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94-1 Research and Development Project

Lead Laboratory Support

Status Report

October 1–December 31, 1995

MASTER

Los Alamos
NATIONAL LABORATORY

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This is the first report in this series.

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Compiled by
Mark Dinehart

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Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

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EXECUTIVE SUMMARY

SALT DISTILLATION

The salt distillation process is designed to separate plutonium pyrochemical salts into a very lean salt fraction (<100 parts per million [ppm] plutonium) and plutonium oxide suitable for storage under DOE Standard 3013-94. The chloride content of the pyrochemical residues are converted into stable, slightly contaminated salt, and the plutonium content is separated into a homogeneous, well-characterized, oxide material suitable for long-term storage.

Distillation separation is based on the large difference in vapor pressures at high temperature between chloride salts that constitute pyrochemical residues and actinide oxides. However, the plutonium content in these salts can be in the form of plutonium trichloride. Vapor pressure differences between alkali and alkaline earth chlorides and plutonium trichloride are too small to effect a good separation; therefore $PuCl_3$ must be converted to an oxide through an oxidation process. Carbonate salts are used as an oxidant to convert all plutonium species into plutonium dioxide. This oxidation process can be ultimately combined with a distillation separation process.

Tests employing existing equipment have been used to determine distillation rates as a function of temperature. A target rate of 3 kg per unit per day had been established for sodium chloride-potassium chloride, however, distillation rates for calcium chloride were found to be too slow at temperatures below 1100°C. Equipment designed expressly for the salt distillation process is now being developed. Tests were conducted this quarter on the high-temperature metal C-ring seals used in the spool connecting the distillation and receiver chambers, which must be at an elevated temperature to permit smooth flow of salt vapors.

Salts in drums at Rocky Flats Environmental Technology Site (RFETS) pose a safety risk. If water is present, its absorption by the salt will cause corrosion and breach of containment; and it will react with any reactive metals present to generate hydrogen gas. While it is theoretically possible to produce a salt of 100 nCi/g (~1 ppm) that would meet the criterion for low-level waste (LLW), efforts are focused on obtaining a product salt that contains <100 ppm plutonium. At this level of contamination, the salts are still transuranic (TRU) waste; but 55-gal. drums can be filled based on a volume limitation of the waste rather than on a radionuclide loading, resulting in a 10- to 100-fold decrease in the number of drums sent to the Waste Isolation Pilot Plant (WIPP).

COMBUSTIBLES

Cryogenic crushing is being developed to reduce bulk items to particles suitable for processing. The following three methods are being evaluated for the destruction of the organic matrix in combustible residues: mediated electrochemical oxidation, catalyzed oxidation, and hydrothermal processing.

Cryogenic Crushing

In order to destroy the organic matrix, many combustible residue materials require size reduction before processing. Among these materials are 1600 polystyrene cubes in storage at Westinghouse Hanford Company (WHC) and contaminated filter units at RFETS. An in-line filter grinder assembly and a cryogenic crusher for polystyrene cube reduction are under development. The filter grinder is based on commercial ice-crusher technology. A prototype is being assembled and will be tested on noncontaminated materials to determine the size of particles. Polystyrene/iron test cubes were fabricated to test a liquid-nitrogen-cooled cryogenic crusher. The test cubes are being evaluated for chemical changes in the polystyrene that may occur during fabrication.

Mediated Electrochemical Oxidation

In the mediated electrochemical oxidation process, an electron transfer mediator is generated at the anode in an electrochemical cell. The mediator reacts with the organic component of a mixed waste, converting it to carbon dioxide. The radioactive component remains in solution and can be recovered or disposed of, depending on the activity level. The process can remove surface contamination from selected matrices. To be effective, the electron transfer mediator must have high positive standard reduction-oxidation (redox) potential, exhibit two stable oxidation states in acidic media, react slowly with the solvent and rapidly with the organic, have reasonably high solubility in aqueous solution, and be recoverable. Oxidation characteristics of the compounds to be destroyed are a major factor. Tests will be conducted first on ion-exchange resin. Bench-scale tests completed to date show that cerium IV is the best mediator of the several that were tested. Cerium IV is quite stable at elevated temperatures and reacts rapidly with the resin to provide complete destruction. Further studies using cerium are currently under way. Parametric studies will determine optimum processing conditions. A pilot-scale oxidation apparatus using a commercially available flat-plate electrochemical cell will be tested in the Los Alamos National Laboratory Plutonium Facility (TA-55).

Catalyzed Oxidation

Catalyzed oxidation of organic compounds utilizes a concentrated solution of ferric chloride, hydrochloric acid, and platinum and ruthenium catalysts in minute amounts. This process destroys solid and liquid organic material within the residue matrix and dissolves radionuclides and active metals. In the process, carbon is oxidized to carbon dioxide by ferric iron, which is reduced to ferrous iron. Oxygen then oxidizes ferrous iron back to ferric iron, producing water; and the solution is regenerated. This project will continue the DETOX^{SM} process development work, which has been demonstrated by Delphi Corporation on liquid organics. Testing of surrogate materials will continue while equipment is prepared for glovebox installation. The corrosive nature of the solution leads to materials concerns. A corrosion-resistant tantalum-lined autoclave is being designed for glovebox testing. The process is being developed for operation in atmospheric pressure, and spent-solution disposal is being investigated. Reliable quantitative analytical methods are not yet available because of the solution's high-chloride content and its tendency to

solidify on cooling to temperatures below ~40°C. Total organic carbon (TOC) is used to determine organic destruction efficiency, but initial analyses have been erratic. Visual and gas-phase analysis appear to confirm results previously obtained by Delphi. In a recent test, observations of an unexpected exothermic reaction followed by a pressure drop during autoclave heat-up indicate that more work is needed to understand the nature of the reactions.

Hydrothermal Processing

Hydrothermal processing oxidizes organics and reduces nitrate components, providing high-destruction and high-removal efficiencies for a wide variety of organic and hazardous substances. For aqueous/organic mixtures, pure organic liquids, or contaminated combustible solids, hydrothermal processing removes most of the organic and nitrate components (>99.999%) and facilitates the collection and separation of the actinides. Results are reported for various noncontaminated compounds. In the process, solids are reduced in size by cryogenic grinding. Organic material is pressurized and mixed with pressurized 30 wt % of hydrogen peroxide. The reaction mixture is fed into a high-temperature, high-pressure reactor and allowed to react for 20–30 s. Organic components of the wastes are oxidized to carbon dioxide by reaction with the water and hydrogen peroxide. Nitrate contaminants also react with the organic material and are converted to a mixture of nitrogen gas and some nitrous oxide. The reactor is fitted with a titanium liner to protect the pressure vessel from corrosion. Speciation of the actinide is not yet certain. Most likely, they are converted either to small insoluble oxide particles that can be separated by filtration or to water-soluble carbonate salts. Implementation of hydrothermal processing will proceed from small-scale testing using surrogate materials, to small-scale contaminated-material testing, then to design and testing of a full-scale unit for surrogates, and finally to full-scale glovebox testing on radioactive materials.

ELECTROLYTIC DECONTAMINATION

The electrolytic decontamination process has been demonstrated to reduce external contamination on long-term storage containers to a level acceptable for removal from the glovebox into the laboratory room.

OXIDE PELLETIZING

The effects of pelletizing on the respirable-particle-size fraction of calcined plutonium oxide was investigated in a small-scale study. An oxide taken from TA-55 vault storage was pressed into compacts. The powder was not milled or sieved, and no binder or lubricant was added. The compacts were calcined at 980°C. The loss on ignition (LOI), mean particle size, and particle size distribution of crushed calcined green pellets was compared to that of the original material. The calcined green pellets had an acceptable LOI. In comparison to the untreated material, particle size was decreased by about half; and the surface area of the powder was greatly reduced. The measured respirable fraction of crushed pellets was not appreciably changed from the original material. Possibly, mean particle size

of crushed pellets was less because pressing broke down agglomerates present in the original material and calcining temperature was not sufficient to sinter particles. The treatment given did not appear to alter the mass fraction of respirable particles. In future tests, lubricants should be added to obtain a higher density pellet; and pellets should be heated to ~1200°C to realize the desired result of having smaller particles agglomerate.
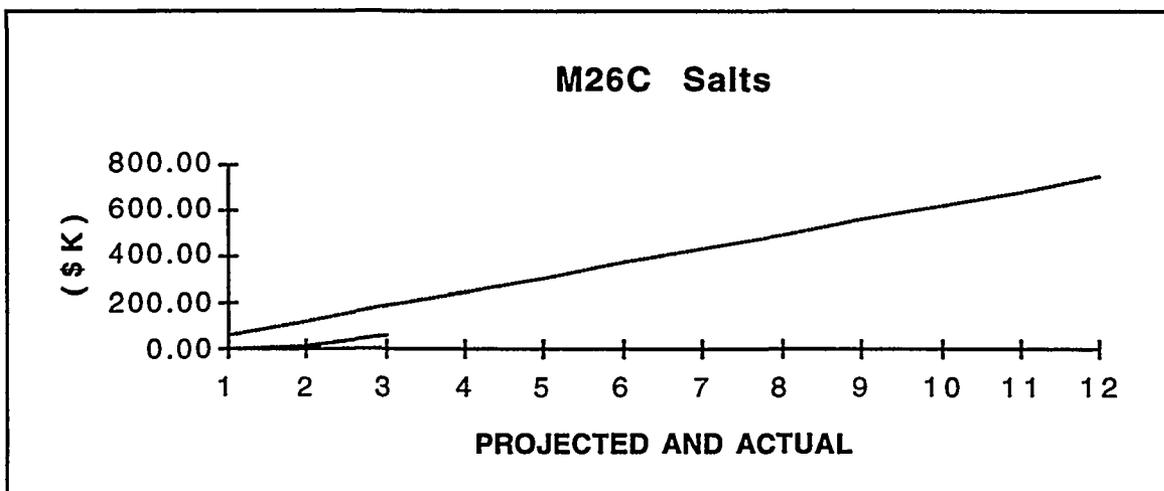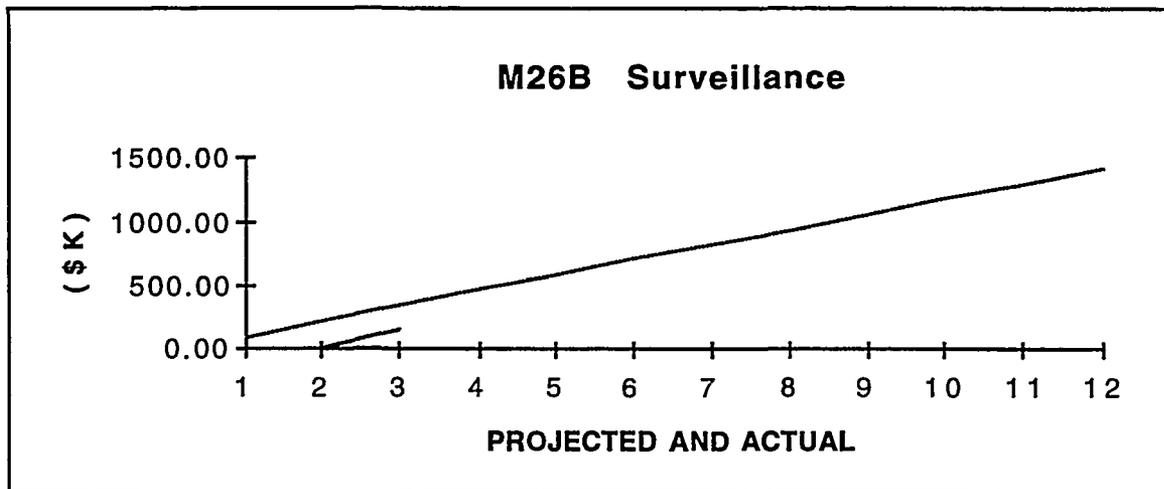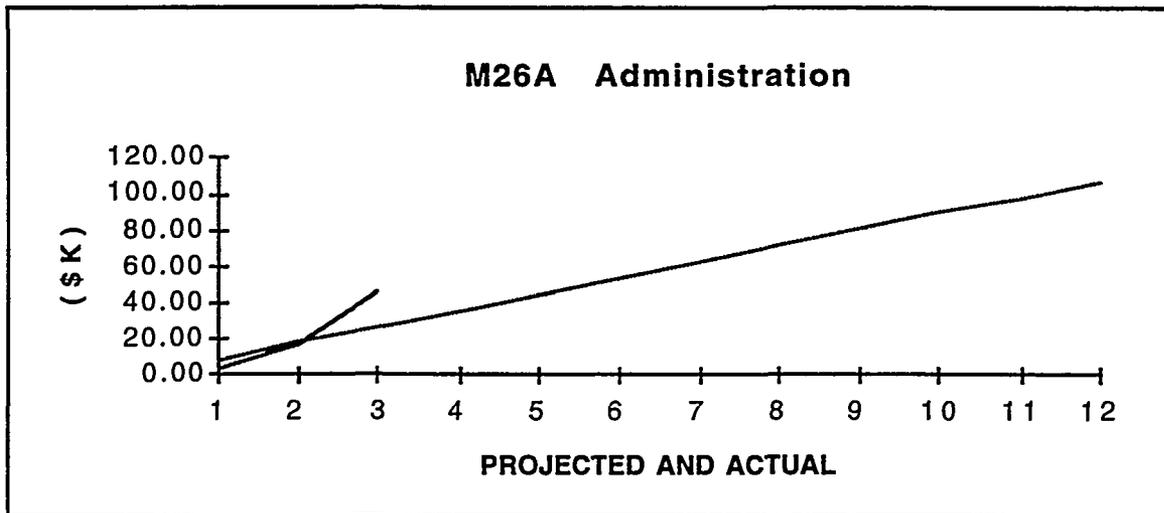
METAL, OXIDE, AND RESIDUE SHELF-LIFE PROJECT

The purpose of the Shelf-Life project is to evaluate the behavior of plutonium metal, oxide, and residues in storage. This project is in support of DOE-STD-3013-94. A test matrix will be developed from the requirements and experience of Los Alamos and other DOE-complex sites. Work done in the DOE complex in the past and recently in the Los Alamos Plutonium Packaging project has established a database on the characteristics and behavior of plutonium oxide. Continued work on the storage of metal, oxide, and residues will build on this knowledge. Although observations suggest that radiolysis of adsorbed water is not a credible pressurization process during storage of pure plutonium dioxide, hydrogen formation by chemical reaction of water is of concern. Experimentation will continue on pure and impure oxides formed from various processes, and experimentation will begin on ash samples. Planning and experimentation will proceed for shelf-life tests on salts.

