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October 21, 1977

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**RESEARCH AND DEVELOPMENT
SEMIANNUAL PROGRESS REPORT
FOR JANUARY THROUGH JUNE 1977**

CHEMISTRY RESEARCH AND DEVELOPMENT

Frend John Miner

Rockwell International

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U. S. DEPARTMENT OF ENERGY
CONTRACT EY-76-C-04-3533

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Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22161
Price: Printed Copy ~~\$5.00~~ ^{6.15} Microfiche \$3.00
Price Is Subject to Change Without Notice

Printed
October 21, 1977

RFP-2680-A
UC-4 Chemistry
TID-4500-R66

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CHEMISTRY RESEARCH AND DEVELOPMENT

Frend John Miner

Chemical Research	-----	James D. Navratil
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Pilot Plant Development	-----	Donald L. Ziegler
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**ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
P. O. BOX 484
GOLDEN, COLORADO 80401**

**Prepared under Contract EY-76-C-04-3533
for the
Albuquerque Operations Office
U. S. Energy Research and Development Administration**

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SUBJECT DESCRIPTORS

Accountability	Formic Acid	Precipitation
Acid	Galvanic Corrosion	Programming
Actinides	Gamma Detection	Purification
Adsorption	Gas Analysis	Pyrochemical Processing
Air Classification	Helium Diffusion	Radiation Detectors
Aluminum	Humidity	Radioactive Waste Processing
Aluminum 5083	Hydrofluorination	Radioactive Wastes
Americium	Impurities	Raschig Rings
Americium Oxides	Incineration	Recovery
Americium Recovery	Incinerator Ash	Reduction
Ash Fusion	Instrumentation and Controls	Refractories
Beryllium	Lathe Coolants	Reverse Osmosis
Beta-Gamma Waste	Leaching	Rotary Kiln
C-Rings	Leak Testing	Safeguards
Calibration Standards	Leco Crucibles	Sampling
Calorimeters	Machining Damage	Separation Processes
Casting	Materials Recovery	Shielding
Chemical Analysis Instrumentation	Measuring Instruments	Shipping Containers
Chemical Preparation	Microprocessors	Slag Resistance
Chemical Milling	Minicomputers	Soils
Chromatography	Molten Salts	Solar Pond Sludge
Cleaning	Molten Salt Residues	Solvent Extraction
Compatibility	Monitoring	Solvents
Control Systems	Nondestructive Analysis	Specific Heat
Corrosion	Nuclear Materials Management	Stainless Steel 304L
Decontamination	Particles	Standard Deviation
Dissolution	Permeability	Statistics
Distillation	Pits	Stress Corrosion Cracking
Efficiency	Plutonium	Tanks
Electronic Equipment	Plutonium Alloys	Thermodynamic Properties
Electrorefining	Plutonium Carbonate	Tilt-Pour Furnace
Enthalpy of Formation	Plutonium Dissolution	Tributyl Phosphate
Evaporation	Plutonium Hydrides	Tungsten
Fast Fluidization	Plutonium Metal	Uranium
Fiberglass	Plutonium Nitrides	Vacuum Furnace
Fiberglass Reinforced Plastic	Plutonium Packaging	Vitrification
Fluidized Bed	Plutonium Processing	Waste Management
Fluidized Bed Incinerator	Plutonium Recovery	Waste Processing
Fluorination	Plutonium Residues	Water Vapor

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977. Production and Production Support programs are identified as PPS.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977. Production and Production Support programs are identified as PPS.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979
Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79,
January 3, 1977. Production and Production Support programs are identified as PPS.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977. Production and Production Support programs are identified as PPS.

†Waste Isolation Pilot Plant.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977. Production and Production Support programs are identified as PPS.

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Process development work is proceeding on a method to convert the residues produced in the fluidized bed incinerator process to a borosilicate glass. A bench-scale, resistance-heated, metal vitrification reactor was installed and operated in a continuous mode. Glass buttons are produced using a free-forming concept. (Special ERDA Funding and PPS*)

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A laboratory-scale fast fluidization unit has been designed for evaluation of this concept for incineration of combustible solids and graphite wastes from nuclear facilities. The laboratory-scale equipment has been requisitioned, and installation will be initiated. (DDS Endeavor 330*)

*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977. Production and Production Support programs are identified as PPS.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977.

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Initial steps in the process have been demonstrated in both the stationary and tilt-pour furnaces with a total of 885 kg of backlog salts processed. Poor metal-salt separation observed in a middle step is attributed to either poor salt-to- metal contact during the equilibration or too high impurity levels in the metal product from the fourth step. Volatile metal solvents have been separated from plutonium-americiu alloy in a research vacuum-melting furnace. A vacuum distillation furnace for separating americiu from plutonium is being installed. (DDS Endeavor 332*)

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1979 Proposed Program for Process Development (NM-01-04) and Related Work, CD77-79, January 3, 1977. Production and Production Support programs are identified as PPS.

RESEARCH AND DEVELOPMENT SEMIANNUAL PROGRESS REPORT FOR JANUARY THROUGH JUNE 1977

CHEMISTRY RESEARCH AND DEVELOPMENT

Frend John Miner

CHEMICAL RESEARCH

James D. Navratil

ACTINIDE RECOVERY AND RECYCLE PREPARATION FOR WASTE STREAMS

Larry L. Martella, James D. Navratil,
Carl E. Plock, and C. Michael Smith

OBJECTIVE

The objective of this program is to evaluate actinide recovery methods and recycle-preparation problems for secondary aqueous waste streams that are likely to be produced during reactor fuel fabrication and reprocessing. Results of this laboratory-scale program, which is being done under contract for Oak Ridge National Laboratory (ORNL), will be used by ERDA and ORNL to determine the feasibility of partitioning actinides from aqueous waste.

PRIOR WORK

No prior work has been done on this project.

ACHIEVEMENTS AND DISCUSSION

Evaluation of recovery methods and recycle-preparation problems for salt waste and wastewater streams was begun. A program plan was written to assist in the planning and management of the program. A preliminary literature search was made of applicable methods

for use on the waste streams. The waste stream compositions were defined and research initiated.

Salt Waste Processing

Three experimental approaches presently planned for processing salt wastes are as follows: bidentate extraction, combination tributyl phosphate-bidentate extraction, and cation exchange. Testing of a bidentate organophosphorous solvent extractant for determining the feasibility of removing actinides from salt waste streams has been initiated. The extractant, dihexyl-N, N-diethylcarbaryl-methylene phosphonate (DHDECMP), was obtained in impure (~50%) form from Wateree Chemical Company, Lugoff, South Carolina. An impurity in the DHDECMP, which prevents efficient stripping of actinides at low acidity, was removed by passing 30 vol % DHDECMP-CCl₄ (carbon tetrachloride) through a bed of Amberlyst® A-26. This bed material is a macroreticular, strong-base, anion-exchange resin in the hydroxide form.

Extraction coefficients for uranium, plutonium, and americium versus nitric acid (HNO₃) concentration are plotted in Figure 1. The americium extraction coefficient in 0.35M HNO₃ is approximately 0.1, but before the impurity in the DHDECMP was removed, the extraction coefficient was 125. The values for uranium at 5, 7, and 9M HNO₃ were all >10³ (and so are off the top of the figure). The high uranium extraction coefficients at low acidity indicate uranium stripping reagents other than water or dilute HNO₃ will be needed.

Various stripping agents were tested for removing uranium from 30 vol % DHDECMP-CCl₄. The extractant, containing 41 g/l uranium, was contacted with the stripping agents four times using an aqueous-to-organic ratio of unity. The percent uranium stripped from the extractant after each contact is plotted in Figure 2. Results show that ammonium sulfate was the most effective stripping agent tested.

A synthetic salt waste solution was prepared and processed by both solvent extraction schemes. Prior to processing, two basic salt wastes (incinerator liquor and analytical waste) were combined and then acidified with 7M HNO₃. The acidification process required care because considerable foam and heat were produced. Filtration after acidification showed no visual solids present in the waste. The composition of the two basic solutions prior to acidification is shown in Table 1.

The problem of actinide removal, especially plutonium, was evaluated using both extraction processes. Figure 3 shows the plutonium and americium analysis of the acidified salt waste after consecutive contacts with 30 vol % tributyl phosphate (TBP)-dodecane and 30 vol % DHDECMP-CCl₄. The results show that the DHDECMP was more effective in removing actinides than TBP.

Wastewater Processing

Reverse osmosis (RO) is being investigated to determine its feasibility for water purification. Figure 4 shows the conceptual flow sheet for purification of wastewater containing insignificant quantities of corrosive anions and low concentrations of impurities and radioactivity. This conceptual flow sheet is based on Rocky Flats experience with RO.¹

Figure 5 shows the conceptual flow sheet for purification of wastewater containing significant quantities of anions and/or detergents. The methods planned for flow sheet testing include adsorption, reverse

osmosis, ultrafiltration (UF), ion exchange, or combinations thereof. Ultrafiltration methods would be used mainly for the removal of detergents and would need to be coupled with an anion removal step such as RO. Use of UF and/or RO methods would reduce the quantities of waste material for incineration compared to adsorption — ion exchange methods. The use of ozonation for destruction of detergents and corrosive anions is also considered feasible.

Also initiated was evaluation of various adsorption materials to remove detergents and anions from wastewater. The initial evaluation will consist of comparing the breakthrough capacity of activated carbons, macroreticular resins, and polyurethanes.

Preliminary breakthrough curves were determined by passing detergent solution (2.6 g/l of Proctor & Gamble Pierce Commercial Laundry Detergent in deionized water) through a column containing about one gram of adsorbent at 10 ml/min. Fractions (100 ml) were collected and analyzed for linear alkylate sulfonates (LAS).

Results of runs using Analab activated coconut carbon, Amberlite® XAD-4 macroreticular sorbent, and Analab polyurethane foam are shown in Figure 6. Foam was substituted for rigid open-pore polyurethane (OPP) because the high pH (~11) of the detergent solution resulted in breakage of the OPP-column bond. Carbon and resin appear to have similar capacities with the carbon having a slight advantage. Discrimination between the two would depend on changing flow rate and/or column design. The foam proved to be inefficient, probably caused by the lack of adsorption sites.

Since solutions of high pH are incompatible with OPP, a pH 3.5 detergent solution was prepared to determine the breakthrough curve of OPP. Runs also were made with XAD-4 resin and two acti-

vated carbons to investigate the effect of pH on the adsorption of LAS. The results in Figure 7 show the OPP and XAD-4 to have the best adsorption capabilities. The decrease in pH enhances adsorption on the XAD-4; there appears to be a decrease in adsorption of the Analab carbon. The low adsorption on the Witco 517 could be caused by the large particle size (20-50 mesh).

FUTURE WORK

The bidentate extraction process will be evaluated further for processing salt wastes. New and recycled extractants will be tested with synthetic waste to determine actinide decontamination factors. The behavior of impurity ions in the process also will be studied.

Evaluation of adsorption materials for removing detergents and corrosive anions from wastewater streams will be completed. Conceptual flow sheets for purifying wastewater using membrane techniques will be evaluated.

REFERENCES

1. R. T. Heitzer and C. E. Plock. "Reverse Osmosis to Achieve Water Control and Recycle," Proceedings of the First Desalination Congress of the North American Continent. Mexico City, Mexico. October 24-29, 1976.

SLUDGE REMOVAL FROM RASCHIG RING FILLED TANKS

Larry L. Martella and James D. Navratil

OBJECTIVE

The objective of this study is to test various solvents for removing sludge from Raschig ring filled tanks. The tanks are used for storing plutonium processing solutions and lathe coolant oil.

PRIOR WORK

Sludge from plutonium process tanks was characterized so that better methods than are now available could be developed for preventing sludge formation in Raschig ring filled tanks or for removing sludge once it is formed. The characterization data suggested that tank leaching methods should be capable of dissolving plutonium dioxide. The data also suggested that improved filtration of aqueous solutions entering the tanks is needed to eliminate the buildup of sludge.

No prior work has been done in testing solvents for removing sludge from tanks used to store spent lathe oil coolant.

ACHIEVEMENTS AND DISCUSSION

Sludge in Raschig ring filled tanks used to store aqueous plutonium solutions is presently removed by flushing with nitric acid (HNO_3). Concentrated HNO_3 (12.5M) is added to the tank. This is followed by sparging with steam until the volume of the acid solution is doubled. A concentration of 0.012M calcium fluoride (CaF_2) formerly was added along with the nitric acid. Solvents other than HNO_3 ; e.g., hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), were not considered because of their incompatibility with the process plus their corrosive effect on process equipment.

Sludge samples were mixed for 30 minutes with 7M HNO_3 and 7M HNO_3 -0.006M CaF_2 at room temperature using a solid-to-liquid ratio of 50 g/l. The residues remaining after dissolving the sludges in the respective solvents were, respectively, 1.5 and 1.4 wt % of the original sludge. The elemental analysis before and after dissolution is shown in Table 2.

Results show that CaF_2 in HNO_3 appeared to reduce the concentration of Nb, Pu, Pb, Si, and Zr over HNO_3 alone; however, the total amount of plutonium in the sludge sample was only reduced from 0.4 to 0.3

milligram per sample by HNO_3 and from 0.4 to 0.1 milligram per sample by $\text{HNO}_3\text{-CaF}_2$. Another test, in progress, supports the conclusion that CaF_2 addition appears to improve sludge removal.

Various organic solvents were considered to remove sludge from tanks used to store spent lathe coolant oil and carbon tetrachloride (CCl_4) mixture. Baker reagent grade CCl_4 , Dow Chlorothene[®] VG technical grade 1,1,1-trichloroethane, and 25 vol % CCl_4 -Texaco 643[®] oil mixture were selected for testing the removal of sludge from Raschig rings. The tests consisted of measuring the weight loss of the sludge-coated rings after solvent contact at 22 °C.

Table 3 summarizes the average weight percent of sludge removed from the Raschig rings using the three solvents. 1,1,1-trichloroethane had a higher average percent weight loss at 10 and 28 minutes compared to CCl_4 or the 25% CCl_4 -Texaco 643 oil mixture. Dow Chlorothene VG brand 1,1,1-trichloroethane was found to be the most effective solvent for sludge removal as well as having the lowest cost per gallon of the solvents tested.

FUTURE WORK

Dissolution tests will be completed on sludge samples taken from tanks used to store plutonium processing solutions.

REMOVAL OF LEAD FROM AMERICIUM PRODUCT

Paul G. Hagan and Gary H. Thompson

OBJECTIVE

The objective is to develop methods for removing contaminant lead from americium. Americium is present in and must be

recovered from molten salt residues by ion exchange, precipitation, and calcination processing. Lead is introduced by lead sheet, foil, and tape used during processing to decrease exposure to operators.

PRIOR WORK

Prior work has been done at Rocky Flats to remove lead from americium recovered from molten salt residues by ion exchange and precipitation. Precipitation of lead as the sulfate is a method commonly used by the Chemical Operations group.

ACHIEVEMENTS AND DISCUSSION

Lead shielding in the form of sheet, foil, and tape is commonly used to reduce exposure to operating personnel during processing of molten salt residues to recover americium-241. Frequently the final americium oxide product is contaminated with up to 1 wt % lead as a result of inclusion of lead or lead corrosion products during processing. Therefore, methods for removing lead were studied.

Investigation has revealed the following:

1. Lead can be removed by precipitating americium oxalate in $\geq 0.3\text{N}$ nitric acid (HNO_3) and allowing the precipitate to equilibrate. The lead remains in solution.
2. The precipitation of lead as the sulfate or sulfide is highly acid dependent.
3. Metathesis of coprecipitated lead and americium oxalate to form the hydroxides does not solubilize the lead.
4. Use of a Jones (metal) reductor column effectively removes lead, but acid present in the feed solubilizes

excessive amounts of the reductant metal. This means a new contaminant is produced.

5. Reduction of acidity by neutralization with potassium hydroxide rather than dilution prior to oxalate precipitation effected substantial decontamination of the americium product lead.

Each of these findings will be discussed in turn.

Table 4 shows the results of lead oxalate solubility as a function of HNO_3 concentration. Lead oxalate was equilibrated overnight in the HNO_3 solutions. The solutions were then filtered and analyzed. As expected, lead oxalate solubility increases with HNO_3 concentration.

Subsequent testing used solutions containing 9.21 grams of Am per litre and 0.320 grams of Pb per litre in HNO_3 of varying concentrations. In one series of tests, precipitates were equilibrated for two hours before filtration; in another, equilibration lasted four days. The results are shown in Table 5.

Lead oxalate solubility increased rapidly with HNO_3 concentration; unfortunately, americium oxalate solubility also increases enough that losses are excessive if filtration is done two hours after precipitation. When the precipitates were equilibrated for four days, however, the lead oxalate redissolved and gave essentially complete lead removal at HNO_3 concentrations of $\geq 0.3\text{M}$. This method offers some promise for lead removal.

Precipitation of lead as the sulfide or the sulfate was effected in cold tests (lead only) in 0.1M HNO_3 ; however, when americium was present, only part of the lead was recovered as the sulfide in 0.1M HNO_3 , and lead sulfate (PbSO_4) did not precipitate at all. (At 0.3M HNO_3 , lead sulfide was not recovered.) The lead sulfide also contained $\sim 5\%$ of the

americium product, indicating coprecipitation. Because of these negative results, this approach was abandoned.

The role played by coprecipitation in these precipitation methods is also suggested by the failure of metathesis to remove any lead from coprecipitated lead and americium oxalates; again, metathesis of lead oxalate only (no americium present) completely solubilized lead at impurity levels. It is possible, however, that equilibrating or aging the precipitates (as with the oxalate- HNO_3 solubility tests) could effect the desired removal of lead.

Metal reductor columns of zinc, aluminum, and cadmium reduced lead from 1670 to < 1 ppm in test solutions; however, acid attack on the metal resulted in a metal contamination level of 10 g/l. Reduction of solution acidity to relieve this problem caused the solution to go acid-deficient and resulted in precipitation of metal hydroxides in the column.

Reduction of the acidity of americium feed solution with caustic rather than by dilution with water prior to oxalate precipitation was also studied. The intent of this approach was to minimize the loss of americium in the oxalate filtrate, reduce the waste volume, and increase lead removal in any lead sulfate precipitation step prior to oxalate precipitation. The latter was based purely on volume and solubility product considerations.

Oxalate precipitations were made with an americium feed solution that had been acid adjusted with 6M potassium hydroxide. The precipitates were easily filtered, and the filtrates and wash solutions combined contained only 3×10^{-3} g/l americium. The elemental analysis of the feed solution and the americium oxide product is shown in Table 6. Also shown are decontamination factors for separation of the elements from americium by oxalate precipitation. Good decontamination factors were found for all of the elements

that were detectable by emission spectrographic analysis. Currently there is no explanation for the decontamination resulting from acid reduction by neutralization rather than dilution.

FUTURE WORK

The promising methods will be studied more closely. Equilibration times between two hours and four days will be studied specifically to determine the time needed for lead oxalate to solubilize. Decontamination resulting from plutonium hydroxide neutralization of excess acid before precipitation as the oxalate will also be studied in an attempt to determine the mechanism of this separation. Other plans are to investigate ion exchange displacement chromatography. The formate system (described elsewhere in this report) will also be investigated to determine its efficiency in lead removal.

CALORIMETRY AND THERMODYNAMICS OF NUCLEAR MATERIALS

Franklin L. Oetting

OBJECTIVE

The objective of this program is to continually evaluate the chemical thermodynamic and calorimetric needs of the nuclear weapons program specifically as they relate to the operation of Rocky Flats. Experimental programs will be developed and implemented to meet these needs. In addition, thermodynamic data related to nuclear materials will be critically evaluated and compiled.

PRIOR WORK

Experimental high-temperature enthalpy data have been obtained for PuN, PuC, Pu₂C₃, and PuO₂. A program for compila-

tion and critical evaluation of thermodynamic data initiated at Rocky Flats in 1974 was actively pursued during an appointment to the International Atomic Energy Agency in Vienna, Austria, from 1974 to 1976. This compilation is being continued at Rocky Flats and will result in the publication of an 11-part series dealing with the thermodynamic properties of all nuclear materials. Two of these parts have been published.^{1,2}

ACHIEVEMENTS AND DISCUSSION

A paper describing the thermodynamic work on PuN has been submitted to the Journal of Chemical Thermodynamics for publication.

Significant progress was made on the acquisition of the adiabatic calorimeter. This calorimeter will be used to accurately measure the high-temperature heat capacity of plutonium metal and the plutonium hydrides. The basic hardware for such a calorimeter was obtained on loan from the National Bureau of Standards, Washington, D.C. with an estimated value of \$4,000 for the silver metal and \$25,000 worth of machining time. LLL supplied \$15,000 to prepare the calorimeter for operation. This includes expenditures for temperature control systems, thermopiles, heaters, and the data acquisition system.

Dr. E. D. West, president of Calorimetrics, Inc., Boulder, Colorado, has been obtained as a consultant to assist in the redesign and construction of the calorimeter. In addition, an evaluation of the type of data acquisition system needed was made and resulted in the outlining of four possible alternative approaches that could be followed.

Installation of a solution calorimeter has been delayed awaiting the installation of a glovebox. The solution calorimeter will be used to measure the enthalpy of formation of compounds in the plutonium-hydrogen system.

The final manuscript of the third part of the critical assessment of thermodynamic data has been sent to Vienna for publication. The manuscript is entitled "The Chemical Thermodynamics of Actinide Elements and Compounds, Part 3, The Miscellaneous Actinide Compounds."

FUTURE WORK

Papers dealing with thermodynamic properties of the plutonium-carbon and plutonium-oxygen system will be prepared and submitted for publication. Thermodynamic properties of plutonium metal and the plutonium-hydrogen system will be measured experimentally, and compilation efforts will continue with emphasis on the actinide alloys, carbides, nitrides, halides, and chalcogenides.

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SECONDARY AMERICIUM RECOVERY

Charlotte E. Alford and
James D. Navratil

OBJECTIVE

The objective is to develop a process for recovering low-level concentrations

of americium from acidic process waste streams.

PRIOR WORK

The bidentate organophosphorous extractant DHDECMP (dihexyl-N, N-diethylcarbamyldimethylene phosphonate) was shown to effectively scavenge americium and plutonium from acidic process waste streams. There was no significant extraction of impurities. Evaluation of extraction chromatography techniques was initiated where bidentate organophosphorous extractants would be used as stationary phases on inert support materials. There was interest in using this technique in the secondary americium recovery process so that existing ion exchange equipment can be used rather than the more expensive solvent extraction equipment.

