oxidation process						9/30
Issue report on crucible oxidation process						
Investigation of Feasibility of Liquation Process						
Determine liquation parameters		1/1	2/28			
Prepare report on feasibility of process			3/3	4/1		
Issue report on feasibility of process				4/1		
Complete liquation process optimization				4/1	6/30	



# Pyrochemical Salt Distillation



## Pyrochemical Salt Filtration

Task Name	1997			
	Qtr 4	Qtr 1	Qtr 2	Qtr 3
<b>Salt Filtration</b>				
Evaluate viability of molten salt filtration process	9/16	12/6		
Define processing parameters needed for implementation	11/18	2/14	2/14	
Prepare report on salt filtration development			2/14	3/14
Issue report				3/14

Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

## Size Reduction/Cryogenic Crushing

Task Name	1997				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Development of High-Efficiency Particulate Air (HEPA) Filters Disassembly Unit					
Present a basic design to Rocky Flats Environmental Technology Site (RFETS) for review and recommend equipment	10/1	10/18			
Purchase equipment and perform nonradioactive demonstration on nonradioactive filters	10/18	12/20			
Supply upgraded equipment with safety and interlock features to RFETS		12/20	3/28		
Install support unit at RFETS	10/1		3/31		9/30
Transfer of Support Technology Regarding Cryogenic Grinding Operations to RFETS	10/1				9/30



## Nitric Acid-Phosphoric Acid Oxidation

Task Name	1997				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Nitric Acid-Phosphoric Acid Oxidation Development					
Install unit in a glovebox	10/1		2/28		
Complete development of in situ monitoring			2/28	4/30	
Complete plutonium fractionation testing			4/30	5/30	
Complete off-gas analysis				5/30	7/31
Complete oxidation testing				5/30	7/31
Complete immobilization studies				5/30	7/31
Issue final report and recommendations				8/1	9/30

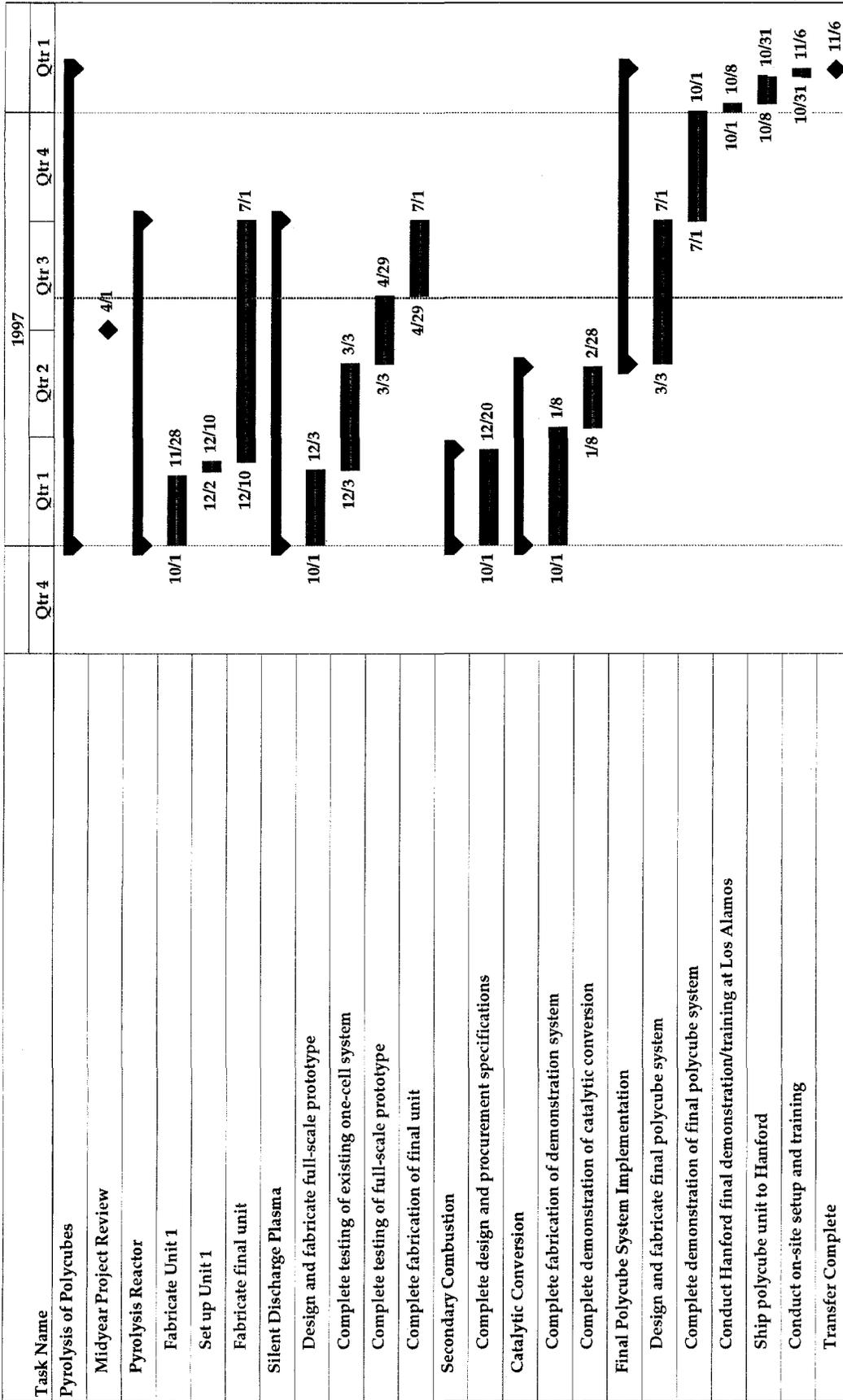


# Catalyzed Chemical Oxidation

Task Name	1996				19
	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
Fabrication of Glovebox System with Delphi Research					
Assemble equipment/test in mockup		5/29		11/22	
Ship glovebox reactor to Los Alamos				11/22	
Deliver operating manual/design report to Los Alamos				11/22	
Evaluation of Final Disposition of Liquid Effluent and Spent Plutonium/DETOX Solution					
Perform experimentation to evaluate liquid effluent and spent solution		3/15		12/13	
Issue report				12/13	
Decision Point on Whether to Continue Installation at Los Alamos or to Transfer to Rocky Flats Environmental Technology Site (RFETS) for Installation					12/31

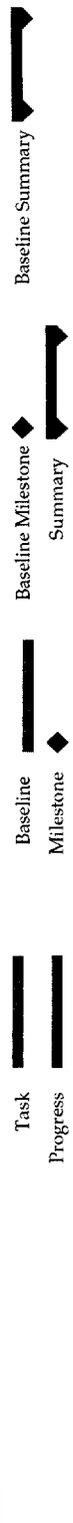


# Pyrolysis—Polycubes



# Washing

Task Name	96				1997				1998				19	
	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 1	Qtr 2
Combinable Washing Experiments														
Install Parr reactor and test glovebox operations		10/1		1/1										
Continue plutonium experiments on baseline wet combustible flow sheet		10/1		12/20										
Revise work scope, as appropriate		10/1		10/1										
Complete review of literature/DOE complex experience for alternate and nitrate flow-sheet development		10/1		10/15										
Organize and update status of contact points		10/15		10/30										
Report on plutonium-surrogate work for baseline process				12/20										
Meet with Rocky Flats Environmental Technology Site (RFETS) contact about treatment technologies for combustible residues				1/15										
Complete and review flow sheet for alternate washing treatments				1/15		2/14								
Revise flow sheets for alternate and nitrate washing processes and obtain final approval				2/17		2/28								
Revise work scope, as appropriate				3/3		3/14								
Conduct scoping experiments for alternate and nitrate flow sheets				3/17		9/15								
Complete summary report on alternate and nitrate flow-sheet development and testing						9/30								
Revise statement of work, as appropriate						10/1								
Continue plutonium experiments on alternate and nitrate flow sheets						10/1								
Perform full-scale demonstration of radioactive materials														
Optimize treatment operating parameters and perform final demonstration														
Prepare final report on full-scale testing and recommend wet combustibles final baseline washing flow sheet (Los Alamos)														
Issue final report														
Train personnel and complete technology transfer to RFETS														



## Mediated Electrochemical Oxidation

Task Name	1997			
	Qtr 4	Qtr 1	Qtr 2	Qtr 3
Mediated Chemical Oxidation Demonstration and Testing Activities				
Determine material balance and liquid waste volume generation (Pacific Northwest National Laboratory)	10/1			9/30
Issue report		12/2	1/15	
Decide status of demonstration and testing activities		1/1	1/31	
Report decision				1/31



# Vitrification Issues with Rocky Flats Environmental Technology Site Ash and Sand, Slag, and Crucible

Task Name	1997					19
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	
<b>Nondestructive Assay (NDA) Constraints and Operating Parameters</b>						Qtr 1 Qtr 2
Obtain ash and glass frit	10/1		1/15			
Generate ash/glass waste forms		1/15	1/31			
Initiate NDA on waste forms		1/31	2/14			
Prepare report on NDA constraints and operating parameters		2/14		5/1		
Issue report				5/1		
<b>Conventional Furnace Melting</b>						
Obtain surrogate compositions	10/1		1/15			
Complete computer modeling for test design		1/15	2/7			
Complete development of glass frit formulation for ash		2/7		4/30		
Complete development of glass frit formulation for sand, slag, and crucible (SS&C)			4/30	5/30	5/30	
Complete variability and verification testing for ash				5/30	6/13	
Complete variability and verification testing for SS&C				6/13	7/15	
Complete analyses on test samples for ash				7/15	7/30	
Complete analyses on test samples for SS&C				7/30	8/4	
Complete flow-sheet development for RFETS				8/4	9/1	
Prepare final report on conventional furnace melting				9/1	9/30	
Issue final report					9/30	



## Vitrification of Rocky Flats Environmental Technology Site Ash

Task Name	1997				19		
	Qtr 4	Qtr 1	Qtr 2	Qtr 3		Qtr 4	Qtr 1
Vitrification of Rocky Flats Environmental Technology Site Ash							
Develop statistically designed experimental program	10/1						12/31
Fabricate glasses and make visual observations		1/1	2/14				
Characterize microstructure of selected glasses			2/14	2/28			
Measure viscosity/liquidous temperature of selected glasses				5/30			7/31
Assess glass performance			3/3	5/2			
Perform plutonium loading tests for glass formation				7/1			8/1
Complete and issue report						8/4	10/1



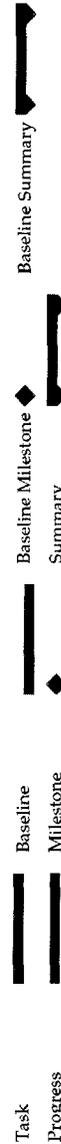
## Maximum Waste Loading of Particulates in the Cement Waste Form

Task Name	1997			
	Qtr 4	Qtr 1	Qtr 2	Qtr 3
Cementation Development and Testing		10/1		
Determine waste form performance standards		12/12		
Complete surrogate preparations		12/23	1/31	
Complete cementation work		2/3	8/1	
Prepare report on cementation			8/4	9/30
Issue report				9/30



# Tomography

Task Name	1996				1997				19	
	Qtr 2	Qtr 3	Qtr 4		Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
Evaluation of Tomographic Gamma Scanner (TGS)	2/23	3/1	4/1	4/30						
Install existing TGS	2/23	3/1	4/1	4/30						
Review failure mechanisms for stored plutonium materials	2/23	3/1	4/1	4/30						
Use computer modeling to evaluate ability of computerized tomography (CT) to detect and quantify changes in stored items	3/1	4/1	4/30	5/21	5/31					
Complete development of CT test objects using surrogate materials	4/1	4/30	5/21	5/31						
Implement test plan for experimental evaluation	4/30	5/21	5/31	7/31	7/31					
Evaluate TGS in comparison to current nondestructive analysis (NDA) technology	5/21	5/31	7/31	8/14	8/30					
Modify existing CT software to detect changes in stored items	5/31	7/31	8/14	8/30						
Complete report documenting TGS evaluation	7/31	8/14	8/30							
Evaluate requirements for facility integration	8/14	8/30								
Complete functional specification for the digital radiography (DR/CT) system										
Prepare draft version of Los Alamos report documenting DR/CT experimental evaluation										
Decide whether to proceed and fund project										
Installation of DR/CT capability										
Complete procurement specification of DR/CT systems										
Initiate procurement specification of DR/CT system										
Initiate facility safety review/modifications for the DR/CT system integration (Savannah River Site [SRS])										
Complete facility integration requirements (SRS)										
Install the DR/CT system at SRS										
Report on complementary measurement techniques for stored-item monitoring										
Complete field test and evaluation of DR/CT on nuclear materials in storage containers										