In a preliminary experiment, four containers holding electrorefining salt, oxidized electrorefining salt, combustibles, and ^{238}Pu-contaminated rags were analyzed. Within a six-month period, no significant changes were detected. The experimental setup was not adequate for precise data acquisition over an extended period, so the experiments were terminated.

Progress is reported on development of several surveillance technologies. Testing is proceeding on the first production bellows for detection of pressure changes in long-term storage containers. Sandia National Laboratories/New Mexico (SNL/NM) has completed the initial scoping and feasibility study for an electronic hydrogen sensor to be placed within a storage container. Real-time radiography equipment purchased by the Plutonium Packaging project will be available for surveillance studies by the Shelf-Life project beginning next quarter. Laser sampling of gases in storage containers has been found to be feasible. A report evaluating the generation of an explosive mixture in plutonium oxide storage containers is complete. For the container configuration analyzed, calculations show that the container would remain intact during laser sampling under worst-case conditions. Acoustic resonance spectroscopy (ARS) has been found to be a feasible method for detecting changes in storage containers and warrants further study. A search of the literature reveals that there exists a high probability that neutron flux differences in several plutonium compounds can be determined. Investigators are developing Raman and laser-induced-breakdown spectroscopy (LIBS) for use in storage surveillance. Sandia National Laboratories/California (SNL/CA) is completing conceptual designs for a long-term storage container for ^{238}Pu.

BUDGET SUMMARY (PROJECTED AND ACTUAL)
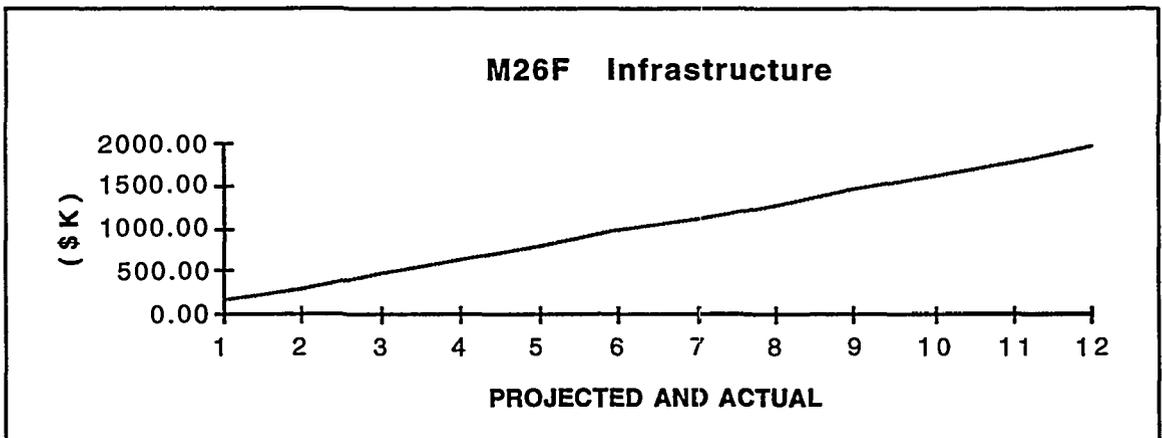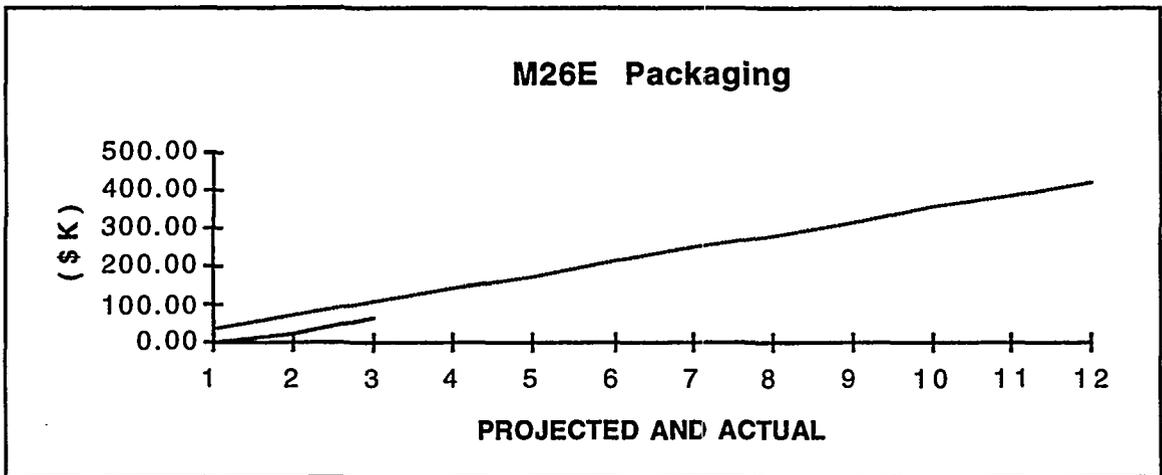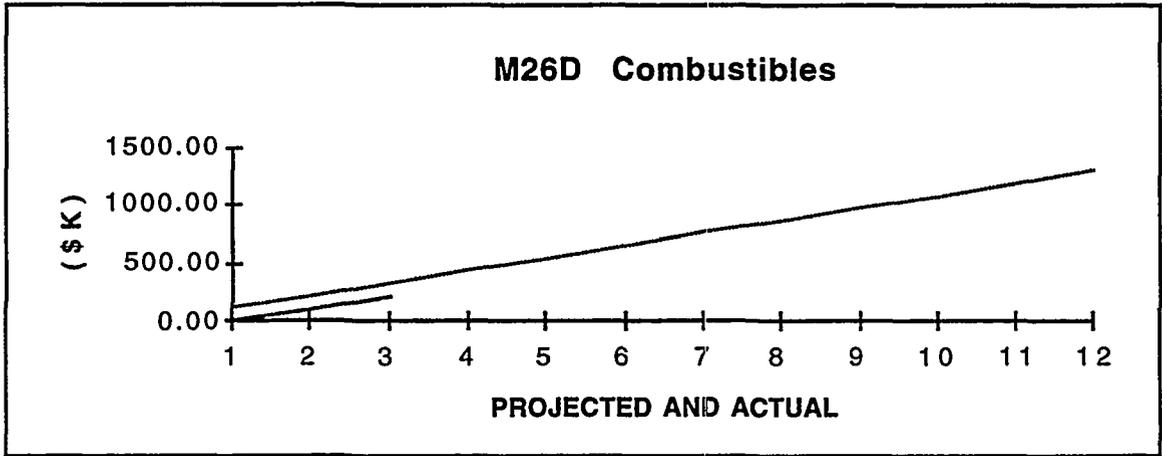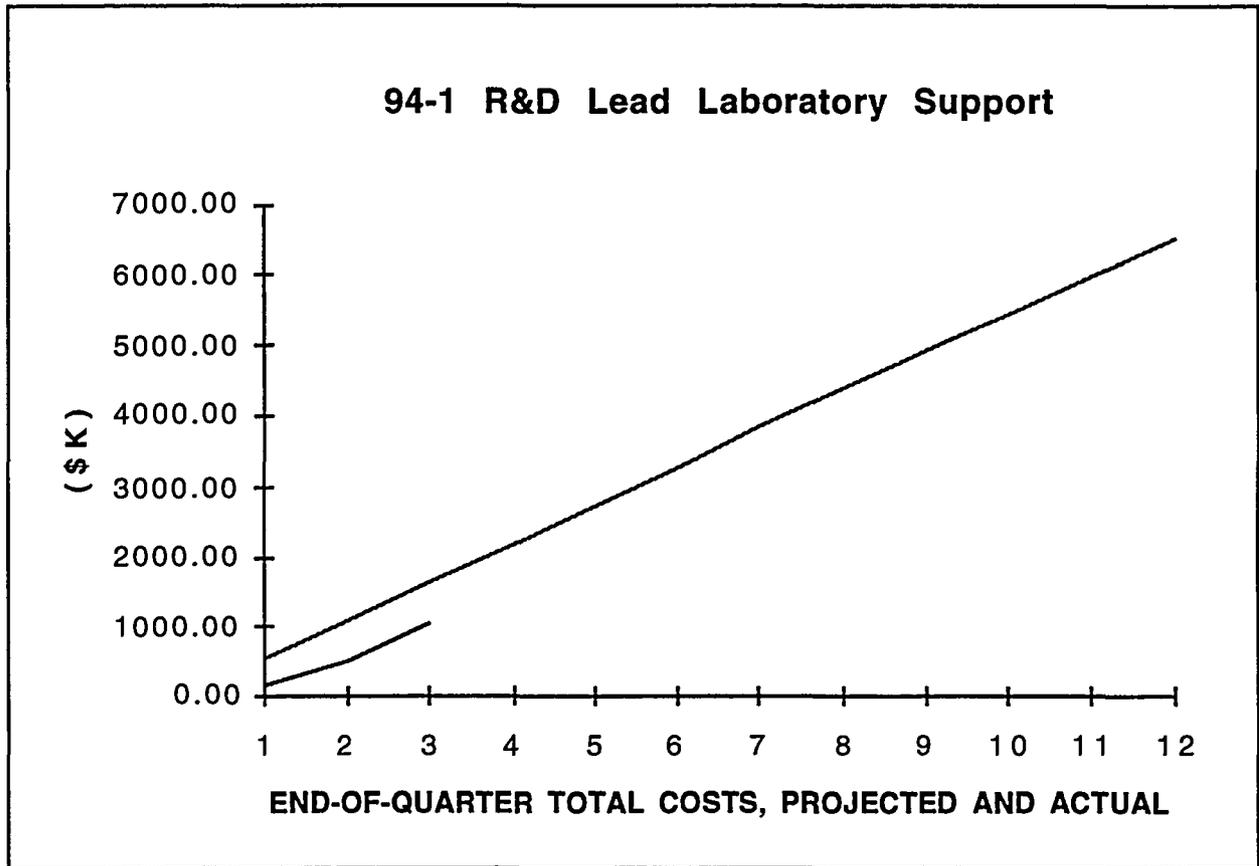
M26A   Administration

M26B   Surveillance

M26C   Salts

M26D Combustibles

PROJECTED AND ACTUAL

M26E Packaging

PROJECTED AND ACTUAL

M26F Infrastructure

PROJECTED AND ACTUAL

94-1 R&D Lead Laboratory Support

END-OF-QUARTER TOTAL COSTS, PROJECTED AND ACTUAL

94-1 RESEARCH AND DEVELOPMENT PROJECT LEAD LABORATORY SUPPORT

STATUS REPORT
October 1–December 31, 1995

compiled by

Mark Dinehart

ABSTRACT

This is a quarterly progress report of the 94-1 Research and Development Lead Laboratory Support Technical Program Plan for the first quarter of FY 1996. The report provides details concerning descriptions, DOE-complex-wide material stabilization technology needs, scientific background and approach, progress, benefits to the DOE complex, and collaborations for selected subprojects. An executive summary and report on end-of-quarter spending is included.

TASK DESCRIPTION

Equipment designed to carry out the salt distillation process will be obtained, assembled, tested, and demonstrated. The salt distillation process is designed to separate plutonium pyrochemical salts into a very lean fraction (<100 ppm plutonium) and plutonium oxide suitable for storage under DOE Standard 3013-94. The chloride content of the pyrochemical residues are thereby converted into stable, slightly contaminated salt; and the plutonium content is separated into a homogeneous, well-characterized, oxide material suitable for long-term storage.

TECHNOLOGY NEEDS

At RFETS, there are 16 metric tons (tonnes) of salts that all combined contain ~1 tonne of plutonium. Eleven tonnes of these salts are composed of a sodium chloride-potassium chloride matrix. The remaining tonnes consist of a calcium chloride matrix. These salt residues are the product of past plutonium processing operations. Residues that possibly are unstable remain in storage after termination of weapons-related activities in the DOE complex. DOE has committed to mitigate the problems associated with 6000 kg of high-hazard pyrochemical salts at Rocky Flats Environmental Technology Site (RFETS) by May 1997 and the problems connected with an additional 4000 kg by December 1997. The high-hazard salts are stored in drums in buildings where workers need routine access. These residues may pose a safety risk if the reactive metals in the residues come into contact with water. Such contact may create hydrogen gas that could cause container pressurization. Even if no hazard from reactive metals is present, these salts can adsorb moisture from the atmosphere, resulting in corrosion and breach of containment.

The full 16-tonne inventory is to be made safe by May 2002. In addition to mitigation of hazards, these residues must also be made acceptable for eventual disposal. An additional 2 tonnes of these salt residues exist at Los Alamos and require stabilization by May 2002.