Over 30 support materials were evaluated for DHDECMP capacity. The highest capacity support materials were also evaluated for their ability to retain the extractant. Results of the evaluations indicated that of the support materials tested, Amberlite® XAD-4 gave the highest capacity for the DHDECMP and maintained the capacity under continued use.

ACHIEVEMENTS AND DISCUSSION

Amberlite XAD-4 macroreticular sorbent was tentatively chosen for further testing because of favorable DHDECMP capacity and low extractant losses. The support material was tested for americium breakthrough capacity. The support material, loaded with a known amount of DHDECMP (0.34 g DHDECMP/ml support), was contained in a 0.6-cm or 1.2-cm bore column with a wet support bed height of 10 cm. The linear flow rate was varied to determine the effect of flow rate on the breakthrough capacity.

Each experiment consisted of passing a synthetic americium feed (0.1 mg/l Am) through the column at a constant flow rate. Fractions (5 ml) of the column effluent were collected and analyzed for americium. The americium breakthrough results are shown in Figure 8. The results show, as expected, that americium breakthrough capacity increases with a decrease in flow rate. The americium breakthrough capacity was $\sim 1 \mu\text{g Am/ml}$ support at 10% breakthrough. This is lower than expected and appears too low for large-scale use.

The americium elution behavior of DHDECMP-loaded Amberlite XAD-4 was studied. The columns were eluted with 0.35M HNO_3 , water, and a 0.35M HNO_3 -0.01M HF solution. Fractions (15 ml) were collected and analyzed for americium. The results of these experiments are presented in Figure 9. The plot is the fraction of americium eluted versus millilitre of eluant passed. The results show that the elution of americium is slow and appears to create too much waste solution for large-scale use.

FUTURE WORK

Smaller bead supports will be tested to improve americium breakthrough capacity and elution. If favorable supports cannot be found, extraction contactor equipment will be tested for the secondary americium recovery process.

EVALUATION OF PRECIPITATION METHODS FOR THE RECOVERY OF PLUTONIUM AND AMERICIUM FROM MOLTEN SALT EXTRACTION RESIDUES

Gary H. Thompson

OBJECTIVE

The objective is to develop a general process for recovering plutonium and

americium from molten salt extraction (MSE) residues.

PRIOR WORK

Prior work has been done at Rocky Flats on the recovery of plutonium and americium from MSE residues by precipitation, solvent extraction, and ion exchange. The precipitation methods described here, however, are new approaches to the problem.

ACHIEVEMENTS AND DISCUSSION

Preliminary investigations have shown that plutonium and americium can be precipitated from solution (prepared by HCl dissolution of plutonium-americium-magnesium-aluminum alloy) as the formates — with good magnesium and aluminum removal. A second method, precipitation with NH_4OH and washing with NaOH, gave poorer decontamination from magnesium and aluminum. A third method, dissolution of the alloy in NaOH (to solubilize aluminum as aluminate ion), proved to be slow and resulted in viscous aluminate solutions that were difficult to filter. Because of the slow rate of dissolution and waste formation with caustic dissolution, this method was abandoned; only the formate and ammonium hydroxide methods will be discussed.

Prior work at Rocky Flats has shown that recovery of plutonium and americium from aluminum and magnesium by conventional precipitation as the hydroxides or oxalates is ineffective. Gelatinous precipitates result with hydroxide, and magnesium is not removed; oxalate is not specific and precipitates most of the species involved. A more selective precipitant is needed.

Formic acid was demonstrated to be a more selective precipitant. This was investigated in the following manner. An alloy comprising 28% plutonium, 2% americium, 60% magnesium, and 10% aluminum was dissolved in 12M HCl with cooling. The

solution was neutralized with NH_4OH to a pH of 8. During this process, the hydroxides precipitate. Formic acid is then added, which dissolves the hydroxide precipitates and precipitates plutonium and americium as the M(III) formates. Magnesium and aluminum do not precipitate and are removed by filtration. Decontamination factors of 58 and 1030 were obtained for aluminum and magnesium, respectively. Recovery was >97% for plutonium and 99% for americium. This process is being optimized by determining the solubility of the formates as a function of formic acid and formate ion concentrations.

Similar experiments with the nitrate system demonstrated that Pu(IV) formate is far more soluble than Pu(III) formate, so precipitation of Pu(IV) formate would not be a viable recovery method. Oxidation of Pu(III) to Pu(IV), however, could prove to be an effective way to separate plutonium and americium once they have been recovered as the M(III) formates.

Another approach investigated was the precipitation of plutonium, americium, and aluminum as the hydroxides by addition of NH_4OH . Magnesium is not readily precipitated from NH_4Cl solutions, and chloride ion was present from the HCl dissolution of alloy. After filtration, the hydroxide precipitate was washed with 8M NaOH to solubilize $\text{Al}(\text{OH})_3$ as $\text{Al}(\text{OH})_4^-$, and again washed with 0.3M NaOH to remove $\text{Al}(\text{OH})_4^-$ and excess Na^+ . The product was dissolved in HNO_3 and analyzed. Recovery of >99% of plutonium and americium was attained with decontamination factors of 34 and 17 for magnesium and aluminum respectively. Decontamination was not as good as with the formate method, and filtration of the hydroxide precipitates was difficult even though magnesium had not precipitated.

FUTURE WORK

As soon as the formate process has been optimized for solubility considerations,

the work on MSE residues will be continued. Methods for recovering or destroying the formate ion left in solution will be investigated since formate waste cannot be evaporated with nitrate wastes. This inability to be evaporated results from HNO_3 and HCOOH reacting with the evolution of NO_x gases. The formate process appears to offer good recovery of plutonium and americium along with good decontamination from common contaminants.

RECOVERY OF PLUTONIUM AND AMERICIUM FROM AN ALUMINUM-MAGNESIUM ALLOY BY A CARBONATE-HYDROXIDE PRECIPITATION PROCESS

Paul G. Hagan and A. D. Mills*

OBJECTIVE

A metallothermic reduction process has been developed at Rocky Flats to separate plutonium and americium from molten salt extraction (MSE) waste salt by concentrating the actinides into an aluminum-magnesium-plutonium-americium alloy. The objective of the work reported here is to develop a process for separating the plutonium and americium from the alloy.

PRIOR WORK

A developmental program was completed that demonstrated a carbonate precipitation process for separating plutonium and americium from MSE waste salts.

ACHIEVEMENTS AND DISCUSSION

A carbonate-hydroxide precipitation process was investigated for separating plutonium and americium from an aluminum-magnesium alloy metal. The

*On loan from the Chemical Operations group.

results from this investigation show that on a one-pass operation, the process removes from 70 to 94% of the aluminum and from 77 to 95% of the magnesium. The recovery of plutonium and americium for return to production is greater than 99%.

The composition of the alloy metal is approximately 15% aluminum, 52% magnesium, 31% plutonium, and 2% americium. For this investigation, two feed solutions were prepared by dissolving, respectively, 30- and 32-gram pieces of the alloy in HCl. To control the rate of dissolution, the alloys were placed in 300 ml of water; concentrated HCl was then added incrementally in 20-ml volumes until the metal was completely dissolved. Time was allowed between additions for the dissolution reaction to subside.

The feed solutions were filtered through a 1.5- μ m filter to remove traces of insoluble tantalum and plutonium oxides that were present in the alloy. Each feed solution was then divided into three equal volumes to provide a total of six solutions for the precipitation studies.

For the carbonate precipitation step, the solutions were first neutralized with Na_2CO_3 to a pH of 1. They were then heated to 95 °C, and a solution of 2M Na_2CO_3 was added at a rate of 0.05 mole carbonate per minute. During the period when the elements were being precipitated from solution, the pH of the solutions was about 5. When the precipitations were complete, the pH rapidly rose to 6.5. The slurries were then cooled to room temperature, and the precipitates were filtered from solution using Whatman® No. 40 filter paper. Following filtration, the precipitates were washed twice with 400 ml of hot water and then dissolved in 300 ml of hot 4M HNO_3 .

For the hydroxide precipitation step, the solutions were slowly added to 600 ml of 10M NaOH. The americium and plutonium were quantitatively precipitated and filtered from solution using a polypropylene pad with a 10- μ m Teflon® filter

backing. Following filtration, the precipitates were washed with 4M NaOH and dissolved in 600 ml of 7.9M HNO_3 -0.1M HF. The solutions were then heated to boiling to dissolve any residual polymerized plutonium.

The results of these precipitations, showing the quantity of the elements in both the filtrate and precipitate, are shown in Table 7.

Although there is no appreciable loss of plutonium or americium, the separation of aluminum and magnesium is not complete. The retention of some of the magnesium is probably caused by the presence of aluminum. During the carbonate precipitation step, which separates the magnesium from the other elements, the aluminum forms an amorphous precipitate that acts as a partial carrier precipitant for the magnesium. The same reasoning is probably true for the retention of some aluminum in the hydroxide precipitation step. The plutonium and americium form rather gelatinous precipitates that also can act as carrier precipitants.

FUTURE WORK

No future work is planned.

EVALUATION OF A COMBINED ANION EXCHANGE — BIDENTATE ORGANOPHOSPHOROUS EXTRACTION PROCESS FOR MOLTEN SALT EXTRACTION WASTE PROCESSING

Larry L. Martella and James D. Navratil

OBJECTIVE

The objective is to test the feasibility of using a combined anion exchange — bidentate organophosphorous solvent extraction process to recover and purify americium and plutonium separately from all types of molten salt extraction (MSE) residues.

PRIOR WORK

A bidentate organophosphorous extractant, DHDECMP (dihexyl-N, N-diethylcarbamy-methylene phosphonate) was shown to effectively extract americium and plutonium from MSE residue consisting of 30 mole % magnesium chloride and equal molar mixtures of potassium and sodium chlorides. Metal ions other than the actinides were not extracted to a significant degree. Selective stripping of plutonium and americium from the organic extractant was not efficient.

ACHIEVEMENTS AND DISCUSSION

An anion exchange — DHDECMP process was evaluated for separating and purifying plutonium and americium from MSE residues consisting of 8 mole % magnesium chloride and equal molar mixtures of potassium and sodium chlorides and aluminum-magnesium and zinc-magnesium alloys.

The 8 mole % MSE salt residue was dissolved in 2M hydrochloric acid (HCl) and adjusted to 7M H^+ with concentrated nitric acid (HNO_3). The MSE alloys, aluminum-magnesium and zinc-magnesium, were dissolved by slowly adding concentrated HNO_3 to 0.35M HNO_3 until the reaction subsided. After dissolution, the solution was adjusted to 0.1M hydrofluoric acid (HF) to remove any polymers or residual plutonium. The solution was then adjusted to 7M H^+ with concentrated HNO_3 . Ferrous sulfamate was added to reduce any plutonium(VI) present. The solutions were then filtered through Whatman® 42 filters and processed as shown in Figure 10.

In the process outline in Figure 10, plutonium was removed from the adjusted feed by passing the feed through a column of Dowex® 1-X4 (50-80 mesh) anion exchange resin. After passing the feed through the column, the resin bed was washed with 7M HNO_3 to remove any remaining americium or impurities. The

plutonium was then eluted with 0.35M HNO_3 and returned to the production stream. The wash and effluent that contained the americium and impurities were combined for further processing by a solvent extraction step.

In the solvent extraction step, the combined effluent and wash solutions were contacted with 30 volume % DHDECMP-carbon tetrachloride (CCl_4) until the americium concentration was below 10^{-2} g/l. Then, using an aqueous-to-organic ratio of 5, residual amounts of extracted impurities were removed from the DHDECMP- CCl_4 mixture by washing with 7M HNO_3 . The americium was then stripped from the organic with water.

Table 8 shows the major impurities in the feed both before extraction and in the americium product strip solutions. The results are representative of three runs with each of the different MSE residues. The results show americium and plutonium were effectively extracted whereas the impurity elements were not appreciably extracted. The process appears to yield a purified americium product.

FUTURE WORK

The laboratory-scale solvent extraction evaluation has been completed. Evaluation of the combined ion exchange — solvent extraction process for aluminum-magnesium MSE alloys will be evaluated on a pilot plant scale.

RECOVERY OF ACTINIDES FROM COMBUSTIBLE WASTES

Everett L. Childs, David L. Cash,
Louis J. Meile, and Gary H. Thompson

OBJECTIVE

The objective of the program is to evaluate methods for actinide recovery

from combustible waste. Current proposals involve incineration of the combustibles and recovery of actinides from the ash. Findings from this laboratory-scale program, which is being done under contract for ORNL, will be used by ERDA and ORNL to assist in determining the feasibility of partitioning actinides from combustible waste.

PRIOR WORK

Prior work has been done at Rocky Flats and elsewhere to recover actinides from combustible waste, but the particular approach used in this program is new for Rocky Flats. The methods being evaluated are extant in the literature; ORNL has limited the evaluation to currently known recovery methods.

ACHIEVEMENTS AND DISCUSSION

Preliminary leaching and dissolution tests were completed using cold ash from the pilot-plant-scale fluidized bed incinerator (FBI) at Rocky Flats. The ashes comprised primary ash (from the heated, fluidized bed of Na_2CO_3); secondary ash (from the catalytic afterburner); and filter fines [from the porous, stainless steel filters used to clean the gas stream prior to the gas reaching the high efficiency particulate air (HEPA) filter system]. Cold ash was used because the FBI system had not been used for contaminated waste.

In preliminary experiments, recovery method efficiency was measured by determining the percent of ash solubilized. Ash was refluxed with 15.7M HNO_3 (leach to solid ratio of 10:1) for three hours. Acid digestion with 95% H_2SO_4 -5% HNO_3 was also done under reflux for two hours at a digestant to solid ratio of 50:1. Fusion at various temperatures and times using NaOH , Na_2O_2 , Na_2CO_3 , 90% Na_2CO_3 - 10% Na_2SO_4 , KHSO_4 , and $\text{K}_2\text{S}_2\text{O}_7$ as fluxes (flux to solid ratio of 10:1) was also investigated. The results are shown in Table 9.

Nitric acid leaching dissolved approximately half of the ash. Acid digestion destroyed ~75% of the ash. The NaOH and Na_2O_2 fusions were most effective. The KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$ were slightly less effective, and the carbonate and carbonate-sulfate were least effective under the test conditions.

The most insoluble material to be reprocessed in the fuel cycle probably will be high-fired PuO_2 from the fuel fabrication process. Therefore, PuO_2 was prepared by firing plutonium oxalate at 925 °C to constant weight. Americium tracer was added (prior to the oxalate precipitation step) to determine the recovery that can be expected for trivalent lanthanides and actinides during the fuel reprocessing.

Because of severe attack on the crucibles, Na_2O_2 was omitted. The prepared oxide was then subjected to the leaching and fusion agents already described. (For these preliminary tests, the pure oxide was used; subsequent tests will use mixtures of ash and PuO_2 .) Test conditions and results are shown in Table 10.

Leaching with concentrated HNO_3 gave poor recovery as expected (no F^-). Acid digestion gave good recovery but required lengthy refluxing; the sulfate system is not a desirable one because of waste considerations. Good results were obtained by NaOH fusion in nickel crucibles, but NaOH fusion in alumina gave poor recovery; additional work is being done to determine the reason for this anomaly. Carbonate and carbonate-sulfate (90% Na_2CO_3 - 10% Na_2SO_4) gave poor recovery, even at 900 °C. Carbonate-nitrate (90% Na_2CO_3 - 10% NaNO_3) gave the best recovery of plutonium and of americium. Fusion with bisulfate and pyrosulfate gave good recovery, but these are poor candidates because of sulfate.

An attempt to prepare contaminated ash by fluidizing ash contaminated with plutonium nitrate at 500 °C was abandoned.

The reason was that nitrate and carbon in the ash reacted violently when heated. Work is now in progress to design a laboratory-scale quartz FBI that will be utilized to burn plutonium-contaminated waste. A heat and material balance has been completed, and final design of the system is underway.

FUTURE WORK

Evaluation of the candidate recovery system (fusion with 90% Na_2CO_3 - 10% NaNO_3) will continue. Optimum operating conditions will be determined by varying such parameters as percent nitrate, flux to solid ratio, temperature, and fusion time. Actinide and fusion product loss to the offgas will be measured. Contaminated waste will be burned in the laboratory-scale FBI unit (now being designed) so that recovery methods can be evaluated using contaminated ash produced by combustion rather than by contaminating cold ash.

EVALUATION OF TRIBUTYL PHOSPHATE IMPREGNATED SORBENT FOR PLUTONIUM-URANIUM SEPARATIONS

Charlotte E. Alford and
James D. Navratil

OBJECTIVE

The objective of this program is to evaluate tributyl phosphate impregnated sorbents for separating uranium and plutonium from mixed actinide residues. These residues presently are processed with a modified Purex solvent extraction process.

PRIOR WORK

No prior work has been done on this project.

ACHIEVEMENTS AND DISCUSSION

A modified Purex process is presently being used to separate small quantities of plutonium-uranium residues. The process consists of selectively extracting uranium from a 5M HNO_3 (nitric acid) - 0.1M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$ (ferrous sulfamate) feed solution with 30-70% TBP (tributyl phosphate)-dodecane. The extractant is washed with 0.35M HNO_3 - 0.1M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$ to remove any residual plutonium. The uranium is then stripped from the TBP with 1M $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulfate).

Use of the process necessitates the need for solvent extraction contractor equipment; however, use of ion exchange column equipment is feasible if extraction chromatography techniques are used with the modified Purex process. These techniques involve the use of a sorbent support containing TBP.

Bayer AG Lewatit® OC-1023 is a new, commercial, extraction chromatography support impregnated with TBP. The support is 20 to 50 mesh polystyrene-divinyl benzene beads with a macroporous matrix. It was tested for uranium-plutonium separation using the modified Purex processing conditions. Uranium breakthrough capacity and elution behavior was determined for the OC-1023.

For the breakthrough capacity and elution determinations, the OC-1023 was loaded into laboratory-scale ion exchange columns. The support was first conditioned with 5M HNO_3 - 0.1M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$. Synthetic feeds containing uranium or plutonium-uranium in 5M HNO_3 - 0.1M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$ were fed to the columns, and fractions of the effluent were collected and analyzed for uranium. The uranium sorbed on the support was then eluted with 1M $(\text{NH}_4)_2\text{SO}_4$. Fractions of the eluate were also collected and sampled for uranium.

The uranium breakthrough capacity and elution results of the QC-1023 under a variety of conditions are shown in Table 11. Results show that the support has a high uranium capacity for 10 g/l uranium feeds. The total uranium capacity of the support was determined to be ~65% of the theoretical TBP capacity. Uranium breakthrough capacity decreased substantially, however, in runs with plutonium feed. This apparently was caused by the presence of plutonium and the low uranium concentration in feed.

Uranium elution results, as shown in Table 11, are in good agreement and show that the uranium can be eluted with a minimum of eluant.

FUTURE WORK

More uranium breakthrough runs will be made with higher uranium concentrations in the mixed actinide feed, and the problem of washing residual plutonium from the resin will be studied. Another support also will be evaluated to obtain extraction chromatography data for comparison to the solvent extraction process.

DECONTAMINATION OF SOIL

Robert L. Kochen and James D. Navratil

OBJECTIVE

The objective of this program is to develop and demonstrate a soil decontamination process for plutonium and americium. The process will be used to decontaminate approximately three acres of Rocky Flats soil presently covered by an asphalt pad.

PRIOR WORK

Preliminary work indicated that mechanical sieving could reduce the

volume of plutonium- and americium-contaminated soil. Screening tests showed that the highest plutonium and americium concentrations were associated with the smallest soil particles. Chemical leaching methods and high-gradient magnetic separations also were evaluated briefly for soil decontamination.

ACHIEVEMENTS AND DISCUSSION

Six different batches of plutonium-contaminated soil, obtained from beneath the asphalt pad, were dry- and wet-screened into various soil fractions. Table 12 shows the weight percents and plutonium and americium analyses of the different soil fractions.

Results show that dry screening did not decontaminate the >4-mm fraction (~60 wt %) of the soil, which consisted mainly of rocks. Wet screening removed contamination from the rocks and also substantially reduced plutonium and americium contamination levels in the 4- to 0.4-mm fractions. The volume of contaminated soil was reduced approximately 65%.

To further decontaminate the 4.0- to 0.4-mm fraction of the soil by wet screening techniques, various reagents were added to the process water to aid in dispersing and decontaminating the soil. A composite soil, consisting of weighted portions of the six pad samples, were attrition scrubbed 10 minutes and wet screened (0.4 mm) with various solutions. The results are presented in Table 13.

The results show that attrition scrubbing reduces the concentration of plutonium and americium in the soil but also reduces the size of the soil fraction (from ~98 to ~80%). The only reagents that appeared to improve the decontamination of soil over water were oxalic acid and Calgon.

Figure 11 shows a conceptual flow sheet for decontaminating the soil. Laboratory-scale testing of the flow sheet indicates that water or Calgon solutions can be recycled once without any loss of decontamination effectiveness.

FUTURE WORK

Further testing of the preliminary process on a larger scale is planned so as to evaluate filtration and other process problems and process parameters. Secondary methods planned for evaluation include foam flotation, density separation, high-gradient magnetic separation, and selective chemical leaching. More exotic soil dispersing agents will also be tested for soil separation by size.

COMPONENT DEVELOPMENT

Richard J. Merlini

ALTERNATE-IMMERSION STRESS CORROSION CRACKING TESTS OF 5083 ALUMINUM FOR THE W-70 MOD 3 AND B77 PROGRAMS

John L. Briggs, Ross J. Jackson,
and Marston R. Dringman

OBJECTIVE

The purpose of this work is to determine if alternate-immersion corrosion tests can be used to reliably predict the susceptibility of 5083 aluminum to stress corrosion cracking (SCC). A stress corrosion cracking acceptance test for this material is needed in sheet and in fabricated form.

PRIOR WORK

No prior work on this objective has been done at Rocky Flats.