# Moisture Probe

Task Name	1997				1998				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Moisture Probe Development	10/1								
Complete bench-top model (Science Applications International Corporation [SAIC])			4/18						
Deliver bench-top model to Los Alamos (SAIC)		1/31	5/16						
Complete standard fabrication (Los Alamos Nuclear Materials Technology Division Nitrate Systems Group)		1/31	4/28						
Complete measurements for field test at Los Alamos		2/28	6/30						
Document/evaluate field test results (conditional upon satisfactory test results and funding)			4/30	8/31					
Initiate procurement of prototype moisture probe					9/1				
Fabricate and deliver prototype moisture probe to Rocky Flats Environmental Technology Site (RFETS)					9/1			6/3	
Test and evaluate prototype system at RFETS						4/1			9/30
Complete testing and evaluation of prototype system at RFETS									9/30



# Acoustic Resonance Spectroscopy

Task Name	1996				1997			
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Acoustic Resonance Spectroscopy								
Evaluate feasibility of detecting gas pressure in a sealed container								
Issue feasibility report								
Evaluate feasibility of gas recognition of hydrogen and helium mixtures								
Complete the design and fabricate containers and experimental setup								
Conduct experiments								
Evaluate feasibility of ARS measurements of gases in double-sealed long-term storage containers								
Complete the design and fabricate containers in experimental setup								
Conduct experiments								
Evaluate gas pressure measurements on long-term storage containers, using argon, helium, and surrogate materials								
Complete the design and fabricate containers and experimental setup								
Conduct experiments								
Decide on conceptual feasibility of ARS techniques for detecting changes in materials in long-term storage								
Continue testing and access measurement techniques								
Continue testing and access measurement systems								
Continue testing and access measurement fixtures								
Continue evaluation and development of ARS for application to shelf-life containers								
Continue software development								



## Nondestructive Assay—Gamma Salts

Task Name	1997				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Nondestructive Assay—Gamma Salts					
Develop and test heterogeneous material parameter sets	10/1		1/20		
Complete heterogeneous parameter testing			1/20		
Develop and test automated parameter sets	10/1			9/1	
Deploy automated parameter set					9/1
Continue testing of additional parameter sets			5/1		9/30

Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

# Calorimetry

Task Name	1997				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Calorimetry	10/1				
Evaluate Mound work and evaluate existing hardware and software		1/1	12/31		
Develop finite element model		1/1	1/20		9/30
Identify operating calorimeter to be used to test model		1/1	2/28		
Construct finite element model		1/1	2/28		
Create drawings or data about test calorimeter				3/3	6/1
Complete testing and evaluate model				6/2	8/1
Compare model and experiment					8/1
Make recommendations for calorimeter design					9/30
Make recommendations for future work					9/30



## Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site

Task Name	1997			
	Qtr 4	Qtr 1	Qtr 2	Qtr 3
Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site (RFETS)	10/1			
Coordinate project requirements, approach, and expected results with Rocky Flats Field Office and the Nuclear Materials Stabilization Task Group		1/1		
Evaluate information on status of stored residues and determine applicability of candidate methodologies		1/2	1/15	
Conduct workshop at DOE headquarters describing risk-based analysis for Los Alamos 94-1 R&D Project implementation		1/15	1/31	
Develop an approach and brief project principles on scope and expected results		1/15	1/31	
Perform preliminary assessments on risk status using available information on residue characteristics, on container degradation, on potential hazards, and on degradation processes			2/3	4/1
Develop plan containing resource and information requirements for in-depth assessments of risk status at RFETS			4/1	5/1



# Actinide Solution Chemistry in Residues and in Residue Stabilization and Treatment Processes

Task Name	1997				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Actinide Solution Chemistry					
Complete acquisition of data on Pu(IV) nitrate system	10/1	11/15			
Complete analysis of Pu(IV) nitrate solution speciation		11/15	12/31		
Complete analysis of Pu(IV) chloride solution speciation		1/1	3/31		
Synthesize Pu(VI) carbonate solids	10/1		3/31		
Synthesize limiting Pu(IV) carbonate	10/1		3/31		
Publish Pu(IV) nitrate results				5/1	
Determine structures of Pu(VI) carbonate solids			4/1	6/30	
Publish Pu(IV) chloride results			4/1		7/31
Complete characterization of limiting Pu(IV) carbonate species					8/1
Complete Pu(IV) nitrate/chloride competition				7/1	9/30
Report on solution thermodynamics of Pu(VI) carbonate solution species					9/30



## Chemical and Physical Interactions of Actinides with Residue Substrates

Task Name	1997				1998				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Surface Interactions									
Procure for investigation residue samples from the Los Alamos National Laboratory Plutonium Facility	10/1		1/31						
Complete resin kinetic studies		2/3		7/31					
Complete resin degradation studies				8/1		9/30			
Present results at national topical meeting					9/30				
Report resin kinetic and degradation studies					10/30				
Complete development of integrated imaging system	10/1					9/30			
Complete spectroscopic studies of plutonium-resin interactions							3/31		
Demonstrate integrated imaging capabilities on plutonium residues							4/1		9/30



# Identification and Characterization of Changes in the Chemical State of Plutonium in Interim Waste Forms

Task Name	96				1997				1998				1999					
	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	
Changes in the Chemical State of Plutonium																		
Synthesize pure plutonium compounds		7/1																
Complete optical spectroscopic characterization	7/1	7/31																
Complete first x-ray absorption spectroscopy (XAS) experiment		8/1	8/30															
Complete first XAS data analysis		9/2		12/31														
Complete initial plutonium structural database			1/1		4/30													
Prepare second set of plutonium samples				5/1		6/30												
Complete second XAS experiment				7/1			9/1											
Complete second XAS data analysis					9/1			1/1										
Incorporate results into plutonium structural database								1/1										
Prepare third set of plutonium samples								5/1										
Complete third XAS experiment								5/1		7/1								
Complete third XAS data analysis								7/1		9/1								
Incorporate results into plutonium structural database										9/1					1/1			
															1/1			
															1/1			4/30



## Actinide-Organic Interactions

Task Name	1997				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Actinide-Organic Interactions					
Retrofit glovebox optical well	10/1	12/20			9/30
Install glovebox according to configuration management	10/1				9/30
Conduct surface characterization experiments	10/1			6/30	9/30
Complete plastics characterization					9/30
Complete cellulose characterization					9/30
Complete rubber characterization					9/30
Conduct actinide-uptake experiments of organic matrices	10/1				9/30
Conduct aqueous-solution actinide-organic oxidation experiments			3/3		9/30
Conduct aqueous-solution radiolytic-degradation and hydrolysis experiments			3/3		9/30

Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

# Corrosion

Task Name	1997				1998				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Corrosion	10/1								
Conduct scanning reference electrode tests coupled with orientation image analyses of common polycrystalline engineering materials									9/30
Conduct scanning reference electrode tests on single-crystal orientations of interest			1/30						9/30
Superimpose maps of texture onto maps of corrosion				7/30					9/30
Conduct surface-enhanced Raman spectroscopy of oxides on textured substrates				9/1					9/30
Set up and begin stress corrosion cracking studies					2/28				9/30
Report on second-year results								9/30	
Correlate SCC crack propagation with orientation									8/31



## Plutonium Diffusion Science

Task Name	1997					19
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	
Plutonium Diffusion Science						Qtr 2
Complete quarterly report			1/15			
Complete analysis of initial samples using secondary ion mass spectrometry	10/1		1/31			
Complete optimization of depth-profiling technique using laser-induced breakdown spectroscopy (LIBS)	10/1		2/28			
Complete quarterly report				4/15		
Complete analysis of initial samples using LIBS			3/3		7/31	
Complete quarterly report					7/15	
Make interim comparison of results obtained by the two techniques						9/30
Issue fiscal year 1998 experimental plan						9/30



# Polymer Filtration

Task Name	1996				1997				1998		
	Qtr 2	Qtr 3	Qtr 4		Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3
Polymer Filtration											
Complete preparation of first systematic series of linear, as compared with branched, polyamine polymers having a range of molecular weights and functionalized at various levels		6/3	6/28								
Initiate testing of appropriate water-soluble polymer for testing with larger-scale equipment for developing engineering model		7/1	9/13								
Complete characterization of the first series of polymers			9/16	9/30							
Complete preliminary size determinations and conduct initial americium and plutonium binding studies			9/16	9/30							
Complete construction of apparatus for fluorescence studies			6/3	9/30							
Initiate fluorescence spectroscopic evaluation of polymers				10/1							
Complete initial evaluation of fluorescence spectroscopy for polymers				10/1	1/15						
Complete initial evaluation of a series of polymers with Raman spectroscopy to determine usefulness as a direct probe of the polymer structure in solution				10/1	1/15						
Complete development of improved synthetic methods for a series of polymers optimized for actinide bonding					1/15	6/30					
Complete initial evaluation of multinuclear nuclear magnetic resonance as a direct probe of polymer structure and complexation reactions in solution					1/15	6/30					
Initiate uranium and neptunium separation studies								8/1			
Complete study to validate the use of polymer filtration as a preconcentration technique for analysis of ultralow actinide levels									9/30		
Report actinide separation results										9/30	



# Polymer Foams

Task Name	1997				1998				19		
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
Polymer Foams	10/1										
Complete first set of actinide removal experiments			12/13								
Prepare and characterize polystyrene/chloromethylstyrene foams		1/1	3/31								
React films and characterize resulting materials		4/1		7/31							
Complete second set of actinide uptake experiments				7/31							
Prepare and characterize polyvinylpyridine foams				8/1	9/30						
Prepare and characterize polyfunctional foams				8/1	9/30						
Select industrial partner					9/30						
Optimize actinide-selective foams				10/1		3/31					
Functionalize chloromethylstyrene foams				10/1		3/31					
React films and characterize resulting materials						4/1				9/30	
Complete third set of actinide uptake experiments											9/30



# Thermodynamics

Task Name	1997					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Thermodynamics	10/1					
Complete experimental studies on vaporization behavior of plutonium oxychloride (PuOCl)		1/3				
Prepare and issue report on thermochemistry of PuOCl		1/3	2/14			
Complete experimental studies on vaporization behavior of americium oxychloride (AmOCl)		1/3	3/28			
Prepare report on thermochemistry of AmOCl			3/28	5/9		
Issue AmOCl report				5/9		
Complete experimental studies on vaporization of mixed halides			4/1	6/13		
Prepare report on modeling of salt distillation process				6/13	7/10	
Issue report on modeling of salt distillation process					7/10	
Complete experimental studies on vaporization of plutonium-zirconium silicate solid solutions				6/13	9/1	
Prepare report on phase stabilities of zircon materials					9/1	9/30
Issue report on phase stabilities of zircon materials						9/30



## Mineral Waste Forms

Task Name	1997					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Mineral Waste Forms						
Complete development of material containment system	10/1		2/14			
Complete preparation and characterization of zircon			2/17	3/14		
Complete initial preparation and characterization of plutonium silicate			3/17		6/13	
Determine solubility limit of plutonium in zircon				6/16		9/12
Issue report on plutonium-zircon process parameters						9/30