SCIENTIFIC BACKGROUND

Distillation separation is based on the large difference in vapor pressures at high temperature between most chloride salts that constitute pyrochemical residues and the actinide oxides. However, the plutonium content in these salts can be in the form of plutonium trichloride. Vapor pressure differences between alkali and alkaline earth chlorides and plutonium trichloride are too small to effect a good separation, therefore $PuCl_3$ must be converted to an oxide through an oxidation process. At Los Alamos, researchers have developed such a process. It uses carbonate salts to act as

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an oxidant, and the method has proved very effective in converting all plutonium species into plutonium dioxide. This oxidation process can be ultimately combined with a distillation separation process.

The vapor pressure of sodium chloride and potassium chloride at 850°C is about 1 torr. The vapor pressure of plutonium dioxide at this same temperature is 10^{-16} torr. This tremendous difference in physical properties forms the basis for a very efficient physical separation. The results of simple modeling indicate that the plutonium concentration in sodium chloride-potassium chloride salts can be reduced to 10^{-10} ppm. While it is theoretically possible to produce a salt that would meet the criterion for low-level waste (LLW) of 100 nCi/g (~1 ppm) efforts are focused on obtaining a product salt that contains <100 ppm plutonium. At this level of contamination, the salts are still transuranic (TRU) waste; but 55-gal. drums can be filled on a volume limitation of the waste rather than a radionuclide loading. This can result in a 10- to 100-fold decrease in the amount of drums sent to the Waste Isolation Pilot Plant (WIPP).

TECHNICAL APPROACH

Uncontaminated salts have been used to verify the feasibility of the salt distillation process. These tests employed existing equipment and have been used to determine distillation rates as a function of temperature. A target rate of 3 kg per unit per day had been established. Results for sodium chloride-potassium chloride indicated that such a rate was easily achievable. Distillation rates for calcium chloride were found to be too slow below 1100°C. These tests with uncontaminated salts have also been used to provide input for equipment designed expressly for the salt distillation process. Focus has now shifted to testing this equipment.

Individual components will be assembled and tested prior to introduction into a glovebox environment. The equipment will then be introduced into an existing plutonium-contaminated glovebox. After assembly in the glovebox, test runs will be conducted using 500 g of uncontaminated salts, progressing to 500-g batches of salts with measured amounts of plutonium dioxide added, 3-kg batches of salts with measured amounts of plutonium dioxide added, 500 g of actual residue salts, and finally full-scale runs using 3 kg of residue salts. Once testing is complete, a demonstration full-scale processing run will be carried out during the rest of the year. These runs will establish reliability and robustness of the process and of the equipment in a full-scale processing environment.

ACCOMPLISHMENTS/PROGRESS

During this quarter all electrical, thermocouple, and vacuum feedthroughs and fittings needed for glovebox installation were purchased and received. A new cover incorporating the appropriate vacuum feedthrough was designed and fabricated to replace the existing furnace well cover. This new cover, along with required fittings and feedthroughs, is now ready to be placed in the glovebox.

The vacuum seals where the distillation and receiver chambers are loaded and unloaded are water-cooled O rings. However, the spool connecting the two chambers must be at an elevated temperature in order to permit smooth flow of salt vapors. A metal C-ring seal in grooved metal flanges was chosen for the spool connector. This type of seal is designed for high temperatures and repeated thermal cycling. Since this is a critical component with which there is not much experience, it was decided to test the seal. A test fixture was fabricated of the same Inconel materials of construction as the designed apparatus, and the same bolt pattern and seal size were also incorporated. The general procedure involved heating and cooling at operating rates and temperatures. Pressure readings were noted every 30 min on both heating and cooling; but, because of the extended time required for cooling, most of the data was collected during this portion of the run.

The acceptable performance criterion for the vacuum seal was established as <0.01 torr. This performance measure was met in the first 6 runs. In run 7, the sealing ability began to deteriorate on cool down, but was still acceptable at high temperatures. However, performance continued to deteriorate in subsequent runs; and by run 13, it was evident that the seal was not performing as required. After run 13, when the test fixture was examined, it was found that the bolts had worked loose during the temperature cycling. A second series of runs was then initiated; and the bolts were checked, with a torque wrench, after every two runs or so. In general, two or three bolts needed to be tightened every time they were checked.

The seal performed better during the second series of test runs. No loss of performance was observed until Run 11, and vacuum levels at 1000°C remained below 0.01 torr until Run 21. This is a marginal performance; and replacement of the seals after 20 runs is possible, but not desirable. Efforts will be made to improve the seal characteristics.

Fabrication of the Inconel parts was delayed a month. Problems were encountered by the manufacturer in machining to the design specifications. These problems now have been solved. All other components and subassemblies have been fabricated and received. Assembly and testing of the entire apparatus is now expected to occur by the end of January 1996. Work has commenced on a standard operating procedure (SOP), and all paperwork and preparations for installation in the glovebox have been completed.

BENEFITS

Separation of the plutonium from the waste salts will lead to a large reduction in the cost of disposal, even if the salts do not meet LLW disposal criteria. Present WIPP Waste Acceptance Criteria (WAC) would result in a maximum plutonium loading of 23 g per 55-gal. drum. In the best possible circumstance this would mean that more than 50,000 drums would be required for sending waste to WIPP. Efforts are under way to modify the WIPP WAC to allow 200 g of plutonium per drum. This would still require 8000 drums. If the plutonium in the salts can be reduced to below 100 ppm, a drum could be filled with salt without impacting even the present 25-g plutonium limit. In this case, about 200 drums would be generated for WIPP

disposal. At a cost of $10 K per drum, the cost savings realized could total many tens of millions of dollars. The separated plutonium, consisting of 1 tonne of plutonium dioxide, could be packaged for long-term storage in accordance with DOE-STD-3013-94. Costs incurred by storage of the plutonium oxide would be greatly offset by savings realized from WIPP disposal. Recent estimates of total cost to process by distillation the salt inventory at RFETS are $71 million, compared to $103 million for disposal at WIPP with modified WIPP WAC and $534 million with present WIPP WAC.

TECHNOLOGY TRANSFER/COLLABORATIONS

At the completion of the production-scale demonstration of salt distillation at the Los Alamos National Laboratory Plutonium Facility (TA-55), the technology will be available for treatment of materials at RFETS.

TASK DESCRIPTION

The task is to develop (1) an in-line cryogenic filter grinder assembly, (2) a cryogenic crusher for polystyrene cube reduction, and (3) a cryogenic shredder for soft combustibles that will provide feed for further processing. The task also includes making polycubes for testing, evaluating size reduction by the various methods, and mixing combustible materials.

TECHNOLOGY NEEDS

In order to destroy the organic matrix, many combustible residue materials require size reduction before processing. Among these are contaminated filter units and 1600 polystyrene cubes in storage at WHC. Technology needs are to understand polystyrene cube pyrolysis and to develop a method to produce suitable feed materials for processing various combustibles.

TECHNICAL APPROACH

In the first quarter, work continued on the development of the in-line filter grinder assembly. Assembly of the prototype is 90% complete. The assembly is an upgraded concept of a commercial ice shaver. A "cold" demonstration was performed with nonradioactive materials in order to determine the particle sizes that can be generated in using the unit. A manual method for feeding the filters is being incorporated on the unit to expedite the test for particle size determination. A motor-driven concept is under consideration and may be incorporated at a later date.

Work on the cryogenic crusher for the polycubes also continued during this quarter. The unit is about 50% complete. The design requires that a polycube be reduced in size from a 2-in. cube to particles that have a major diameter of less than 0.040 in. Processing will be performed with the polycube chilled in liquid nitrogen prior to attempts at crushing and fragmenting. The crusher will also be cooled.

ACCOMPLISHMENTS/PROGRESS

Polystyrene test cubes were formed from mixtures of iron particles and polystyrene powder. The need to evaluate chemical changes caused by heat required the use of polystyrene cube composites, as well as cubes of

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polystyrene. An effort was initiated to form billets of styrene, machine them into cubes, and subject the cubes to pyrolysis. Four cubes were fabricated and delivered to the chemist for processing.

An effort was initiated to fabricate approximately 60 cubes of styrene for future pyrolysis tests. Thirty composite styrene and iron polycubes will also be required for the pyrolysis and the cube crushing efforts. Procurement of these materials was initiated.

BENEFITS

Size reduction is crucial to the success of most of the candidate combustible processes.

TECHNOLOGY TRANSFER/COLLABORATIONS

Reducing the size of combustibles will prepare wastes for any one of several processing operations now being developed for use throughout the complex. The crygenic filter shredder is ready for use in preparing RFETS filters for processing.

TASK DESCRIPTION

The purpose of this work is to determine the applicability of mediated electrochemical oxidation as a viable technology for the treatment of combustible waste and for the removal of surface contamination from selected matrices. This technology will also be evaluated against alternative treatment technologies to determine which is best suited for treatment of a given waste.

TECHNOLOGY NEEDS

Mediated electrochemical oxidation is a semi-mature technology that has been demonstrated at a bench-scale level for the destruction of selected organic compounds. This technology has applications throughout the DOE complex. Continuing technology development needs include the following: (1) determining the appropriate electron transfer mediator for the treatment of a selected residue, (2) optimizing the process parameters to guarantee the highest process efficiency and throughput, and (3) demonstrating the process on actual mixed-waste residues on a pilot- and full-production scale.

SCIENTIFIC BACKGROUND

In the mediated electrochemical oxidation process, an electron transfer mediator is generated at the anode in an electrochemical cell. The mediator then reacts with the organic component of a mixed waste, converting the organic component to carbon dioxide. The radioactive component remains in solution and can be recovered using standard recovery processes; or it can be disposed of, depending on the activity level.

The critical component in this process is the electron transfer mediator. To be effective, it must have a high positive standard reduction-oxidation (redox) potential, exhibit two stable oxidation states in acidic media, react slowly with the solvent and rapidly with the organic compound in the waste, have reasonably high solubility in aqueous solution, and be recoverable/recyclable. Only a limited number of chemical species satisfy all or even some of these criteria. The mediators identified thus far include silver II, cobalt III, cerium IV, and permanganate (manganese VII).

A second critical component is the oxidation characteristics of the organic compound to be destroyed. Each compound or class of compounds has its own unique oxidation characteristics, including relative ease of oxidation. For example, simple chlorinated hydrocarbons like chloroform and carbon tetrachloride are

destroyed at high efficiencies at room temperature; whereas others compounds such as alcohols, ketones, and carboxylic acids, require elevated temperatures to achieve complete conversion to carbon dioxide. This variation in oxidation characteristics has an impact on the selection of a mediator. All four of the listed mediators are reasonably stable at room temperature, but silver II and cobalt III have limited stability in aqueous solution at elevated temperatures.

TECHNICAL APPROACH

The first mixed waste targeted for treatment studies is spent ion-exchange resin, which has been identified as a potential safety concern at RFETS. Bench-scale experiments will determine which of the mediators is best suited for destruction of the resin. Parametric studies will be conducted to determine optimum process operating conditions. Simultaneously, a pilot-scale apparatus will be designed, constructed, and installed in the Los Alamos National Laboratory Plutonium Facility (TA-55). Results of the bench-scale studies will be used to establish pilot-scale parameters for the treatment of actual spent ion-exchange resins.

Two alternative treatment technologies, hydrothermal processing and catalyzed oxidation, will be developed concurrently with this study, using the same mixed-waste feeds. At the completion of these studies, an evaluation of all three technologies will be conducted to determine which one should be further developed for implementation on a full-production scale.

ACCOMPLISHMENTS/PROGRESS

Using silver II, cobalt III, cerium IV, and permanganate as the electron transfer mediators, we have completed a series of bench-scale studies on the mediated electrochemical destruction of ion-exchange resins. Because of the relatively inert nature of the organic matrix, it has been necessary to run the reaction at elevated temperatures, approximately 80°C, to bring about complete destruction in a reasonable amount of time. The overall reaction efficiencies, using either silver and cobalt, increase with rising temperature. This is a somewhat surprising result, since the stability of both mediators decreases with rising temperature. This finding would suggest that the mediator reacts more rapidly with the ion-exchange resin than with the solvent or that the products of the decomposition reaction are themselves active oxidation reagents; for example, hydroxyl radicals. Permanganate was found to be an unsuitable mediator, since it reduces to insoluble manganese dioxide during the reaction and it cannot be regenerated electrochemically. Preliminary results with cerium are encouraging. Cerium appears to be quite stable at elevated temperatures and reacts rapidly with the resin to provide complete destruction. Further studies using this mediator are currently under way.

A pilot-scale mediated electrochemical oxidation apparatus that uses a commercially available flat-plate electrochemical cell has been installed in TA-55 and is currently being used to complete a series of experiments involving the electrochemical treatment of spent electrorefining salts. At the completion of these

studies, scheduled for mid-January 1996, this apparatus will be used for mediated electrochemical oxidation studies. An SOP is already in place for this process, so no further administrative action should be necessary to begin the pilot-scale studies.

BENEFITS

Treatment of mixed waste using mediated electrochemical oxidation has several attractive features. The process completely destroys the organic component of the waste, converting it to harmless carbon dioxide. This operation converts the waste category from mixed to radioactive, and this conversion has a dramatic favorable impact on the waste disposal method and the associated costs. The reaction solution can be used repeatedly, so there is minimal waste generation and also minimal chemical reagent consumption. Mediated electrochemical oxidation is easily controlled with a power supply and operates at room temperature or at a slightly elevated temperature and also at ambient pressure; so there are few safety concerns. Process operating costs are quite low relative to the costs of competing technologies. Because of these features, mediated electrochemical oxidation should easily gain high public acceptance as a treatment process.

TECHNOLOGY TRANSFER/COLLABORATIONS

The entire combustibles program is being carried out in collaboration with personnel at RFETS. As the project progresses, this collaboration will include hands-on participation by RFETS personnel at Los Alamos. In addition, the RFETS prioritized combustibles treatment list serves as a guideline for selecting wastes to be evaluated by mediated electrochemical oxidation and by other treatment processes currently under development.