ACHIEVEMENTS AND DISCUSSION

Tests were performed to qualify incoming 5083 aluminum plate and subsequent pressed parts produced at Rocky Flats. The tests were conducted to determine the susceptibility of 5083 alloy to stress corrosion cracking. The test specimen geometry was conventional C-rings; the test environment was alternate immersion in a 3.5% NaCl solution at 26.7 °C, the test duration was 30 days, and the stress level 30,000 psi (210 MPa). The tests were carried out in accordance with ASTM recommended practice G44-75 for alternate-immersion stress corrosion testing in 3.5% NaCl solution. To conform with the ASTM recommended practice, a test room with controlled humidity (45 ±5%) and temperature (26.7 °C) was set up. In addition, an alternate-immersion test system (Figure 12) was designed and built for the corrosion studies.

Test samples (stressed C-rings of 5083 aluminum) were placed in the upper sample immersion tank. The 3.5 wt % aqueous salt solution is pumped to this tank until the C-ring samples are completely immersed for 10 minutes. The sample tank is then drained, and the specimens are allowed to air dry for 50 minutes. The test apparatus continues to operate through the immersion-drying cycle for 30 days.

For these tests, short transverse C-ring type specimens were machined from the plate so that the centerline of the specimen, which is the area of maximum applied stress, represents the centerline of the plate. A sketch of the specimen orientation in relation to the rolling direction of the plate is shown in Figure 13.

Three sizes of C-ring specimens were used: 0.750-, 0.700-, and 0.500-inch O.D. with wall thicknesses of 0.060, 0.056, and 0.040 inch, respectively.

After cleaning, the C-ring specimens were stressed by a bolt and nut to reduce the ring diameter. The following formula was used to determine the desired stress:

$$\Delta = \frac{f\pi D^2}{4EtZ}$$

where:

- Δ = change of outside diameter required for desired stress,
- f = desired stress in psi,
- t = wall thickness in inches,
- D = mean diameter (O.D. - t) in inches,
- E = modulus of elasticity in psi,
- Z = a constant (function of ring D/t)

During testing, the specimens were examined daily. The presence of cracks was determined by visual inspection with the aid of a 10X magnifier. Special attention was paid to the edges of the C-rings where cracks would be expected to form. If there was doubt as to whether a crack had nucleated or if it was merely pitting attack, the area was noted and subsequent metallographic examinations were directed to this area of the specimen.

The first alternate-immersion SCC tests were performed on three sets of C-rings fabricated from as-received 5083 aluminum. Results of the tests are shown in Table 14.

All three sample sets failed the SCC test since ASTM test requirements state that "no more than two specimens (from a sample population of nine) shall exhibit cracks." The need was evident for a suitable heat treatment to eliminate the apparent sensitization of the as-received material.

Two additional specimen sets with experimental heat treatments and part-forming parameters were examined by alternate-immersion testing. This

testing was performed as follows: Two sets of eight 0.5-inch O.D. C-rings were fabricated from Parts 230-15 and 230-45, which were formed at 230 °C. Eight C-rings was the maximum number that could be machined from each production part. This deviation was recorded as per ASTM specifications, which requires a sample population of nine C-rings. No cracks were detected for either set of eight C-rings after the 30-day alternate-immersion test.

The next test series consisted of two sets of 14 C-rings fabricated from 0.75-inch sheet material that had been annealed at 400 °C for three hours. Fourteen 0.700-inch O.D. C-rings were removed from the 0.75-inch sheet. After the sheet was rolled to 0.50 inch, an additional fourteen 0.500 O.D. rings were fabricated from the rolled sheet. No cracks were detected for any of the C-rings in this test series.

The next test series consisted of the first set of 32 acceptance C-rings (0.50-in. O.D.) taken from parts fabricated as follows:

1. Solutionize 3 hours @ 400 °C, water quench,
2. Cross roll 20-25% @ 23 °C,
3. Form @ 175 °C,
4. Stabilize @ 150 °C.

[The acceptance tests will be performed on seven production parts (16 C-rings per part) for a total of 112 C rings.]

Twenty-three of the 32 C-rings showed visual cracks within the first seven days of the alternate-immersion test; 17 (of the 23) showed cracks after four days of test, as shown in Table 15. After the first seven days of test, no cracks were detected for the remainder (23 days) of the test duration.

The susceptibility of the acceptance test parts (formed and stabilized in a sensitization range of 65-205 °C) to

stress corrosion cracking indicates the need for improved fabrication procedures for 5083 aluminum.

Reproducibility of the controlled test environment to produce stress corrosion cracks in susceptible material (i.e., as-received sheet and fabricated parts) indicates the method is suitable for process prove-in SCC tests.

FUTURE WORK

Further alternate-immersion tests will be performed to complete acceptance tests.

COMPATIBILITY OF NON-NUCLEAR WEAPONS METALS WITH PROCESS MATERIALS

John L. Briggs and Marston R. Dringman

OBJECTIVE

The objective of these tests is to determine the compatibility of process materials with non-nuclear weapons metals.

PRIOR WORK

The results of other compatibility studies have been reported in previous classified semiannual progress reports.

ACHIEVEMENTS AND DISCUSSION

As part of a continuing program, the compatibility of all non-nuclear weapons metals with selected, currently used processing materials has been determined by corrosion and residue removal tests.

The compatibility tests were performed employing total immersion corrosion tests (NACE Standard Method TM-01-69) except for non-fluid materials, which were performed by contacting metal coupons with the materials.

All of the coupons were pretreated by surface finishing with 120 grit abrasive paper, rinsed in distilled water, rinsed in acetone, air dried, and weighed to the nearest 0.1 mg. The metal coupons then were immersed in or (in the case of non-fluid materials) placed in contact with the various corrosive materials and stored for 10 days at room temperature 23 ± 2 °C).

At the end of the test period, the coupons were removed as were loose corrosion products, if any. After visual examination, the coupons were reweighed for corrosion rate determinations. Following the corrosion tests, the coupons that had been exposed to the corrosive environments were cleaned with an aqueous detergent as follows:

1. Ultrasonically clean in detergent (Oakite NST Aluminum Cleaner, 20 ml/l at 55 ± 5 °C) - 5 minutes
2. Rinse in distilled/demineralized water - 5 minutes
3. Rinse in distilled/demineralized water - 5 minutes
4. Air dry

The coupons were then analyzed for residue by infrared, atomic absorption, and emission spectrographic techniques.

Table 16 summarizes the new process materials and non-nuclear weapons metals that were tested.

All materials listed in Table 16 proved compatible except the Tool Rite H-12-17, which was not compatible with the three aluminum alloys tested. In addition, other tests were made in which 5083 aluminum and U-0.75 Ti alloy were tested for compatibility with 26 currently used non-nuclear metals. No incompatibility was detected for any of the materials with these two production metals.

FUTURE WORK

Further compatibility studies will be performed as required for new weapons metals and process materials.

CORROSION TESTS OF WATER-SHIELDED PLUTONIUM PALLET-CONTAINERS

John L. Briggs, Robert L. Kochen,
and Martson R. Dringman

OBJECTIVE

The purpose of this study was to determine the possible effects of galvanic corrosion in plutonium storage containers and to select a suitable dye leak detector for addition to the shielding water in the storage containers.

PRIOR WORK

Previous studies were performed that showed Rocky Flats tap water was suitable for use as shielding water in the storage containers.

ACHIEVEMENTS AND DISCUSSION

Corrosion tests were performed to determine if corrosion would occur in plutonium storage containers containing solutions of shielding water and dye. The stability of several dye solutions was also examined in this study.

Eight pallet-containers, as shown in Figure 14, were obtained for the water-dye corrosion tests. Experimental tap water — dye solutions were made up as shown in Table 17.

Photographs were taken of the storage containers' interior surfaces for a visual record of corrosion. The dye-treated water was then added to the pallet-containers. The container

orifices were closed with rubber stoppers, and the pallet containers were stored for 12 months at ambient temperature (21 ± 2 °C). After storage, the containers were drained of dye-water, the dye-water solution was tested for pH change, and the interior of each container was again photographed for visual corrosion effects.

After 12 months of storage, the pontacyl carmine dye — water solutions were nearly colorless and would therefore be unacceptable for leak detection. The Rhodamine B dye — water solution was slightly faded in color intensity after container storage. The Rhodamine WT dye — water (both pH 6.5 and pH 8) showed no diminished color intensity after one year of storage in the containers. The color intensity of the test dye solutions was compared visually with new dye solutions. The pH of all the dye-water solutions showed no significant change after the 12-month storage period. No significant visual corrosion was detected for either the 304L stainless steel or the lead components of any of the storage containers.

The results of corollary galvanic corrosion tests (Table 18) showed that the Rhodamine WT solution (pH 8) exhibited the lowest corrosion rates for the galvanic couples. Some weight loss was determined for the 304L stainless steel in the pH 6.5 Rhodamine WT solution indicating the higher pH solutions is more suitable for corrosion resistance.

The results of these tests have shown that Rhodamine WT dye (pH 8) is a suitable leak detector for use in the shielding water of the storage pallet-containers. This dye was recommended for treatment of Rocky Flats tap water for filling the storage containers.

FUTURE WORK

No further work is planned.

SELECTION OF A METAL FOR FABRICATING A BERYLLIUM CHEMICAL-MILLING TANK

Marston R. Dringman and John L. Briggs

OBJECTIVE

The objective of this work was to select a material to resist a solution of mixed acids used for chemical-milling beryllium.

PRIOR WORK

Previous studies were performed to select a corrosion-resistant tank fabricating material for a chemical-milling solution composed of a mixture of phosphoric, sulfuric, and chromic acid.

ACHIEVEMENTS AND DISCUSSION

The current corrosion tests were performed to select a suitable fabricating material for beryllium chemical-milling tanks. The acid milling solution is composed of 50 vol % lactic acid, 40 vol % phosphoric acid, and 10 vol % water.

Sample coupons of 15 metal alloys were selected for preliminary screening tests. The samples were sanded with 120-grit silicon carbide paper, aqueous detergent washed, rinsed, air dried, and weighed to the nearest 0.1 mg. The samples were then immersed in the mixed acid solution at 75 ± 2 °C and stored for 24 hours. After terminating the test, the samples were removed from the solution, cleaned, rinsed, air dried, and weight losses were measured for gravimetric corrosion rate determinations by the following formula:

$$\text{mpy} = \frac{(534)(\text{mg})}{dAt}$$

where:

mpy = mils penetration per year

mg = milligram weight loss

d = density of material

A = area of material in square inches

t = time in hours

The results of the 24-hour test are shown in Table 19.

Three of the alloys (Hastelloy B, Hastelloy C, and Inconel 625) exhibited minimal corrosion rates and were selected for extended (287 hours) exposure to the mixed acids. Fusion welded coupons of each of the three alloys were also tested. After 287 hours immersion in the acid mixture at 75 °C, the coupons were removed, cleaned, and weighed. Results of the 287-hour test are shown in Table 20.

No excessive corrosion was exhibited by any of the alloys shown in Table 20, and any of the three materials would be satisfactory for service in the mixed acid environment.

FUTURE WORK

Materials-selection corrosion tests will be performed as required.

OPTIONS FOR PROCESSING AND PACKAGING TRANSURANIUM-CONTAMINATED SOLAR EVAPORATION POND SLUDGE

Kazuji Terada

OBJECTIVE

The objective of this work was to evaluate fixation and drying processes for solar evaporation pond sludges. An additional objective was the identification of packaging options.

PRIOR WORK

In prior years, sludge in the solar evaporation ponds was allowed to sun-dry and then was shoveled into waste packages for shipment to the Idaho National Engineering Laboratory.

ACHIEVEMENTS AND DISCUSSION

New procedures were evaluated for packaging sludges to conform with plant policy of eliminating off-site release of radioactive contamination.

Two fixation and five drying processes were compared from the viewpoint of economics, developmental work necessary, and processing time. Table 21 summarizes the different options and costs based on the sludge being packaged in fiberglass reinforced plastic (FRP) coated plywood boxes. Calculations showed that the cost of packaging and shipping the sludge in boxes was less than in steel drums with polyethylene liners.

The two fixation processes involved mixing the sludge with a solidifying agent. In one case, about 10% cement is mixed into the sludge. The other process is the commercial Chemfix process* where proprietary ingredients are added to the sludge by an outside contractor.

The drying processes evaluated involve dehydration by (1) solar evaporation in controlled environments, (2) filtration, (3) steam heat, and (4) filter press. Solar evaporation under a plastic air house and solar heated chambers were evaluated. The primary virtue is fuel economy. Filtration and use of a steam-heated "porcupine" dryer in Buildings 774 and 374, respectively, have the advantage of utilizing existing equipment.

As shown in Table 21, processing in Building 374 is the least desirable option because of high cost and the long processing time required. Vacuum filtration in Building 774 also requires long processing times and will remove only a small percentage of the water, at most about 20%.

Sludge fixation has the advantages of requiring little developmental work and having processing rates that could be adjusted to complete the work within a selected time span. Without a dewatering step, however, this method necessitates packaging, shipping, and storing a large quantity of water as contaminated waste.

Solar drying techniques are highly attractive in this period of energy consciousness, but energy cost to dry the sludge is very small compared to the total cost. Solar drying processes also require relatively large amounts of developmental work. Note that development costs are not included in Table 21.

The use of a filter press to dewater and form cakes that could be readily handled was recommended as the most attractive of the options on the basis of cost, minimum developmental work, and flexibility of processing rates. Flexibility of process rates, as shown in Table 21, is a characteristic enjoyed by other sludge processing options as well. Since these options are not dependent on existing facilities, equipment and facilities can be acquired on the basis of processing rate requirements.

FUTURE WORK

A laboratory-scale filter press will be installed and operated to obtain information necessary to determine filter-press operating parameters and pressed sludge characteristics.

*Proprietary process of Chemfix Corporation, Pittsburgh, Pennsylvania.

LOW WATER-VAPOR PERMEATION SHIPPING BAGS FOR THE W-70 PROGRAM

Kazuji Terada

OBJECTIVE

The objective of this work is to design a low-cost, low water-vapor permeation shipping bag for a critical W-70 part.

PRIOR WORK

No prior work has been done on this objective at Rocky Flats.

ACHIEVEMENTS AND DISCUSSION

Several materials were tested as potential enclosures for this component. The criteria used for material selection were sealability, low cost, and low water-vapor permeation rates. Polyethylene, vinylidene chloride - vinyl chloride copolymer and a laminate of fabric-aluminum-polyethylene were selected for evaluation because they met these criteria. The first two were selected from among other polymers specifically because of their reported low water-vapor permeation constants.¹ Heat sealability was provided by vinylidene chloride - vinyl chloride copolymer being laminated to a polyvinyl acetate - polyethylene copolymer.

No special test for polyethylene was necessary as polyethylene film is heat-sealed routinely on plant site. The aluminum laminate, however, required a special sealer. Test seals were made with the equipment of a local vendor at his location. Seals of this material are effected through the polyethylene. Visual inspection and manual tear tests showed excellent seals.

The water-vapor permeation test consists of monitoring sealed bags for moisture content. The vinylidene chloride - vinyl chloride copolymer was not tested, however, because the only available material was so thin (~0.2 mil) it formed permanent crease marks in which leaks could occur. Dow Chemical, a major producer of the copolymer, does not market thicker films. The polyethylene and aluminum laminate were 4 and 12 mils thick, respectively. The polyethylene was tested as a double bag with a silica gel desiccant between the bags to decrease water transmission. Analysis showed that moisture content of the inner polyethylene bag increased from 450 to a maximum of over 3000 ppm in three days and decreased to 1750 ppm over the next week. The decrease was attributed to a combination of variable laboratory humidity and desiccator effects. The measured water-concentration changes in the bag atmosphere were consistent with those calculated from permeation rates.

The change in moisture content of the aluminum laminate bag is shown in Figure 15. Tests were incomplete as of this writing, but extrapolation of the data indicates a moisture concentration of 450 ppm would be reached 9 weeks after the bag is sealed; 450 ppm is the current upper limit of allowable moisture concentration.

FUTURE WORK

Moisture concentration in the aluminum laminate bag will continue being monitored.

REFERENCES

1. Modern Plastics Encyclopedia, 1974-1975, p. 732, McGraw-Hill Inc., New York.

LEAK CHECK OF WASTE BOXES COATED WITH FIBERGLASS REINFORCED PLASTIC

Marston R. Dringman and Kazuji Terada

OBJECTIVE

The objective of this work is to develop a leak-check method for fiberglass reinforced plastic (FRP) waste boxes. This test will be used as one of the receiving acceptance tests.

PRIOR WORK

Two leak-check techniques have been studied. One involved immersion of a pressurized box in water; the other utilized "helium leak-check" methods. The helium test was rejected because it could not be used to recheck a repaired box. Helium absorbed by the plywood "bleeds" out and confuses subsequent tests. The water immersion test was not used because only a small portion of the box surface could be checked per immersion.

ACHIEVEMENTS AND DISCUSSION

The procurement specification for FRP-coated boxes requires the FRP to "be free of leak paths to the plywood as determined by a water immersion test or equivalent." No leak test is currently being performed. The necessity for leak tests became apparent when rain water flowed through the bottom of some boxes stored outdoors.

Three methods of leak-testing boxes were evaluated. The first, a method using a Tesla coil, was rejected because of the lack of a suitable conductive paint. The method was based on spark formation between a high voltage source and a conductive surface. The surface was formed by applying a conductive paint on the plywood before application of the FRP. Where there is a leak, a spark would

trace the leak path through the FRP to the conductive paint. Of two paints evaluated, one lacked sufficient conductivity and the other had no adhesion to the FRP.

The second method, which utilized a detector, was also rejected. It consisted of filling the box with dioctylphthalate (DOP) smoke and using a detector to locate the leak sites. This method was rejected because of the long time required to completely scan the box exterior with the detector.

Soap solution applied over a slightly pressurized box was selected for further development because of its overall simplicity. Tests showed an internal air pressure of less than 0.25 psi is sufficient for the leak test. This should present no safety hazard as a box can be pressurized to about 5 psi before venting.

To leak-test the box by this method, it will be necessary to temporarily seal the open top to pressurize the box. It was decided this could be best accomplished by inverting the box on its top on a special lid. This would facilitate leak checking the bottom. Equipment to perform these operations is being acquired and installed.

FUTURE WORK

Development work on a temporary lid to seal the box will be continued. In addition, various foaming agents and application techniques will be studied.

INSTRUMENTATION AND STATISTICAL SYSTEMS

Richard N. Chanda

A CRATE COUNTER

Ronald A. Harlan, Grover J. Cunningham,
Jorge L. Martinez, and George P. Minges

OBJECTIVE

The objective of this work is to design and construct a crate counter capable of estimating the plutonium in waste placed in 1.22- X 1.22- X 2.13-m crates. The estimate will provide accountability for normal operating loss and minimize the possibility of discarding significant quantities of plutonium.

PRIOR WORK

Construction of the crate counter has been completed.

ACHIEVEMENTS AND DISCUSSION

A crate has been modified to receive plutonium calibration sources in transverse aluminum tubes. The Chemistry Standards Laboratory is cooperating to simulate waste matrices. Bundles or packages of the simulated waste will fill the standard crate for calibration. These experiments are essentially ready to begin. Figure 16 shows the counter with the standard crate in place and ready to be rolled inside on the internal conveyor.

FUTURE WORK

Calibration experiments will be performed. When a calibration is available, the machine will be turned over to the Waste Management department for routine use. It is expected that studies will continue on counter response to various wastes for approximately one year.

INVENTORY VERIFICATION AND CALIBRATION EXPERIMENTS DURING 1976-1977

Charles D. Zeis, Ronald A. Harlan,
and James L. Lawless

OBJECTIVE

The objectives are to provide a data base for nondestructive assay (NDA) calibration in package counters and to provide better plutonium inventory values in process residues stored at Rocky Flats. An immediate goal is the statement of estimated bias in certain categories of residue so that inventory corrections can be made.

PRIOR WORK

The present work is a continuation of similar studies dating back to 1964. Instrumentation and Statistical Systems share in this work through participation in the Measurement Control Task Force and by designing sample plans and calibration models, analyzing and interpreting the data, and implementing calibration. The NDA devices covered by this project are the Can Counter, the Helix Counter, the Waste Packaging Facility (WPF) South Drum Counter, and WPF North Drum Counter. The reference assay technique is calorimetry. Part of the calorimetry is performed at Mound Laboratory (Miamisburg, Ohio) and part at Rocky Flats.

ACHIEVEMENTS AND DISCUSSION

Several significant developments occurred during this reporting period. First, a proposal was prepared by Rocky Flats to change the inventory verification and calibration experiments so that all calorimetry could be done at Rocky Flats under Energy Research and Development Administration (ERDA) supervision. Secondly, results of the 1976 study were received from ERDA and Mound, and the data were analyzed. Finally, calibration adjustments were made on the North Drum Counter,

and a calibration experiment was completed for the South Drum Counter.

With regard to the first development, a committee was formed to study and formulate a procedure for the changeover. Safety aspects, cost, and expediency were reviewed, and a proposal was submitted to ERDA's Albuquerque Operations Office. Conditional acceptance for the proposal was obtained for years subsequent to 1977; however, one more sample exchange involving Mound must be successfully completed. A sampling plan was drawn up for this exchange. It included 16 items from the electrorefined salts category, 8 ash items, and 6 ash heel items for a total of 30 items to be sent to Mound. In addition, 30 items from graphite scarfings and unpulverized sand slag and crucible (USS&C) categories will be studied at Rocky Flats. All 60 items will be calorimetered by Rocky Flats Chemistry Standards Laboratory. The 60 items were selected after studies of these inventories were carried out to choose optimal sample allocations. A tentative sample set was then chosen.

The second development can be summarized by reporting that the 1976 bias estimates obtained from the sample exchange were essentially in agreement with the 1975 ones for ash, ash heels, and USS&C categories. Table 22 gives a summary of these estimates. Recommendations have been made to adjust the ash and ash heels inventories and to adjust the Helix Counter calibration for these categories.

Estimated standard deviations of individual measurements also were obtained and are given in Table 23. The large standard deviation for USS&C (21% of the total grams Pu) indicates that other measurement techniques, such as calorimetry or neutron coincidence, should be developed for certain kinds of materials that are not entirely suitable for gamma ray counting for reasons such as attenuation and lumpiness.

A lengthy calorimetry study of molten salt residues was completed in the North

Drum Counter, and a gamma-ray calibration was implemented.

The experimental portion of a study of insulation for the South Drum Counter is complete, and data are being reduced prior to calibration changes. The study represents several months of effort.