## Synthesis and Structural Characterization of Plutonium (IV) and Plutonium (VI) Phosphates

Task Name	1997				1998					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Plutonium (IV)(VI) Phosphates	10/1									
Complete synthesis and characterization of binary U(VI) phosphates			3/28							
Complete synthesis and characterization of binary Pu(VI) phosphates			4/1							
Complete structural and compositional characterization of ternary U(VI) and Pu(VI) phosphates				8/1			9/30			
Complete synthesis and characterization of binary U(IV) phosphates								9/30		
Complete synthesis and characterization of binary Pu(IV) phosphates									3/31	7/30
Complete structural and compositional characterization of ternary U(IV) and Pu(IV) phosphates									8/3	9/30



## Plutonium Phosphate Solution Chemistry

Task Name	1997					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Plutonium Phosphate Solution Chemistry						
Complete studies on the precipitation of plutonium by organic precipitants from concentrated phosphoric acid solutions and characterize solid phases produced	10/1					8/29
Complete investigation of plutonium coprecipitation with inorganic phosphates	10/1					8/29
Characterize physical properties of plutonium phosphate solutions at elevated temperatures	10/1					9/30
Develop process for recovery of plutonium from phosphoric acid concentrated solutions	10/1					9/30



# Molten Salt/Nonaqueous Electrochemistry

Task Name	1997					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Molten Salt/Nonaqueous Electrochemistry						
Recruit and hire a postdoctoral fellow	10/1	1/2				
Set up room-temperature molten salts (RTMS) capability	10/1	12/30				
Issue quarterly report		1/2				
Study chemical behavior of uranium in RTMS system		1/2	7/1			
Issue quarterly report			3/31			
Publish results of uranium study in refereed journal					7/1	
Issue quarterly report					7/1	
Present results of uranium study at American Nuclear Society meeting						8/25
Study chemical behavior of near actinides in RTMS				7/1		9/30
Issue quarterly report						9/30



## Improved Methods for the Detection of Alpha-Emitting Isotopes in the Environment

Task Name	1997					
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Alpha Isotope Monitoring						
Complete evaluation of more selective extractants for the Photon Electron Rejecting Alpha Liquid Scintillation (PERALS) system			3/3	4/1		
Complete testing of curve-fitting procedures in order to improve isotopic information			4/1	5/30		
Complete testing of commercially available resins in order to concentrate and separate isotopes				6/2	8/1	
Complete studies on applying PERALS to plutonium process waste					8/1	9/1
Issue report on applying PERALS to aqueous low-level alpha waste						9/1



# Project Management

Task Name	1997				19		
	Qtr 4	Qtr 1	Qtr 2	Qtr 3		Qtr 4	Qtr 1
Administration of Fiscal Year 1997 (FY97) 94-1 Research, Development, and Testing (RD&T) Project	10/1		12/31				
Complete FY97 technical program plan			2/1				
Issue FY97 first quarterly report			2/13				
Conduct Technical Advisory Panel (TAP) core technology review				5/1			
Issue FY97 second quarterly report			4/1				
Conduct mid-year program review				5/30			
Assist TAP/Plutonium Focus Area in R&D plan revisions for fiscal year 1998 (FY98)				6/2		8/29	
Solicit proposals for FY98 technical program plan				6/2		8/29	
Draft FY98 technical program plan					9/1	9/30	
Issue FY97 third quarterly report					8/1		
Issue FY97 fourth quarterly report						10/15	
Issue FY98 technical program plan							11/3



# Catalyzed Chemical Oxidation—Radioactive Demonstration at Los Alamos

Task Name	1997				1998				19		
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
Radioactive Demonstration of Catalyzed Chemical Oxidation—unfunded											
Decide whether to continue Los Alamos National Laboratory installation or transfer to Rocky Flats Environmental Technology Site (RFETS) for installation		12/31									
Installation at Los Alamos											
Conduct compliance, configuration management, and reviews											
Write operating procedure		1/9	3/14								
Obtain treatability study permit		1/1		6/13							
Complete configuration management review at Los Alamos Plutonium Facility		1/9		6/13							
Issue authorization basis				6/15							
Conduct installation activities											
Modify glovebox				6/16		9/30					
Install unit							1/30				
Assess readiness							2/2	2/27			
Have equipment ready for testing with radioactive materials										2/27	
Demonstrate process											
Conduct 100-g-scale surrogate test								3/2	3/31		
Conduct 500-g-scale surrogate test									4/1	4/30	
Complete surrogate test										4/30	
Conduct test on applicable radioactive combustible materials										5/1	10/30
Issue final report on radioactive tests											10/30



## Mediated Electrochemical Oxidation—Development Activities beyond Rocky Flats Environmental Technology Site Rebaseline Exercise

Task Name	1997				1998				1999			
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Mediated Electrochemical Oxidation (MEO) Demonstration and Testing Activities—unfunded	[Task Bar]											
Pacific Northwest National Laboratory MEO Demonstration and Testing Activities	[Task Bar]											
Obtain environment, safety, and health (ES&H)/National Environmental Policy Act (NEPA) regulatory approval for surrogate and actual waste testing	12/2											
Calculate balance-of-process design for Full-Flo filter processing	12/2	1/2										
Conduct bench-scale testing on radioactive Full-Flo filter core samples	12/2	5/30										
Prepare report on core filter testing		5/30	6/30									
Issue report on core filter testing			6/30									
Conduct radioactive testing of whole Full-Flo filters		6/2	9/30									
Issue final letter report on radioactive filter testing				10/31								
Evaluate and design filter housing	12/2	3/20										
Modify MEO cell		3/21	5/30									
Conduct nonradioactive testing of integrated MEO system		6/2	8/29									
Issue final letter report on nonradioactive testing and process optimization				10/31								
Complete balance-of-process design and fabrication for filter-processing system			10/1	4/30								
Transfer MEO filter-processing system to Rocky Flats Environmental Technology Site (RFETS)				12/1	4/30							
Design support for RFETS system			10/1	9/30								
Conduct on-site participation at RFETS for installation and testing			10/1	9/30								



## Mediated Electrochemical Oxidation—Development Activities beyond RFETS (Continued)

Task Name	1997				1998				1999				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Mediated Electrochemical Oxidation (MEO) Demonstration and Testing Activities—unfunded													
Lawrence Livermore National Laboratory MEO Demonstration and Testing Activities													
Obtain ES&H and NEPA regulatory approval for surrogate testing		11/1	12/31										
Conduct laboratory-scale studies in support of conceptual design		11/1	6/30										
Complete conceptual design of pilot-scale MEO cellulosic treatment system			6/2	7/31									
Construct and install pilot-scale MEO treatment system			8/1	9/30									
Issue progress report								9/30					
Test cellulosic residues treatment using pilot-scale system					10/1			3/31					
Issue progress report								3/31					
Design production-scale MEO cellulosic treatment system								3/31	5/29				
Construct and test production-scale MEO treatment system								6/1	9/30				
Obtain permit for use of production-scale MEO system at RFETS								4/1	9/30				
Transfer and install production-scale MEO system at RFETS									10/1				3/31



## Appendix B



### Unfunded Projects



## **Storage Issues**

### **Plutonium Disposition Methodology**

**Date Issued:** November 16, 1996

**Principal Investigator:** Mark A. Robinson

**Budget:** Fiscal Year 1997      \$400 K

**94-1 IP Milestone:** None

**R&D Plan:** 3.3

#### **Objective**

Plutonium disposition methodology (PDM) will result in the disposition of residue inventories in a manner that minimizes costs, personnel exposures, and waste generation rates. At the same time, this research will maximize plutonium recovery for programmatic purposes. This disposition process is intended to expedite 94-1 stabilization activities by identifying materials that are more appropriate for discard than for stabilization and storage.

This research will result in replacing economic discard limits with discard limits that are based on more viable considerations than the cost of special nuclear material (SNM) production. More viable considerations include minimization of waste and environmental impacts, worker safety, storage and processing risks, safeguards, transport and disposal criteria, and comprehensive costs associated with implementation of discard limit selections.

#### **Scope**

During fiscal years 1995 and 1996, the Los Alamos National Laboratory Nuclear Materials Technology (NMT) Division performed a series of "straw man" inventory evaluations that quantitatively assessed consequences of material disposition alternatives. This effort resulted in disposition methodology being endorsed by both the DOE Albuquerque Operations Office (DOE/ALO) and the Office of Safeguards and Security (NN-51). DOE/ALO also presented this approach informally to the New Mexico Environment Department (NMED) and obtained NMED concurrence with the general disposition rationale.

Now that the methodology has been developed and accepted, we plan in fiscal year 1997 (FY97) to complete data-gathering necessary for disposition of the entire Los Alamos Plutonium Facility (TA-55) inventory. Prerequisite data for these evaluations include the following:

- a predictive personnel exposure model for processes and residue matrices,
- characterization data for all residue matrices, and
- data for recovery process efficiency and waste generation rates.

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We also need to develop, as input to the disposition process, a predictive dose model, a comprehensive characterization document, and a comprehensive inventory assessment quantifying SNM concentrations and bulk quantities of residue matrices. We will develop these products by statistical analysis of inventory data and will augment them by process knowledge from materials custodians. Finally, we will statistically analyze processing records, review published recovery methods, and consult subject-matter experts in order to quantify recovery process efficiencies and waste generation rates.

Once we obtain prerequisite data, we will use the quantitative models we have developed in order to accomplish inventory disposition and discard-limit development. These models quantify the consequences of selecting proposed disposition alternatives and discard limits in terms of personnel exposure, waste generation, recovered SNM, and overall costs. Thus, we have a concrete basis for alternative selection. These models also facilitate "high-grading" of inventories so that return on investment, in terms of recovery/stabilization resources, is maximized. By the end of FY97, we will develop disposition of historical residue inventories and discard limits.

### **Benefits**

The mandate to implement PDM has both inherent benefits and liabilities.

One benefit is that PDM provides a mechanism for identifying inventory subsets (from personnel exposure, waste generation, and resource expenditure perspectives), when appropriate, to discard materials. Sometimes, such discarding is preferable to the across-the-board recovery and stabilization that is implied as necessary under 94-1 stabilization commitments. Such dispositions, in fact, reduce the risks associated with storing potentially reactive residues by allowing facility recovery/stabilization resources to be directed toward richer and higher hazard materials.

The liability is that with the previous method, economic discard limits are subject to cancellation at any time. Consequently, completing inventory evaluation and disposition is urgent. The DOE/ALO presented PDM to the NMED as assurance that Los Alamos residues will be proactively dispositioned and not "stored in lieu of abandonment" as occurred at RFETS. So, funding for this project is important because of safeguard and security issues and because of potential savings in the complex-wide life-cycle costs of 94-1 stabilization activities.

**Stabilization Process Development**  
**Ceramification of Rocky Flats**  
**Environmental Technology Site Incinerator Ash**

**Date Issued:** September 19, 1996

**Principal Investigators:** A. G. Phillips (Rocky Flats Environmental Technology Site)  
T. S. Rudisill (Savannah River Site)

**Budget:** Fiscal Year 1997      \$275 K

**94-1 IP Milestone:** IP-ES-025

**R&D Plan:** 4.3.5.2.4

**Objective**

Ceramification is a low-temperature chemical ceramic process that can reduce the potential for dispersion of plutonium residues at Rocky Flats Environmental Technology Site (RFETS). This technology will be especially valuable in the event of a catastrophic building accident. Ceramification combines plutonium oxide powders together in a bonded structure that is in turn bonded to the dual-purpose process vessel and ultimate disposition container. The process can have significant cost savings in the handling of powder residues and the final building specifications for a plutonium repository. Ceramification can bond residue powders together using the nitrates of either plutonium, cerium, or zirconium. The product prepared by ceramification can be the final form or an intermediate form that can be further processed using vitrification or other conventional ceramic practices.

**Scope**

This program will extend demonstration tests recently completed at the Savannah River Technology Center. The primary activities include the following:

- continuing water adsorption tests using previously prepared ceramic coupons,
- further optimizing the ceramification process,
- preparing representative samples for shelf-life studies at Los Alamos National Laboratory,
- extending the ceramification process to selected residues, and
- conducting dissolution studies to measure the recoverability of plutonium from the ceramic.