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TASK DESCRIPTION

Catalyzed oxidation of organic compounds, using a concentrated solution of ferric chloride, hydrochloric acid, and platinum and ruthenium catalysts in minute amounts, was developed by Delphi Research, Inc., under the trade name DETOX. The development work was supported for four years by Los Alamos and for many years by other sites, including RFETS and Mound Laboratory, Miamisburg, Ohio.

Specifically, the objectives of the test program are to

- Reproduce optimum conditions developed by Delphi on liquid organics;

- Demonstrate the DETOX process on solid organic wastes, such as ion-exchange resins;

- Develop reliable analytical methods for gas and liquid phase analysis;

- Demonstrate, with continued usage, the resistance of tantalum to the DETOX solution at autoclave process conditions;

- Design and build an autoclave assembly that can be used safely and efficiently in a glovebox to process radioactive wastes;

- Determine whether the process can be run at lower temperatures and pressures; and

- Determine treatment and disposal of spent DETOX solution.

TECHNOLOGY NEEDS

Combustible residues must be stabilized for long-term storage or for disposal. This process achieves this goal by the destruction (oxidation) of all solid and liquid organic material within the residue matrix and by solution of all radionuclides and active metals.

SCIENTIFIC BACKGROUND

The following reactions illustrate the destruction of the organic matrix by the DETOX solution:

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$$C + 4Fe^{+3} + 2H_2O \rightarrow CO_2 + 4Fe^{+2} + 4H$$

and

$$4Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O \ .$$
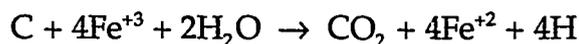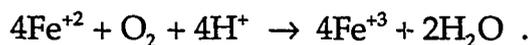
The reactions show that carbon is oxidized to carbon dioxide by ferric iron, which is reduced to ferrous iron. Oxygen then oxidizes ferrous iron back to ferric iron, which produces water and regenerates the solution, which can be reused. The solution must be disposed of only when its composition has changed significantly, for example, due to overloading with metals or radioactivity.

The reactions are simplified, since in the process there are many complex interactions between the oxidants (ferric and oxygen), catalysts (platinum and ruthenium), and phases (solid, liquid, and gaseous). If the organic compounds are chlorinated or sulfonated, hydrochloric acid or sulfur dioxide is formed. With very few exceptions, if metals are present, they are dissolved in the solution. The solubility of metals is generally very high.

The approximate process conditions developed by Delphi are 30–240-min residence time at 150°–200°C, with 100–150-pounds-per-square-inch, gauge (psig) oxygen overpressure, and 5–30 g of organic per 1500 ml of solution. The optimum solution composition consists of 6-M ferric chloride and 1-M HCl with 100 ppm of the noble metal catalysts platinum and ruthenium. The operation can be run continuously, especially on liquid organics. Solid organics must be reduced in size, for example by cryogenic grinding, and are pumped into the autoclave as a slurry or are dry-fed with a feeder. Fresh oxygen is added to the autoclave as needed. The gas bleed goes through a scrubber for removal of hydrochloric acid, which is returned to the autoclave. A high degree of organic oxidation was demonstrated by Delphi on a variety of organics.

TECHNICAL APPROACH

This project will continue the DETOX process development work using both nonradioactive ("cold") and plutonium-contaminated ("hot") organic wastes. Testing on "cold" organic wastes will verify the effectiveness of the process for this application, followed by testing at TA-55 using "hot" wastes in an autoclave set up in a glovebox.

The potential for running at atmospheric pressure, at least on some organics, will influence the design of the equipment to be installed in a glovebox. Running at atmospheric pressure, or actually under slight vacuum, offers many advantages, including the following: (1) no energy accumulated as pressure, (2) no possibility of leaks, (3) easier feeding of solid organics, and (4) cheaper construction materials. Before design work begins, the kinetics of oxidating various combustibles in the autoclave under standard DETOX-solution conditions and at atmospheric pressure with the modified solution should be compared. We propose this investigation as an important part of the program for the next quarter.

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The process must be optimized from beginning to end, including solution disposal. Hydrolysis to produce ferric oxide is feasible. Operating conditions must be optimized; and the fate of other metals, especially plutonium surrogate, must be determined in order to optimize the disposal flow sheet. This is another area in which we propose to concentrate our efforts during the next quarter.

These investigations will provide an improved flow sheet. Mass balances will be calculated. A process accountability flow diagram will be prepared for the glovebox installation. Equipment and instruments will be researched to provide safe and practical operation. Operating and safety documents will be written, and a permit will be obtained. This process will begin in the second quarter of this fiscal year.

ACCOMPLISHMENTS/PROGRESS

The DETOX process is conducted at relatively low temperatures and pressures, the solution solubilizes metals, and the solution is reusable. The solution can treat a wide variety of materials including organic liquids and solids; and the reaction products are primarily CO_2, H_2O, and soluble metals. However, since the solution solubilizes most metals, there were concerns about materials of construction for the autoclave. A study contracted to the Colorado School of Mines by RFETS showed that tantalum was resistant to the DETOX solution at operating conditions. During the first half of FY95, a tantalum autoclave was purchased to use for testing.

The testing conducted at Delphi focused primarily on the destruction and treatment of surrogate liquid organics. During the first half of FY95, the bench-scale testing of surrogate samples at Delphi was completed, and subsequent testing at Delphi for Los Alamos was stopped. At the end of FY95, the equipment purchased under the subcontract with Delphi was transferred to Los Alamos for use in continuing development of this technology on radioactive wastes, especially on plutonium-contaminated combustibles. This development will require installation in a glovebox of equipment and other enhanced features. Also, the Los Alamos principal investigators believe they can improve the process in some areas, specifically operation at low pressure, disposal of the used ferric chloride solution, and optimization of conditions for specific combustibles. Efforts have focused on investigating and improving three main areas of the catalyzed oxidation process: (1) autoclave operation, (2) development of atmospheric operating conditions, and (3) spent-solution disposal.

An important improvement to this technology was operation at lower pressure. The boiling point of solutions with various compositions was determined. A solution boiling at 175°C was tested under a slight negative pressure on a few organic compounds. Carbon dioxide was generated, indicating that organic oxidation took place. The kinetics of oxidation must be compared with the standard conditions for the process operating in an autoclave.

The new 1-gal. tantalum autoclave purchased by Delphi was set up in a batch mode. Testing showed that this autoclave is not appropriate for installation in a glovebox. There are penetrations through the autoclave head for gas-in and gas-out, a pressure sensor, a thermocouple, a safety disk, and an organic feed. The penetrations are sealed against the inside tantalum liner with Teflon washers that creep at 150°–200°C. Keeping the autoclave leak-free under these conditions is difficult. The 1-gal. size is also cumbersome and would be difficult to operate in a glovebox. The competitive bidding for an improved design of a smaller autoclave has begun.

Improvement to the technology can also be made in the area of solution disposal. Disposal of spent DETOX solution by precipitation of metals as hydroxides is possible, but filtration and washing of the gelatinous precipitate is difficult. The neutralized solution also is a heavy chloride brine that may still be radioactive. Hydrolysis of the solution at elevated temperature was tested. This process produces a coarse ferric oxide and a scrubber solution of hydrochloric acid, so many possibilities open up for solution disposal. Such possibilities are (1) stabilization of the ferric oxide and other metal oxides in cement or glass or (2) washing of the ferric oxide if other metals are left as chlorides. Future work must optimize hydrolysis conditions and define whether to dispose of metals.

Pressure Testing in the Tantalum Autoclave

The equipment transferred from Delphi to Los Alamos consisted of one 1-gal. titanium autoclave that was badly corroded and not usable, one 1-gal. titanium autoclave that was partially corroded but in working condition, and one new 1-gal. tantalum-lined autoclave that was missing several parts needed for operation. It was therefore apparent that several adjustments to the original test plan were needed. First, the "cold" testing was delayed while parts were ordered and delivered to make the tantalum autoclave operational. To help alleviate the delay, some "cold" tests were run in the workable titanium autoclave while we waited for the parts for the tantalum autoclave. Second, the 1-gal. autoclaves with their associated heaters and stirring assemblies are too large and too heavy to be set up and used in a glovebox. And finally, tests run using these autoclaves have shown that 1500 ml of solution used to conduct tests is probably too large a volume for tests using plutonium-contaminated resins, because too much waste solution is generated for disposal.

Initial Autoclave Testing. Exploratory tests were run in the 1-gal. titanium autoclave at 175°–200°C using commercial ion-exchange resins. The resins were no longer visually detectable at the end of the tests. At 175°C, TOC analyses showed that about 80% of the resin was destroyed in 240 min. When tests were run at 200°C, corrosion of the titanium autoclave continued to the point that it is now no longer in working condition. Subsequently, parts for the tantalum autoclave arrived, and testing resumed both on ion-exchange resins and on liquid organics.

A test was run using DETOX solution with no added oxygen pressure and no organic. The purpose of the test was to determine the observed pressure in the system as a function of temperature. The results are interesting because the vapor pressure of the solution was significantly lower than that of water. For example, at

200°C, the pressure observed for solution was about 100 psig. The vapor pressure of water at this temperature is ~200 psig.

Quantitative results are not yet available because we are working on reliable analytical methods. The solution is difficult to analyze because of its high chloride content and its tendency to solidify on cooling below about 40°C. TOC analysis will be used to determine organic destruction efficiency, but initial analyses have been erratic. Samples of fresh solution with no organic have shown high-TOC contents, so analysis of treated solutions is suspect. Visually, and by gas-phase analysis for CO_2, we have confirmed that the process appears to be working well. Our results agree with those obtained by Delphi.

A series of tests were run at 150°, 175°, and 200°C, mostly using ion-exchange resins and some using organic liquids. Gas-phase analysis has shown that, as expected and in agreement with Delphi findings, the reaction rate increases significantly in this temperature range. There was a measurable rate at 150°C, but the rates at 175° and 200°C were much faster. To process a wide variety of organic wastes in a reasonable time period, operation at a minimum of 175°C is recommended.

An interesting effect that we have observed during all of the autoclave tests, and to our knowledge one not reported by Delphi, is that the solution seems to absorb significant quantities of oxygen the first time it is used. In the autoclave tests that were run, the solution and the organic to be oxidized were sealed at ambient temperature within the autoclave. Then 150 psig of oxygen overpressure was added to the autoclave. Ideally, once the oxygen pressure stabilizes, the reactor is heated to the programmed temperature and the pressure in the system is 150 psig plus the vapor pressure of the DETOX solution at temperature. In a recent test, a highly exothermic reaction was noticed at about 105°C during heat-up: immediately the pressure dropped and more oxygen had to be added. On reheating this solution after use, neither the oxygen consumption nor the exothermic reaction was observed. It appears that the high oxygen consumption and exothermic reaction may indicate that the initial solution undergoes a phase transformation. More work is needed to determine what happens to the DETOX solution during heat-up and oxygen addition.

Autoclave Design. Probably the most important result of the initial test program has been the evolution of an autoclave design for glovebox testing. The 1-gal. autoclave was a modified design of a titanium autoclave. The autoclave shell is a tantalum lining over a titanium body. The stirring assembly, thermowell, and all internal parts are tantalum. In our studies to date, we have found that tantalum is a heavy, soft, but somewhat friable metal. When tubing has been bent to make connections to the head assembly, care has to be taken not to go beyond about a 45° angle; or the tubing breaks. Swage-lock fittings are difficult to use, since each time the fitting is tightened, the tantalum tends to creep and to break after a few uses.

The magnetic drive for the autoclave has been reliable and leak-free for the most part. However, the head assembly has been the biggest problem during operation. The head is titanium with a tantalum-lined face that is exposed to the interior of the autoclave. The tantalum lining so far has proved to be suitable and corrosion-

resistant in testing. The major problem has been related to the fittings connected to the head. Through each hole in the head passes a removable tantalum nipple that is threaded on the end that passes through the head. A large tantalum bolt is welded to the other end of the nipple that extends into the autoclave. The threaded bolt allows for attachments to be made in the autoclave and is meant to fit snugly against the tantalum-lined face. Additional bolts are used to secure the nipples to the autoclave head from the outside of the head. Around the nipple we have placed Teflon gaskets that help to seal the welded bolt against the head as the nipple is tightened into place.

Although, the use of the nipples provides a great deal of flexibility to the system, nipples tend to leak; and they must be tightened for each test because the Teflon gaskets deform at the test temperatures. The autoclave design for the glovebox will be made with a solid tantalum head. Holes will be drilled and threaded so that attachments will be made directly to the cooler part of the head and will be sealed with Teflon tape: leaking should be eliminated. Also, all external tubing connections and fittings will be made with titanium and titanium tubing, which bends easier, seals better, and lasts much longer with Swage-lock-type connectors. Only the internal wetted parts need to be made from or lined with tantalum.

One final area of autoclave design that is important is agitation. In the testing done to date, it is apparent that during organic destruction using the DETOX solution, many organics are converted to gaseous phases during treatment. Therefore, agitation in the autoclave is very important, since the organic in the gas phase needs to be recontacted with the solution. Impeller design and some form of gas recirculation will be part of the autoclave designed for the glovebox operation.

Future Testing Required. The preliminary results indicate that the process should work on resins and has application to a variety of organic and combustible wastes. The main problem to overcome is related to materials. In tests conducted to date at Los Alamos, wetted tantalum parts have shown no corrosion. While waiting for the 1-L autoclave to arrive, we plan to continue running "cold" tests on organic wastes in the available autoclave in order to establish conditions of time, temperature, oxygen overpressure, and organic charge for optimum destruction of organics.