FUTURE WORK

The Rocky Flats Chemistry Standards Laboratory is currently calorimetering samples of the items sent to Mound to again compare calorimetry between the two plants. This data analysis will be carried out by the Instrumentation and Statistical Systems group. Results of the 1977 experiment will be analyzed, and corrective action will be taken if needed.

The new insulation calibration for the South Drum Counter will be instituted. Concurrent studies of filter media and cemented insulation or filter media will be completed, and an internally consistent set of calibrations for these three materials will be implemented.

Black salts and white salts produced by molten salt extraction will be calibrated on the North Drum Counter. In addition, calibrations will be obtained on molten salt residues in a new packaging configuration.

RADIOMETRIC MONITORS AND ASSAY COUNTERS FOR THE NEW PLUTONIUM RECOVERY FACILITY

James L. Lawless and Francis X. Haas

OBJECTIVE

The objective is to develop design criteria for radiometric instruments to be installed in the new plutonium recovery facility.

PRIOR WORK

Conceptual designs were developed for several of these instrument systems during the early stages of the building layout. Others were added to the list of requirements to conform to recent measurement control and safeguards criteria.

ACHIEVEMENTS AND DISCUSSION

These instruments logically fall into two groups: (1) monitoring systems used for safety and process control and (2) systems used to assign a plutonium assay value to materials for accountability and safeguards.

Priority is presently being given to assurance that sufficient cable runs and computer interfaces are installed in the recovery facility by the contractor. Table 24 shows a list of required functions and the computers to which each function must communicate; i.e., the Mod Comp 2/25 data acquisition computer or the Digital Equipment Corporation PDP 11/45 stacker-retriever computer.

Concurrently, conceptual designs are being formulated for the spent resin and oxide counters.

FUTURE WORK

Work will continue on specifications for cabling and computer interfacing together with designs for the monitors and counters.

ADDITIONAL FOUR-LITRE SAFEGUARDS CALORIMETER

George P. Minges

OBJECTIVE

The objective is to provide increased four-litre sample throughput to generate additional data for the calibration of radiometric counters and for the Mound Exchange Verification Program.

PRIOR WORK

An additional four-litre calorimeter has been designed and fabricated and is now in use by the Rocky Flats Standards Laboratory.

ACHIEVEMENTS AND DISCUSSION

The additional twin-cell calorimeter has been fitted with a third, nonidentical reference cell. Several months of evaluation of this system has shown no identifiable degradation of sensitivity or stability of the calorimeter. This new reference cell now frees the identical reference cell for use as a sample cell, thus doubling the throughput of the calorimeter.

The electronic scanner purchased for this calorimeter has been redesigned, modified, and interfaced to the additional four-litre calorimeter for use as an active, nondisturbing cell scanner. Use of this scanner has shown that a single, highly stable digital ratio meter can (1) scan multiple calorimeters and cells and thereby reduce the complexity of the system, (2) eliminate duplication of expensive readout devices, and (3) decrease the overall number of instruments requiring Standards Laboratory calibration. Several months of evaluating this portion of the calorimeter has shown no identifiable degradation of the sensitivity or stability of the calorimeter.

FUTURE WORK

The original four-litre calorimeter will be modified and fitted with the non-identical reference cell and interfaced to the scanner. This will then free another reference cell for use as a sample cell.

The next step in calorimeter design will be to interface and develop the algorithms for a microprocessor to control and read out the calorimeter data — hopefully to include equilibrium end-point prediction.

Development of these systems will be applied to the design of the calorimeters for Building 371, the new plutonium processing facility.

UPGRADING OF EXISTING ROCKY FLATS PERSONNEL DOORWAY MONITORS AT GUARD POSTS

Grover J. Cunningham and
Jorge L. Martinez

OBJECTIVE

The objective is to upgrade the levels of response on existing personnel doorway monitors to comply with Energy Research and Development Administration's SNM standard in ERDA MC-2405, Appendix I.

PRIOR WORK

The Rocky Flats personnel doorway monitor was approved in June 1976 by the Energy Research and Development Administration. Prior to December 1976, one system was completed and met the sensitivity specifications.

ACHIEVEMENTS AND DISCUSSION

Four additional personnel doorway monitors were updated to comply with the ERDA specification. Each system was adapted with larger, integrally mounted 5.08- X 2.54-cm NaI(Tl) detectors along with several electronics modifications. This adaptation included the replacement of outdated UDD's (updating digital discriminators) with the newer microprocessor-based digital comparator.

The five Rocky Flats personnel doorway monitors now meet all requirements of the ERDA standard.

FUTURE WORK

No future work is planned for these five personnel doorway monitor installations.

PORTAL MONITOR FOR HIGH BACKGROUND APPLICATIONS

Grover J. Cunningham, Jorge L. Martinez,
and George P. Minges

OBJECTIVE

A need has developed on the plant site for a 1.2-m wide portal monitor capable of meeting specifications under ERDA MC-2405, Appendix I.

PRIOR WORK

The performance of an improved, safe-guards, personnel doorway monitor has been reported previously. This system meets ERDA specifications listed under ERDA MC-2405 for portal widths up to 122 cm, when operated in a background of 10 to 15 microroentgens per hour; however, it fails under higher background conditions.

ACHIEVEMENTS AND DISCUSSION

The system under development is similar to the "Improved Safeguards Personnel Doorway Monitor" previously reported. The major differences between the two systems are the number of detectors used, the lead shields enclosing the detectors, and the microprocessor-based discriminator used to make the logical decisions in the electronics.

The new system utilizes 10 sodium iodide detectors arranged in 5 tubes per bank mounted at each side of the door frame. Each tube is encased in a cylindrical lead shield 0.635-cm thick to minimize ambient background. In addition, the tubes are positioned 45.72 cm from each other for proper coverage of the detecting volume. Slots 1.27-cm wide by 2.54-cm long have been cut at the crystal end of the detector shield. This increases detection sensitivity along the vertical plane close to the detector surface (see Figure 17).

The microprocessor-based discriminator uses a sliding background concept for average background update. Preliminary data indicate satisfactory sensitivity.

FUTURE WORK

Further tests will be conducted on this system in a background of 25 to 30 microroentgens per hour to ensure compliance with specifications required by the ERDA standard.

SINGLE-CHANNEL MICROPROCESSOR-BASED PORTAL DISCRIMINATOR

George P. Minges

OBJECTIVE

Totally digital discriminators are needed to improve the sensitivity, reliability,

and cost of safeguards personnel and vehicle portal radiation monitors.

PRIOR WORK

Two different and unique microprocessor-based discriminators have been designed and built in laboratory prototype (See the next subject in this report). The evaluation, testing, and success of the single channel unit indicated a great need for the immediate use of this unit at existing portal systems.

ACHIEVEMENTS AND DISCUSSION

A mass-produceable, single-channel device based on the earlier prototypes has been designed, tested, and put into a small-scale test production phase. Five of these units, which are simpler and less expensive than the earlier prototypes, have been fabricated and will be installed at existing portals.

The new units utilize a commercially available single-board 8080 A microprocessor and a single in-house custom-built electronics board along with associated hardware and cabinet for a total parts cost of under \$500. The units require no special skill to fabricate and can be built in less than a week. When fabrication is complete, the units require no adjustments or calibrations other than a routine final test. Software has been rewritten for this new, single-board microprocessor. At the same time, improvements such as numerical rounding in the statistical calculations performed by the unit have been added. The production units have also been designed to easily interface with the expected future requirements of the plant's overall alarm system.

FUTURE WORK

At this time, the design of the single channel units is considered complete.

The training of Maintenance personnel along with proper documentation will complete the project.

SECOND GENERATION MICROPROCESSOR PORTAL DISCRIMINATOR

George P. Minges

OBJECTIVE

Testing, evaluation, and debugging of the recently completed four-channel differential discriminator is needed to determine its capabilities and to determine the direction of future studies.

PRIOR WORK

A microprocessor-based, four-channel discriminator was designed and fabricated. Its prime purpose was to increase the sensitivity of portal monitoring equipment; however, the unit could also be used to replace four separate discriminators at four remotely located portals.

ACHIEVEMENTS AND DISCUSSION

The multiple-channel discriminator has been tested, and all programming errors have been eliminated. Testing has shown that the expected increase in sensitivity has been accomplished, but that the false alarm rate also increased at approximately the same rate. Thus, the only advantage realized has been a visual indication to the security inspector as to where the alarm occurred; e.g., the head, foot, chest, or waist area. This advantage alone does not at this time justify the added expense of this unit.

While testing the four-channel unit, it became obvious that the hoped-for increase in portal sensitivity could be achieved by proper summing and further manipulation by the microprocessor of

the four separate input signals. The microprocessor can be further utilized to generate and synthesize signals that are not now available from existing hardware.

FUTURE WORK

Future work will be a straightforward matter of algorithm and accompanying software changes or modifications.

INVENTORY VERIFICATION INSTRUMENT

Grover J. Cunningham and
Jorge L. Martinez

OBJECTIVE

The objective of this work was to verify location and identify material type (plutonium or uranium) of parts stored on conveyor lines outside dryboxes.

PRIOR WORK

No previous work on this objective has been done at Rocky Flats.

ACHIEVEMENTS AND DISCUSSION

Parts containing special nuclear material (SNM) are transported on conveyor lines inside dryboxes within the plutonium fabrication and foundry areas. An instrument has been assembled to verify location, material type (uranium or plutonium), and number of parts in storage at the beginning and end of every shift.

The system was assembled from available instrumentation and consists of a Ludlum Model 135 counting system with a 3.81-cm photomultiplier tube and a 2.54- X 2.4-cm NaI(Tl) gamma detector. A lead shield and collimator (Figure 18) was used to attenuate background radiation to obtain

maximum response from each part. The detector and shield were placed on top of the stainless steel drybox approximately 0.61 metre from the passing part. Response of the counting system was sufficient not only to verify location but to distinguish between plutonium and uranium on the strip chart recorder.

FUTURE WORK

Based upon the successful operation of this system, others will be assembled as needed.

BUILDING 991 VERIFICATION SYSTEM

Francis X. Haas and Ronald A. Harlan

OBJECTIVE

A procedure was developed to verify the presence of pits and buttons shipped to and from Rocky Flats through the shipping and receiving facility. Gamma-ray and neutron radiation emitted by the items are used to identify each item as to its type.

PRIOR WORK

This project was initiated during the last reporting period. Preliminary gamma-ray data were acquired on a portion of the part types to be surveyed using a SAM II,* stabilized assay meter. A SNAP II neutron detector was ordered to help compliment the gamma-ray data toward verifying the identity of part types.

ACHIEVEMENTS AND DISCUSSION

The identification of pit types is verified by measuring the 384 keV gamma rays and fast neutrons emitted by each unit. The shielding and collimation on each detector allows it to be placed on top of the drum containing the item and to view only the pit in the drum under surveillance.

The operating procedure developed allows for a rapid verification of each item. Four drums, placed in a square array on an aluminum pallet, are unloaded from the dock by a fork lift truck and placed in the counting area. A 12-second count of each drum is made using each instrument. The neutron and gamma-ray counts obtained are compared to values listed in a table for each pit type. If the counts are within the limits specified, the part is verified as to type. If the part fails the test, the drum is set aside and surveyed by both the gamma-ray and neutron detectors viewing the drum from the side. The counts obtained in this configuration are compared to limits tabulated in a second table. Failure of an item's counts to fall within the specified limits requires immediate visual verification of the item.

FUTURE WORK

No additional work will be required until FY-78 when a fully automated and computerized system will be installed. This system will include a Ge(Li) spectrometer for monitoring items for other radioactive contaminants. Liason will be maintained with the user.

*Eberline Instrument Company, Santa Fe, New Mexico.

WASTE VERIFICATION COUNTING SYSTEM FOR WASTE ISOLATION PILOT PLANT

James L. Lawless

OBJECTIVE

Under the terms of a six-month development contract with Sandia Laboratories in Albuquerque, Rocky Flats is undertaking the conceptual design of a radiation monitoring system for trans-uranium (TRU) waste packages arriving for storage at the Waste Isolation Pilot Plant (WIPP) salt mine repository near Carlsbad, New Mexico.

PRIOR WORK

This is a new project.

ACHIEVEMENTS AND DISCUSSION

As presently conceived, the fully automated system would perform four separate functions:

1. Electronic transfer of label information (by means of a modified Universal Product Coding system, for example) into the WIPP computer.
2. Radiation "signature" verification (i.e., verification by passive radiation measurements that a waste package, or array of packages, is as described by the shipper).
3. Direct measurement of surface alpha contamination.
4. Measurement of surface dose rate levels.

A conveyor belt system would automatically divert waste packages requiring decontamination or special handling because of high radiation levels and those whose radiation signatures indicate a mistake in the description of the

package (or, conceivably, tampering during shipment). This monitoring system is not intended to "assay" incoming packages; that remains the responsibility of the shipper.

The conceptual design of the system will be completed by September 30, 1977.

FUTURE WORK

It is expected that a follow-on contract will be awarded for FY-78 to construct and evaluate a prototype verification system.

STATISTICAL DESIGN FOR PLUTONIUM AND AMERICIUM SOIL STANDARDS

Merril W. Hume

OBJECTIVE

Soil standards for americium-241 and virtually isotopically pure plutonium-239 were developed by the Rocky Flats Chemistry Standards Laboratory. Statistical evaluations of these soil standards are required to assign reference values to the standards.

PRIOR WORK

This is part of the continuing effort at Rocky Flats Plant to develop standards to enhance measurement capability and quality control procedures.

ACHIEVEMENTS AND DISCUSSION

Two activity levels of soil standards were fabricated for plutonium and for americium. The levels were approximately 10 and 1 disintegrations per minute per gram (dpm/g). Sixteen samples of each standard, in addition to 32 blank samples, of plutonium and americium were to be

analyzed by each of three laboratories. Thus, for plutonium and for americium, each laboratory was to analyze, randomly the blind, 48 samples (16 each of the 10 dpm/g, 1 dpm/g, and blank standards for each of the two elements). The participating laboratories were Rocky Flats, LFE*, and Eberline†.

To date, all analyses have been completed by LFE; Rocky Flats has completed the plutonium portion; and results are slowly becoming available from Eberline. Eberline is using these standards as part of the quality control program for soil samples associated with current litigation (M. Church, et al); thus, complete results will not be available for some-time. Preliminary analyses indicate that the Rocky Flats results for plutonium are significantly higher in both mean and variability than those of LFE. Also, tracer yield recovery does not appear to be a viable measure of analytic capability.

FUTURE WORK

A complete statistical analysis will be performed when all of the data are available. It is apparent that some interlaboratory differences will need to be resolved.

LEUKEMIA AND SUICIDE STATISTICS

Merril W. Hume

OBJECTIVE

The Rocky Flats Plant has recently been accused of not only contaminating the

environs but also of causing undue health risks to plant workers and to people living in the plant vicinity. Statistics concerning leukemia and suicides were compiled to investigate possible casual effects of the Rocky Flats Plant.

PRIOR WORK

Almost routinely, the Rocky Flats Plant has been attacked by the news media or by agencies such as the Jefferson County Health Department as being detrimental to health. Past studies have investigated Rocky Flats employees' deaths attributable to cancer, cardiovascular diseases, and all causes combined. None of the results support the accusations.

ACHIEVEMENTS AND DISCUSSION

Leukemia deaths for the last seven years were compiled for the seven counties that comprise the Denver Standard Metropolitan Statistical Area (SMSA). These data were examined for an increasing trend in leukemia deaths; no trends were found to be significant. Similar results were found for leukemia incidents occurring in the Denver SMSA; however, data from the Colorado Department of Health concerning leukemia incidents is not too reliable since all cases are not reported.

Suicides of Rocky Flats Plant employees were compiled for the past six years. Using the corresponding Rocky Flats Plant population, suicide rates were computed. These were compared to both the United States and Colorado State suicide rates. No significant evidence was found to cause alarm with the Rocky Flats Plant suicide history.

FUTURE WORK

Future work will be limited to input for the ERDA-sponsored study conducted by LASL of assessing health effects of radiation exposure to plutonium workers.

*Environmental Analysis Laboratories,
LFE Corporation, Richmond, California.

†Eberline Instrument Company, Santa Fe,
New Mexico.

PLUTONIUM MEASUREMENT CAPABILITY
AT ROCKY FLATS

Elizabeth L. Baker

OBJECTIVE

This work was initiated to evaluate the capability of measurement devices such as balances, counters, and chemical analyses used to determine plutonium content.

PRIOR WORK

Earlier efforts have focused on evaluating various techniques used to measure plutonium. Several control programs have been set up to calculate statistics such as bias, precision, and outliers on each method. These programs include the Measurement Control Program, Continuous Inventory Verification Sampling Plan, Weight Measurement Control, and Plutonium Precision. Reports from these programs have been and are being generated regularly.

ACHIEVEMENTS AND DISCUSSION

Information, where it existed, on the bias and precision of measurement devices was compiled out of reports from several control programs. To complete the information, data files were generated that contained the raw data used in these reports. These data and a review of the statistical techniques used in the control programs have shown that many of the statistics used are inappropriate for the data. This results in much of the information provided by the reports being invalid.

FUTURE WORK

A thorough examination of past data is currently being made to determine what statistical methods can be used to glean

meaningful information from the data. The control programs themselves will then be revised and rewritten where necessary.

REPORT GENERATION AND
PROGRAM MAINTENANCE

Elizabeth L. Baker

OBJECTIVE

The objective of this work is to maintain several computer programs that generate regular reports for various plant functional groups.

PRIOR WORK

This has been an ongoing function for several years.

ACHIEVEMENTS AND DISCUSSION

Reports have been prepared regularly for the Sample Exchange program, MUF* control chart, and Safety programs. Concurrently, program modifications have been made where necessary. In addition, history files have been maintained and updated; e.g., MBA's† have been added or deleted in the MUF file. Special programs have been written on request by Safety to generate one-time reports.

FUTURE WORK

Program maintenance services will be provided as needed.

*Material Unaccounted For

†Material Balance Area

STATISTICAL CONSULTING

Charles D. Zeis, Elizabeth L. Baker,
and Merril W. Hume

OBJECTIVE

The objective of this effort is to provide guidance and technical services of a statistical nature to Rocky Flats groups upon request. Included are experimental designs, sampling plans, analysis of data, programming support, and other related technical services.

PRIOR WORK

This has been an ongoing function for a number of years.

ACHIEVEMENTS AND DISCUSSION

Sampling plans and analyses have been provided for testing air filters for Industrial Engineering and for cost factors involved in site-return processing for Process Chemistry and Engineering. Sensitivity levels and false alarm probabilities associated with portal radiation monitors have been supplied to Instrumentation and Statistical Systems.

Assistance has been given to Environmental Sciences in studying methods to determine contours of plutonium in soil and in devising a soil sampling plan for cesium-137. Programming and statistical support in determining summary statistics for weather and air pollution over Denver and Rocky Flats was also provided for Environmental Sciences. Nuclear Materials Control has been provided with information on variability of plutonium measurements for work they are doing regarding Material Unaccounted For (MUF's) observed at Rocky Flats.

FUTURE WORK

Several of the above programs receive assistance on an ongoing basis. Future requests of a like or similar nature are expected.

CORRELATION SPECTROPHOTOMETRIC
ANALYSIS OF PROCESS MATERIALS

Charles M. Johnson and L. Harry Faber

OBJECTIVE

The objective of this project is to develop an analyzer to determine various compounds in gaseous and liquid materials used in production processes. The development of these analyzers is important for detecting constituents of process streams for control purposes. There presently are no analyzers available to perform this function.

PRIOR WORK

Basic conceptual work on the principle of filter correlation spectrometers has been explored through the development of a gas-filter correlation spectrometer for the detection of HCl and HF gases.

ACHIEVEMENTS AND DISCUSSION

The principle of filter correlation spectrometry enhances the sensitivity of the compound of interest and nullifies interfering substances. The energy beam passes alternately through the reference cell plus sample cell and the sample cell. Because both light beams see any interfering compounds, interferences are blanked out of the chopped signal. Appropriate solid state electronics compare and amplify the resultant signal with a greater signal-to-noise ratio than available in common spectrometers. With the use of selective band pass filters,

light sources, and detectors, this principle can be used for ultraviolet, infrared, or visible spectrometry.

The gas-filter correlation spectrometer received from Science Application, Inc. (SAI), has been redesigned and is being rebuilt. The sample cell and associated electronics have been separated to facilitate the placement of the sample cell in a hot area. The electronics have been improved with the addition of a higher quality power supply and a more stable preamp for the infrared sensor. Testing is in progress, and further improvements will be added where needed.

FUTURE WORK

Following laboratory checkout, the gas unit will be installed and the process tested. Prime candidates for liquid analysis will be chosen and the instrument design work begun.

MICROPROCESSOR CONTROLLER FOR STACK GAS ANALYZERS

L. Harry Faber and Charles M. Johnson

OBJECTIVE

The objective of this project is to develop and fabricate hardware and software for a solid state microprocessor-based valve and data controller to replace an electro-mechanical relay controller.

PRIOR WORK

The original dual-gas analyzer system with control unit has been purchased and installed. The original controller failed and is incapable of any additional control functions.

ACHIEVEMENTS AND DISCUSSION

The stack-emission gas monitoring system is being expanded to analyze a third gas, carbon dioxide (CO₂), for boiler-fire control purposes.

A microprocessor controller has been designed and fabricated that will not only control the various valving functions of the system but will differentiate and send informational signals to the Hewlett-Packard 21MX minicomputer data acquisition system and to the individual digital meters for the boiler operators' control room. This controller was designed specifically to be housed in the original control cabinet (Figure 19).

The heart of the controller is a Pro-Log Corporation one-card 8-bit microprocessor system utilizing the Intel 8080A microprocessor chip. The size of this system is excellent for this dedicated control application. Cost of all parts amounts to less than \$500. The system has the capability of 1K bytes of RAM (Random Access Memory) and 4K of EPROM (Erasable Programmable Read Only Memory). Approximately 30 percent of this memory has been used for this control program.

A remote panel with Velonex Impac[®] Digital panel meters provides the boiler operators with a readout for each stack (Figure 20). The meters are controlled by the microprocessor control system and are updated every five minutes. Controls provided at the remote panel will permit continuous monitoring of one boiler exhaust on a real-time basis, but the controls will revert back to the auto sequencing mode after a preset time delay.

FUTURE WORK

The controller is now complete and following bench testing will be mounted in the existing analyzer main-cabinet system in the boiler plant. The next step in this project will be interfacing

of a Hewlett-Packard 21MX computer for data logging and report generation.