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A major objective of this program is to complete optimization of the fiscal year 1996 (FY96) ceramification work, in which SRS and RFETS researchers demonstrated immobilization of plutonium oxide using the metal nitrates of plutonium, cerium, and zirconium. A limited number of ceramic coupons produced during proof-of-principle tests are available for water adsorption tests and semiempirical crush tests that measure the dispersibility of the product. Additional ceramic coupons will be produced in fiscal year 1997 (FY 97) to facilitate the ease of implementing the ceramification technology at RFETS and at other DOE facilities. Water adsorption and crush tests will also be performed for these coupons. As a continuation of the process demonstration, a test sample or samples will be produced for shipment to Los Alamos to perform long-term shelf-life studies that monitor the water adsorption characteristics of the coupon(s) stored in selected hardware.

Ceramification is being proposed to stabilize/immobilize three different residues at RFETS. These include sand, slag, and crucible; ash; and scrapings from graphite casting molds. The primary goals of this technology are to simultaneously stabilize any chemically reactive or physically unstable constituents and immobilize the residue as a nondispersible material suitable for transport and long-term storage. The well-bonded, porous, compact product made by this process should more than adequately satisfy these requirements. We will perform experiments, using surrogates and the actual materials, when possible, to demonstrate the applicability of the ceramification process to these residues.

The remaining task included in the FY97 program involves dissolution studies to measure the recoverability of plutonium from the ceramics produced by the ceramification process. Potential future uses may require dissolution and recovery of the plutonium as a purified material. Dissolving selected coupons will provide a measure of recoverability and will allow for recycle of the plutonium for additional experiments.

### **Benefits**

Ceramification is a pragmatic approach to readily and rapidly stabilizing and immobilizing plutonium oxide powders at RFETS. Because ceramification is capable of producing a pure solid storage item, the process provides a resource with flexibility for future needs and uses (i.e., mixed-oxide fuel production). Product additives can be uniformly distributed in high percentages for strength and physical property modification, neutron absorption, and proliferation enhancement. This flexible process can cope with plutonium metal, nitrates, oxides, and many residue forms.

Ceramification provides a reduction in the dispersibility of plutonium compounds and consequently reduces safety hazards involved with storage and transport. A nondispersible product reduces potential contamination of personnel, facilities, and equipment during handling of materials. The process produces a homogeneous product with extremely high loading of plutonium oxide. The final volume, compared to the starting materials, ranges from a sharp reduction to a slight increase, thereby requiring fewer and possibly no additional packaging vessels.

## Stabilization Process Development: Measurement of Moisture in Pyrochemical Salts

**Date Issued:** November 11, 1996

**Principal Investigator:** Lewis Baylor (Savannah River Technology Center)

**Budget:** Fiscal Year 1997      \$250 K

**94-I IP Milestone:** None

**R&D Plan:** None

### Objective

Thousands of kilograms of plutonium-bearing pyrochemical salts have been designated as needing conversion to a more stable, lower-risk form. Los Alamos National Laboratory personnel are developing technology to stabilize the reactive metals in the salts and minimize corrosion caused by moisture. *In situ* measurement of moisture content will aid in control of the stabilization process. Savannah River Technology Center (SRTC) researchers have experience with remote moisture measurements by fiber-optic near-infrared (NIR) spectroscopy. This experience will be used to develop a system to perform this measurement.

### Scope

SRTC personnel have extensive experience in the development and application of fiber-optic spectroscopy systems for remote measurement of radioactive materials. Their experimenters have developed a prototype near-infrared system for measuring moisture content in radioactive waste tank salts at Hanford Site. The system successfully measured moisture over a range of 0 wt %–60 wt % in waste simulants.

The purpose of this work will be to build on the prior SRTC development to produce a system capable of measuring moisture content in the various pyrochemical salt forms associated with the stabilization process and long-term storage. The performance of two different near-infrared spectrometers will be evaluated for this application. After satisfactory demonstration of the basic concept, specific spectrometer hardware will be selected for application. Fiber-optic probes will be designed and fabricated, including an *in situ* probe with a sealed feed-through for a long-term storage container. Software and mathematical models will be optimized for this application. An integrated prototype system will be assembled and demonstrated on actual materials either at SRTC or at Los Alamos.

### Benefits

*In situ* measurement of moisture content will aid in control of the stabilization process for salts. Determining moisture content before final packaging for disposal will provide confidence in the stabilization process. SRTC personnel have experience with remote moisture measurements by fiber-optic NIR spectroscopy, and their experience will help develop a system to perform this measurement.

**Stabilization Process Development**  
**Electrochemical Scrubbing**  
**of Rocky Flats Environmental Technology Site Residues**

**Date Issued:** September 19, 1996

**Principal Investigators:** Alice Murray (Savannah River Site)  
William Averill (Colorado School of Mines)

**Budget:** Fiscal Year 1997      \$350K

**94-1 IP Milestone:** None

**R&D Plan:** None

**Objective**

The current residue stabilization program (RSP) for Rocky Flats Environmental Technology Site (RFETS) is focused on satisfying commitments made to the Defense Nuclear Facilities Safety Board (DNFSB) for the safe, interim storage of RFETS residues. However, for many of these residues, that course of action will not yield a disposable waste form that meets the safeguards and security guidance that was issued in July 1996 by the DOE Office of Safeguards and Security.<sup>1</sup> From a safety and economic perspective, it is desirable for the RFETS residues to be handled and treated only once in order to meet the criteria for safe, interim storage and for waste disposal.

**Scope**

To meet the interim safe storage criteria, some RFETS residues require processing in order to stabilize reactive species. Under the current RSP, the principal means for such stabilization is oxidation. Both muffle furnaces (for ash-type residues) and pyrochemical stationary furnaces (for salt residues) will be used for oxidation. One way to modify the RSP is to develop and implement technologies that will use the planned pyrochemical stationary furnaces for the simultaneous oxidation of reactive species and concentration of plutonium into a separate phase. The stabilized residue matrix would meet the waste disposal guidance. The plutonium concentration may meet the DOE long-term storage standard for plutonium metal and oxide (DOE-STD-3013),<sup>2</sup> or it may require further processing to meet the criteria.

Researchers propose a two-step flow sheet to treat several RFETS residues in order to meet safe interim storage criteria and the safeguards and security guidance for waste disposal. The treated bulk residue matrix will be nonreactive and suitable for waste disposal, and the plutonium concentrate will be in a form suitable for stabilization at Savannah River Site (SRS). This technology will be directed primarily at the pyrochemical salt residues but could have applications for the ash-type residues (both incinerator ash residues and sand, slag, and crucible residues). The first step is an electrochemical scrubbing process that oxidizes reactive species while concentrating the plutonium into an alloy. Essentially, the first step is an adaptation of the Hall-Heroult Cell that is used in electrowinning aluminum metal from molten cryolite baths. The second step involves the processing at SRS of the alloy into a form suitable for safe, interim storage.

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### **Benefits**

As mentioned, this technology currently is used for the commercial production of aluminum metal, but it has never been applied as residue treatment technology. Researchers will do the proof-of-principle demonstration with salts that contain a plutonium surrogate. Next a demonstration of radioactive salts will be done. Those salts will be compounded to simulate typical RFETS pyrochemical salt residues. Both the proof-of-principle and radioactive demonstrations will be done using equipment and personnel at the Savannah River Technology Center and personnel from RFETS. The demonstration with radioactive materials also will establish whether the alloy is suitable for stabilization at SRS.

This successful demonstration of this technology for pyrochemical salt residues will open the door for the use of this technology on other RFETS residues, specifically the ash-type residues. The same flow sheet will be used as for the pyrochemical salt residues, but a diluent salt will be added to the residue matrix. The diluent salt will be the molten medium that will allow for intimate contact of the plutonium species and other reactive species with the anode. The RFETS transuranic (TRU) pyrochemical salt waste is a good candidate for the diluent salt. Researchers propose the use of this TRU waste so that the overall amount of salt waste sent to the Waste Isolation Pilot Plant will not be increased. Proof-of-principle experiments and a demonstration with radioactive materials will need to be done. Some RFETS incinerator ash is at SRS and could be used for the radioactive demonstration, thus eliminating the need to compound a suitable surrogate residue.

### **References**

1. E. J. McCallum, "Additional Attractiveness Level E Criteria for Special Nuclear Material (SNM)," DOE Office of Safeguards and Security memorandum (July 22, 1996).
2. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).

**Stabilization Process Development**  
**Solubilization of Plutonium in Rocky Flats Environmental**  
**Technology Site Ash-Type Residues**

**Date Issued:** September 19, 1996

**Principal Investigators:** Alice Murray (Savannah River Site)  
David Karraker (Savannah River Site)

**Budget:** Fiscal Year 1997      \$230 K

**94-I IP Milestone:** IP-ES-025

**R&D Plan:** 4.3.5.3.1

**Objective**

The current residue stabilization program (RSP) for Rocky Flats Environmental Technology Site (RFETS) is focused on satisfying commitments made to the Defense Nuclear Facilities Safety Board (DNFSB) for the safe interim storage of those residues. However, for many of the residues at RFETS, that course of action will not yield a disposable waste form that meets the safeguards and security guidance that was issued in July 1996 by the DOE Office of Safeguards and Security.<sup>1</sup> From a safety and economic perspective, it is desirable for the RFETS residues to be handled and treated only once to meet the safe, interim storage criteria and the waste disposal criteria.

**Scope**

Researchers propose a two-step flow sheet in order to treat the ash-type residues at RFETS in order to meet safe interim storage criteria and the safeguards and security guidance for disposition at the Waste Isolation Pilot Plant. The first step is the simultaneous stabilization of the residues matrix and solubilization of the plutonium oxide. The treated residue will be shipped to Savannah River Site (SRS) where the residue will be processed so that the plutonium is in a form that is suitable for safe, long-term storage. The solubilization of the plutonium oxide is necessary to assure that the dissolution of the treated ash-type residue proceeds in a safe manner with respect to criticality safety concerns.

The solubilization is based on the conversion of the insoluble plutonium oxide to a more soluble compound. That conversion involves the oxidation of plutonium(IV) with the formation of an alkali-plutonium oxide to the more soluble valences of plutonium(V) or plutonium(VI). Applicable reactions are reported in the literature for the formation of lithium- and sodium-plutonium oxides. The ternary oxide is produced from the reaction of plutonium oxide with the appropriate alkali oxide or peroxide at temperatures in the range of 700°C–900°C. The ternary oxide will be suitable for dissolution in the F-Canyon at SRS.

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### **Benefits**

This process has only been done in the laboratory and has not been applied for production use. However, the development of this process to a point that it is suitable for a residue treatment technology should not be difficult. The technology will not require any new equipment designs. That is, the pyrochemical stationary furnaces planned for Building 707 at RFETS will be suitable for this process. The procedure will be similar to the pyrochemical salt oxidation procedure and will result in a simplified training program for the operators.

RFETS RSP personnel plan to calcine the ash to meet the criteria for safe, interim storage. That calcination will not result in a waste form that is suitable for disposal. One approach is to convert the plutonium to a form that is suitable for storage according to DOE standard DOE-STD-3013.<sup>2</sup> Conversion at SRS requires a readily soluble plutonium oxide that is absent in high-fired ash. Some type of solubilization of the plutonium oxide is required for the F-Canyon facilities to be used in a safe and efficient manner. Reaction of plutonium oxide to form an alkali-plutonium oxide is one way to obtain a soluble plutonium species suitable for processing in F-Canyon.

### **References**

1. E. J. McCallum, "Additional Attractiveness Level E Criteria for Special Nuclear Material (SNM)," DOE Office of Safeguards and Security memorandum (July 22, 1996).
2. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).