As the testing progresses, we will characterize the solution and gas phases. An important part of this phase of the test program will be to determine analytical methods to characterize both the gas phase during reaction and the reacted solution. This will be critical to determining how effectively and completely the organic-type materials are destroyed during processing. These data will provide information needed to calculate mass balances.

Disposal of the Solution by Hydrolysis

Results to Date. A survey of the literature on ferric salts shows that ferric iron in sulfate and chloride solutions tends to hydrolyze to the ferric oxide at elevated temperature. The reaction in the chloride system can be written as

$$2\,FeCl_3 + 3\,H_2O \rightarrow Fe_2O_3 + 6\,HCl$$
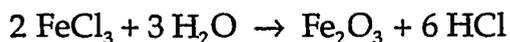
Hydrolysis, therefore, produces two streams—solid ferric oxide and hydrochloric gas. In addition, if the ferric chloride solution contains water in excess of the stoichiometric requirement, it evaporates at high temperature. Ferric oxide is easy to stabilize, if needed, in cement or glass. If other metals are present, such as plutonium, they may also hydrolyze to the oxide form, in which case they can be stabilized as well. If they stay as chlorides, they can be washed from the iron oxide. The hydrochloric gas and the water can be scrubbed in a water scrubber, as commonly practiced in some industries. The hydrochloric acid generated in the scrubber can be reused to produce more ferric chloride.

A test was run where $FeCl_3 \cdot H_2O$ was heated to increasingly higher temperatures, and the released hydrochloric gas and water vapor were measured. This salt, $FeCl_3 \cdot 6H_2O$, melts at about 60°C. A standard DETOX solution contains more water and some hydrochloric acid. This salt was selected to prevent overloading the scrubber with large amounts of water and acid.

As the ferric chloride was heated to 125°C, some water was released, but no HCl. When the temperature was increased to 150°C, more water came out but virtually no HCl. Note that more water was released as the temperature rose from 125° to 150°C than when the temperature stabilized. This was owing to the fact that the full wattage was applied to the heating mantle only as temperature was far from the control set point and that a fraction of the wattage was applied at equilibrium around the set point. At 150°C, about 2 moles of water had evaporated. More water was released on the way to 175°C, but some HCl was released as well. However, the highest release of HCl occurred above 175°C.

The test was run over an 11-h period, and complete hydrolysis was not achieved. The amount of water, ferric chloride, and ferric oxide can be calculated at each point of the test. At the end, about 60% of the ferric chloride was hydrolyzed.

Faster hydrolysis can be obtained by leaving the full wattage on the vessel. It must be ensured that the rate of water release is not such that the anhydrate $FeCl_3$ is produced before hydrolysis is complete. Hydrolysis cannot proceed without water. Obtaining water, however, should be easy. A water-cooled condenser can return the evaporated water as needed while letting the hydrochloric gas pass through to the scrubber. Then, the condenser can be turned on and off to maintain a constant composition of the solution, the volume of which shrinks while more ferric oxide is produced. The ferric oxide produced in the above test was relatively coarse and easy to wash and filter.

Future Testing Required. Future testing must address several issues. Hydrolysis conditions must be optimized, and complete hydrolysis must be demonstrated. The operating conditions must maintain enough water to bring hydrolysis to completion but run at a temperature high enough for fast hydrolysis. Hydrolysis of the standard DETOX solution must be demonstrated as well. It is expected that conditions will be quite similar, with only higher release of water and hydrochloric acid at the beginning because of the presence of free phases of these compounds. The strength of the hydrochloric acid produced in the scrubber must be determined to define its recycling. The fate of radioisotope surrogates during hydrolysis must be

determined. Whether oxide or chloride is mixed with ferric oxide will shape the disposal of the flow sheet. The metal compounds present after hydrolysis will be determined by analytical techniques, such as assays and x-ray diffraction. When appropriate, washing and filtration of entrained chlorides will be tested.

Oxidation of Organics at Atmospheric Pressure

Results to Date. During hydrolysis testing of spent solutions, results showed that several ferric chlorides formed, depending on solution temperature and composition. A literature survey showed that some of the ferric chlorides of general formula $FeCl_3 \cdot nH_2O$ boil at high temperature. If one of the chlorides had a boiling point in the range of 150°–200°C, it might be possible to conduct organic oxidation at atmospheric pressure.

The test results show that a ferric chloride solution boiling at 175°C can be obtained by evaporating water from the molten salt $FeCl_3 \cdot 6H_2O$. Hydrolysis did not occur to any great extent at this temperature. The composition of the ferric chloride compound at this temperature was between 2.5 and 3 moles of water.

A solution was prepared with a boiling point of 175°C in an agitated enclosed glass vessel at a slightly negative pressure to atmospheric pressure. Once the solution had stabilized, the temperature control set point was lowered to 170°C and a water-cooled condenser was turned on to prevent further evaporation. To collect any hydrochloric acid gas, air was circulated through the vessel, out through the condenser, and through two water scrubbers in series. The scrubber solution was titrated for hydrochloric acid at regular intervals. A few organics were fed to this solution. After adding an organic compound, the gas was analyzed for carbon dioxide. A gas chromatograph was not available, so CO_2 was approximately determined using Draeger tubes.

With O-xylene, carbon dioxide generation peaked quickly. O-xylene is gaseous at this temperature and significant amounts reported to the scrubber. This effect would also be observed during continuous autoclave operation. A "cold" trap would be needed to collect volatile organics entrained in the bleed stream. The volatile organics can then be pumped back to the autoclave. Solids, such as ion-exchange resins and nitrile gloves, were oxidized at a steady rate. Catalysts were not added to the solution for these tests.

Future Testing Required. Kinetics of operation at 175°C with the modified ferric solution must be determined for typical combustible organics and compared with kinetics at the same temperature with the standard DETOX solution and also with kinetics at higher temperatures with the standard solution. A choice of operating conditions can then be made.

Hydrolysis of the solution at 175°C was slow, but nevertheless it occurred. The rate of hydrolysis during the test reported previously was about 5%/h of the total ferric chloride. The acid captured in the scrubber could be returned to the vessel. Acid concentration in the scrubber cannot exceed 40% or 470 grams per liter (gpl), which is the maximum concentration for HCl. In fact, the concentration will be limited to a

somewhat lower level. For example, at 30% or 345 gpl, with a specific gravity of 1.149, there is 804 gpl of water or a ratio of 2.33 $H_2O:HCl$. To maintain equilibrium and boiling temperature, the water vapor and HCl gas exiting the vessel must be equal to the acid returned. Control of boiling temperature and composition of the gas exiting the vessel can be achieved by turning the condenser on and off.

It must be noted that autoclave operation faces the same considerations as does hydrolysis. Gaseous HCl and water vapor also exit with the bleed. Water evaporation can also be controlled with a condenser. However, the solution contains free hydrochloric acid and water. We are not aware of reports from Delphi on the respective vapor pressures of water and hydrochloric acid in the gas. If the ratio $HCl:H_2O$ is too high, it will exceed the maximum concentration in the scrubber, water make-up will be needed, and the DETOX solution composition will change. The autoclave pressure will change until the water vapor pressure is high enough and the $HCl:H_2O$ ratio is adequate. HCl and water vapor pressures, at temperatures between 150° and 200°C, must be determined for the DETOX solution.

TASK DESCRIPTION

Researchers will design, build, and test a hydrothermal processing unit for the destruction of plutonium-contaminated combustible solid and liquid wastes.

TECHNOLOGY NEEDS

Operations at DOE facilities have created a large legacy of combustible wastes such as rags, plastics, polystyrene cubes, and organic solvents that are contaminated with TRU materials, other radioactive elements, and strong oxidizers such as nitrates. In some cases, these wastes are an acute safety hazard because of the production of flammable gases from organic decomposition initiated by radioactive decay. Technologies are needed that can mitigate the hazards associated with these wastes. These technologies need to be robust, able to treat a wide variety of waste matrices, able to produce a minimum amount of secondary wastes, and, if possible, compact enough to fit into existing facilities without major modifications.

SCIENTIFIC BACKGROUND

Oxidation of the organic and reduction of the nitrate components of combustible waste will mitigate safety hazards, reduce waste volume, and facilitate separation of radioactive elements. Hydrothermal processing (reactions in hot water) provides high-destruction and high-removal efficiencies for a wide variety of organic and hazardous substances. For aqueous/organic mixtures, pure organic liquids, or contaminated combustible solids, such as ion-exchange resins, plastic filters, and cellulose rags, hydrothermal processing removes most of the organic and nitrate components (>99.999%) and facilitates the collection and separation of the actinides. A schematic of a laboratory-scale process unit is shown below in Figure 1.

Organic material is pressurized and mixed with pressurized hydrogen peroxide (30 wt %). For pumping solids, the solids are first reduced in size by cryogenic grinding, then mixed with water. The reaction mixture is fed into a high-temperature, high-pressure reactor and allowed to react for 20–60 seconds. At the end of the reactor, cold water is added to help cool the mixture and to facilitate transport of any insoluble solid material that may have been formed in the reactor. The mixture is further cooled in a heat exchanger and then depressurized. In the reactor, the organic components of the wastes are oxidized to carbon dioxide by reaction with the water and hydrogen peroxide. Nitrate contaminants also react with the organic material and are converted to nitrogen gas and some nitrous oxide. Heteroatoms, such as chlorine, sulfur, and phosphorus, are oxidized and converted to acids or salts depending on the pH of the solution. At temperatures above 500°C,

reactions are rapid; and greater than 99% conversion can be achieved in seconds. The reactions are carried out entirely in an enclosed pressure vessel and in dilute concentration so that the heat of reaction is absorbed by the water and the temperature can be maintained at any desired level, typically in the range of 400°–550°C. The reactor is fitted with a titanium liner to protect the pressure vessel from corrosion. The speciation of the actinides in the hydrothermal reactor is not yet certain; they most likely will be converted to either small insoluble oxide particles that can be separated by filtration or to water-soluble carbonate salts. Since the reactions are rapid, the volume of the reactor is small (200 ml). Consequently, the amount of radioactive material and the stored energy are small. During the last quarter, Los Alamos studied the reactions and treatment of a wide variety of organic wastes using nonradioactive simulants. The results of these studies are given in Table I.
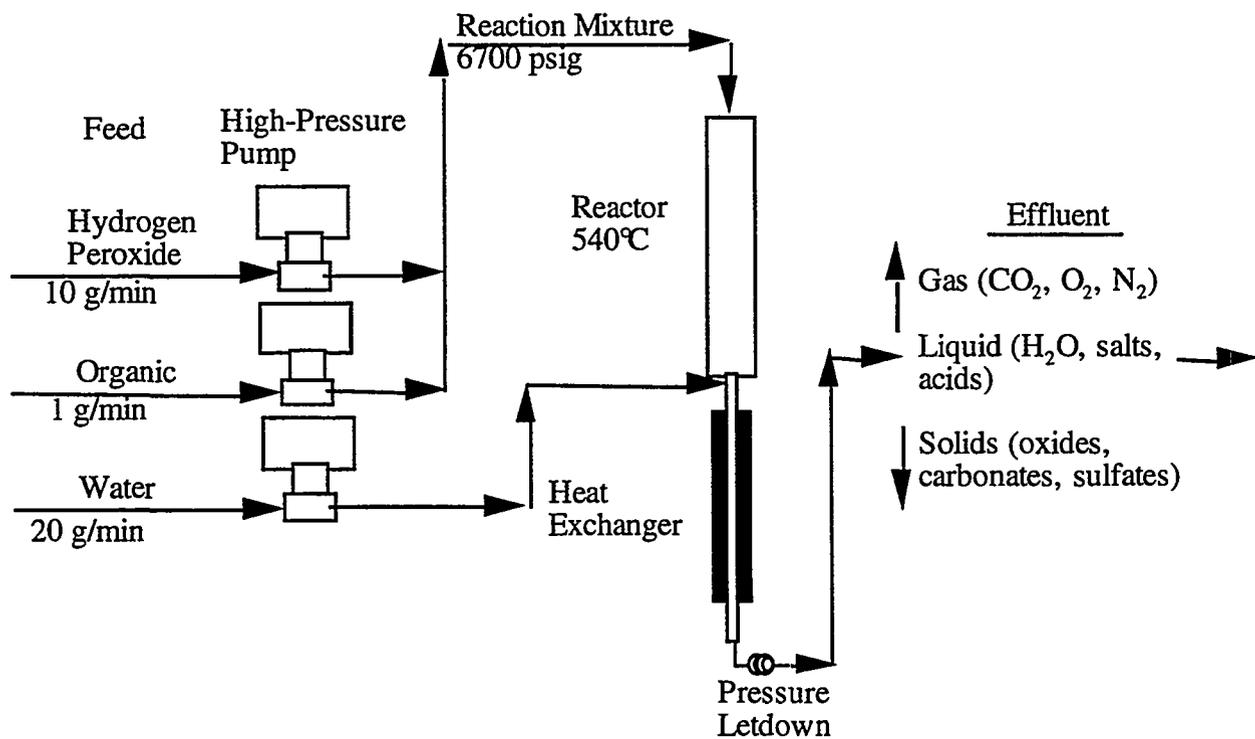

Figure 1. Process flow diagram: laboratory-scale unit.

TECHNICAL APPROACH

Implementation of testing of hydrothermal processing of TRU-contaminated combustibles will be done in the following four steps:

- Design and test small-scale unit (2 g/min) using nonradioactive simulants;

- Design and test small-scale unit with TRU-contaminated material;

- Design and test full-scale unit (20 g/min) using nonradioactive simulants; and

- Design and test full-scale unit with TRU-contaminated material.