DOCUMENTATION OF LARGE-SCALE PROGRAMMABLE LOGIC CONTROLLER SOFTWARE

David E. Hausburg

OBJECTIVE

The purpose of this work is to develop a standard method for documenting programmable logic software with minimum design-engineering drafting services.

PRIOR WORK

Programmable logic controller (PLC) technology is being applied to the Water Control and Recycle Project.

ACHIEVMENTS AND DISCUSSION

Alarm functions for the Water Control and Recycle project have been finalized. A portion of the PLC software to effect 8 of the required 65 alarm functions has been programmed into the PLC process simulator. Satisfactory operation of the eight alarm functions has been achieved in the process simulator.

The ladder diagram for the 65 alarm functions has been produced with the process simulator and a teletype. Layout work of the ladder diagram and reproduction of "C" size blue-line prints is complete. Mnemonics have been assigned to the alarm input and output functions.

FUTURE WORK

Similar documentation of the process control functions for the Water Control and Recycle project is required to complete this project. A report concerning the interrelationship of the

documentation to the process is also required for use by the Utilities Department and the Maintenance Department.

PROGRAMMABLE CALCULATOR-BASED INSTRUMENTATION SYSTEM APPLICATION

David E. Hausburg

OBJECTIVE

The objective of this work is to apply programmable calculator-based instrumentation technology to solve problems associated with the development and evaluation of process instrumentation and to provide proof-of-principle data.

PRIOR WORK

Investigations into the use of a programmable calculator instrumentation system for small experimental process-control projects has been undertaken.

ACHIEVEMENTS AND DISCUSSION

It was proposed that a conductivity measurement instrument be installed in the mist tank of a Nash pump vacuum system. The system is to alarm when the mist tank caustic solution becomes acidic. The user required a proof-of-principle experiment before installing the instrument. Data from these experiments were obtained using a Tektronix calculator-instrumentation system (Figure 21). In addition to the testing of these data, the results were plotted on an x-y plotter, which is associated with the instrumentation system.

FUTURE WORK

Design and development of new instruments will require proof-of-principle experiments or evaluation, and the programmable calculator-based instrumentation system will be applied as required.

AUTOMATIC SEQUENCER FOR WASTE-LINER FLAME SEALER

Frederick L. Crawford

OBJECTIVE

The objective of this project is to design, fabricate, and install an automatic sequencing system for sealing plastic waste containers.

PRIOR WORK

This is a new project.

ACHIEVEMENTS AND DISCUSSION

A flame sealer to seal lids on plastic 55-gallon drum liners is currently undergoing testing by the Component Development group. A system for automating and sequencing this sealer has been designed and fabricated (Figure 22). When a plastic container is placed on a turntable and the sealer system started, the automatic sequencer takes over and controls removal of the excess material around the area to be sealed, the flame sealing operation, and finally a cooling step. Operational tests show the system works satisfactorily.

In areas where open flames cannot be tolerated, a design has been prepared where hot air will be used to make the seal (Figure 23).

FUTURE WORK

Future work relates to safety. In the event one or more of the flames used in the sealing operation goes out, the entire fuel supply should be automatically shut down. A design for accomplishing this has been prepared, and the necessary parts are on order.

PILOT PLANT DEVELOPMENT

Donald L. Ziegler

DEVELOPMENT OF A FLUIDIZED BED INCINERATION PROCESS

Andrew J. Johnson, James R. Sheets,
Dean A. Burton, Scott C. Burkhardt,
and Alfred L. Johnston

OBJECTIVE

The objective of this program is the development of a fluidized bed incineration system for processing combustible waste containing radioactive contaminants. The system is being developed to achieve substantial weight and volume reductions of both solid and liquid wastes as they are reduced to a dry, nonflammable residue suitable for storage, actinide recovery, or additional waste fixation operations.

The fluidized bed process is a relatively new incineration concept that has some advantages over conventional incinerator systems. In situ neutralization of acid gases is utilized to decrease equipment corrosion and eliminate the need for aqueous offgas scrubbing. In addition, the fluidized bed incineration with catalytic afterburning permits low-temperature operation and eliminates the need for refractories while producing a residue that is amenable to subsequent actinide recovery processes.

PRIOR WORK

The entire system is now in a canyon-type enclosure for operation with plutonium-contaminated waste. All pertinent operations can be controlled through gloves from the operational side of the canyon wall. Residue removal locations, such as cyclone discharges, are contained in a separate glove box to reduce radioactive contamination of the canyon area. The plant now incorporates all shredding and air-classification systems necessary to incinerate solid waste as well as a storage and pumping system for burning combustible liquids.

The tramp metal content (8.5 wt %) of production-generated, solid, combustible waste necessitated the addition of an air classifier to the system. A general type of classifier proved troublesome in operation; consequently, a unit was designed, fabricated, and installed as a replacement for the first unit. The improved air classifier, as installed, has only one mechanical moving part besides the blower. This is a remotely controlled, movable baffle for adjustment of the throat area to control separation efficiency by varying the cross sectional area.

A test burn of high efficiency particulate air (HEPA) filters was made to test the feasibility of incineration as a disposal method. The shredding and air classification system performed well; framing nails torn loose during shredding were dropped out while media and wood chips were air conveyed to the screw feed hopper. Because of the shredded filter material being only slightly compressible, the five-to-one compression ratio screw experienced stalling and resulted in uneven feeding into the incinerator. Investigation of other feeding options, such as a lower compression ratio screw or mixing HEPA's with general waste was started.

ACHIEVEMENTS AND DISCUSSION

Tributyl Phosphate (TBP)

Nuclear facilities that use the Purex or Thorex process for actinide separation generate waste-organic-solvent solution containing the tributyl phosphate extractive agent and its decomposition products. The high radioactivity of some of the processed material causes partial decomposition of the TBP and changes its extractant properties. The most practical method for disposal at the present time is by incineration. Incineration methods tried previously resulted in the production of large amounts of soot and the volatilization of phosphorous pentoxide (P_2O_5). The P_2O_5 , considered to be phosphoric acid anhydride, is a flammable solid that readily absorbs moisture to form phosphoric acid. This acid is corrosive to ferrous metals and alloys.

The mixed-bed fluidized bed incinerator (FBI) should be a promising incinerator for this material. A primary bed containing sodium carbonate (Na_2CO_3) could react with the phosphate released during combustion to form the thermally stable sodium phosphate. The solvent, similar to other hydrocarbons previously burned in the FBI, should pose no new problems.

Laboratory Scale FBI Tests

A 115-mm-dia. quartz laboratory-scale FBI was used for the initial tests. This allowed small batches of test material to be burned under easily controlled conditions, with the quartz equipment affording visual observance of the incineration process. A solution of approximately 10% TBP in solvent was prepared and injected into the bed with a diaphragm-metering pump fed from a calibrated reservoir. Two series of tests were run: (1) A primary bed of oxidation catalysts only was used to simulate conventional incineration and

(2) A mixed primary bed of Na_2CO_3 and oxidation catalyst was used to produce a neutralization reaction and tie up phosphate. At the conclusion of each run, samples of residue and deposits from various parts of the system were submitted for analysis.

Results

Incineration of the TBP-solvent mixture in catalyst only gave a random depositing of phosphorous compounds in different parts of the incineration system. The water scrubber at the exit of the system was not effective in trapping phosphorous, and an average of only 2.2% of added phosphorous was recovered over three incinerator runs.

The second series of tests using a mixed bed of Na_2CO_3 , and the catalyst was much more successful. Table 25 gives the results, as calculated from analyzed samples, on the average of two incinerator runs.

Results indicate that phosphate is retained in the bed by reaction with the sodium carbonate bed materials. The proposed reaction, shown below, would form the thermally stable tribasic sodium phosphate:

Samples were submitted for scanning electron microscope and X-ray analysis in an attempt to positively identify the exact sodium phosphate compound formed, but results have been inconclusive.

FUTURE WORK

Successful results from laboratory-scale incineration indicated that a pilot plant run could be made on a larger scale. The pilot plant run will be made with the solvent type (Texaco® P-4, a dodecane type hydrocarbon) presently in use at Savannah River Plant.

A ram-type feeder is being tested as a method of injecting noncompressionable waste into incinerators. This type of ram differs from those used to shove packaged or loosely packed waste into a fire box. The test ram is for moving tightly packed shredded waste as a slug into the incinerator; the waste forms a gas-tight seal. An experimental model is being fabricated for initial trials.

ROTARY KILN INCINERATOR DEVELOPMENT

Alton R. Teter, Peter T. Faccini,
Doyle L. Mitchell, Carl E. Plock,
Loyal F. Richmond, David L. Cash,
and Herb N. Robinson

OBJECTIVE

The objective of this program is to develop process design information, evaluate conventional refractories, and develop a refractory system for a rotary kiln incinerator for processing beta-gamma waste for the Savannah River Alternate Fuel Cycle program. One portion of the project will be concerned with the development of superior kiln and of afterburner refractories for long-term use in the incinerator. The second portion of the program will be to develop methods for remote removal, repair, and replacement of the refractories. An existing pilot-scale rotary kiln incinerator will be modified for evaluation of the most suitable refractory system and for development of process design information.

The primary chamber of the Savannah River Laboratory (SRL) rotary kiln incinerator is expected to be approximately 0.91 m inside diameter and 3.66 m long. Initial design criteria provide for a one-hour residence time for solid waste in the rotary portion of the system and a five-second residence time for the gas, soot, and tar in the afterburner. The chamber in the rotary kiln is intended to be operated at approximately 800 °C; the

afterburner chamber will be operated at approximately 1000 °C.

Shredded and prepackaged waste will be fed into the incinerator at a rate of 23.1 kg every six minutes. In addition to the solid waste, solvents (kerosene and tributyl phosphate) from fuel element processing will be fed into the rotary kiln incinerator chamber at the rate of 27.2 kg per hour. It is anticipated that the intermittent solid-waste feeding will result in severe temperature and atmosphere cycling conditions, which will be detrimental to the refractory lining.

The combined solid- and liquid-waste feed composition for the SRL rotary kiln incinerator is shown in Table 26.

The percent of ash that will result from burning of the above materials and the chemical composition of the ash from each material has been obtained from literature. This information has been used to calculate the approximate total ash composition, which is listed in Table 27.

PRIOR WORK

A production-scale rotary kiln incinerator is being installed in a plutonium recovery facility at the Rocky Flats Plant. A pilot-scale rotary kiln incinerator was operated during 1973 and 1974 to supplement design information and to develop operating criteria for the production incinerator. This pilot-scale rotary kiln incinerator will be utilized in the refractory and process development work for the SRL program.

ACHIEVEMENTS AND DISCUSSION

Refractory Studies

Two hundred seventy kilograms of simulated nonradioactive waste was burned to generate ash for the refractory slag tests. The actual chemical analyses of the resulting ash composition has not been completed. Laboratory fusion tests

indicate that the ash melts and forms a corrosive glass in the temperature range of 1050 to 1150 °C.

The following types of refractory bricks and castables have been purchased for laboratory scale evaluation: alumina of 70, 80, 90, and 99% concentrations; 90% magnesia; 50% chromia; zircon; silicon carbide; and silicon oxynitride. These refractory materials will be evaluated for thermal shock resistance, slag resistance, abrasion resistance, and penetration of radiation material during simulated incinerator operating conditions.

Tests have been started for evaluating the slag resistance of refractory materials at temperatures of 800, 1000, and 1200 °C. These temperatures were selected to approximate the expected operating range for the incinerator and afterburner refractories. The materials' slag resistance will be studied using 90- and 1000-hour cup tests in an oxidizing atmosphere. The 90-hour tests will be used to eliminate a large number of candidate refractories prior to the 1000-hour test.

Cups used for the tests are 25.4-mm cubes cut from bricks. The cups have a drilled hole in the center for holding molten slag. Lids composed of the same material as the cups will be used above the slag cups to collect volatile products that may form during the melting. The samples and cups are removed from the furnace each 24 hours during the 90-hour tests. This is done to determine the extent of the reaction with respect to time. After the 90-hour tests in an oxidizing atmosphere have been completed and the most suitable refractories have been selected, the cup tests will be repeated in a reducing atmosphere. These additional tests will be conducted because it is expected that periodic reducing conditions will be experienced in the rotary kiln incinerator as a result of batch feeding.

The castable refractories used for the cup tests will be molded, dried, and fired at 1000 °C. The same test procedures will be followed with castable cups as are being followed with the brick cups.

The cup will be sectioned for evaluation to determine the extent of slag penetration and attack. The sections then will be examined to determine the depth of penetration, erosion, cracking, and bloating. Petrographic techniques will be employed to determine if the slag is filling the refractory porosity with no reaction or if there is a chemical phase change present at the interface of the refractory.

Pilot Plant Design

A screw feeder has been designed that will be capable of feeding 4.5 to 36.4 kg per hour of shredded feed. This feed will have the same composition as the feed anticipated for the SRL Alternate Fuel Cycle rotary kiln incinerator. It has been calculated that 8.4 kg/hr of shredded feed (paper, plastic, rubber) and 1.0 kg/hr of tributyl phosphate in kerosene will be required to simulate the SRL waste feed rate for the Rocky Flats rotary kiln incinerator pilot plant. This assumes that the proposed SRL rotary kiln incinerator will be 0.91 m inside diameter and 3.66 m long. It has also been estimated that if the Rocky Flats rotary kiln pilot plant incinerator were fed on a continuous basis, as much as 27.3 kg/hr of shredded feed and 3.23 kg/hr of liquid waste could be incinerated.

An afterburner for the Rocky Flats rotary kiln pilot plant incinerator is also being designed. The afterburner will be used to ensure complete combustion of the off-gas, which could include fly ash, hydrocarbons, and carbon monoxide. The afterburner will have to be capable of raising the off-gas temperature from 760 to 1000 °C and be capable of maintaining that temperature for 0.5 second or

longer. Sufficient oxygen must be provided to produce a turbulent condition in the afterburner for good mixing and complete combustion.

The off-gas cleanup system will follow the afterburner and will be used to remove any particulates and any acid gases such as hydrogen chloride or sulfur dioxide. It will also be necessary to reduce the exhaust gas temperature from approximately 1000 to 22 °C. The primary equipment in the off-gas cleanup system will be a venturi scrubber, a packed tower, heat exchangers, high efficiency particulate air (HEPA) filters, and a blower.

Preliminary flow sheets with a material and energy balance has been completed. In addition, an activity matrix chart has been prepared to chart the cost and manpower requirements for the entire project. The project has been divided into 19 different tasks, and each task has been entered on the activity matrix for cost and manpower requirements.

Process Design Evaluation

A study has been initiated to evaluate the proposed SRL rotary kiln incinerator for the Alternate Fuel Cycle. This study will include the following:

1. The comparison of batch feeding by a ram to a continuous-type feeding and what effects each system will have on the capacity of the rotary kiln incinerator and off-gas system.
2. The effect that temperature cycling will have on the rotary kiln incinerator and afterburner and what damage, if any, this cycling may cause on the combustion equipment.
3. A comparison of the SRL proposed off-gas system to other types of off-gas cleanup equipment.

FUTURE WORK

The 90- and 1000-hour slag tests will continue. Tests will be instituted for evaluating thermal shock resistance, abrasion resistance, radiation material penetration, and the resistance of castables and prefired refractories in simulated rotary kiln incinerator operating conditions.

When fabrication and installation of the rotary kiln pilot plant incinerator equipment has been completed, runs will be made to test the feasibility of the incinerator system. This system will include the feed system, refractories, incinerator design, afterburner, and the off-gas system. Operational parameter development of the rotary kiln incinerator will be the subject of long-term runs and will establish combustion feed rates and the relationship of those rates with off-gas system flow rates.

FLUIDIZED BED INCINERATION SYSTEM FOR ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION DEFENSE WASTE

Lewis L. Richey, Peter T. Faccini,
and Pen K. Feng

OBJECTIVE

The two-fold objective of this project is to demonstrate the adaptability of the fluidized bed process for combustion of a wide variety of waste materials and to prove scale-up information developed on pilot plant equipment. The process is being scaled up to a capacity of about 82 kg/hr, which will correspond to a heat release rate of 1,600,000 kJ/hr. To effect optimum control with minimum personnel, the equipment will be instrumented with remote actuators in a control room. Data acquisition, in-process calculations, documentation of incinerator performance, inventory control of nuclear materials, and on-line process control will be obtained by use of a minicomputer.

PRIOR WORK

Previous activities consisted of containment-area construction, an equipment Title II review, laboratory-scale tests, and electronic hardware requisitioning. Containment-area construction consisted of continuing the removal of interfering ducts and piping; installing the main electrical feeder lines, motor control center, and area lighting; and erection of the block walls and hollow metal doors. The Title II review of equipment and equipment installation involved design specification and the fabrication and installation of process equipment, ducting, instrumentation, and utilities to individual pieces of equipment. Laboratory-scale tests were initiated and completed to develop design criteria for (1) full-scale equipment for "tramp" metal removal from the primary fluidized bed, (2) high-temperature gas filters for particulate removal from the off-gases, and (3) a methanol preheater for heating the catalytic afterburner to operating temperature. The data acquisition and control hardware was also specified and requisitioned.

ACHIEVEMENTS AND DISCUSSION

Construction work on the containment structure, block walls, doors, mezzanines, plus utilities to the area, was completed in April 1977. A beneficial occupancy inspection was held on April 7, 1977. On April 11, Rockwell Maintenance began installation of the process equipment, "canyon" wall, air supply ducting, and electrical supply to individual pieces of equipment. Because of alignment problems in the containment area, additional installation tasks, and past due equipment deliveries, equipment installation is about one month behind schedule. Additional personnel have been assigned to the project to recoup some of the lost time. Without a major effort and additional funding, all of the lost time cannot be regained.

During this report period, a "control print" procedure has been implemented and a "control print" engineer assigned to the project. With this procedure, modifications to equipment installation can occur rapidly and can provide documentation to correct design errors, safety hazards, or cumbersome operations not previously recognized. This system is well suited to development projects where changes in equipment or operation will occur as better information is developed. This system eliminates the need for returning to facilities engineering for design changes. Also eliminated is the time-consuming rescheduling of jobs in engineering for those changes.

Work on the process monitoring and control system is continuing. This system utilizes a Digital Equipment Corporation (DEC) programmable data processor-11/10 (PDP-11/10), Foxboro Spec 200, and Interspec hardware to receive process signals, convert them to digital format, store those values, and display them on a cathode ray tube (CRT) monitor. Also included in this system are control loops initially used for local manual and automatic control. Eventually the loops were used for on-line computer control. The 52 process sensors and 10 control loops monitoring and controlling the process have been specified along with a remote weighing station microprocessor for inventory control of feed material. All hardware items have been received, and assembly of the system has begun.

FUTURE WORK

Equipment installation will continue. With no additional delays, installation could be completed by October 1977. Delivery of major pieces of equipment are still expected to be completed in June 1977. Equipment shakedown and cold testing with simulated waste should start about November 1977. The February 1978 date for demonstrated operation on contaminated waste has become more difficult to achieve, but is still a goal that may be obtained.

FLUIDIZED BED INCINERATOR ASH IMMOBILIZATION

Leong Q. Fong, David J. Peterson,
Roger A. Santeramo, and James W. White

OBJECTIVE

The objective is to develop a method for immobilizing residues obtained from incineration of nuclear wastes. The methods selected should produce a product that is environmentally safe for transportation and long-term storage. The final product should be in a physically stable form having good mechanical strength so that it does not dust or fracture during transportation and handling. In addition, the product should be inert to atmospheric conditions and insoluble in water to minimize the spread of contamination if the outer container fails during storage.

PRIOR WORK

Work has been conducted at the Rocky Flats plant on forming glass from contaminated first- and second-stage waste treatment sludges, insulation, scrap glass, and incinerator ash. Lead borosilicate compositions were developed for forming glass from fluidized bed incinerator ash. Sintering, plastic bonding, plastic coating, and cementing were investigated as alternatives to vitrification for immobilizing fluidized bed incinerator ash. Glass additives of boric acid (H_3BO_3) and sodium carbonate (Na_2CO_3) were added to the waste containing Fluidized Bed Incinerator (FBI) ash, diatomite filter aid, and mineral resin to produce glass at a 1000 °C melt temperature. Vitrification reactors, both Joule-heated and standard resistance types, have been designed and are being fabricated. Pellets of various sizes were prepared by pouring the molten glass into graphite molds.

ACHIEVEMENTS AND DISCUSSION

The feed material used in a development program for the residue fixation process has been prepared to simulate waste materials generated in nuclear fuel plants. The feed is prepared from chemical compounds and ERDA transuranic (TRU) wastes generated at Rocky Flats Plant. General low-specific-activity (LSA) waste and nonradioactive contaminated high efficiency particulate air (HEPA) filters from exhaust plenums have been burned in the pilot plant FBI. Other FBI ash residues were obtained by incineration of nonradioactive tributyl phosphate (TBP) solvent mixture and organic ion exchange resins. Noncontaminated diatomite filter aid, mineral resin, Na_2CO_3 , and H_3BO_3 are used to complete the mixture of materials for the vitrification feed. The waste blend, feed, and product compositions are tabulated in Table 28.

Initial assessment of feed streams and material balance calculations indicates that the feed streams are converted to 74.5 wt % glass and 25.5 wt % off-gas. The glass product contains 67.1 wt % contaminated waste material and 32.9 wt % additives, which are in the form of boron oxide (B_2O_3) and sodium oxide (Na_2O). The calculated chemical compositions of the glass and off-gas products are also shown in Table 28.

A bench-scale, resistance-heated, metallic vitrification reactor was designed, fabricated, and installed. The reactor chamber is designed for low-temperature (1000 °C) melting operation. Resistance type furnaces consume less power because they can be more completely insulated and have shown a history of long operating times when the elements are properly protected from products of the melt reaction. Use of the resistance type furnace would provide a system in which a metal reaction chamber could be easily changed out in a remote type operation without creating a large amount of contaminated insulation waste. No cooling water will be required for oper-

ation of a resistance-heated vitrification reactor. The reactors have been operated continuously to produce glass buttons 20 mm in diameter by 6 mm thick. The free forming concept involves periodically releasing a gob of molten glass onto a rotating flat plate by using a reciprocating plunger in the product discharge tube. This forming concept is simple to operate, does not require a high temperature mold, and does not require a special atmosphere.