## Stabilization Process Development Hydrothermal Oxidation

**Date Issued:** October 1996

**Principal Investigators:** Steven J. Buelow  
Laura A. Worl

**Budget:** Fiscal Year 1997 \$800 K

**94-1 IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.5

### Objective

One of the most complex problems facing DOE is the expedited treatment of mixed wastes generated by operations at DOE facilities. A large legacy of created hazardous wastes (such as organic solvents and nitrates) are contaminated with transuranics. In some cases, these wastes are an acute safety hazard because of the production of flammable gases from organic decomposition initiated by radioactive decay. Remediation or elimination of these mixed wastes is a seemingly formidable task. The objective of this Los Alamos National Laboratory work is to evaluate and demonstrate a hydrothermal unit for processing and stabilizing mixed-waste legacy residues at the Los Alamos Plutonium Facility (TA-55).

### Scope

Hydrothermal processing can eliminate mixed-waste streams by the complete oxidation of the organic components and by reduction of the nitrate components in the waste. This process will mitigate safety hazards and will reduce radioactive waste volumes. Hydrothermal oxidation provides high destruction and removal efficiencies for a wide variety of organic and hazardous substances. For aqueous/organic mixtures, pure organic-liquid hydrothermal processing removes most organic and nitrate components (>99.999%) and facilitates collection and stabilization of the actinides.

The work proposed here will utilize hydrothermal processing at TA-55 to demonstrate stabilization of mixed-waste legacy residues that are present at the site. The target streams are identified under a recent treatability study notification to the Hazardous and Radioactive Waste Bureau of the New Mexico Environment Department, with the intent to conduct nine mixed-waste treatability studies at TA-55, a total of 41.5 kg mixed waste. Streams to be studied include hazardous solutions that contain plutonium or other actinides and liquids such as acetone, methylene chloride, nitric acid, and tributyl phosphate. Goals will be the successful elimination of the mixed waste.

We propose to eliminate as much as 41.5 kg of mixed-waste residues with hydrothermal processing. In fiscal year 1996, the laboratory-scale equipment for hydrothermal processing was assembled and installed for operation under the 94-1 R&D Program. This unit is capable of processing organic material at a rate of 0.1–0.5 kg/h. The work will require the support of two full-time technicians, one full-time staff member, and one half-time staff member.

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Initial feeds to be treated will include organic-bearing analytical solutions and spent solvent extraction solutions. We will analyze the effluent streams to determine the partitioning of the radionuclides between the solid and liquid phases and the amount of incomplete oxidation products in the liquid effluents. Our objective is to reduce the volume of mixed waste to zero by destroying it.

### **Benefits**

The primary benefit will be the elimination of mixed waste. Technologies, such as hydrothermal processing, that destroy organic material will also effect a large reduction in the volume and the mass of the actinide-containing material that must be stored. In addition, the extensive safety hazards that are inherent in mixed wastes will be completely mitigated after treatment with hydrothermal processing. Secondly, permitting incineration of plutonium-contaminated combustibles has been and will continue to be considerably difficult. Despite this fact, incineration is considered the alternate operable technology. Successful demonstration of an alternate mixed-waste treatment technology would be extremely beneficial.

**Stabilization Process Development**  
Catalyzed Chemical Oxidation—  
Radioactive Demonstration at Los Alamos  
**Work Breakdown Structure No.: 1.2.2.3**

**Date Issued:** November 30, 1996

**Principal Investigators:** Charles Brown (Kaiser-Hill company, Rocky Flats  
Environmental Technology Site)  
Wayne H. Smith

**Budget:** Fiscal Year 1997      \$750 K

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.3

### **Objective**

This process will stabilize combustible residues for long-term storage or disposal. This stabilization is achieved by destruction (oxidation) of all solid and liquid organic materials within the residue matrix and by dissolution of all radionuclides and active metals. The result of the process is that no combustible material or hydrogen-generating constituents remain. The actinides can be separated and stored as a salt or oxide; or the actinides can be disposed of with the other metal salts and insoluble materials, such as polyethylene or polyvinyl chloride. Space constraints within gloveboxes and criticality requirements can be met because of the relative small size of the required reaction vessels. The chemistry of the process will deal with the multiple hazardous-waste codes associated with residues at Rocky Flats Environmental Technology Site (RFETS) that are regulated by the Resource Conservation and Recovery Act (RCRA).

### **Scope**

Development to date has focused on the Delphi Research, Inc., DETOX<sup>SM</sup> process and has been highly successful. Delphi Research, Los Alamos National Laboratory, and RFETS now have 2 years of experience operating this process with surrogate materials at the 4-L reactor vessel size, full scale for residue processing. A full-scale demonstration using actual plutonium residues is now needed. Reconfiguring and upgrading the current development system for glovebox operation will be required, followed by testing and demonstrating with radioactive materials.

The process uses iron with a combination of homogeneous metal catalysts, such as platinum and palladium, in a chloride solution. This is a variation of wet chemical oxidation, in which the metals in solution play the major role in the destruction of the organic material. The process operates at 200°C and 0.7 megapascals (Mpa) or 100 pressure per square inch (psi). Bench-scale testing of a variety of surrogate materials has demonstrated that the DETOX process can produce a wide variety of residues, including those contaminated with mercury and cyanide. The average destruction rate for combustible-type materials is 0.2 kg/h in 2 L of solution in a 4-L stirred reaction vessel. Process information on surrogate destruction; process information

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on the fate of cyanide and nitric acid in the DETOX solution; and component testing on stirrers, solid feed, condenser design, and secondary reactors have been incorporated into the design of the proposed pilot-plant system. Researchers on an independent study conducted by the Materials Department at the Colorado School of Mines have identified the construction materials that offer the greatest corrosion resistance for this application. Delphi Research completed a process design and a safety review for a low-level mixed-waste pilot demonstration system that is currently being fabricated.

The activities funded for catalyzed chemical oxidation in fiscal year 1997 include the final procurement of the glovebox reactor from Delphi Research. A decision regarding the continuation of this project is required. Los Alamos personnel made a continuation request to RFETS/Kaiser-Hill Company, and this request will serve as a decision point regarding the continued funding and scheduling of this project. The factors necessary to reach this decision include the following:

- Which site can best handle the installation and testing of the prototype unit with radioactive materials—RFETS or Los Alamos?
- Does the site installation and test schedule meet the needs of the various sites; i.e., is the radioactive materials development and test schedule compatible with site integrated stabilization management plans so that milestones can be accomplished?
- Which site or sites will require this stabilization process?
- Does the process place the material in an acceptable end-state, or is additional handling required?

### **Benefits**

Although the relative hazards of combustible residues is dependent upon the type of residue, the potential system safety problems with combustible residues include the following:

- radiolytic generation of hydrogen and other flammable and corrosive gases from hydrogenous material, plastic packaging material, and reactive metals;
- production of reactive and pyrophoric metals;
- production of nitrated organics and other fuel mixtures;
- production of plutonium metal and organohalide mixtures; and
- degradation of plastic packaging material.

By the destruction of the organic matrix, this research, development, and testing effort will aid in the stabilization and safer storage of these high-risk combustibles.

## Milestones

### Radioactive Demonstration

of Catalyzed Chemical Oxidation ..... December 31, 1996–October 30, 1998

1. Decide whether to continue Los Alamos installation  
or to transfer to RFETS for installation. .... December 31, 1996

Installation at Los Alamos ..... January 1, 1997–October 31, 1998

1. Conduct compliance, configuration  
management, and reviews ..... January 1–June 13, 1997  
Write operating procedure ..... January 9–March 14, 1997  
Obtain treatability study permit ..... January 1–June 13, 1997  
Complete configuration management  
review at Los Alamos Plutonium  
Facility ..... January 9–June 13, 1997  
Issue authorization basis ..... June 15, 1997
2. Conduct installation activities ..... June 16, 1997–February 27, 1998  
Modify glovebox ..... June 16–September 30, 1997  
Install unit ..... September 30, 1997–January 30, 1998  
Assess readiness ..... February 2–27, 1998  
Have equipment ready for testing  
with radioactive materials ..... February 27, 1998
3. Demonstrate process ..... March 2–October 30, 1998  
Conduct 100-g-scale surrogate test ..... March 2–31, 1998  
Conduct 500-g-scale surrogate test ..... April 1–30, 1998  
Complete surrogate test ..... April 30, 1998  
Conduct test on applicable radioactive  
combustible materials ..... May 1–October 30, 1998  
Issue final report on radioactive tests ..... October 30, 1998

This proposed project and schedule involve actual installing and testing, with radioactive materials, the 2-L glovebox unit currently being fabricated by Delphi Research. Installing and testing the unit at Los Alamos requires prioritization in the Nuclear Materials Technology Division integrated project plan. The schedule for installation and demonstration at RFETS is thought to be similar to the time and costs required to complete the demonstration task at Los Alamos.

## Stabilization Process Development

### Mediated Electrochemical Oxidation—Development Activities beyond Rocky Flats Environmental Technology Site Rebaseline Exercise Work Breakdown Structure No.: 1.2.2.6

**Date Issued:** October 28, 1996

**Principal Investigators:** Jeff Surma (Pacific Northwest National Laboratory)  
Dean Kurath (Pacific Northwest National Laboratory)  
Martyn G. Adamson (Lawrence Livermore National Laboratory)  
Bryan Balazs (Lawrence Livermore National Laboratory)  
Wayne H. Smith

<b>Budget:</b> Fiscal Year 1997	\$1000 K (PNNL \$750 K, LLNL \$250 K)
Fiscal Year 1998	\$1300 K (PNNL \$900 K, LLNL \$400 K)
Fiscal Year 1999	\$1050 K (PNNL \$750 K, LLNL \$300 K)
Fiscal Year 2000	\$200 K (PNNL \$100 K, LLNL \$100 K)

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.6

### Objective

The purpose of this work is to continue developing mediated electrochemical oxidation (MEO) as a viable technology for the treatment of combustible residues and for the removal of surface contamination from selected matrices. The final goal is to demonstrate the feasibility of this process using real combustible waste as feed and to oversee the installation of a full-production-scale unit at Rocky Flats Environmental Technology Site (RFETS).

### Scope

MEO has been demonstrated successfully for the treatment of selected combustible residues. However, this technology has not been demonstrated on the residues at RFETS. The scope of this project is threefold:

- to design and test a pilot-scale MEO unit that is capable of treating RFETS residues,
- to test this apparatus with radioactive materials and on real or surrogate residues, and
- to design, test, and install a full-production-scale unit for use at RFETS.

MEO can destroy the organic component and recover the radioactive component of selected mixed wastes. For example, chlorinated hydrocarbons, such as tetrachloroethylene, carbon tetrachloride, and chloroform, have been very efficiently converted to carbon dioxide at room temperature; while other organic materials, such as polypropylene and polyethylene, are fairly

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inert. Thus MEO would be an ideal technology for the treatment of a waste such as that found on polyethylene process line filters (Full-Flo™) contaminated with carbon tetrachloride and plutonium. Treatment with the MEO process would convert the carbon tetrachloride to carbon dioxide, dissolve the plutonium for subsequent recovery by standard recovery procedures, and leave the filters free of both organic and radioactive contamination, ready for packaging and shipment to the Waste Isolation Pilot Plant as transuranic or possibly low-level waste. A similar scenario can be envisioned for the high-efficiency particulate air filter residues. These two filter residues combined represent approximately one-third of the total bulk combustible residues at RFETS.

One approach to treating the filters is to flow the MEO solution through the filter, either in the same direction or counter to the original flow pattern in an effort to flush the system of organic and radioactive contamination. One of the goals of the proposed research is to design and test an apparatus capable of accomplishing this task. One problem that may be encountered by this approach is channeling the solution through the noncontaminated portions of the filters with insufficient contact of the solution with the contaminated portions.

A second approach to be tested is to first shred the filters, using the recently developed cryoshredding technology. This pretreatment would increase the total processing time but would also significantly increase the exposed surface area and improve the efficiency of the extraction process. The shredded material would be packed into a containment vessel, and the MEO solution would be passed through. A totally different equipment design would be necessary for this approach.

After all the plutonium has been removed, the residue will be washed with water in order to remove the residual nitric acid solution. Then the residue will be dried before it is packaged in waste drums. The MEO solution would be recycled until the plutonium content reached a specified level. The solution would then be treated to recover the plutonium for separate packaging and storing. The wash, dry, and solution treatment steps in the process require further development and are the focus of this proposed work.