At each step, the reactor design will be analyzed and optimized for safety and operability; the reaction kinetics and products will be measured over a range of temperatures, pressures, and residence times; a reactor model will be developed and validated; and the corrosion and wear of reactor components will be evaluated. The effluent streams will be analyzed to determine the partitioning of the radionuclides between the solid and liquid phases and the amount of incomplete oxidation products, such as carbon monoxide, methane, and hydrogen, in the gas phase.

ACCOMPLISHMENTS/PROGRESS

During the final quarter of FY95, the hydrothermal processing of a variety of nonradioactive waste simulants was tested. A summary of these tests and results are given in Table I.

During the first quarter of FY96, a small-scale hydrothermal unit for the treatment of TRU-contaminated combustible material was designed, using the results from the simulant experiments. The process flow diagram and schematics of the layout of the unit are given in Figures 1-4. Significant effort has been devoted to safety documentation and glovebox preparations for equipment installation in the Los Alamos Plutonium Facility. Environment, Safety, and Health (ES&H) safety reviews are in progress. All of the required documentation is currently on schedule.

For glovebox preparation, several items have been addressed. They include a general glovebox cleanup, preparation of required materials, and generation of work orders. Glovebox drawings have been updated for the required work. The necessary power feedthroughs have been fabricated for glovebox installation. The work orders will equip the glovebox with all necessary panels for the power feedthroughs, a reagent transfer device, and electric power required for the equipment. The work on the requested work orders has begun.

TABLE I: Summary of Waste Treatment Studies

Waste Type	Composition	Reaction Conditions	Results[*]
Hydraulic jack oil	98% hydrocarbons, sulfur-related compounds, no silicone	550°C, 44 MPa, 60 s, 34 wt % H_2O_2	25,000 ppm TOC reduced to <5 ppm, effluent contained 300 ppm sulfate, pH~2.3
Vacuum pump oil	Olefin: $(CH_2)n$, where 20<n<40	550°C, 44 MPa, 60 s, 34 wt % H_2O_2	40,000 ppm TOC reduced to <5 ppm
Heavy mineral oil	Paraffin C_nH_{2n+2}, where n~34	550°C, 44 MPa, 60 s, 34 wt % H_2O_2	40,000 ppm TOC reduced to <5 ppm
Tributyl phosphate	$(C_4H_9O)_3PO$	550°C, 44 MPa, 60 s, 34 wt % H_2O_2	Effluent pH~2.
Diesel oil #2	Hydrocarbons: C_{15} to C_{25}	550°C, 44 MPa, 60 s, 34 wt % H_2O_2	25,000 ppm TOC reduced to <5 ppm
Toluene	C_7H_8	550°C, 44 MPa, 60 s, 34 wt % H_2O_2	30,000 ppm TOC reduced to <5 ppm
Carbon tetrachloride	CCl_4	450°C, 60 MPa, 80 s, titanium-lined reactor	CCl_4, 11,500 ppm reduced to <0.5 ppm (>99.995% destruction)
Trichloroacetic acid	CCl_3COOH	500°C, 60 MPa, 30 s, titanium-lined reactor	CCl_3COOH, 1000 ppm reduced to <1 ppm
Trichloroethylene	C_2Cl_3H	500°C, 60 MPa, 30 s, titanium-lined reactor	C_2Cl_3H, 1000 ppm reduced to <1 ppm
1,1,1 Trichloro-ethane	CCl_3CH_3	500°C, 60 MPa, 30 s, titanium-lined reactor	CCl_3CH_3, 1000 ppm reduced to <1 ppm
Cation-exchange resin	$(C_8H_8SO_3)n$, 50-100 mesh, 50 wt % water	500°C, 44 MPa, 60 s, 34 wt % H_2O_2	Effluent TOC <1 ppm

[*] For all waste types, the total organic carbon (TOC) levels were below detection limit.
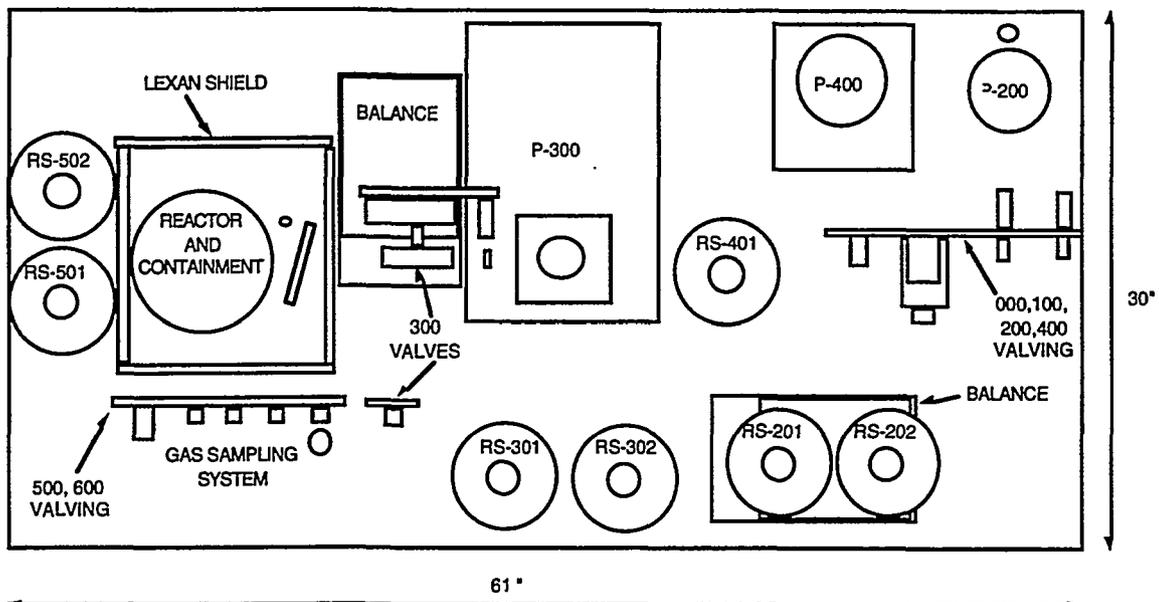
Figure 2. Schematic of reactor layout in glovebox (top view).
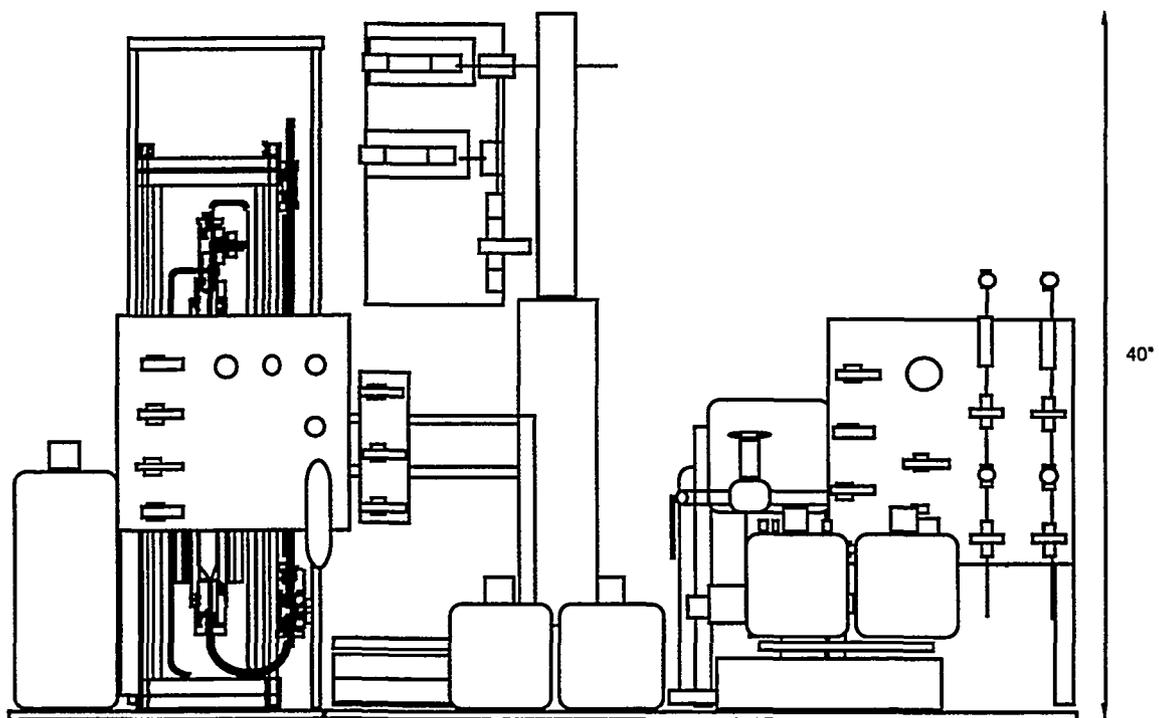
Figure 3. Schematic of reactor layout in glovebox (front view).
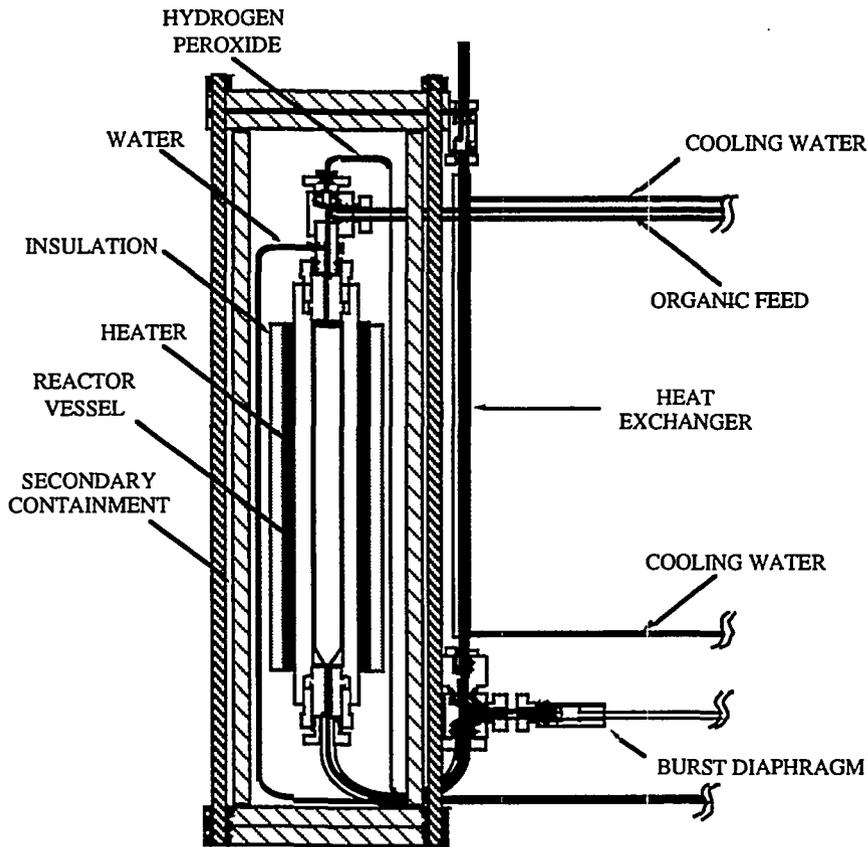
Figure 4. Detailed schematic of reactor and secondary containment.

Also during this quarter, the components for the reactor were ordered and the assembly of the reactor was initiated. The completion of this reactor is scheduled for the end of January 1996.

BENEFITS

This project will provide the information on effectiveness, operability, and cost needed to evaluate hydrothermal processing, a technology for the treatment of TRU-contaminated combustible organics. If the technology is successful, the project will produce an operating and tested full-scale treatment unit. This unit will be able to treat approximately 15,000 kg of residue per year.

TECHNOLOGY TRANSFER/COLLABORATIONS

In addition to building and testing hydrothermal units for TRU-contaminated combustible wastes, Los Alamos is also building and testing a hydrothermal unit for the treatment of low-level mixed wastes at Los Alamos, is collaborating with a consortium led by General Atomics Cooperation to build a skid-mounted unit for the treatment of U.S. Navy shipboard wastes, and is negotiating a cooperative research and development agreement (CRADA) with an environmental company to develop hydrothermal processing technology for the treatment of industrial wastes. The size of hydrothermal units for these projects range from 60,000 to 1,000,000 kg of organic waste per year.

TASK DESCRIPTION

The task is to decontaminate material containers so that these containers can be released into the laboratory room for handling outside the glovebox environment.

Electrolytic decontamination is a technology under development for several applications. The original purpose of the technology was to decontaminate equipment and uranium weapons parts for disposal at RFETS, and it has been successfully demonstrated for these applications. Its potential for providing contamination-free containers as part of an automated system led to the integration of electrolytic decontamination with the Sandia National Laboratories/New Mexico (SNL/NM) can-out system, a robotic-assisted method for removing filled storage containers from the glovebox. The technology is also being applied as the means of container decontamination in the Advanced Recovery and Integrated Extraction System (ARIES) pit conversion project. These several projects each receive separate funding. The 94-1 R&D project supports electrolytic decontamination to demonstrate its utility in removing contamination from the exterior of long-term storage containers.

TECHNOLOGY NEEDS

Repackaged containers must be contamination-free for out-of-line storage, and container weld ends must remain hermetically sealed after cleaning.

SCIENTIFIC BACKGROUND

The stainless steel material container to be decontaminated (anode), a stainless steel containment fixture (cathode), and sodium nitrate aqueous solution (electrolyte) are configured as an electrolytic cell.

A low-DC voltage and current density are applied to the cell to cause the iron, chromium, and nickel in the stainless steel to oxidize and dissolve into the solution; meanwhile, plutonium-containing particles embedded in the surface of the stainless steel container are removed to the solution. As electrolysis progresses, the solution becomes basic and forms solid precipitates with the dissolved metal ions. The precipitates trap the plutonium-containing particles and separate from the solution. Then the solution is filtered to remove the precipitates and is reused.