Corrosion studies indicate a metallic vitrification reactor is feasible for processing simulated wastes from nuclear facilities. Ten samples consisting of stainless steel, Hastelloy, Inconel, and Incoloy-type metals were partially submerged in molten waste-material glass and held in an electric resistance furnace at 1000 °C for two weeks. These metal samples were exposed only to the molten glass and not to actual process-operating conditions involving generated corrosive gases from the glass melt reaction. Three metals (Inconel 600, Inconel 690, and Incoloy 825) showed promise. Inconel 690 appeared to have the greatest corrosion resistance. The estimated corrosion rate is approximately 10 mils per month.

Product integrity at a permanent repository will depend on physical and chemical characteristic of the environment and of the glass composition. Internal buildup of helium in the glass from contained plutonium, one of the factors affecting product integrity, was modeled mathematically. The model was developed to predict the time period for the glass to fracture when the helium gas concentration, generated during alpha decay of contained plutonium waste, exceeds its maximum solubility in a borosilicate glass. Data from the model were generated by numerical methods using a computer program. At an initial plutonium concentration of 0.3% plutonium oxide (PuO_2), the size (0.5- to 1.27-cm diameter spheres) of the glass product does not significantly affect the calculated fracture time period because

of high helium generation and low helium diffusion rates in the glass. Over 2000 years will elapse before the undiffused helium gas will exceed its solubility at the glass yield strength. The 0.3% concentration is the expected average plutonium concentration in glass produced from a nuclear plant waste.

FUTURE WORK

Continued effort is being conducted to finalize the types of equipment required for the vitrification process. A preliminary process flow diagram and design criteria is being prepared, and engineering design is being implemented for a 4.5 kg/hr, canyon-type pilot plant.

FAST FLUIDIZED BED INCINERATION PROCESS

Seng F. Chung

OBJECTIVES

The objectives of this program are

1. To develop and adapt the fast fluidization techniques for use in the combustion of radioactive waste materials.
2. To develop technical information so that the advantages of fast fluidization can be identified and compared to the slow fluidized-bed incineration process at the Rocky Flats Plant.
3. To develop process design information for a fast fluidization technique for burning solid radioactive waste and scrap graphite.

PRIOR WORK

This is a new program.

PROCESS DESCRIPTION

Figure 24 shows the flow diagram of the fast fluidized-bed incinerator process. An air-nitrogen mixture is heated to the desired temperature and is brought to a reactor for the combustion of wastes. The fluidized bed reactor consists of two portions. The lower portion, about 3 feet high and 4 inches in diameter, is filled with sodium carbonate. Waste material is fed into this portion by a screw conveyor. The primary purpose of this lower chamber is to neutralize acid gases and to decompose the waste material. The superficial air velocity at this chamber is about 1.5 to 2 ft/sec.

The upper portion of the reactor is a fast fluidized bed, 15 feet long and 3 inches in diameter. An air velocity of about 15 ft/sec will be used in this second chamber to develop fast fluidization conditions. Fine-size oxidation catalyst particles are fluidized in this portion to furnish complete combustion of hydrocarbons. The high air velocity causes large slip velocities between gas and solids and results in a vigorous and extensive solid backmixing. Thus, it provides an intimate catalyst-gas contact to promote the rate of combustion. Catalysts are recycled through the primary cyclone back to the bottom of the fast fluidized bed. The flue gas passes through the secondary cyclone and the sintered metal filter before being sucked out by an air ejector.

The advantages of the fast fluidization process over conventional fluidization are as follows:

1. High capacity
2. Excellent gas-solid contacting
3. Better solid mixing
4. Excellent thermal uniformity and high heat-transfer rate

5. Less volume required
6. Less cross sectional area and floor space required
7. Ease in handling solids that do not flow freely and solids that tend to agglomerate.

ACHIEVEMENTS AND DISCUSSION

Preliminary studies on the fast fluidization technique were conducted during this report period. These studies included the conceptual design, material and heat balance, selection and sizing of equipment, and design of a fast fluidized bed unit. The procurement of equipment and instruments has begun.

FUTURE WORK

Future work will include installation of the unit, testing and modification of equipment, and development of process information using simulated radioactive wastes.

PROCESS CHEMISTRY AND ENGINEERING

Edward D. Erickson

INCINERATOR ASH DISSOLUTION IN HYDROCHLORIC ACID

Kay K. Kunert

OBJECTIVE

The objectives of this project are to investigate the dissolution of incinerator ash in hydrochloric acid solutions and to develop a method for converting a plutonium chloride solution to a plutonium nitrate solution.

PRIOR WORK

The dissolution of plutonium containing incinerator ash in HCl solutions has been investigated.¹

ACHIEVEMENTS AND DISCUSSION

A solution of HCl-HF-SnCl₂ has been shown to give excellent dissolution of plutonium from incinerator ash residues. Because of the problems caused by tin in production processes, it is desirable to remove the tin from solution before further processing.

Twenty-gram batches of ash were leached at boiling in 200-ml solution. Each combination of reagents was repeated twice. Dissolutions were done using the following combinations of reagents:

- (1) 6M HCl
- (2) 6M HCl — 0.5M HF
- (3) 6M HCl — 0.5M HF — 0.2M SnCl₂

Table 29 shows the results of the dissolution tests. The excellent dissolution of plutonium without the SnCl₂ reducing agent was unexpected and is apparently due to the particular makeup of the incinerator ash used. To ensure complete plutonium dissolution from all batches of incinerator ash, however, a reducing agent will be required in the HCl-HF solution. The data in Table 29 also show the improved dissolution with the addition of the SnCl₂ reducing agent.

An ion exchange process was studied to determine the feasibility of removing the chloride and tin impurities from the plutonium solution and converting it to a nitrate solution. A 50-ml Pyrex column was used, packed with Dowex[®] 1-X4 nitrate form anion resin. The resin size range was 50 to 100 mesh. The feed solution used was obtained from the dissolution of incinerator ash in 6M HCl — 0.2M SnCl₂. The column was loaded at

approximately 1 ml/min. Removal of the chloride and tin impurities was accomplished using 8 to 13 column volumes of 7.2M nitric acid (HNO_3) — 0.5M HF wash solution. Three to four column volumes of 0.35M HNO_3 was used to elute the plutonium from the column. Table 30 shows the results of the ion exchange runs for various elements.

Effluent from the process contained 4×10^{-3} g Pu/l solution and the wash contained 7×10^{-4} g Pu/l, which are both below the 1.38×10^{-2} g Pu/l discard limit for ion column effluent.

FUTURE WORK

No future work is planned using HCl for the recovery of plutonium from incinerator ash. Future work will include (1) the dissolution of residues other than incinerator ash in HCl, and (2) the effect of FeCl_2 and CuCl , as replacements for SnCl_2 , on HCl dissolution.

REFERENCES

1. D. L. Ziegler, John W. Lindsay, and John K. Fraser. Evaluation of Methods of Recovering Pu from Incinerator Ash. RFP-1723. Dow Chemical U.S.A., Rocky Flats Plant. August 16, 1971.

CHEMICAL MILLING SURFACE FINISH STUDY

Robert L. Riegel

OBJECTIVE

The objective of this work is to compare the beryllium surface finish produced by various new chemical milling solutions. The goal is to improve the beryllium surface finish on production parts. This work is being performed as part of a long range study of methods to remove machine damage from beryllium surfaces.

PRIOR WORK

The process used for chemical milling has been reported previously,¹ as have the initial studies of surface finish obtained by chemical milling.

ACHIEVEMENTS AND DISCUSSION

Six different chemical milling solutions (Table 31) were tested on HP-50 and Select S-65 beryllium coupons to determine which solution produced the best surface finish. The term "Select" S-65 beryllium is used because special batches of S-65 beryllium having higher than average impact strength were chosen for the tests. The HP-50 coupons used were smaller than the Select S-65 coupons because of a shortage of the HP-50 material. The HP-50 coupons were 0.25 X 2 X 0.06 inches. The Select S-65 coupons were 1 X 3 X 0.06 inches.

Three coupons of each material were chemical milled in 500 ml of each solution shown in Table 31. The coupons were inspected for blemishes under magnification (60X). The surface finish was then measured using a Profilometer Type QA Amplimeter. The results are given in Table 32.

Past experience has shown that the coupon size affects the surface finish obtained by chemical milling: a better surface finish is obtained on a small coupon than on a larger one. Also, experience has shown that the finish produced by chemical milling is dependent upon the initial surface finish of the starting material. For this reason, the results shown in Table 32 can be considered only as relative and should be used to compare solutions and not beryllium materials.

Lawrence Livermore Laboratory (LLL) Solution produced a better surface finish than the Rocky Flats (RF) Production Solution. The surfaces from the LLL Solution were also blemish free while

surfaces from the Production Solution had slight cratering in both kinds of beryllium.

The effect of beryllium part size is illustrated by comparing surface finishes obtained on coupons with those obtained on W-79 parts, each made with the same type of beryllium. Using the RF Production Solution, surface finishes of from 10 to 17 microinches were obtained on coupons. On W-79 parts made of the same beryllium, the surface finish varied from 30 to 45 microinches.

FUTURE WORK

Hazard rating, corrosion studies, and waste disposal studies will be done on the LLL Solution.

REFERENCES

1. R. L. Riegel, E. L. Childs, and K. R. Souply. Chemical Milling of Beryllium for Machining Damage Removal. RFP-2174. Dow Chemical U.S.A., Rocky Flats Division. July 8, 1974.

PLUTONIUM RECOVERY FROM LECO CRUCIBLE RESIDUES

Kay K. Kunert

OBJECTIVE

The objective of this project was to evaluate methods for recovering plutonium from Leco crucible residues.

PRIOR WORK

The dissolution of Leco crucible residues containing iron in nitric acid - hydrofluoric acid (HNO_3 -HF) solutions was investigated on a laboratory scale. The

residues were not readily soluble in HNO_3 -HF solutions, but a pretreatment with sodium hydroxide - fluoride ion (NaOH-F^-) was found to improve their solubility

ACHIEVEMENTS AND DISCUSSION

Leco crucible residues are generated by the Analytical Laboratory during analysis of carbon in plutonium metal. The residue consists of an aluminum silicate crucible, plutonium metal, and an accelerator used to ensure complete combustion of the sample. Before mid-1972, tin was used as the accelerator. From mid-1972 until late 1975, iron replaced the tin and in the latter part of 1975, the accelerator was changed to copper. Crucible residues with the iron and copper accelerator are the only ones being considered at this time. During the analysis of the plutonium metal, a temperature of $\sim 2000^\circ\text{C}$ is reached. The high temperature causes silica to be leached from the crucible and creates an extremely hard, refractory material containing plutonium. The silica and the hardness of the material make recovery of the plutonium difficult.

Tests were conducted to determine the feasibility of using wet ash hydrofluorination as a pretreatment in processing Leco crucible residues that contain iron as the accelerator. Tests were also made to determine the ability of an HNO_3 -HF mixture used by Chemical Operations to process other Leco crucible residues that contain copper as the accelerator.

Fluorination of Leco Crucible Residues Using Anhydrous Hydrogen Fluoride Gas

The effect of fluorination on dissolution of Leco crucible residues containing iron was studied using a process consisting of the following steps:

1. Coarse grinding of crucible material.

2. Magnetic separation of the plutonium-rich kernel from the crucible material.
3. Fine grinding of the plutonium-rich kernel in a ball mill.
4. Hydrofluorination of one-half of the ground material.
5. Dissolution of the ground material — both fluorinated and nonfluorinated.

Coarse grinding of the material to approximately 0.25-inch pieces is necessary for effective magnetic separation. Fine grinding causes the plutonium to be separated from the magnetic iron, thus destroying the mechanical separability of the material. Table 33 shows the results of the magnetic separation.

After fine grinding in the ball mill, one-half of the plutonium-enriched material was fluorinated and leached. Fluorination was done in the wet ash hydrofluorinator by Chemical Operations. The feed material was wet with water and contacted with anhydrous hydrogen fluoride gas for 30 minutes. Following hydrofluorination, the material was water washed on an R-6* filter pad. The material was leached using 32 litres of 12M HNO_3 — 0.5M F^- in an air lift dissolver. Calcium fluoride was used as the source of fluoride ion. The dissolver was heated to reflux temperature, and the solution was boiled for three hours. The solution was then filtered on another R-6 filter with a new pad to prevent contamination from previous use. The heel was scraped off the pad, and both the heel and the pad were dried. The filtrate and the heel were sampled for a chemical analysis of plutonium

*An R-6 filter is a specially made 18-inch-diameter filter pan with a polypropylene cloth filter pad.

content, and the filter pad was gamma and neutron counted to determine residual plutonium content.

The remaining one-half of the plutonium-enriched material from the ball mill was leached using the same procedure as above except without the fluorination step. A new R-6 filter pad was used for this dissolution for material balance purposes. Table 34 shows plutonium balances for both processes. The data are the results of one run. They indicate that better dissolution of plutonium is achieved without fluorination pretreatment than with it.

Plutonium Recovery from Leco Crucible Residues Containing Copper as the Accelerator

In March 1975, the Analytical Laboratory purchased a Leco analyzer that operated better with copper than with iron as an accelerator. Dissolution methods used for leaching iron-bearing Leco crucibles were tested for leaching the residues containing copper. The following solutions were investigated:

12M HNO_3 — 0.5M HF with

10M NaOH — 0.1M F^- preleach

12M HNO_3 — 0.5M HF

7M HCl — 0.2M SnCl_2 — 0.5M HF

Table 35 compares the results with the leach solutions. The best dissolution was obtained with the HCl — SnCl_2 — HF system with 99% of the plutonium dissolving with a single 2-hour contact. The dissolution obtained with HNO_3 — HF resulted in ~97% plutonium recovery after 2 contacts. In all cases, the heels were below the discard level of 6.0×10^{-3} g Pu/l for Leco crucible residues. There was no significant improvement in the dissolution when the NaOH preleach was used.

The data show that plutonium can be effectively recovered from Leco crucible residues containing copper with HNO_3 - HF.

FUTURE WORK

No future work is planned.

INDUCTION-HEATED TILT-POUR FURNACE

James B. Knighton, Robert G. Auge,
Ray E. Giebel

OBJECTIVE

Induction-heated, tilt-pour furnaces will be used in Building 371, the new Plutonium Recovery Facility. A prototype tilt-pour furnace has been installed in Building 776. The objectives of the development program are to develop a basic tool for equilibration of molten salt - metal phases and to gain early experience with the prototype furnace. Required modifications and demonstration of automatic operation with a sequence panel are necessary prior to start-up of the furnaces in Building 371. Molten salt extraction, electrorefining, and other pyrochemical processes such as pyroredox, oxide reduction, and salt cleanup need to be demonstrated in the tilt-pour furnace.

PRIOR WORK

The molten-salt extraction process has been successfully demonstrated using a tungsten crucible to contain and equilibrate the molten salt and metal phases.

ACHIEVEMENTS AND DISCUSSION

A total of 23 kg Pu were processed by electrorefining in the tilt-pour furnace. Six kg met the specifications for ultra-

pure plutonium. More testing is required to establish electrorefining as a routine operation for the furnace.

The sequence panel for automatic operation has been interfaced with the prototype furnace. Significant electronic modification of the sequence panel was necessary.

The pyroredox process has been successfully demonstrated. The process, as illustrated in Figure 25, was demonstrated on four impure plutonium buttons. An overall yield of 84% was obtained, based upon impure metal feed. Levels of boron, chromium, copper, iron, gallium, molybdenum, nickel, lead, and silicon were significantly reduced; however, the levels of aluminum, carbon, tantalum, and tungsten increased. This may be attributed to impurities in the tungsten crucible that had been used previously for salt cleanup processing. High levels of zinc remained in the product metal because excess zinc chloride was used in the oxidation step. Plutonium concentrations in the residue salts were below discard levels.

Three steps of the salt cleanup operation have been successfully demonstrated. These were (1) magnesium reduction of plutonium and americium chloride from the molten-salt extraction salt into zinc alloy, (2) concentration and purification of the plutonium and americium by oxidation into a salt phase with zinc chloride, and (3) reduction of the plutonium and americium from the salt phase, using calcium metal. It was found impractical to use the same furnace for oxidations and reductions. At least two furnaces would be necessary for salt cleanup using this process.

FUTURE WORK

Removal of zinc by vaporization from the pyroredox process metal product will be evaluated in a vacuum casting furnace. The tilt-pour furnace will continue to

be used as a basic tool for the salt cleanup effort and other pyrochemical operations.

RECOVERY AND PURIFICATION OF AMERICIUM FROM AN ALUMINUM — AMERICIUM OXIDE MIXTURE

Donald L. Baaso

OBJECTIVE

The objective of this project was to separate and purify the americium from an aluminum — americium oxide mixture for the Lawrence Livermore Laboratory (LLL). The product requested by LLL was to include one batch of high purity (99.9% pure) americium oxide for Oak Ridge National Laboratory (ORNL), and a second batch, which was to be as pure as practical, for LLL.

PRIOR WORK

No prior work has been done at Rocky Flats on this project.

ACHIEVEMENTS AND DISCUSSION

Feed material consisted of americium oxide mixed with aluminum metal powder. Part of the material was pressed in aluminum capsules. The americium was separated from the aluminum — americium oxide by selective dissolution. Precipitation and ion exchange techniques were used for purification of the americium. The process used is shown in Figure 26. The initial separation of aluminum from americium was achieved by selective dissolution of the aluminum in a sodium hydroxide (NaOH) solution. Oxalate precipitations in subsequent steps gave further purification.

Rare earth contamination was reduced using a fluoride precipitation technique.

Silver, which was added in the fluoride precipitation step, and lead were removed as insoluble chlorides. The plutonium was removed by anion exchange. These techniques were used sequentially, as shown in Figure 26, to produce two batches of high purity americium oxide.

Selective dissolution of the starting material was accomplished by slowly adding the Al-AmO₂ mixture to 5M NaOH — 1M NaNO₃. The aluminum solubility and dissolver size dictated that this be done in four batches. Nitrate ion was added to suppress hydrogen evolution. The caustic filtrates had up to 106 g/l aluminum, which caused salting in one batch. This batch had to be diluted to 30 g/l to keep the aluminum in solution. The insoluble AmO₂ was combined into one batch and dissolved in 7.5M HNO₃ — 0.1M HF in preparation for further treatment.

The americium was precipitated from the first nitrate solution by adjusting the acidity to 0.6M H⁺ and adding sufficient oxalic acid to precipitate the americium and make the solution 0.5 molar. The higher aluminum concentration in the first nitrate solution complexed some of the oxalic acid, thus requiring a higher oxalic acid concentration than in subsequent precipitation. The subsequent oxalate precipitations were made at an acidity of 0.1M H⁺ and with the solution 0.1M in oxalic acid. Precipitations were made at ~50 °C, cooled, and digested for 16 hours at room temperature.

The rare earths were removed by precipitating them as fluorides while holding the americium in the soluble, hexavalent state with ammonia persulfate [(NH₄)₂S₂O₈] and argentous oxide (Ag₂O). This was done in two batches to keep the solution volume below 500 ml for handling convenience. Each batch contained ~20 grams of americium in 400 ml, 0.1M HNO₃. The solutions were heated to 80 °C and made 0.25M in (NH₄)₂S₂O₈, 0.002M in Ag₂O, and digested 40 minutes at 80 °C.

The rare earths were then precipitated by making the solutions 0.2M in fluoride, digesting 3 to 5 minutes, and then removing the fluoride precipitate by filtration. Ascorbic acid was used to reduce the americium back to the trivalent state where it was precipitated as an oxalate and calcined to the oxide. The oxide from both batches was combined and dissolved in 500 ml, 6M HNO₃ in preparation for silver and lead removal.

The silver and lead were removed by precipitation as chlorides. The solution was adjusted to 0.1M H⁺ and made 0.1M in NH₄Cl. After a 16-hour digestion, the precipitate was removed by filtration. The americium was converted to an oxide by the oxalate precipitation-calcination method and redissolved in 400 ml of 7.5M HNO₃ in preparation for plutonium removal.

The plutonium was removed by sorption on Dowex 1-X4 nitrate-form resin. This step was repeated because analytical results showed poor plutonium decontamination after the first pass. The first run solution was adjusted with 0.007M hydrazine and 0.007M sodium nitrate to stabilize plutonium in the tetravalent state. The solution was digested for 30 minutes before ion exchanging. The second-run solution was adjusted with only sodium nitrite and digested 24 hours. The solutions were run through a 28-mm dia. X 18-cm bed of resin at 10 ml/min. The americium was washed through with 4 column volumes of 7.5M HNO₃ and then converted to the oxide by the oxalate precipitation — calcination method. The final oxide was calcined for 8 hours at 660 to 700 °C.

The starting americium, analyzed after the first dissolution and oxalate precipitation, contained 5000 ppm aluminum. The product of the short process (two dissolutions and two oxalate precipitations) was 99.7% pure with plutonium and lead being the major impurities. The product of the full process was 99.9% pure. Impurities above the detectable

limits are reported in Table 36. The high purity batch (99.9%) was shipped to ORNL and the 99.7% batch will be shipped to LLL.

FUTURE WORK

No future work is planned on this project.

PLUTONIUM RECOVERY FROM BACKLOG SALTS

James B. Knighton, Ray E. Giebel,
and James W. Berry

OBJECTIVE

At Rocky Flats, americium is separated from plutonium metal in a molten-salt extraction process. The product salt from this extraction process is subsequently fed into an aqueous process for recovery of plutonium and americium. During the past several years, a backlog of salt has built up while waiting for aqueous processing. The objective of this project is to develop and demonstrate pyrochemical methods for recovering plutonium and americium from these salts on a production basis.

PRIOR WORK

Process steps necessary for plutonium and americium recovery from backlog salts were described in a previous, classified progress report. The first three steps in the process (zinc-magnesium reduction, zinc chloride oxidation, and calcium reduction) were demonstrated on a production scale.

A high-temperature vacuum furnace for separating relatively high volatile metals such as magnesium, calcium, and zinc from plutonium-americium alloys was checked out in the pyrochemical laboratory in Building 779.

The separation of americium from plutonium by vacuum distillation on a small scale has been reported by investigators at other sites.¹

ACHIEVEMENTS AND DISCUSSION

The first three steps in the salt clean-up process have been run on a production basis in the stationary furnaces. To date, 885 kg of backlog salt have been fed to the process.