Treatment of filters by MEO dissolves the contamination and destroys the organic residue but does not attack the hard plastic matrix to any appreciable extent. However, some organic materials are destroyed by this treatment. They include cellulosic materials, such as paper, cloth, cardboard, and wood. These materials also make up a significant fraction of the residues at RFETS. A second phase of this project will be to design and test an MEO system capable of destroying these combustibles residues with subsequent recovery and disposal of the contained plutonium.

Much of the development work on the MEO process in this country has been done at Pacific Northwest National Laboratory (PNNL) and Lawrence Livermore National Laboratory (LLNL), either separately or in collaboration. Both sites have in place a pilot-scale apparatus capable of conducting tests on surrogate waste materials. This equipment can also be easily modified to accommodate the proposed residue treatment flow sheet for combustible residues at RFETS. In order to expedite the necessary further development of MEO technology for this purpose, both sites need to be involved in this activity. The higher priority at this time is treatment of the filter media. Developing a process to treat these residues is best done at PNNL. Unlike LLNL, PNNL has the capability to perform radioactive tests on actual residues from RFETS or, if shipping is a

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problem, of using identical contaminated filters generated at Hanford Site. While the filter work proceeds at PNNL, a similar concurrent development of treating cellulosic materials will take place at LLNL. The latter work is potentially more challenging and may require a longer time to achieve.

In fiscal year 1997 (FY97), work at PNNL will involve application of MEO technology to the treatment of filter media. The first step in this process will be to estimate the volume of waste water generated in treating these residues to make certain that the MEO process fits into the RFETS general cleanup scheme. Then actual radioactive testing will be conducted using filters obtained either from RFETS or from Hanford Site. A first phase will involve process optimization using samples from actual filters, followed by a second phase in which whole filter elements will be treated in a prototypic demonstration. Paralleling the radioactive testing will be a subtask that involves developing an MEO treatment system design for use at RFETS. An MEO system that was fabricated for service at Hanford will be tested with nonradioactive materials during FY97 at PNNL. This system may be modified for the filter treatment application if such modification is deemed necessary. The process will ultimately be transferred to RFETS for testing and implementation in actual filter processing. PNNL personnel will participate in the subsequent design, balance-of-process fabrication, installation, and testing of the filter processing MEO system at RFETS.

The FY97 work at LLNL will involve modification of existing equipment to handle cellulosic residues and studies of process optimization. Personnel from PNNL, LLNL, and Los Alamos National Laboratory will continue to serve as technical consultants to the project during its application at RFETS.

### **Benefits**

One of the conclusions of the combustible residues trade study<sup>1</sup> is that no one technology, other than possibly incineration, is capable of treating the full suite of combustible residues. However, it is unlikely that incineration is a viable option because of the difficulty and uncertainty in getting a permit. Therefore, we are left with the realization that at least two technologies will be necessary to deal with the RFETS combustible residues. The current thinking is to use MEO to remove the contamination from the surface of hard plastics, such as filter materials and plastic bottles. Another chemical oxidation technique will be used to treat the remaining residues. The advantages of using MEO to treat filter media are (1) that this technology has already been demonstrated to be applicable to the treatment of selected combustible residues and (2) that obtaining a permit to operate should not be difficult because this technology is an ambient temperature, ambient pressure, aqueous process. These two factors should expedite implementation at RFETS. Implementation will also be aided by the direct participation of site personnel during the evaluation studies. If we can also demonstrate that MEO will treat the majority of the remaining residues, we have the added benefits of using a technology that has already been installed and permitted and that can be used with only minor modifications.

### **Reference**

1. "Department of Energy Plutonium Combustibles Trade Study," U.S. Department of Energy report (December 1996).

## Milestones

MEO Demonstration and Testing Activities .....	November 1, 1996–September 30, 1999
PNNL MEO Demonstration and Testing (D&T) activities .....	December 1, 1996–September 30, 1999
1. Obtain environment, safety, and health (ES&H) and National Environmental Policy Act (NEPA) regulatory approval for surrogate and actual waste testing .....	December 2, 1996
2. Calculate balance-of-process design for Full-Flo filter processing .....	December 2, 1996–January 2, 1997
3. Conduct bench-scale testing on radioactive Full-Flo filter core samples .....	December 2, 1996–May 30, 1997
4. Prepare report on core filter testing .....	May 30–June 30, 1997
5. Issue report on core filter testing .....	June 30, 1997
6. Conduct radioactive testing of whole Full-Flo filters .....	June 2–September 30, 1997
7. Issue final report on radioactive filter testing .....	October 31, 1997
8. Evaluate and design filter housing .....	December 2, 1996–March 20, 1997
9. Modify MEO cell .....	March 21–May 30, 1997
10. Conduct nonradioactive testing of integrated MEO system .....	June 2–August 29, 1997
11. Issue final report on nonradioactive testing and process optimization .....	October 31, 1997
12. Complete balance-of-process design and fabrication for filter-processing system .....	October 1, 1997–April 30, 1998
13. Transfer MEO filter-processing system to RFETS .....	December 1, 1997–April 30, 1998
14. Design support for RFETS system .....	October 1, 1997–September 30, 1998
15. Conduct on-site participation at RFETS for installation and testing .....	October 1, 1997–September 30, 1999
LLNL MEO D&T activities .....	November 1, 1996–March 31, 1999
1. Obtain ES&H and NEPA regulatory approval for surrogate testing .....	November 1–December 31, 1996
2. Conduct laboratory-scale studies in support of conceptual design .....	November 1, 1996–June 30, 1997
3. Complete conceptual design of pilot-scale MEO cellulosic treatment system .....	June 2–July 31, 1997
4. Construct and install pilot-scale MEO treatment system .....	August 1–September 30, 1997
5. Issue progress report .....	September 30, 1997
6. Test cellulosic residues treatment using pilot-scale system .....	October 1, 1997–March 3, 1998

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7. Issue progress report..... March 31, 1998
  8. Design production-scale MEO cellulosic treatment system ..... March 31–May 29, 1998
  9. Construct and test production-scale MEO treatment system ..... June 1, 1998–September 30, 1998
  10. Obtain permit for use of production-scale MEO system at RFETS ..... April 1–September 30, 1998
  11. Transfer and install production-scale MEO system at RFETS..... October 1, 1998–March 31, 1999

**Stabilization Process Development**  
**Process Analytical Chemistry—**  
**Aqueous Stabilization Processes**

**Date Issued:** November 30, 1996

**Principal Investigators:** James T. Dyke  
Kevin J. Kuhn  
Dianna S. Blair (Sandia National Laboratories, New Mexico)

**Budget:** Fiscal Year 1997      \$300 K

**94-1 IP Milestone:** None

**R&D Plan:** None

**Objective**

The purpose of this work is to provide technologies for real-time monitoring of aqueous processes that are currently being tested and used for stabilizing plutonium residues. A number of chemical parameters influence the efficiency of aqueous plutonium recovery operations being used in stabilization activities. By providing real-time analytical information on these parameters, process engineers can optimize the processes so as to minimize the volume of waste generated during stabilization.

**Scope**

The composition of the waste matrices that require stabilization are highly variable in content. Therefore, to properly control the stabilization process, we need to provide real-time monitoring of important process parameters in order to provide smooth and efficient process operation. At the same time, we need to minimize generation of additional waste as a byproduct of stabilization activities. If these process parameters are not monitored on a batch-by-batch basis, then the processing envelope must be specified on a worst-case basis. This worst-case processing envelope creates an envelope in which excess reagents are used, excess wash volumes are generated, and potential loss of plutonium to the waste streams is present. The use of real-time monitoring will allow the process envelope to be adjusted for each particular feed batch, leading to efficient processing and minimizing waste. Conditions in which plutonium could be lost to the waste streams are identified, and corrective actions can be taken to minimize this risk.

Studies have identified several process parameters that effect efficiency.<sup>1,2</sup> These parameters include the following:

- aqueous phase plutonium concentration,
- plutonium oxidation state,
- concentration of interfering complexing agents,

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- nitric acid concentration, and
  - nitrate concentration in waste solutions.

Researchers on this project will develop and test on-line instrumentation, based on previous laboratory studies, to provide real-time monitoring of these parameters. The instrumentation will be turn-key systems that are suitably rugged for use in a process environment.

**Proposed analytical techniques.** The on-line instrumentation would be based on two analytical platforms: optical absorption spectroscopy<sup>3-6</sup> and flow-probe chemical sensors.<sup>7</sup> Nitrate concentration by means of flow-probe technology is ongoing work at Los Alamos National Laboratory to implement an on-line nitrate monitor based on the flow-probe technology. The technology has been shown to be feasible through a laboratory prototype of monitoring nitrate at 5-45 parts per million (ppm). This work should be readily transferable to this application.<sup>8</sup>

Optical absorption spectroscopy will be used for plutonium concentration, plutonium oxidation state, and interfering complexing agents. Flow-probe technology will be used for nitric acid and nitrate concentrations. Both analytical platforms make use of fiber-optic spectroscopy, a technology that has been proved to be compatible with glovebox operations and that provides the ability to analyze process solution in the glovebox line while keeping more complex instrument components outside the glovebox for easier maintenance.

### **Benefits**

On-line monitoring of actinide compounds during purification and stabilization processes is currently not performed in the DOE weapons complex. However, active on-line process control and monitoring can reduce costs related to energy consumption, materials reprocessing, process efficiency, and waste generation.

This work draws on expertise that resides at both Los Alamos and Sandia National Laboratories, New Mexico (SNL,NM). Both laboratories have ongoing research efforts in the areas of analytical chemistry and sensor technologies. Furthermore, Los Alamos researchers have extensive experience in actinide chemistry and in deploying instrumentation in glovebox environments, and SNL,NM personnel have experience in systems integration and in deployment. This collaboration will bring the strengths of these two laboratories to bear on the solution to the problem.

### **References**

1. James T. Dyke, Roderick S. Day, Alvin R. Vigil, and Jacob M. Espinoza, "Analytical Survey of the Nitrate Anion-Exchange Recovery of Plutonium," Los Alamos National Laboratory report LA-11611 ECI (April 1990).
2. James T. Dyke, Glenn E. Bentley, J. R. Bruninga, Donald A. Burns, et al., "Plutonium Recovery Modification Program: Process Analytical Chemistry Support Study," Los Alamos National Laboratory report LA-12083-MS (July 1991).
3. Roderick S. Day, Alvin R. Vigil, and S. Fredric Marsh, "A Visible/Near IR Spectral Database for Plutonium Solutions of Known Nitric Acid, Fluoride, and Oxalate Composition," Los Alamos National Laboratory report LA-11480 (April 1989).

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4. W. P. Carey, James T. Dyke, and Lawrence E. Wangen, "Spectrophotometric Method for Monitoring a Plutonium Oxalate Precipitation Process Using Partial Least-Squares Regression," Los Alamos National Laboratory report LA-11508 (July 1989).
  5. Ellen A. Stallings, James T. Dyke, and S. Fredric Marsh, "Spectrophotometric Analysis for the Prediction of Distribution Ratios and Estimation of Plutonium Complexation in Nitrate Process Solutions," Los Alamos National Laboratory report LA-11696 (March 1990).
  6. S. Fredric Marsh, Roderick S. Day, and D. Kirk Veirs, "Spectrophotometric Investigation of the Pu(IV) Nitrate Complex Sorbed by Ion-Exchange Resins," Los Alamos National Laboratory report LA-12070 (June 1991).
  7. Kevin J. Kuhn and James T. Dyke, "A Renewable-Reagent Fiber-Optic Sensor for Measurement of High Acidities," *Anal. Chem.* 68(17), 2890-2896 (1996).
  8. James T. Dyke, Los Alamos National Laboratory, unpublished data.