TECHNICAL APPROACH

Preliminary "hot" demonstration tests of electrolytic decontamination of material containers were conducted.

ACCOMPLISHMENTS/PROGRESS

Three empty externally contaminated 304 stainless steel material containers, which had been contaminated in the glovebox line of the repackaging project, were decontaminated to below the specifications for release into the laboratory room. The swipable limit for room release is 20 disintegrations per minute (dpm)/100 cm^2. For the sides of the containers, contamination was reduced from an average direct alpha contamination reading of 25,000 dpm/100 cm^2 and an average swipable alpha contamination reading of 5000 dpm/100 cm^2 to not detectable and no swipable. For the weld ends of the containers that make contact with the glovebox floor, these hermetically sealed containers were cleaned from an average direct alpha contamination reading of 200,000 dpm/100 cm^2 and an average swipable alpha contamination reading of 10,000 dpm/100 cm^2 to less than the required 500 dpm/100 cm^2 direct and no swipable.

After cleaning, these containers were leak-tested for the presence of helium to 1×10^{-7} std cm^3/s as required by DOE-STD-3013-94. Also, the containers had been tested prior to cleaning. No detectable leaks were found in either test. The recycled electrolyte was analyzed by liquid scintillation and gas-proportional alpha counting, and no detectable plutonium could be found. Precipitate analysis verified plutonium contamination in the precipitate. An ultrafiltration testing report was issued. Ultrafiltration would be an upgrade to the Buchner funnel currently used.

BENEFITS

Once the material can is set up in the fixture, no more handling by operators is required during the decontamination process. This minimizes radiation exposure to personnel. The electrolyte solution is recycled, which minimizes waste generation.

TECHNOLOGY TRANSFER/COLLABORATIONS

This project has collaborative efforts with SNL/NM for the automatic bagless can-out system and with Lawrence Livermore National Laboratory (LLNL), who are partners with Los Alamos in the ARIES project.

TASK DESCRIPTION

Plutonium oxide was pressed into pellets without the use of binders or lubricants and was calcined to test the effect of pelletizing before calcining on the mass fraction of respirable particles.

TECHNOLOGY NEEDS

Significantly reducing the mass fraction of respirable particles would have a positive impact on the safety of handling, packaging, facilities, and shipping.

SCIENTIFIC BACKGROUND

Respirable particle size is considered to be in the range ≤ 3 μm. Basic work on plutonium oxide particle size has been conducted by Los Alamos chemists using equipment available at TA-55. Previous work has shown a decrease in the mass fraction of respirable particle size after heating bulk oxide to 950°C for 2 h.

TECHNICAL APPROACH

The approach was to compact PuO_2 material and characterize the pellets using existing fuel pellet pressing equipment and to calcine the green pellets in the plutonium oxide packaging line with furnaces used to stabilize oxides for packaging. The pellets were then subjected to crushing and impact tests, and particle size and surface area measurements were made on the initial oxide and on the crushed calcined pellets.

ACCOMPLISHMENTS/PROGRESS

The plutonium oxide tested was formed from the decomposition of Pu^{+3} oxalate precipitated from a plutonium nitrate solution. The material was calcined at approximately 600°C for 6 h before it was sent to the vault in 1992. Plutonium content and impurities were determined at that time. The results are shown in Table I.

TABLE I. Chemical and Isotopic Analyses Results for PuO_2 Used in This Study

Isotopics			
Pu-238	**Pu-239**	**Pu-240**	**Pu-241**
0.017	93.6	6.06	0.304
Chemistry			
	Am	**Th**	**U**
	<10	<20	15
Ag	**Al**	**B**	**Be**
<1	5	<10	<1
Bi	**Ca**	**Cd**	**Cr**
50	7500-75000	<10	10
Cu	**Fe**	**Mg**	**Mn**
<1	20	5	<1
Mo	**Na**	**Ni**	**Pb**
<20	100	7	<5
Si	**Sn**	**Zn**	
140	<5	<5	

The sample was 87.4 mass % plutonium. The largest impurity was calcium at <75,000 ppm. When the storage container was opened, the material was agglomerated. Material analyzed for particle size and surface area was forced through a 20-mesh sieve to break down agglomerates before the analysis was performed. Loss-on-ignition, particle size, and surface area analysis of this material are shown in Table II.

The oxide was pressed into compacts using a punch-and-die set with a nominal diameter of 0.665 in. and a hand-operated hydraulic press. The oxide was charged to the die just as it came from the storage container. No binder or lubricant was added, and the powder was not milled or sieved. Compacts of acceptable integrity were obtained using a forming pressure of 55,650 psig. A crack was seen across the flat surface of some of the pellets. After pressing parameters were determined, six compacts having the following characteristics were fabricated:

- Diameter: 0.674 in.,

- Length: 0.245 in.,

- Weight: 5.01 g, and

- Density: 32% theoretical density (TD). PuO_2 TD = 11.46 g/cm^3

The compacts were heated in air at a rate of about 190°C/h to 980°C at which they were held for 2 h, then cooled at the same rate. As soon as the compacts were removed from the furnace, two of them were submitted for analysis of loss on ignition (LOI). The LOI was done by heating the sample to 950°C in air and calculating the weight lost. The results of the LOI analysis are presented in Table II.

Another two parts were crushed by placing one at a time in the hydraulic press in a fixture that had its surfaces aligned with those of the flat faces of the compact. The compact was compressed just as it had been pressed, but without the constraints of the die around the sides. The line pressure at which the part failed was recorded. The crushed parts were then collected by inverting a small 80-mesh sieve with a catch pan on the bottom over the fixture and then inverting the complete assembly to catch all the material on the sieve and in the pan below. This was done so that none of the finer particles could escape during collection of the sample. The sieve and the catch pan were then transferred to the glovebox for analysis of particle size and surface area. Both the >80-mesh (>180 μm) and the <80-mesh (<180 μm) fractions of the crushed part were weighed and the <80-mesh material was analyzed for particle size distribution and surface area. These results are presented in Table II. After the above two fractions were weighed, the sieve and pan were observed to be covered with a layer of dust. The pan and sieve were weighed, wiped clean, and weighed again; and the difference was recorded as lost fines.

The particle size distribution was measured using a Lasentech LAB-TECH 1000 analyzer, a laser system that employs a light-scattering method to measure particles suspended in deionized water. These measurements, which go up to 250 μm, are reported as a percentage of the total particles counted that are within various spherical equivalent sizes scaled in microns. Mass distributions were calculated from the measurement, assuming a density for the oxide and spherical equivalent particles. Surface areas were determined with a Quantachrome Corporation Nova 1000 sorption analyzer, using the Braunauer-Emmet-Teller method and nitrogen as the adsorbate.

The remaining two compacts were crushed by dropping a 4-kg weight a distance of 30 cm onto the flat surface of each part. The parts were placed one at a time in a depression in a steel plate. A cylinder was placed on end in the depression over the part. Holes were drilled in the side of the cylinder to let air escape as the weight dropped, because the fit around the weight was snug in order to assure that the weight dropped straight onto the compact. The weight was dropped down the cylinder onto each part. After the drop, the weight and cylinder were carefully removed; and a stack of two sieves and a catch pan were inverted over the crushed part to collect the sample, as we had done with those crushed in the press. The 60-mesh (250 μm) and 80-mesh (180 μm) U.S. Standard sieves were used. The weights of material collected on each sieve, of that collected in the pan, and of the lost fines are presented in Table III. The material in the pan (<80-mesh) was analyzed for particle size distribution and surface area. The results are reported in Table II.

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TABLE II. Loss on Ignition, Particle Size, Surface Area, and Fraction <3 μm

Sample	LOI (wt %)	Mean Particle Size (μm)	Surface Area (m²/g)	Fraction <3 μm (wt %)
Material from Vault	2.21	17.8	67.5	9.3×10^{-5}
2 Pellets Calcined,	0.049 and 0.054			
2 Pellets Crushed in Press		9.9 and 7.3	2.0 and 1.8	6.8×10^{-5}
2 Pellets Crushed by Weight		7.0 and 6.8	1.4 and 1.3	6.0×10^{-4}

TABLE III. Mass of Crushed Calcined Compacts

Sample ID	Mass >60-mesh (>250 μm) (g)	Mass <60/>80-mesh (<250/>180 μm) (g)	Mass <80-mesh (<180 μm) (g)	Mass of Lost Fines (g)
2 Pellets Crushed in Press		4.2172 and 4.0106	0.5429 and 0.6414	0.0324 and 0.0499
2 Pellets Crushed by Weight	2.1451 and 3.1245	0.2071 and 0.3647	0.6582 and 1.2236	0.1736 and 0.0940

Despite the high-pressing pressure, the green density of the compacts is low relative to the 60-65% TD that is usually reached when pressing fuel pellets. The springback of the diameter of the compacts was 9 mils, or 1.35%, which is high and probably accounts for the cracks that occurred. If a binder and lubricant were added to the powder and the powder were conditioned by milling, higher green density and less springback would have occurred, and the cracks may have been eliminated.

Calcining at 950°C brought the LOI down to an acceptable level for long-term packaging, decreased the mean particle size by about half, and greatly reduced the surface area of the powder. The compacts were not measured after the calcining because they were too fragile. Therefore, a final density was not determined; but the parts did not appear to have sintered at all.

The first part that was compressed yielded at a line pressure of 1400 psig. The second part was compressed to a line pressure of 5000 psig and never exhibited a clearly discerned failure. Nevertheless, the parts looked alike after the pressure was applied. The parts that the weight was dropped on looked similar to those that were crushed in the press, except that the fragments were more scattered.

We suspect that the mean particle size in all the crushed samples is less than in the as-received material because the high pressure used to form the compacts broke down the agglomerates present in the original materials, and the calcining temperature was not sufficient to sinter any particles together. As a result, the mass fractions of particles <3 µm in all three samples are within an order of magnitude of each other. The mass of the >80-mesh material was added to the mass of the <80-mesh sample when calculating the fraction of particles smaller than 3 µm; but the mass of the lost fines was not added, nor were the lost fines in the <80-mesh sample analyzed with the Lasentech analyzer. Because some of this dust surely included particles smaller than 3 µm, this bias should be considered when evaluating these results. The calculations were done this way to be consistent with past data reported. We recommend that in the future the sieves and pan be rinsed with the deionized water used as the suspension fluid in the analysis so that this dust is collected and included in the analysis and calculations.

We conclude that the treatment given the PuO_2 powder in this test did not alter the mass fraction of <3-µm particles. In future tests, lubricants and possibly a binder should be added to the powder before pressing to obtain a higher-density compact. The compacts should be heated to a temperature above the sintering threshold for PuO_2, probably >1200°C, to realize the desired result of having smaller particles agglomerate.

TECHNOLOGY TRANSFER/COLLABORATIONS

This work was done to satisfy safety study requirements at RFETS.

TASK DESCRIPTION

To enhance the understanding of plutonium storage issues, the Shelf-Life project evaluates the behavior of plutonium metal, oxide, and residues in storage. The data gathered from experimentation is used to establish the parameters for the safe storage of plutonium-bearing materials. Both treated and untreated materials are placed in experimental containers for surveillance evaluation. Shelf-life testing includes compatibility testing of plutonium oxides and residues with container materials. The project will better characterize oxides and residues and provide a means to confirm the processing necessary for stabilization. When feasible, the demonstration of commercially available technologies will be incorporated into this project. A test matrix will be developed from the requirements and experience of Los Alamos and other DOE-complex sites. The project supports DOE-STD-3013-94 storage standard for oxide and development of interim storage standards.

TECHNOLOGY NEEDS

The DOE manages a significant quantity of solid process residues in matrices that include impure oxides and metals, salts, combustibles, ash, dissolver heels, sludges, contaminated glass and metal, and other items, most of which are currently in a configuration that is not suitable for long-term storage. Processing, treatment, stabilization, and/or repackaging are required to secure residues in a safe, stable form. There is a need to understand fundamental and potential problems for the safe long-term storage of plutonium metal, oxides, and residues. To do this we must enhance the basic understanding of existing stored metal, oxide, and residues including such characteristics as gas-phase generation/recombination, equilibrium effects, corrosion of materials and containment, and thermodynamic and kinetic behavior with time. We must close gaps in the present knowledge of water-dependent salt corrosion as a function of concentration and of the effect of radiolysis within salts. Noninvasive, non-waste-producing techniques must be developed for surveying plutonium-containing materials in storage. Corrosion-resistant shipable containers and weld closures are needed for use with existing or stabilized residues.

SCIENTIFIC BACKGROUND

Previous work done in the DOE complex and in the Los Alamos Packaging project during FY94 and FY95 has empirically established a database on the characteristics and behavior of plutonium oxide. Continued work on the storage of metal, oxide, and residues will build on this knowledge.

The following categories have been tentatively identified to undergo further analysis:

- Plutonium metal;

- Oxides; and

- Residues chosen from the following categories:
  - metal alloys,
  - ash,
  - sand, slag, and crucible,
  - pyrochemical salts, and
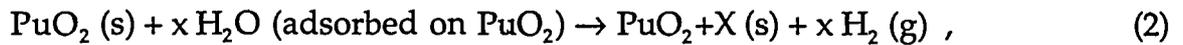 - combustibles.

Plutonium Metal

An extensive database has been established for plutonium metal that has been stored within pits over the past 50 years. These materials have been thoroughly characterized, and it is felt that a minimal R&D effort is required to ensure the safe storage of plutonium metal in accordance with DOE-STD-3013-94.