Tantalum crucibles used to hold ceramic crucibles in the first three steps were failing rapidly because of leaks and breakage of the ceramic crucibles. The tantalum crucibles have been replaced by stainless steel sleeves placed in small tantalum backup cups that last indefinitely.

The salt product from the first step consists of two phases: one of which is white in color, contains about 30 ppm plutonium, and is discardable. The other salt phase is black in color, or black salt, and may contain plutonium concentrations greater than the discard limit. It may therefore require further processing. Analytical results for this black salt, which is usually about 25% of the total salt phase, indicate it consists of oxides and small metal droplets dispersed in a salt matrix. Using a molten salt filtration technique, about 80% of the salt matrix has been separated from the black constituents. To filter the black salt, vacuum is applied across a porous carbon frit contained in a steel vessel.

Steps 1, 2, and 3 of the salt cleanup have been demonstrated in the tilt-pour furnace; however, for the process to be efficient, two tilt-pour furnaces are needed. One would be dedicated to the oxidation process and the other to the reduction process.

The fourth step in the process, which is vacuum melting (separation of the more volatile solvent metals from americium and plutonium), has been demonstrated in an experimental vacuum-melt furnace. Some splattering of the material within the distillation crucible is occurring. This splattered material adheres to the sides of the magnesium oxide (MgO) crucible. Methods such as burning and hydriding are being explored to recover the splattered plutonium. A hydriding procedure is being considered along with some changes in operating parameters (temperature and pressure) to eliminate the problem.

The condensate product (zinc, magnesium, and calcium) is being sampled and analyzed and then returned to the early stages of the salt cleanup process as a reagent. This has reduced the generation of residues and has eliminated one area of plutonium loss.

Step 5 (americium extraction) is currently being performed in stationary cells on the plutonium-americium alloy, which is the distillation residue in Step 4. Both two-stage and three-stage countercurrent extractions have been performed. In each mode of operation, metal-salt separations were poor. This may be attributed to either poor salt-to-metal contact during the extraction process or to the unexpected high impurity levels in the alloy product from the fourth step. This problem is undergoing investigation.

In the final step, the americium will be separated from plutonium by vacuum distillation. Additional equipment remaining to be installed for the americium vacuum still include the induction coil, still, and collector. These are being designed and the distillation procedure is being developed at LLL. The design and development work is in the final stages.

FUTURE WORK

Efforts will continue toward reducing the quantity of recycle material (from black salts and ceramic crucible breakage) and to process the recycled material pyrochemically. An effort will be made to solve the problems encountered in the fourth and fifth steps of the process. This effort will include improving the salt-metal contact in the furnace together with investigating the sources of impurities and methods for their removal.

Studies will continue on operating parameters for the separation of high vapor pressure metals from plutonium-amerium alloys. The main effort will be aimed at eliminating the splattering problem. A secondary effort will be directed towards hydriding the splattered material away from the ceramics.

The americium distillation equipment will be installed and distillations begun. Special handling problems such as possible radiation exposure will need to be solved as the problems arise.

REFERENCES

1. E. H. Kobisk, Manager. Target Preparation Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Private communications. August 10, 1976.

PREPARATION OF PLUTONIUM-238 METAL ROD

William V. Conner

OBJECTIVE

The objective of this project was to prepare a plutonium metal rod enriched in plutonium-238. This project was undertaken in response to a special

order received from Lawrence Livermore Laboratory. The rod was to be less than 0.2 in. in diameter and contain approximately 12 wt % ^{238}Pu . In addition, the ^{238}Pu content of the rod was to be approximately twice the ^{240}Pu content.

PRIOR WORK

No prior work has been done on this project.

ACHIEVEMENTS AND DISCUSSION

A 6.3-g batch of plutonium containing 5.1 g of ^{238}Pu was received as oxide from LLL for this project. This oxide had been in storage at LLL for several years, and the history of this material was unknown. Therefore, to assure a reactive oxide, this material was dissolved in nitric acid and the plutonium was precipitated with oxalic acid. The plutonium oxalate precipitate was calcined at 600 °C for 6 hours and converted to plutonium dioxide (PuO_2).

The PuO_2 was converted to plutonium tetrafluoride (PuF_4) using fluorine (F_2) gas in a Monel fluorination vessel. A neutron counter was used to monitor the increased neutron emission rate that occurred as the PuO_2 was converted to PuF_4 .

The PuO_2 was contacted with F_2 for 37 minutes using a F_2 flow rate of 400 cm^3/min . A 98.7% conversion to PuF_4 was achieved. Operating conditions for the fluorination are given in Table 37. The $^{238}\text{PuF}_4$ was then mixed with war reserve (WR) stream isotopic PuF_4 , and the mixed fluorides were reduced to metal in a sealed stainless steel reaction vessel. Table 38 shows the composition of the charge used for the reduction. Calcium metal was used to reduce the PuF_4 , iodine was added to provide additional heat ($\text{Ca} + \text{I}_2 \rightarrow \text{CaI}_2 + \text{Heat}$), and the calcium chloride was added to improve the metal yield. The reduction produced a

39.75-g metal button for a 97% metal yield.

A vacuum casting furnace was used to cast the metal button into the required rod. The metal was heated to 950 °C in a melting crucible of oxidized tantalum metal and was bottom poured into the calcium fluoride — coated graphite rod mold that had been heated to 700 °C. The casting produced a 0.185-in.-diameter by 2-in.-long rod. Analysis of a sample from the casting showed the rod contained 11.359% ^{238}Pu and 5.475% ^{240}Pu . The complete isotopic and impurity analysis are given in Table 39. The high copper and nickel impurity levels were caused by contamination from the Monel fluorination reactor. The metal, reburned skull oxide from the casting, and the reduction residues were all shipped to LLL.

FUTURE WORK

No future work is planned on this project.

BACKLOG REDUCTION THROUGH IMPROVED ASH DISSOLUTION TECHNIQUES

Charles E. Baldwin

OBJECTIVE

The objectives are to determine methods for controlling heel disposition and for increasing dissolution efficiency to
(1) improve plutonium recovery and
(2) accelerate the backlog reduction.

PRIOR WORK

Previous attempts at achieving continuous discardable ash heels were precluded by the absence of control over plutonium levels in the resulting heels. The result was the mixing of low- and high-

level plutonium heels that never allowed the heels from subsequent leachings to reach the discard level.

In April 1976, studies were completed on an evaluation of dissolution efficiencies obtained using SS&C (sand, slag, and crucible), SS&C heel, and calcium fluoride as fluoride ion sources required for dissolution. From this study, it was concluded that the use of calcium fluoride, as opposed to SS&C or SS&C heel, improved dissolution efficiency and resulted in lower plutonium levels in resulting heels.

In August 1976, further studies indicated that discardable heels could be produced by careful segregation of heels by plutonium concentration, campaigning of ash/ash heel to prevent cross-contaminating of high- and low-level plutonium-containing heels, and the use of calcium fluoride only in low-level heels.

ACHIEVEMENTS AND DISCUSSION

Beginning in October 1976, a coordinated effort was begun to start segregating ash/ash heel into specific categories (referred to as levels) based on plutonium concentration as follows:

420 (Ash)*	
<u>Level</u>	<u>Pu Concentration (g/g)</u>
Level 0	0 → 0.0046
Level 1	0.0047 → 0.0090
Level 2	0.0091 → 0.0300
Level 3	0.031 → 0.0500
Level 4	0.051 → Up

*Discard Limit - 4.7×10^{-3} g/g

421 (Ash Heel)*

<u>Level</u>	<u>Pu Concentration (g/g)</u>
Level 0	0 → 0.0060
Level 1	0.0061 → 0.0090
Level 2	0.0091 → 0.0300
Level 3	0.031 → Up

*Discard Limit - 6.1×10^{-3} g/g

One dissolver line, Line 23, was dedicated to processing Level 1 ash heels using calcium fluoride. The remaining lines, 24 and 25, continued to process the high levels of ash/ash heel. Table 40 is a summary of the results achieved in Line 23 since processing began on low-level heels in October 1976.

Prior to October 1976, the percentage of discardable ash heels obtained during normal operations was usually less than 1%. From October 1 to November 1, approximately 37% of the heels were below the 2.7×10^{-3} g/g discard limit. On November 8, 1976, the economic discard limit for ash heel was raised from 2.7×10^{-3} g/g to 6.1×10^{-3} . From November 1 through March 1, approximately 99.5% of the heels were below the 6.1×10^{-3} g/g discard limit. Processing of Level 1 ash heels was completed March 1 and processing of Level 2 ash heels begun. A material flow for the first quarter of 1977 is shown in Figure 27.

FUTURE WORK

Additional studies such as optimizing fluoride and acid concentration are necessary to improve dissolution efficiency. In addition, new guidelines for determining economic discard limits of heels need to be considered.

Figure 1. Effect of Nitric Acid Concentration on Actinide Extraction Coefficients

Figure 2. Evaluation of Uranium Stripping with 30% DHDECMP-CCl₄ (Aqueous-to-Organic Ratio = 1)

Figure 3. Results of Actinide Removal with TBP and DHDECMP

Figure 4. Conceptual Flow Sheet for Water Purification

Figure 5. Conceptual Flow Sheet for Wastewater

Notes

C_0 = 134 mg/l linear alkylate sulfonates (LAS)

$\frac{C}{C_0}$ = LAS concentration in effluent divided by LAS in influent

Flow Rate 13 ml/min

Figure 6. Breakthrough Curves for Adsorbents Alkaline Detergent (pH 12)

Figure 7. Breakthrough Curves for Adsorbents Acidified Detergent (pH 3.5)

Notes

C_0 = 134 mg/l LAS

$\frac{C}{C_0}$ = LAS concentration in effluent divided by LAS in influent

Flow Rate = 10 ml/min

Figure 8. Americium Breakthrough on Amberlite XAD-4

Figure 9. Americium Elution Results on Amberlite XAD-4

Figure 10. Conceptual Flow Sheet for Processing Pyrochemical Residues

Figure 11. Conceptual Flow Sheet of Primary Soil Decontamination Process

21093-3

Figure 12. Alternate-Immersion Stress Corrosion Test System

Figure 13. Orientation of C-Ring in Relation to Plate

20310-8

Figure 14. Building 371
Plutonium Pallet-Container

Figure 15. Change of Moisture
Content in the Aluminum
Laminate Bag

21646-9

Figure 16. Crate Counter for Normal Operating Loss Determinations (A standard crate is shown loaded at left, and several of the 10 neutron-sensitive, lithium-loaded scintillation detectors also are shown in position.)

21742-3

Figure 17. Gamma Detector and Lead Shield
Used With the 1.2-m Portal Monitor

Figure 18. Lead Shield for Inventory Verification Instrument

21809-1

Figure 19. Control Cabinet for Dual-Gas Analyzer System

Figure 20. Remote Panel with Velonex Impact[®] Digital Panel Meters

21809-2

21152-4

Figure 21. Tektronix Programmable Calculator and X-Y Plotter

Figure 22. Waste-Liner Sealer Wiring Diagram for Gas Burner

Figure 23. Waste-Liner Sealer Wiring Diagram for Hot-Air Torch

Figure 24. Flow Diagram of Fast Fluidized Bed Incineration Process

Figure 25. Pyroredox Process

Figure 26. Aluminum - Americium Oxide Processing Diagram

Figure 27. Material Flow - Ash/Ash Heel Dissolution
December 27, 1976 to March 24, 1977

TABLE I. Basic Solution Prior to Acidification

<u>Incinerator Liquor</u>	
Na_2CO_3	1.36 <u>M</u>
Na_3PO_4	0.46 <u>M</u>
NaCl	0.52 <u>M</u>
Na_2SO_4	0.37 <u>M</u>
NaNO_3	0.07 <u>M</u>
Pu	0.00004 <u>M</u>
Am	0.000004 <u>M</u>
U	0.0042 <u>M</u>
Fission Products	0.14 g/l
<u>Analytical Waste</u>	
HNO_3	1.5M
HCl	0.1 <u>M</u>
NaNO_3	0.005 <u>M</u>
$\text{K}_2\text{Cr}_2\text{O}_7$	0.005 <u>M</u>

TABLE 2. Elemental Analysis of Sludge Before and After Dissolution

Element	Elemental Analysis (wt %)		
	Sludge ^a	Sludge After 7M HNO ₃ Contact	Sludge After 7M HNO ₃ -0.006M CaF ₂ Contact
Al	0.05	0.5	0.5
B	0.01	0.04	0.05
Cu	0.02	0.05	0.05
Fe	1	5	5
Mg	0.03	0.5	0.5
Mo	<0.01	0.05	0.1
Na	0.3	0.1	0.5
Nb	0.01	0.1	0.01
Ni	0.2	0.5	0.5
Pb	0.03	0.05	0.01
Pu	0.004	0.2	0.1
Si	0.5	2	0.2
Sn	0.02	0.1	0.2
Sr	<0.01	0.05	0.05
Ta	<0.01	0.05	0.05
Zr	<0.01	0.1	0.05
Zn	0.01	0.1	0.1

a. Sludge sample from vacuum receiver tank.

TABLE 3. Average Percent Sludge Removed from the Raschig Rings by the Solvents

Solvent	Sludge Removed (avg wt %)	
	After 10 minutes	After 28 minutes
25 vol % CCl ₄ -Texaco 643 oil mixture	55 ±7	64 ±3
CCl ₄	79 ±4	80 ±4
1,1,1-Trichloroethane (Dow Chlorothene VG)	84 ±5	91 ±4

TABLE 4. Solubility of Lead Oxalate as a Function of Nitric Acid Concentration

HNO ₃ Concentration (mol/l)	Lead Concentration* (g/l)	Lead Solubilized (%)
0.1	0.014	1.4
0.3	0.036	3.6
0.5	0.300	30
0.7	0.830	83
0.9	0.900	90
1.1	0.993	99

*Results of single determinations.

TABLE 5. Solubility of Lead and Americium Oxalates as a Function of Nitric Acid Concentration and Equilibration Time

	Concentration*				
	<u>HNO₃</u> <u>(mol/l)</u>	<u>Pb</u> <u>(g/l)</u>	<u>% Total</u> <u>Pb</u>	<u>Am</u> <u>(g/l)</u>	<u>% Total</u> <u>Am</u>
Feed		0.320	100	9.21	100
	0.1	0.055 ±0.011	17	0.004 ±0.002	0.04
Filtrates	0.3	0.114 ±0.012	36	0.013 ±0.007	0.14
After	0.5	0.121 ±0.016	38	0.059 ±0.041	0.64
Two Hours	0.7	0.142 ±0.007	44	0.146 ±0.066	1.58
Equilibration	0.9	0.183 ±0.011	57	0.295 ±0.295	3.20
	0.1	0.177 ±0.030	55	0.006 ±0.002	0.07
Filtrates	0.3	0.333 ±0.073	100	0.057 ±0.039	0.41
After	0.5	0.270 ±0.019	84	0.136 ±0.028	1.48
Four Days	0.7	0.333 ±0.126	100	0.470 ±0.346	5.10
Equilibration	0.9	0.263 ±0.032	32	0.963 ±0.346	10.5

*Mean ± standard deviation of duplicate samples.

TABLE 6. Analysis of Americium Feed Solution and Americium Oxide Product

<u>Am Feed Solution (g/l)</u>	<u>Am Oxide Product (g/g)</u>	<u>Decontamination Factors</u>
H ⁺ , 3.33M		
Am, 0.62	0.825	
Pu, 0.004	0.003	
Al, 0.10	1.0×10^{-4}	1.3×10^3
Ca, 0.20	7.5×10^{-4}	3.5×10^2
Cr, 0.02	6.0×10^{-5}	4.4×10^2
Cu, 0.01	$<1.0 \times 10^{-5}$	$>1.3 \times 10^3$
Fe, 0.30	2.0×10^{-4}	2.0×10^3
K, 10.0	1.0×10^{-2}	1.3×10^3
Mg, 0.5	8.0×10^{-4}	8.3×10^2
Mn, 0.006	$<1.0 \times 10^{-5}$	$>8.0 \times 10^2$
Ni, 0.04	$<1.0 \times 10^{-5}$	$>8.3 \times 10^3$
Pb, 0.14	3.25×10^{-3}	57
Si, 0.02	4.0×10^{-3}	6.6
Ti, 0.02	$<1.0 \times 10^{-5}$	$>2.6 \times 10^3$

TABLE 7. Results from Carbonate-Hydroxide Precipitations
(results expressed in grams)

Element		Sample 1 Aliquants			
		1	2	3	
Pu	Filtrate	0.016	0.015	0.009	Avg. 99.57
	Precipitate	3.32	3.01	2.90	
	% Recovered	99.52	99.50	99.69	
Am	Filtrate	0.001	0.002	0.001	Avg. 99.44
	Precipitate	0.26	0.23	0.23	
	% Recovered	99.62	99.14	99.57	
Al	Filtrate	1.03	1.33	1.74	Avg. 90.02
	Precipitate	0.19	0.13	0.10	
	% Separated	84.43	91.09	94.56	
Mg	Filtrate	6.62	8.03	9.14	Avg. 94.64
	Precipitate	0.48	0.38	0.46	
	% Separated	93.24	95.48	95.21	
		Sample 2 Aliquants			
		1	2	3	
Pu	Filtrate	0.022	<0.01	0.01	Avg. >99.31
	Precipitate	2.04	2.14	1.85	
	% Recovered	98.93	>99.53	99.46	
Am	Filtrate	<0.001	<0.001	<0.001	Avg. >99.29
	Precipitate	0.14	0.15	0.13	
	% Recovered	>99.29	>99.34	>99.24	
Al	Filtrate	0.85	0.99	0.72	Avg. 70.34
	Precipitate	0.34	0.27	0.46	
	% Separated	71.42	78.57	61.02	
Mg	Filtrate	2.08	2.77	2.18	Avg. 82.75
	Precipitate	0.46	0.35	0.63	
	% Separated	81.89	88.78	77.58	

TABLE 8. RESULTS OF PROCESSING MOLTEN SALT
EXTRACTION RESIDUES

Major Elements (mg/sample) for Al-Mg Alloy						
	<u>Am</u>	<u>Pu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Na</u>
Feed Before Processing	23	0.04	19	158	459	78
Strip Solution	18	0.004	0.57	<0.1	<0.1	0.23
	<u>K</u>	<u>Ca</u>	<u>Cl</u>	<u>F</u>		
	136	2	207	56		
	<0.1	0.79	<0.1	7		
Major Elements (mg/sample) for Zn-Mg Alloy						
	<u>Am</u>	<u>Pu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Na</u>
Feed Before Processing	30	0.08	30	11	135	63
Strip Solution	14	0.04	6	<0.6	<0.3	<0.6
	<u>K</u>	<u>Ca</u>	<u>Cl</u>	<u>F</u>	<u>Zn</u>	<u>Pb</u>
	113	<0.75	905	144	2940	9
	<0.3	<0.3	3	<1	<0.3	<0.3
Major Elements (mg/sample) for 8 mole % Salts						
	<u>Am</u>	<u>Pu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Na</u>
Feed Before Processing	5.5	0.2	3	<2	120	800
Strip Solution	2.5	0.07	3	<2	<0.1	1
	<u>K</u>	<u>Ca</u>	<u>Cl</u>	<u>F</u>	<u>Zn</u>	<u>Pb</u>
	1500	0.3	3500	63	<0.2	0.6
	1	0.1	3	0.2	<0.2	<0.3

TABLE 9. Ash Destruction by Leaching, Digestion, and Fusion

Leach to Solid Ratio of 10:1
 Digestant to Solid Ratio of 50:1
 Flux to Solid Ratio of 10:1

Method	Temperature (°C)	Time (hr)	Ash Destroyed (mean wt % $\pm$ standard deviation)		
			Primary	Secondary	Filter Fines
15.7M HNO ₃ leach*	(reflux)	2	57	36	51
H ₂ SO ₄ -HNO ₃ digestion* (95% H ₂ SO ₄)	(reflux)	2	75	80	68
NaOH fusion*	500	0.5	60	66	44
NaOH fusion	500	2	68 $\pm$ 4.8	63 $\pm$ 0.80	64 $\pm$ 8.6
NaOH fusion*	800	2	81	81	74
Na ₂ O ₂ fusion	500	0.5	80 $\pm$ 4.4	75 $\pm$ 6.2	70 $\pm$ 3.2
Na ₂ CO ₃ fusion	500	0.5	33 $\pm$ 2.7	51 $\pm$ 3.1	19 $\pm$ 2.0
Na ₂ CO ₃ -Na ₂ SO ₄ fusion	800	2	34 $\pm$ 7.1	57 $\pm$ 3.7	19 $\pm$ 1.8
KHSO ₄ fusion	500	2	59 $\pm$ 10	60 $\pm$ 9.3	60 $\pm$ 8.9
K ₂ S ₂ O ₇ fusion	500	2	59 $\pm$ 6.3	54 $\pm$ 4.9	64 $\pm$ 8.9

*Single determination

TABLE 10. Actinide Recovery by Leaching, Digestion, and Fusion

Leach to Solid Ratio of 250:1
 Digestant to Solid Ratio of 100:1
 Flux to Solid Ratio of 100:1

Sample: Am-traced PuO_2
 (2.27×10^{-4} g Am/g Pu)
 fired at 925 °C to
 constant weight

Method	Temperature (°C)	Time (hr)	Actinide Recovery (mean wt % ± standard deviation)			
			Pu		Am	
15.7M HNO_3 leach†	(reflux)	12	0.09		3.5	
H_2SO_4 - HNO_3 digestion†	(reflux)	12	94		88	
H_2SO_4 - HNO_3 digestion†	(reflux)	16	97		96	
NaOH fusion*	500	2	98	±0.97	96	±0.89
NaOH fusion**	500	2	34	±4.6	32	±4.0
Na_2CO_3 fusion	900	2	7.7	±2.5	6.9	±0.35
Na_2CO_3 - Na_2SO_4 fusion	900	2	6.3	±3.9	6.7	±1.2
Na_2CO_3 - NaNO_3 fusion	900	2	98	±2.3	98	±2.6
KHSO_4 fusion	500	2	95	±2.8	94	±3.5
$\text{K}_2\text{S}_2\text{O}_7$ fusion	500	2	92	±5.3	89	±5.0

†Single determination

*Ni crucible

**Alumina crucible

TABLE 11. Uranium Breakthrough Capacity and Elution Results

Feed Composition		Flow Rate (ml·cm ⁻² ·min ⁻¹)	Column Dimensions, dia. X height (cm)	Uranium Breakthrough Capacity ^a	Uranium _b Elution ^b
U (g/l)	Pu (g/l)				
10.3	0	10.7	0.6 X 13	46	--
10.3	0	1.0	2 X 20	56	6.9
0.074	10.5	1.7	1.2 X 10	0.5	10.8
0.074	10.9	2.0	1.2 X 15	2	--

a. Grams of uranium fed to one litre of support when the ratio of uranium concentration in the effluent to feed reached 0.01.

b. Column volumes of 1M (NH₄)₂SO₄ to elute 95% of the uranium from the support.