## **Stabilization Process Development**

### **Process Analytical Chemistry—Pyrochemical Salt Distillation**

**Date Issued:** November 30, 1996

**Principal Investigators:** James T. Dyke  
Kevin J. Kuhn  
Dianna S. Blair (Sandia National Laboratories, New Mexico)

**Budget:** Fiscal Year 1997      \$300 K

**94-I IP Milestone:** None

**R&D Plan:** 4.3.1.2.2

#### **Objective**

Researchers on the pyrochemical salt distillation project, currently ongoing at Los Alamos National Laboratory, separate plutonium-containing pyrochemical salts into a very lean salt fraction (<100 parts per million [ppm] plutonium) and plutonium oxide suitable for storage under the DOE standard DOE-STD-3013.<sup>1</sup> The chloride content of the pyrochemical residues is converted into stable, slightly contaminated salt; and the plutonium content is separated into a homogeneous, well-characterized oxide material that is suitable for long-term safe storage. Process monitoring and control of plutonium salt concentration in the lean salt fraction is of concern because actinide levels suitable for disposal at the Waste Isolation Pilot Plant (WIPP) must be met. Distilled salt grab sampling and transportation to allow laboratory-based analysis does not provide rapid enough turnaround time to provide adequate process control. Typical laboratory analysis can take up to 2 weeks, during which the salt cakes must be held in temporary storage. After analysis is performed, the salt cakes can then be packaged and disposed of. An analysis method that can monitor the lean salt fraction during distillation will eliminate the need for salt cake storage and can identify process upsets in near real time.

#### **Scope**

The vacuum pyrochemical salt distillation method currently being explored at Los Alamos for stabilization of electrorefining, molten salt extraction, and direct oxide reduction salts is considered a baseline technology. When the process is brought on-line, process monitoring to quantify actinide content in the lean salt fraction will provide a means to verify waste acceptance requirements (at WIPP) and to reduce process waste generated by system upsets. The goal of this work is to implement process measurement capabilities on the lean salt fraction that is produced by the distillation process. Candidate technologies for this on-line monitoring of actinides include the following: (1) optical absorption techniques, (2) mass spectrometry, (3) prompt gamma emission, and (4) alpha scintillation.

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This work explores the capabilities of these techniques for low-level actinide detection (<100 ppm plutonium) in a process environment. Issues to be addressed include the adaptability of instrumentation to glovebox processing lines, sampling interfaces, potential interferences, and analytical figures of merit. Engineering to minimize the operational complexity of the analysis instrument is also necessary in order to provide a turn-key system for use by a nonexpert operator.

### **Benefits**

On-line monitoring of actinide compounds during purification and stabilization processes is currently not performed in the DOE weapons complex. However, active on-line process monitoring and control can reduce costs related to energy consumption, materials reprocessing, process efficiency, and waste generation.

This work draws on expertise that resides at both Los Alamos and Sandia National Laboratories, New Mexico (SNL,NM). Both laboratories have ongoing research efforts in the areas of analytical chemistry and sensor technologies. Furthermore, Los Alamos researchers have extensive experience in actinide chemistry and in deploying instrumentation in glovebox environments, and SNL personnel have experience in systems integration and in deployment. This collaboration will bring the strengths of these two laboratories to bear on the solution to the problem.

### **Reference**

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).

## **Stabilization Process Development**

### **Process Analytical Chemistry—Mediated Electrochemical Oxidation**

**Date Issued:** November 30, 1996

**Principal Investigators:** James T. Dyke  
Kevin J. Kuhn  
Dianna S. Blair (Sandia National Laboratories, New Mexico)

**Budget:** Fiscal Year 1997      \$300 K

**94-1 IP Milestone:** None

**R&D Plan:** 4.3.4.2.6

#### **Objective**

The purpose of this work is to provide technologies for real-time monitoring of the mediated electrochemical oxidation (MEO) process. MEO is currently being tested to establish viability of the technology for treating combustible residues and for removal of surface contamination from selected matrices.

#### **Scope**

MEO is one of the baseline technologies that are suitable for the treatment of combustible residues and for removal of actinide surface contamination from selected waste matrices. The composition of these waste matrices are highly variable in organic and plutonium content. Therefore, to properly control the process, real-time monitoring of important process parameters is needed. Key parameters include the following:

- aqueous phase plutonium concentration,
- activity of the mediator metal ( $\text{Ag}^{2+}$ ),
- concentration of soluble organics,
- nitric acid concentration, and
- nitrate concentration in the rinse solution.

Measuring aqueous phase plutonium content will provide a comparison to initial nondestructive assay (NDA) measurements of plutonium. This comparison between the two methods will help determine the extent of plutonium removal from combustible residue. Mediator activity will provide a measurement of the combined generation/utilization rate of the mediator. Coupled with the measurement of the aqueous plutonium, this measurement will provide input to the process engineer as to whether the mediator is being used to remove actinide contamination or whether the mediator is being consumed by other reactions, such as destruction of

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organic materials. Monitoring nitric acid content will help maintain process operation in optimal ranges. Monitoring the soluble organics and the nitrate levels of rinse solutions will assist in controlling characteristics of process-generated waste with the goal of meeting discard criteria.

The proposed work will coordinate with process development activities to establish the required concentration ranges of the key parameters and to develop at-line and on-line analytical methods for monitoring and controlling these parameters. We will develop and test prototype instruments that are suitably rugged for use in a process environment.

**Proposed analytical techniques.** We plan to use the following analytical techniques.

- *Studying plutonium concentration by means of optical spectroscopy.* Los Alamos National Laboratory has experience in monitoring plutonium concentration by using optical spectroscopy in aqueous plutonium processing streams.<sup>1</sup> Mass balance comparison between initial NDA values for plutonium and plutonium concentrations in the aqueous phase will be a valuable diagnostic tool for solution channeling problems in filter materials.
- *Studying mediator activity by means of electrochemical techniques.* The original principal investigators on R&D Plan 4.3.4.2.6 may provide the best guidance in this area and will be solicited for technical assistance.
- *Studying soluble organics by means of infrared spectroscopy.* SNL,NM researchers have experience in monitoring organic concentrations in electroless copper plating baths.<sup>2</sup>
- *Studying nitric acid concentration by means of flow-probe technology.* This technique has been successfully demonstrated for monitoring nitric acid concentration from 0.1 to 14 M.<sup>3</sup> This work was a joint research effort of Los Alamos; SNL,NM; and the University of Washington and was funded by EM-50.
- *Studying nitrate concentration by means of flow-probe technology.* Los Alamos researchers are currently implementing an on-line nitrate monitor based on flow-probe technology. The technology has been shown to be feasible through a laboratory prototype of monitoring nitrate at 5–45 parts per million (ppm). Our work should be readily transferable to this application.

Coordinating and integrating the output signals from all five sensing formats will be an important part of developing a turn-key system for process use.

### **Benefits**

On-line monitoring of actinide compounds during purification and stabilization processes is currently not performed in the DOE weapons complex. However, active on-line process control and monitoring can reduce costs related to energy consumption, materials reprocessing, process efficiency, and waste generation.

This work draws on expertise that resides at both Los Alamos and SNL,NM. Both laboratories have ongoing research efforts in the areas of analytical chemistry and sensor technologies. Furthermore, Los Alamos researchers have extensive experience in actinide chemistry and in

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deploying instrumentation in glovebox environments, and SNL, NM personnel have experience in systems integration and in deployment. This collaboration will bring the strengths of these two laboratories to bear on the solution to the problem.

### References

1. James T. Dyke, Roderick S. Day, Alvin R. Vigil, and Jacob M. Espinoza, "Analytical Survey of the Nitrate Anion-Exchange Recovery of Plutonium," (ECI) Los Alamos National Laboratory report LA-11611 (April 1990).
2. Dianna S. Blair, "Monitoring the Composition of Electroless Copper Baths Using Quantitative Infrared Spectroscopy," Sandia National Laboratories, New Mexico report SAND 91-0925 (1990, unpublished).
3. Kevin J. Kuhn and James T. Dyke, "A Renewable-Reagent Fiber-Optic Sensor for Measurement of High Acidities," *Anal. Chem.* **68**(17), 2890-2896 (1996).

## **Stabilization Process Development**

### **Process Analytical Chemistry—Pyrochemical Salt Oxidation**

**Date Issued:** November 30, 1996

**Principal Investigators:** James T. Dyke  
Kevin J. Kuhn  
Dianna S. Blair (Sandia National Laboratories, New Mexico)

**Budget:** Fiscal Year 1997      \$300 K

**94-1 IP Milestone:** IP-3.3-012A

**R&D Plan:** 4.3.1.2.1

#### **Objective**

The proposed residue stabilization process for pyrochemical salts is based on the use of standard pyrochemical furnaces with chemical oxidants. The amount of chemical oxidant required and the choice of furnace operating parameters, such as process time, are determined by the composition of feedstock material. The feedstock material is a highly heterogeneous matrix because it originates from many sources, such as electrorefining, molten salt extraction, or direct oxide reduction salts. A primary concern in salt oxidation is determining the optimal amount of chemical oxidant to add to a particular batch and to ensure that the excess oxidant is completely reacted before the salts are processed by salt distillation. Analysis of the off-gas during the process, coupled with analysis of feedstock, will allow the pyrochemical furnaces to operate under optimal conditions with minimal production of additional salts as a byproduct of the oxidation process. Continuous analysis of the off-gas will allow feedback control for adding chemical oxidant.

#### **Scope**

Researchers seek to develop process analytical support for the salt oxidation process. Two opportunities exist for analytical measurements to provide information on critical processing parameters: (1) off-gas analysis during the process to provide active feedback control for adding the chemical oxidant and (2) feedstock analysis to identify reactive metal content of the feed.

The primary choice of chemical oxidant is currently sodium or calcium carbonate. Presently, an estimated excess of carbonate is added, with the estimate being based on a carbonate-to-plutonium ratio. This ratio may or may not account for all the reactive metal content of a particular feed batch. At the end of the process, the excess carbonate is reacted with added titanium metal. Adding a recipe quantity of chemical oxidant does not always ensure efficient process operation. Monitoring the chemical composition of furnace gas effluent for the oxidation byproducts provides a method to confirm that pyrochemical salts are being fully oxidized. The proposed work will develop methods for off-gas analysis to follow byproducts from the reaction of carbonate with the reactive metals and with the plutonium chloride. We expect the off-gas to contain carbon monoxide and carbon dioxide. The results of the continuous off-gas analysis will be used to control the addition of carbonate and to verify that excess carbonate was removed by reaction with titanium metal.

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Monitoring the reactive metal content of feedstock material before adding it to the salt oxidation furnace is important because this reactive metal content is directly related to the optimum amount of chemical oxidant that should be added for efficient salt oxidation. The heterogeneous nature of the feedstock complicates measuring of reactive metal content. Therefore, bulk methods of sampling and analysis are required in order to obtain reliable information. Digital radiography is a bulk analysis technique that can be used. As part of the 94-1 R&D Project surveillance and monitoring activities, digital radiography (R&D Plan 7.2.2.1) is under development to nondestructively gain information on metal, oxide, and residues that are in storage throughout the DOE complex. This technique could be used to analyze the feedstock for metals that will be oxidized in the pyrochemical furnace and to provide an accurate measure of the stoichiometric amount of chemical oxidant required for processing.

### **Benefits**

To the process engineer, monitoring byproducts from the chemical oxidant confirms that the process is efficiently converting feedstock to oxides. Identifying optimal oxidant additions and furnace operation parameters that happen during residue stabilization activities will provide reductions in costs associated with energy consumption, materials reprocessing, process efficiency, and waste generation. Successful use of digital radiography for measuring metal content in the feedstock will provide a quantitative value for the amount of chemical oxidant to be added for complete conversion to a stable metal oxide.

This work draws on expertise that resides at both Los Alamos National Laboratory and Sandia National Laboratories, New Mexico (SNL,NM). Both laboratories have ongoing research efforts in the areas of analytical chemistry and sensor technologies. Furthermore, Los Alamos researchers have extensive experience in actinide chemistry and in deploying instrumentation in glovebox environments; and SNL,NM personnel have experience in systems integration and deployment. This collaboration will bring the strengths of these two laboratories to bear on the solution to the problem.