Plutonium Oxide

Although the requirements for storing metal and some alloys are well established from work with plutonium weapons components, a similar knowledge base for plutonium oxide does not exist; and PuO_2 chemistry needs to be further defined for safe storage. Potential difficulties associated with oxide storage arise primarily from a combination of its chemical and physical properties. As a consequence of high surface area and strong chemical affinity of surface sites, the dioxide can adsorb several mass percentages of molecular species from the atmosphere. Polar molecules, such as water, are strongly bound to the oxide surface. Radiolysis and chemical reaction of adsorbates have potential for producing unacceptably high pressures of noncondensable and reactive gases during storage. For example, the amount of water present at the 1-mass-% level is capable of producing a pressure of about 50 atmospheres of hydrogen and oxygen in a typical storage vessel. The hazard posed by possible rupture of an oxide storage vessel is considered to be significant, because a large mass fraction of the material resides in the size range considered to be dispersable. Previous oxide data is summarized, and new work is discussed by John M. Haschke and Thomas E. Ricketts in "Plutonium Dioxide Storage: Conditions for Preparation and Handling," Los Alamos National Laboratory report LA-12999-MS (August 1995).

During FY95, pressurization processes were investigated. Two processes could lead to excessive pressurization of oxide-containing vessels during extended storage. As described by the following equations, these processes are (1) radiolytic

decomposition of water and other adsorbates on the oxide and (2) chemical reaction of adsorbed water to form high-stoichiometry oxide and hydrogen:

$$H_2O \text{ (adsorbed on } PuO_2\text{)} \xrightarrow{\text{alpha-particle}} H_2(g) + 1/2 O_2 (g) \ , \tag{1}$$

$$PuO_2 (s) + x H_2O \text{ (adsorbed on } PuO_2\text{)} \rightarrow PuO_2+X (s) + x H_2 (g) \ , \tag{2}$$

when (g) refers to the gas phase and (s) to the solid.

The packaging philosophy at Los Alamos is to adequately calcine the oxide and thereby limit to a safe level the maximum possible pressure increase in a storage container. However, knowledge about the rate of these reactions is necessary in order to define possible risks associated with improperly fired materials and to establish a basis for surveillance frequency for oxide containers. If the rates of the reactions are so slow that significant pressure is not generated over a period of 50–100 years, requirements for firing and surveillance could possibly be relaxed. Water is the species that is most tenaciously retained during firing and most rapidly re-adsorbed upon exposure to air. The main objective of kinetic studies is to identify relevant radiolytic and chemical processes and to define the rates at which noncondensable gases are formed from water.

Although observations suggest that radiolysis of water is not a credible pressurization process during storage of plutonium dioxide, formation of hydrogen by chemical reaction of water is of concern. However, for a given amount of residual water on the oxide, the maximum pressure achieved by the reaction is two-thirds of that for radiolysis. In a typical storage configuration (3 kg of oxide in a container with 2 L free volume), a maximum hydrogen pressure of about 150-psi H_2 will be generated by reaction of 0.5 mass % water. If equation (2) proceeds at the rate measured for water-saturated oxide, the H_2 pressure will increase by about 2.7 psi per year and the maximum pressure for 0.5 mass % water will be reached in about 55 years. This annual increase is considered to represent the worst-case situation because the rate of equation (2) is expected to have a dependence on water concentration with less rapid rates being observed for fired oxide than for water-saturated material.

Residue Categories

Storage of residue materials (<50 wt % plutonium) will initially be the same issues as are investigated for oxides and metals; i.e., pressure build-up, corrosion, flammable gas mixtures, pyrophoricity, and affects of moisture. Because of the multiple-compound nature of residues, as well as water content, corrosivity, and gas generation, these residues are difficult to categorize. Some residues will lend themselves to stabilization; others must be processed to remove the plutonium.

TECHNICAL APPROACH

Metal

A minimal endeavor will be conducted for metal evaluation to include periodic surveillance of metals stored in containers with pressure-sensitive devices. These data will be collected on a regular basis within the Packaging project, and the data will be available for evaluation. The containers will be available for further study coordinated between the Packaging and Shelf-Life projects.

Oxide and Residues

Residue studies to target specific problems within the DOE complex began on materials available in the Los Alamos inventory. Personnel at other sites will be contacted to obtain their input to the planning and decision process and, if possible, samples of their materials.

NOTE: Los Alamos does not intend to store residues beyond the end-point of the 94-1 stabilization project.

Selection of materials for study is based on potential and perceived storage risk as well as on availability of analytical equipment and personnel. With the selection of plutonium oxides and residues, experimenters will record the following:

- The problem chosen for study and its importance to the complex,

- Information expected to be gained,

- Types of measurements to be conducted,

- A projected lifetime for each container,

- Approved procedures to be used in the experimentation, and

- Comments on the experimentation.

Monitoring of materials in containers will be performed under the following conditions by pressure-volume-temperature (PVT) and noninvasive test capabilities:

- Containers treated and untreated at room temperature,

- Containers treated and untreated at elevated temperature,

- Selected containers initially evacuated, and

- Selected containers evacuated and back-filled with inert gas (helium or argon).

Planned or possible analytical approaches include the following:

- PVT measurements,

- Surface studies,

- Corrosion testing,

- Mass spectroscopy to identify gases generated,

- Thermogravimetric analysis,

- Microbalance,

- Raman spectroscopy,

- Laser-induced breakdown spectroscopy (LIBS), and

- Infrared backscattering.

Oxides and Oxide-Like Materials. Experimentation will continue on pure and impure oxides formed from various processes, and experimentation will begin on ash samples. The studies will address dispersable and respirable fractions, pressure generation, and compatibility with the storage containers. Experimentation will be conducted to determine particle size/surface area, particle size distribution, moisture uptake, gas generation and recombination, production of hyperstoichiometric oxide, and material/container compatibility. Valuable information has already been recorded for pure oxides from several sources.

Characterization of each matrix is residue category-specific. Oxide or oxide-like materials may require the following analyses:

- LOI measurement of the untreated material taken from the vault,

- LOI on the matrix heated to 950°C,

- Surface morphology (particle size and surface area),

- Wt % plutonium and homogeneity of plutonium in the matrix,

- Carbon content of the untreated material taken from the vault, and

- Carbon content of the matrix after heating.

By the end of this quarter, oxides and ash are to be placed in experimental containers.

Salts. Salts may be corrosive and react with their storage containers because they have affinity for water ranging from waters of hydration to deliquescence, thus

exhibiting innocuous-to-very-corrosive properties. Knowledge of the behavior of salt in storage is basic to decisions on interim or long-term storage configurations. Experimentation will address properties of pure and actinide-containing residue salts, corrosivity of salts on containers, and radiolysis effects within a salt. Individuals currently working on the salt questions within the DOE complex will contribute to the planning for this experimentation, which is in the early stages. Initial information will be gathered by means of a literature study. Existing pyrochemical salts will be characterized. Analyses may include water vapor determination with several salts; the evaluation of drying techniques, including microwaves; and water determination using infrared techniques. PVT measurements, mass spectroscopy, gas analysis, and Raman spectroscopy may be used.

Advanced Technologies

The Shelf-Life project initiated development of and will continue interaction on noninvasive nondestructive waste-minimizing methods of analysis. Progress is reported on the following tasks, each of which is included as a work package in the 94-1 Research and Development Lead Laboratory Technical Program Plan:

- Digital Radiography (Real-Time),

- Tomography,

- Pressure-Sensitive Devices,

- Laser Sampling,

- Acoustic Resonance Spectroscopy, and

- Nondestructive Assay (neutron counting).

Also, progress is reported on producing a long-term storage container for ^{238}Pu and on noninvasive analytical techniques.

ACCOMPLISHMENTS/PROGRESS

Metal

A basis for continuing surveillance of metal-filled containers has been established within the Los Alamos Plutonium Packaging project. The Packaging project has completed nine quality-assured double-welded containers for pure plutonium metal, and these containers meet the DOE standard. Each container holds slightly more than 4 kg of metal. Two of the nine packages contain aneroid bellows, which will indicate pressure changes. Bellows will be placed in a statistical sampling of metal containers. Until real-time radiography is available at the Plutonium Facility in mid-FY96, a base line for each bellows will be established using film radiography.

As part of the Packaging project surveillance program, the boundary containers will be periodically checked for leaks, and the total containment system will be weighed.

Oxides and Oxide-Like Materials/Residues

Shelf-Life Project—Container Prototype I. The first set of four shelf-life tests (Container Prototype I) tests were completed. In this preliminary set of experiments, PVT studies of residues were conducted on samples of electrorefining salt, combustibles, oxidized electrorefining salt, and incinerated ^{238}Pu-contaminated rags.

In a six-month period, no significant changes were detected within the four containers. The experimental setup was not adequate for precise data acquisition over an extended period, and the experiments were terminated.

Shelf-Life Experiments—Container Prototypes II and III. The oxide/ash studies will proceed with new test setups. A preliminary test plan has been drafted and is being used in establishing an experimental matrix to satisfy DOE-complex needs. For oxide and ash, the design for a container has been approved. Containers will be fabricated this quarter. A sampling manifold is available. A data acquisition system must be ordered. Experimental goals are well developed. Samples of oxides of various weight percentages of plutonium and of ash must be selected and characterized. Experiments are to be initiated by the end of this quarter.

Goals for the experimentation on salts must be developed and candidate materials identified. For salts, a manifold has been designed for installation into an existing glovebox. Containers have been designed and fabricated and await intrumentation. Hardware is to be delivered this quarter. A data acquisition system is available.

Advanced Technologies

Pressure-Sensitive Devices. The initial scoping and feasibility study for a hydrogen sensor to be placed inside a welded container was completed by SNL/NM. It indicates the feasibility of the detection of hydrogen pressure from 1x10^{-6} torr to atmospheric pressure and of the telemetry required to process the signals through the stainless steel can. SNL/NM will provide a written report on their work to date and will proceed in developing experimental devices for use in shelf-life testing.

In addition to the electronic devices under development at SNL/NM, the Shelf-Life project will continue development of the pressure-sensitive bellows, which are welded onto the lid of the material (inner) container of the long-term storage container system and are measured using radiography. This device was designed in cooperation with the vendor, Miniflex Corporation, and is in use within the Plutonium Packaging project. With support from the Los Alamos National Laboratory Technology and Safety Assessment Division's statistics group (TSA-1) for test design and data evaluation, Packaging personnel and the vendor have conducted tests to determine the response of the bellows to increasing pressure in the container. As a result of this testing, a production specification was established for bellows. Testing will be completed with a series of tests done on the production bellows using the Plutonium Facility's real-time radiography

equipment. A report on the testing and response of the bellows will be provided by TSA-1 personnel. The Shelf-Life project is continuing bellows development with an aim to providing a more robust bellows integrated with container design.

Real-Time Radiography. Equipment purchased by the Packaging project will be installed in the Plutonium Facility during the second quarter and will be placed in use for initial inspection of production long-term storage containers. This equipment will be used to complete qualification of the bellows. A Savannah River Site (SRS) collaborator has been named to cooperate in development of real-time radiography for use with surveillance of stored materials within the DOE complex.

Tomography. SRS has also agreed to provide a collaborator for development of surveillance of materials in storage by means of computerized tomography and investigations of tomographic gamma scanning. Los Alamos and SRS investigators will meet during the second quarter to lay out specific approaches to the collaboration.

Laser Sampling. Laser sampling of gases in several container configurations has been investigated and is found to be feasible. Initial scoping and designing of a sealable laser head will be completed during the second quarter. A report evaluating the generation of an explosive mixture in a plutonium oxide storage container and the ability of the container to withstand excess pressure is complete. For the prototype SRS Bagless Transfer System container, the calculations show that the container would remain intact under worst-case conditions.

Acoustic Resonance Spectroscopy (ARS). Initial scoping experiments using ARS for gas identification and pressures have been completed. The feasibility study indicates that this method is viable for noninvasive surveillance. The progress report will be completed this quarter.

Nondestructive Assay (Neutron Counting). A search of the literature reveals that, with recent advancements in equipment for neutron counting, a high probability exists that neutron flux differences in several plutonium compounds can be determined. Investigations will be conducted within the Core Technology section of the Los Alamos Technical Program Plan.

Noninvasive Analytical Methods. Initial planning meetings were held with investigators who are developing Raman spectroscopy and LIBS for use with materials in long-term storage. They will design and fabricate containers and conduct experimentation using these methods. After their initial demonstrations, Raman spectroscopy and LIBS will be demonstrated on prototype containers filled with storage materials. These studies are being conducted as a part of the Shelf-Life project.

Plutonium-238 Long-Term Storage Container. Design concepts for a long-term storage container for ^{238}Pu are being studied by Sandia National Laboratories/ California (SNL/CA). They have proposed two alternative approaches to the design of a container using a quartz filter to allow generated helium to escape. Their report will be completed after a conference between their investigators and Los Alamos

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personnel, scheduled to take place in February. No further studies on this container are planned.

BENEFITS

Problems with storing plutonium-bearing materials are being identified. Enhancement of surveillance techniques has been demonstrated, and development continues. Materials that must be processed to remove the plutonium for safe storage will be identified. Deleterious effects of water will be further defined. Eliminating corrosion problems and pressure buildup within containers will vastly improve the safe storage of plutonium-bearing materials.

TECHNOLOGY TRANSFER/COLLABORATIONS

The Shelf-Life project has set meetings with RFETS and SRS to obtain their input to the experimental matrix. Los Alamos collaborated on digital radiography and laser sampling with SRS, and these interactions will continue. The development of electronic pressure-sensitive devices is conducted by SNL/NM in cooperation with the Shelf-Life project, and the bellows development will continue in close coordination with the vendor, Miniflex Corporation of Ventura, California.