TABLE 12. Characterization Results of Various Soil Samples

	<u>>4.0 mm Fraction</u>			<u>4.0 to 2.4 mm Fraction</u>		
	<u>P-1*</u>	<u>P-2</u>	<u>P-3</u>	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>
DRY SCREENING:						
wt %	62	63	61	4	4	5
Pu (d/m/g)	100	160	153	130	390	414
Am (d/m/g)	180	130	17	38	51	55
	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>
wt %	64	56	58	5	5	4
Pu (d/m/g)	100	530	405	3,200	2,000	2,000
Am (d/m/g)	23	59	500	7,000	380	390
WET SCREENING:	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>
wt %	62	63	61	4	4	4
Pu (d/m/g)	<5	<5	<5	19	33	47
Am (d/m/g)	<5	<5	<5	<5	<5	<5
	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>
wt %	64	56	58	4	4	4
Pu (d/m/g)	<5	<5	<5	100	130	370
Am (d/m/g)	<5	<5	<5	32	30	81
	<u>2.4 to 0.42 mm Fraction</u>			<u><0.42 mm Fraction</u>		
	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>
DRY SCREENING:						
wt %	10	9	11	24	24	23
Pu (d/m/g)	430	840	1,200	6,200	12,000	14,000
Am (d/m/g)	66	130	140	920	1,800	1,500
	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>
wt %	13	15	12	18	24	26
Pu (d/m/g)	6,800	5,800	3,700	63,000	36,000	45,000
Am (d/m/g)	1,200	1,000	820	6,800	6,100	7,400
WET SCREENING:	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>
wt %	9	9	11	25	24	24
Pu (d/m/g)	24	30	--	7,400	12,000	11,000
Am (d/m/g)	<5	<5	16	930	1,800	1,900
	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>
wt %	12	13	10	20	27	28
Pu (d/m/g)	140	236	680	49,000	39,000	44,000
Am (d/m/g)	190	40	140	7,000	7,000	8,300

*P-1 to P-6 = Six soil samples obtained from beneath the asphalt pad.

TABLE 13. Attrition Scrubbing and Wet Screening a Composite Soil with Various Solutions*

Solution	4.0- to 0.4-mm Samples (wt %)	Pu (d/m/g)**	Am (d/m/g)
Water ^a	96.7	740	120
Water	79.5	130	32
Water	78.8	120	25
Hot Water (~80 °C)	80.1	180	35
Anionic Surfactant ^b	85.0	220	47
Cationic Surfactant ^c	79.5	170	36
Detergent ^d	86.9	460	61
0.1M Oxalic Acid	78.8	68	21
0.1M Citric Acid	--	160	32
0.1 wt % Sodium Silicate	--	150	27
5 wt % Calgon ^e	82.1	140	18
10 wt % Calgon	80.5	66	15

*Composite soil of weighted portions of six samples from under the asphalt pad. 4.0 to 0.4 mm. Pu = 3700 d/m/g; Am = 630 d/m/g.

**d/m/g - disintegrations per minute per gram.

- a. No attrition scrubbing
- b. Sodium dioctyl sulfosuccinate
- c. Alkylamine-guanidine polyoxyethanol
- d. Basic H, Shaklee Products Company
- e. Sodium hexametaphosphate

TABLE 14. Results of C-Ring Tests on
As-Received 5083 Aluminum

<u>Sample Set Number</u>	<u>Identification</u>	<u>Number of C-Rings Tested</u>	<u>Number of Visual Failures</u>	<u>Average Time to Failure (days)</u>
1	Batch A000763 (1.0 in. thick)	9	3	6
2	Alcoa 5083-H321 (1.0 in. thick)	9	4	16
3	#153271-3 (0.75 in. thick)	9	7	5

TABLE 15. Stress Corrosion Acceptance Test Results
for 5083 Aluminum Production Parts

<u>Sample Identification</u>	<u>Number of C-Rings Tested*</u>	<u>Number of Visual Failures</u>	<u>Average Time to Failure (days)</u>
4A2	8	7	5
1-2	8	4	5
6E-2	8	7	5
7A2	8	5	5

*Eight C-rings is the maximum number of specimens that can be machined from each production part.

TABLE 16. Compatibility Test Materials and Metals

<u>New Process Materials</u>	<u>Weapons Metals Tested</u>
3M Adhesive Tape	*
Tuck Adhesive Tape	*
NDT Varnished Part Holder	*
Texaco Rust Proof	*
Chemform 1000 Epoxy	Beryllium
Taylor Hobson Impression Table	Beryllium
Tool Rite H-12-17	6061 Al, 1100 Al, 5083 Al†
Tool Rite J-4-13	6061 Al, 1100 Al, 5083 Al
CX30S Cinn Milacron	304L, S/S††, 21-6-9 S/S, A286 S/S, 6061 Al, 1100 Al, 7075 Al
Sun CS06020	A286 S/S, 304L S/S, 21-6-9 S/S, U - 6.5 Nb
Esterbrook Feltrite Pen (PFR)	A286 S/S, 304L S/S, 21-6-9 S/S, U - 6.5 Nb
RubberJel	Beryllium
Tim Sol	*

*Weapons metals include: 316, 303, 304L, A286, 21-6-9, and 321 stainless steels; 6061, 1100, and 5083 aluminum; U - 6.5 Nb alloy, tuballoy; Monel; and beryllium.

†Incompatible because of tarnish.

††S/S - stainless steel.

TABLE 17. Water-Dye Solutions for Pallet-Container

<u>Pallet-Container Number</u>	<u>Dye Type^a</u>	<u>Dye Concentration</u>	<u>Total^b Volume (litres)</u>	<u>Final pH^c</u>
1&2	Rhodamine B	0.02 g/l	10	8
3&4	Rhodamine WT	0.1 ml/l	10	8
5&6	Pontacyl Carmine	0.1 ml/l	10	8
7&8	Rhodamine WT	0.1 ml/l	10	6.5

- a. All of the dyes were amine hydrochloride base dyes.
- b. After 10 litres were added, the top of the exposed mild steel band was immersed two inches below the fluid surface.
- c. NaOH was used to adjust the pH to 8; H₂SO₄ was used to adjust the pH to 6.5

TABLE 18. Gravimetric Galvanic Corrosion Test Results

<u>Couple Number</u>	<u>Dye Type</u>	<u>Concentration</u>	<u>pH</u>	<u>Corrosion Rate (mpy)*</u>	
				<u>304L S/S**</u>	<u>Lead</u>
207	Rhodamine B	0.02 g/l	8	0	0.13
208	Rhodamine B	0.02 g/l	8	0	0.14
209	Rhodamine WT	0.1 ml/l	8	0	0.06
210	Rhodamine WT	0.1 ml/l	8	0	0.03
211	Pontacyl Carmine	0.1 ml/l	8	0	0.08
212	Pontacyl Carmine	0.1 ml/l	8	0	0.03
213	Rhodamine WT	0.1 ml/l	6.5	0.05	0.06
214	Rhodamine WT	0.1 ml/l	6.5	0.05	0.06

*mils penetration per year

**S/S - Stainless Steel

TABLE 19. Results of 24-Hour Corrosion Tests

<u>Alloy</u>	<u>mpy*</u>	<u>Alloy</u>	<u>mpy</u>
304L	2350	E-Brite 26-1	14
304L welded	1232	Haynes 30-6B	256
316	8	Haynes 30-25	3
316 welded	22	Titanium	894
Inconel 625	0.3	Hastelloy B	0.1
Inconel 600	102	Hastelloy C	0.3
Incoloy 825	2	Hastelloy N	0.5
Incoloy 804	399	Hastelloy G	0.9
Incoloy 800	58		

*mils penetration per year

TABLE 20. Results of 287-Hour Corrosion Test

<u>Alloy</u>	<u>mpy* (welded)</u>	<u>mpy (not welded)</u>
Hastelloy B	0.5	0.35
Hastelloy C	0.25	0.26
Inconel 625	0.23	0.36

*mils penetration per year

TABLE 21. Costs of Packaging and Transporting
Sludge in Plywood Boxes Coated with
Fiberglass Reinforced Plastic

<u>Processing Methods</u>	<u>Process Time (Number of 8-hour shifts per acre-foot of sludge)</u>	<u>Cost per Acre-Foot of Sludge (\$K)</u>
Fixation		
Cement	flexible	495
Chemfix*	flexible	449
Dehydration		
Steam heat in Building 374	750	984
Filtration in Building 774	600	540
Solar evaporation under plastic air sheets	flexible	332
Solar evaporation in a drying chamber	flexible	337
Filter press	flexible	344

*Proprietary process of Chemfix Corporation, Pittsburgh,
Pennsylvania.

TABLE 22. Estimated Biases

1975 Exchange, 1976 Exchange, and Pooled*
(95% statistical confidence level significance)

Biases on Inventory Items

	<u>Ash (% High)</u>	<u>Ash Heels (% Low)</u>
1975 Experiment	+3.8	-4.4 Sept. 1974-Jan. 1975 -5.1 Jan.-May 1975
1976 Experiment	+4.4	-8 overall
Pooled Estimates	+4.1	-6.4

Biases on Current Measurements

	<u>Ash (% High)</u>	<u>Ash Heels (% Low)</u>	<u>USS&C†</u>
1975	+2.9	Unbiased	-
1976	+3.7	-3.0	0
Pooled Estimates	+3.3	-1.5	-

*"Pooled" refers to pooling of the various time periods where each year gets equal weight.

†Unpulverized sand slag and crucibles.

TABLE 23. Estimated Random Error* Standard Deviations of Individual Measurements

	<u>Inventory</u>	
	Standard Deviation for Ash (%)	Standard Deviation for Ash Heels (%)
1975 Experiment	6	3.8 Sept. 1974-Jan. 1975 16.8 Jan.-May 1975
1976 Experiment	7	7.0 overall
Pooled Estimates	6.5	10.0

	<u>Current Measurements</u>		
	Standard Deviation for Ash (%)	Standard Deviation for Ash Heels (%)	Standard Deviation for USS&C† (%)
1975 Experiment	4	6	-
1976 Experiment	6	5	21
Pooled Estimates	5	6	-

*Random error does not include systematic error or anything other than deviations between standard values (by calorimetry) and corrected observed values. The true standard deviation of measurements will be larger because of unaccounted-for errors (systematic or otherwise) that change over time.

†Unpulverized sand slag and crucibles.

TABLE 24. Computer Communications for Radiometric Instrumentation

<u>Computer</u>	<u>Monitors</u>	<u>Number</u>	<u>Purpose</u>
Data Acquisition	Molten Salt	10	Prevent double loading of buttons.
Mod Comp 2/25	NaF Traps	8	Detect saturation of NaF filters.
	Ion-Column Breakthrough	3	Detect ^{241}Am breakthrough on ion-columns.
	LSA* Incinerator	1	Monitor output of LSA incinerator.
	<u>Counters</u>		
Stacker-Retriever PDP 11/45	Can Counters	4	Assay miscellaneous process residues.
	Ge(Li) Package	1	Assay molten salt residues.
	Ge(Li) Liquids	1	Assay dissolver liquids.
	Spent Resin	1	Assay ion column spent resin.
	Oxide	1	Assay calcined oxide.
	Calorimeters	20	Assay metal/oxide receipts and shipments.

*LSA - low specific activity

TABLE 25. Phosphate Recovery from
Na₂CO₃-Catalyst Bed Incineration

	<u>Weight (g)</u>	<u>Percent of Total (%)</u>
Added PO ₄ as TBP	181.1	
Recovered PO ₄		
Primary Bed	179.1	98.9
Cyclone	7.2	4.0
Scrubber	0.4	0.2
		<hr/>
		103.1

TABLE 26. Rotary Kiln Incinerator
Waste Composition

<u>Material</u>	<u>Weight Percent</u>
Paper	39.99
Polyvinyl chloride	7.91
Polyethylene	22.76
Rubber (Neoprene)	18.81
Kerosene	9.47
Tributyl phosphate	1.06
	<hr/>
	100.00

TABLE 27. Calculated Savannah River Laboratory
Incinerator Ash Composition

<u>Oxide</u>	<u>Weight Percent</u>
Aluminum Oxide (Al_2O_3)	22.36
Silicon Dioxide (SiO_2)	33.66
Sodium Oxide (Na_2O)	11.19
Phosphorous Pentoxide (P_2O_5)	6.50
Titanium Dioxide (TiO_2)	7.65
Lead Oxide (PbO)	0.29
Stannic Oxide (SnO_2)	0.24
Ferric Oxide (Fe_2O_3)	0.07
Magnesium Oxide (MgO)	8.05
Calcium Oxide (CaO)	0.02
Chromic Oxide (Cr_2O_3)	0.02
Cadmium Oxide (CdO)	0.02
Zinc Oxide (ZnO)	9.93
Total	100.00

TABLE 28. Waste Blend, Feed, and Product Composition of the Vitrification Process

Waste Blend Composition (wt %)	Feed Composition (includes additives) (wt %)	Product Composition (wt %)
<u>FBI* ASH</u>	NaCl 1.5	<u>GLASS</u> 74.5
Alpha Ash 51.8	Cr ₂ O ₃ 3.2	NaCl 2.0
TBP Ash 1.8	Al ₂ O ₃ 13.7	Cr ₂ O ₃ 4.2
HEPA Ash 10.9	SiO ₂ 20.6	Al ₂ O ₃ 18.4
Organic Resin Ash (future)	Fe ₂ O ₃ 0.3	SiO ₂ 27.6
	CaO 1.3	Fe ₂ O ₃ 0.4
<u>ILW†</u>	Na ₂ O 0.4	CaO 1.7
Diatomite 20.8	MgO 1.9	Na ₂ O 19.4
Mineral Resin 14.7	H ₃ BO ₃ 28.9	MgO 2.6
100.0	Na ₂ CO ₃ 22.8	B ₂ O ₃ 21.9
	Na ₂ SO ₄ 1.5	Na ₂ S 1.1
	Na ₂ PO ₄ 1.2	P ₂ O ₅ 0.7
	H ₂ O 0.8	100.0
	C 1.9	
	100.0	<u>OFF-GAS</u> 25.5
		H ₂ O 45.0
		CO ₂ 55.0
		100.0 100.0

*FBI - Fluidized Bed Incinerator

†ILW - Intermediate Level Waste

TABLE 29. Plutonium Dissolution from Incinerator Ash

<u>Batch</u>	<u>Percent of Plutonium Dissolved</u>				
	<u>HCl^a</u>	<u>HCl^b</u>	<u>HCl-HF^a</u>	<u>HCl-SnCl₂^b</u>	<u>HCl-SnCl₂^a</u>
1(1960) ^c	99	-	98.6	(d)	(d)
2	94	-	(d)	(d)	(d)
3(1970) ^c	87	90	(d)	97.5	96.3

a. Three-hour residence time at boiling.

b. One-hour residence time at boiling.

c. Date ash was generated.

d. These tests were not performed because of good dissolution in HCl and HCl-HF solutions.

TABLE 30. Material Distribution and Decontamination

<u>Element</u>	<u>Element in Fraction (%)</u>			<u>Decontamination Factor</u>
	<u>Effluent</u>	<u>Wash</u>	<u>Eluate</u>	
Pu	0.6	1.5	98.0	--
Sn	0.1	99.7	0.2	496
Cl	78.2	20.8	0.9	122
Fe	52.5	47.4	0.1	1050

TABLE 31. Chemical Milling Solutions Used
For Surface Finish Study

<u>RF Production Solution</u>	<u>LLL Solution</u>
750 ml/l H_3PO_4	50 parts by vol. Lactic Acid
71 g/l CrO_3	40 parts by vol. H_3PO_4
30 ml/l H_2SO_4	10 parts by vol. H_2SO_4
200 ml/l H_2O	10 parts by vol. H_2O
Temp. 70 °C	Temp. 75 °C
<u>Kawecki Berylco Solution</u>	<u>RF Polishing Solution</u>
10% by vol. HNO_3	600 ml/l H_3PO_4
1.5% by vol. HF	150 ml/l H_2SO_4
0.5% by vol. H_2SO_4	50 ml/l HNO_3
Balance H_2O	6 g/l $CuSO_4 \cdot 5H_2O$
Temp. Room Temperature	Balance H_2O
	Temp. 100 °C
<u>MAB-204-M Etchant #1</u>	<u>MAB-205-M Etchant #2</u>
20% by vol. HNO_3	50 g CrO_3
1% by vol. HF	25 ml H_2SO_4
Balance H_2O	450 ml H_3PO_4
Temp. 25-30 °C	Temp. 60 °C

Reagents Used

H_3PO_4	85%
H_2SO_4	96%
HNO_3	70%
HF	50%
CrO_3	99%
Lactic Acid	85%

TABLE 32. Surface Finishes Obtained from
Chemical Milling Coupon Tests

<u>Solution</u>	<u>Finish (microinch^a)</u>		<u>Remarks</u>
	<u>Select S-65</u>	<u>HP 50</u>	
Starting Surface Finish	10	10	
RF Production Solution	17	10	a few craters
LLL Solution	8	4	no surface blemishes
Kawecki Berylco Solution	50	40	very dull finish
RF Polishing Solution	13	5	much cratering in S-65
MAB-205-M Etchant #1	40	13	few blemishes
MAB-205-M Etchant #2	50	40	pitting

a. Arithmetic average of three runs.

TABLE 33. Distribution of Plutonium after Magnetic Separation

	<u>Material Weight (kg)</u>	<u>Total Weight (%)</u>	<u>Plutonium Weight (g)</u>	<u>Total Pu (%)</u>	<u>Plutonium Concentration (g Pu/g material)</u>
Starting material	40.0	100	986	100	0.025
Plutonium-enriched material	4.5	11	846	87	0.186
Crucible	35.5	89	124	13	0.002

TABLE 34. Effect of Wet Ash Hydrofluorination on Plutonium Dissolution

Dissolution without Fluorination

<u>Total Pu^a</u>	=	<u>Pu dissolved</u>	+	<u>Pu remaining in Heel</u>	+	<u>Pu remaining in Filter Pad</u>
231 g		157 g		68 g		6 g
		68.0%		29.4%		2.6%

Dissolution with Fluorination

<u>Total Pu^a</u>	=	<u>Pu remaining in HF filter pad</u>	+	<u>Pu Dissolved</u>	+	<u>Pu remaining in Heel</u>	+	<u>Pu remaining in Filter Pad</u>
320 g		12 g		157 g		145 g		6 g
		3.8%		49.0%		45.3%		1.9%

a. Total material accounted for after dissolution

TABLE 35. Dissolution of Copper-Accelerated
Leco Crucible Residues

Leach Solution	12M HNO ₃ — 0.5M HF with 10M NaOH — 0.1M F ⁻ Preleach	12M HNO ₃ — 0.5M HF	7M HCl — 0.2M SnCl ₂ — 0.5M HF
Temperature	Reflux	Reflux	Reflux
Solid to Liquid Ratio	1:10	1:10	1:10
Residence Time	2 hours each pass	2 hours each pass	2 hours
Contacts with fresh solution	1 NaOH 2 HNO ₃	2	1
Total Residue Dissolved (%)	55	23	16
Plutonium Dissolved (%)	99	97	99
Plutonium in Heel (%)	1*	3*	1*

*g Pu/g solid ranged from 2×10^{-4} to 9×10^{-4} g/g

TABLE 36. Detectable Impurities in Americium Oxide

<u>Impurity</u>	<u>First Sample* (ppm)</u>	<u>Short Process Product (ppm)</u>	<u>Full Process Product (ppm)</u>
Ag	<10	<10	<10
Al	5000	<10	<10
Ca	50	<10	100
Fe	300	<10	<50
K	<10	100	100
Mg	<10	<10	100
Pb	1000	420	<10
Pu		1850	410
Si	100	100	50
Tm	300	<50	<50
Y	300	100	100

*After dissolution and one oxalate precipitation.

TABLE 37. Operating Conditions for
Conversion of $^{238}\text{PuO}_2$ to PuF_4

<u>Starting PuO_2 Weight (g)</u>	<u>Final PuF_4 Weight (g)</u>	<u>Conversion to PuF_4 (%)</u>	<u>Starting Neutron Flux (counts/min)</u>	<u>Ending Neutron Flux (counts/min)</u>
7.1	7.9	98.7	10,000	58,000

TABLE 38. Composition of Reduction Charge

<u>$^{238}\text{PuF}_4$ (g)</u>	<u>WR Stream Isotopic PuF_4 (g)</u>	<u>Total Pu (g)</u>	<u>Calcium (g)</u>	<u>Iodine (g)</u>	<u>Calcium Chloride (g)</u>
7.9	45.4	41.3	22.3	21.8	3.8

TABLE 39. Analysis of Plutonium-238
Enriched Metal Rod

A. Mass Spectrographic Isotopic Analysis

<u>Isotope</u>	<u>Weight Percent</u>
Pu-238	11.359
Pu-239	82.753
Pu-240	5.475
Pu-241	0.375
Pu-242	0.038

B. Emission Spectrographic Impurity Analysis*

<u>Element</u>	<u>Content (g/g Pu)</u>
Al	105
B	5
Be	0.2
Ca	300
Cr	50
Cu	1,000
Fe	123
Ga	73
Mg	10
Mn	35
Ni	2,000
Si	131
Ti	5

*Only detectable impurities are listed. Elements not listed were below detection levels for the method used.

TABLE 40. Level 1 Ash Heel Processing -
Line 23

<u>Time Period</u>	<u>Input</u>		<u>Output (Heels)</u>		
	<u>Net (kg)</u>	<u>SS* (kg)</u>	<u>Net (kg)</u>	<u>SS (kg)</u>	<u>Discard (%)</u>
4th Qtr '76	893.7	6.8	724.2	2.3	99.5
Jan/Feb '77	846.0	6.0	676.0	2.3	99.5

*SS - stainless steel