## Stabilization Process Development Process Analytical Chemistry—Washing

**Date Issued:** November 30, 1996

**Principal Investigators:** James T. Dyke  
Kevin J. Kuhn  
Dianna S. Blair (Sandia National Laboratories, New Mexico)

**Budget:** Fiscal Year 1997      \$300 K

**94-I IP Milestone:** IP-3.3-017

**R&D Plan:** 4.3.4.2.7

### Objective

Researchers on this project will provide technology for monitoring chemical parameters that will influence the effectiveness of the washing flow sheets for stabilization of combustible residues.

### Scope

The proposed wash procedure for plutonium stabilization of selected combustible residues is a batch process. Combustible residues are highly variable in their plutonium and organic content, making processing time highly variable. Monitoring important process parameters is necessary in order to properly control stabilization processes. Target process parameters that require monitoring include the following:

- plutonium concentration in the liquid phase,
- soluble organics concentration,
- nitric acid concentration, and
- nitrate concentration in the rinse solution.

*Proposed analytical techniques.* We will use the following analytical techniques:

- *Studying plutonium concentration by means of optical spectroscopy.* Los Alamos National Laboratory personnel have experience in monitoring plutonium concentration by using optical spectroscopy in aqueous plutonium processing streams.<sup>1</sup> Mass balance comparisons between initial nondestructive assay values for plutonium and aqueous-phase plutonium concentrations could be a valuable diagnostic tool for identifying channeling problems in filter materials.

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- *Studying soluble organics by means of infrared spectroscopy.* Sandia National Laboratories, New Mexico (SNL,NM) personnel have experience in monitoring organic concentrations in electroless copper plating baths.<sup>2</sup>
  - *Studying nitric acid concentration by means of flow-probe technology.* This technique has been successfully demonstrated for monitoring nitric acid concentration of 0.1–14 M.<sup>3</sup> The process was the result of a joint research effort at Los Alamos; SNL,NM; and the University of Washington and was funded by EM-50.
  - *Studying nitrate concentration by means of flow-probe technology.* Ongoing work at Los Alamos to implement an on-line nitrate monitor based on flow-probe technology has shown to be feasible through laboratory prototype monitoring of nitrate at 5–45 parts per million (ppm). This analytical technique should be easily adapted to our research.

Coordinating the output signals from all four analytical techniques will be an important part of developing a turn-key system for process use.

### Benefits

On-line monitoring of actinide compounds during purification and stabilization processes is currently not performed in the DOE weapons complex. However, active on-line process control and monitoring can reduce costs related to energy consumption, materials reprocessing, process efficiency, and waste generation. This work draws on expertise that resides at both Los Alamos and SNL,NM. Both laboratories have ongoing research efforts in the areas of analytical chemistry and sensor technologies. Furthermore, Los Alamos researchers have extensive experience in actinide chemistry and in deploying instrumentation in glovebox environments, and SNL,NM personnel have experience in systems integration and in deployment. This collaboration will bring the strengths of these two laboratories to bear on the solution to the problem.

### References

1. James T. Dyke, Roderick S. Day, Alvin R. Vigil, and Jacob M. Espinoza, "Analytical Survey of the Nitrate Anion-Exchange Recovery of Plutonium," (ECI) Los Alamos National Laboratory report LA-11611 (April 1990).
2. Dianna S. Blair, "Monitoring the Composition of Electroless Copper Baths Using Quantitative Infrared Spectroscopy," Sandia National Laboratories, New Mexico report SAND 91-0925 (1990, unpublished).
3. Kevin J. Kuhn and James T. Dyke, "A Renewable-Reagent Fiber-Optic Sensor for Measurement of High Acidities," *Anal. Chem.* **68**(17), 2890-2896 (1996).

## Surveillance and Monitoring

### Position-Sensitive Boron-Loaded Scintillating-Optical-Fiber Neutron Counting System for Assay of Plutonium in Lean, Highly Impure Residues

**Date Issued:** November 20, 1996

**Principal Investigators:** Teresa L. Cremers  
Phyllis A. Russo

**Budget:** Fiscal Year 1997      \$300 K

**94-1 IP Milestones:** IP-3.3-022

**R&D Plan:** 7.2.2.7

### Objective

Los Alamos National Laboratory researchers on this project will evaluate a position-sensitive boron-loaded scintillating-optical-fiber neutron counting system. This neutron detection system consists of boron-loaded plastic fibers that are assembled in long, wide ribbons. Researchers optically couple both ends of these bundled ribbons to a photo multiplier tube (PMT). The neutron detection system, which is based on new sensor technology, allows the continued use of current, commercially available neutron assay software and of associated hardware.

### Scope

The primary neutron signal from the boron-loaded fibers is the scintillation produced by the energetic charged particle that is released in the  $(n,\alpha)$  reaction between a thermal neutron and  $^{10}\text{B}$ . The fibers are also sensitive to gamma-rays. By appropriate choice of fiber diameter, scintillations in a single fiber that arise from gamma-ray interactions will give rise to smaller pulse heights than those from neutron capture, enabling rejection of gamma-ray signals by pulse-height discrimination.

Several benefits are realized by coupling the PMTs to the optical fibers at each end of the ribbons. Position-sensitive PMTs (PSPMTs) are used on one end of the optical fibers. The principal benefit is reduction of detector to gamma rays by applying logic to multiple output signals for the different position. The result is that the neutron-to-gamma-ray efficiency ratio is improved over competing types of detectors. Requiring a coincidence between the PSPMT signal at one end and the standard PMT signal at the opposite end of the fiber reduces PMT noise or dark current signals.

Thin moderator layers can be inserted between the fiber ribbons in order to optimize neutron detection efficiency and to improve sensitivity to true coincident fission neutrons. Thus, by modeling to determine the best moderator position and placement, we can optimize the counter design for improved sensitivity for neutron counting of materials with high  $\alpha$ - $n$  neutron yields such as spent americium-extraction salts.

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Our proposed work is broken out in three stages. The first stage (through fiscal year 1997) is development of the detection system. We will purchase a position-sensitive boron-loaded scintillating-optical-fiber neutron counter from the Bicron Corporation. This counter is a capital equipment item consisting of a pair of PSPMTs, multiple-fiber ribbons, a common PMT, coupling hardware, and readout electronics. This project stage includes mathematical modeling of the counter in order to optimize efficiency and sensitivity for detection of true time-correlated neutrons. The first stage also includes developing hardware and software capability for rapid discrimination and logical sorting of pulses and linkage to the electronics. The second stage (fiscal year 1998) is characterizing detection system response to sources of random and coincident neutrons and gamma rays. The third stage (fiscal years 1998 and 1999) is characterizing detection system response to plutonium-bearing materials, including spent americium extraction salts.

### **Benefits**

This work can extend quantitative analysis of plutonium by neutron counting to include materials that are lean and highly impure (such as molten-salt extraction residues) and to other difficult-to-measure isotopes and matrices.

## **Surveillance and Monitoring**

### **Advanced Tomographic Gamma Scanner Development**

**Date Issued:** November 30, 1996

**Principal Investigators:** Thomas H. Prettyman  
Lynn A. Foster

<b>Budget Request:</b> Fiscal Year 1997	\$250 K Operating/\$50 K Capital
Fiscal Year 1998	\$800 K Operating/\$50 K Capital
Fiscal Year 1999	\$100 K Operating/\$20 K Capital

**94-1 IP Milestone:** IP-3.3-022

**R&D Plan:** 7.2.2.2

#### **Objective**

We will develop a state-of-the-art tomographic gamma scanner (TGS) for the Los Alamos National Laboratory Plutonium Facility (TA-55) Building PF-4. Our purpose will be to improve accountability measurements of product materials, process residues, and waste. The advanced TGS will make possible high-accuracy assays of impure, nonuniform, and inhomogeneous materials, such as pyrochemical salts, in containers ranging from small cans to 208-L drums. Severe matrix effects and contamination with high levels of  $^{241}\text{Am}$  can make these items difficult or impossible to assay by standard nondestructive assay (NDA) methods, including segmented gamma scanning (SGS) and passive neutron coincidence counting. The new instrument will be designed to measure these materials with high accuracy and meet or exceed the sensitivity and throughput of gamma-ray instruments currently in use in the PF-4 count room.

#### **Scope**

The purpose of this project is to develop and implement a state-of-the-art gamma-ray NDA instrument for use in the nation's only operating plutonium production facility. The instrument, an advanced TGS, will provide fast, accurate assays of a wide range of materials, including product materials, process residues (such as pyrochemical salts), and contaminated waste. The instrument will be used both for accountability measurements of items under safeguards and for safeguards-termination measurements on waste. The throughput and accuracy of the instrument will make possible the measurement of a number of materials categories that, with existing instrumentation, could only be measured accurately by calorimetry corrected for isotopics. Consequently, a number of functions currently reserved for passive neutron counting will be done by the new scanner.

The technology underlying the new instrumentation is tomographic gamma scanning. Tomographic gamma scanning was developed by the Los Alamos safeguards program to provide high-accuracy assays of samples that contain nonuniform and inhomogeneous materials. With tomographic gamma scanning, low-resolution images of gamma-ray attenuating material within an item are formed, using transmission computerized tomography. These images are used to correct gamma-ray emission computer tomography for attenuation by nonuniform

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matrix materials, enabling accurate assays of gamma-ray emitting material in the sample. High-resolution gamma-ray spectroscopy is used for both the transmission and emission imaging modes, allowing individual gamma rays to be measured in the complex gamma-ray spectra characteristic of special nuclear materials, minor actinides, and their daughters. Gamma-ray spectroscopy also enables the TGS to detect and correct for source self-attenuation, for example, by plutonium-metal shot that is often found in process residues.

A prototype TGS is currently set up at Building PF-4 and is being evaluated for use in measuring pyrochemical salts. Preliminary results of the evaluation are quite promising, with TGS outperforming both SGS and passive neutron coincidence counting for samples containing electrorefining and molten-salt extraction salts. Improvements in the design of the prototype, both from the standpoint of throughput and ease-of-use, are desired before implementation of the TGS in the Building PF-4 count room.

The TGS proposed for this project will have a number of features that will enable it to function effectively in the count-room environment. The advanced TGS will be capable of assaying two-to-three items per hour with the same sensitivity and accuracy as the prototype scanner. We will achieve the target throughput by using two or more intrinsic germanium detectors. One of these detectors will be optimized for isotopics measurements, and software will be provided to perform peak search and identification, as well as plutonium isotopics. We will use automated, variable-geometry collimators to adjust spatial resolution of the scan so as to accommodate different package sizes and to facilitate high-resolution region-of-interest (ROI) scans. In addition, we will develop an adjustable source filter and governor to automatically control transmission source intensity and to enable a higher dynamic range for gamma-ray transmission measurements. Both the ROI scanning and the adjustable source filter are new features that will enable the TGS to produce accurate assays of dense items and items that have large amounts of special nuclear material.

The software package for advanced TGS will provide for data acquisition and control, tomographic reconstruction and image rendering, and data archiving. The software will be able to execute a variety of scan protocols, including traditional low-resolution scans and high-resolution region-of-interest scans. The flexibility in scanning protocol will enable a "graded approach" to safeguards assay, in which assay accuracy can be adjusted according to the amount of materials in the sample. We will implement methods to preset scan time in order to achieve target precision requirements for safeguards and waste screening. The improved TGS software will include a user-friendly interface that will be easy for count-room technicians to learn and operate.

***Budget and Schedule.*** This project will consist of three phases leading to the installation of an advanced TGS in the Building PF-4 count room. Installation will take place within 2 years from the beginning of the project and full operation will begin within the third year. In the first phase, we will develop a design package for the advanced TGS hardware and data acquisition and analysis software. This part of the project will last approximately 6 months. The second phase will involve procuring scanner hardware, fabricating the TGS, installing it in the facility, and completing acquisition and analysis software development. We will complete this part of the project by the end of the second year. The final phase will involve acceptance testing and physics support needed to integrate the instrument into the facility.

