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Printed
November 8, 1978

RFP-2803
November 8, 1978

MASTER

CHEMISTRY RESEARCH AND DEVELOPMENT
PROGRESS REPORT
FOR JULY 1977 THROUGH APRIL 1978

Frend John Miner

Chemical Research ------------------- James D. Navratil
Process Chemistry and Engineering ----------- Edward D. Erickson

Rockwell International

Energy Systems Group
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

U. S. DEPARTMENT OF ENERGY
CONTRACT DE-AC04-76DPO3533

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 Microfiche $3.00
Price Is Subject to Change Without Notice

RFP-2803
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RFP-2803
UC-4 CHEMISTRY
TID-4500-R66

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ROCKWELL INTERNATIONAL
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GOLDEN, COLORADO 80401

Prepared under Contract DE-AC04-76DPO3533
for the
Albuquerque Operations Office
U.S. Department of Energy

SUBJECT DESCRIPTORS

Actinides
Adsorption
Alkali Metals
Americium
Americium Recovery
Ash Fusion
Calorimeters
Chromatography
Crucibles
Dissolution
Distillation
Electrorefining
Enthalpy of Formation
Formic Acid
Hydrochloric Acid
Incinerator Ash
Ion Exchange
Leaching
Materials Recovery
Molten Salt Residues
Molten Salts
Plutonium
Plutonium Dissolution
Plutonium Fluoride
Plutonium Hydrides
Plutonium Metal
Plutonium Nitrates
Plutonium Peroxide
Plutonium Processing
Plutonium Recovery
Plutonium Residues
Precipitation
Purification
Pyrochemical Process
Radioactive Waste Processing
Radioactive Wastes
Recovery
Reverse Osmosis
Separation Processes
Soils
Solvent Extraction
Specific Heat
Thermodynamic Properties
Tilt-Pour Furnace
Tin
Tributyl Phosphate
Tungsten
Uranium
Vacuum Furnace
Waste Management
Waste Processing
Zinc

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CALORIMETRY AND THERMODYNAMICS OF NUCLEAR MATERIALS 1

Investigations into the thermodynamic properties of plutonium metal and the plutonium-hydrogen system are currently underway. A compilation of the thermodynamic properties of all actinide materials is also in progress. In addition several miscellaneous production and process problems are being investigated from a thermodynamic viewpoint. (DDS Endeavor 112*)

ACTINIDE RECOVERY AND PURIFICATION 2

Several process methods are being evaluated for actinide recovery efficiency and product purification. The formate system was evaluated but rejected as a possible process because of concentration requirements and reactivity with nitric acid. (DDS Endeavor 113)

OPTIMIZATION OF THE CATION EXCHANGE PROCESS FOR RECOVERING AMERICIUM AND PLUTONIUM FROM MOLTEN SALT EXTRACTION RESIDUES 3

A program was begun to optimize the cation exchange process used to recover americium and plutonium from molten salt extraction (MSE) residues. Preliminary results show that macroporous resin is more efficient than gel-type resin. (DDS Endeavor 113)

DECONTAMINATION OF SOIL 3

Primary and secondary processes have been tested to reduce the volume of Rocky Flats soil contaminated with plutonium and americium. (DDS Endeavor 331)

SECONDARY ACTINIDE RECOVERY 5

Bidentate organophosphorous extractants and extraction chromatography techniques were tested for their effectiveness in removing plutonium and americium from acidic process waste streams. (DDS Endeavor 333)

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1980 Proposed Program for Process Development (NM-01-04) and Related Work, CD 77-4282, December 30, 1977. Production and Production Support programs are identified as PPS.

EVALUATION OF TRIBUTYL PHOSPHATE-IMPREGNATED SORBENT FOR PLUTONIUM-URANIUM SEPARATIONS 7

Bayer AG Lewatit® OC-1023, a macroporous sorbent impregnated with tributyl phosphate, was tested for the separation of uranium and plutonium from mixed actinide residues. (DDS Endeavor 333*)

COMPARISON OF CATION EXCHANGE RECOVERY OF ACTINIDES FROM THE NaCl-KCl-$MgCl_2$ AND $CaCl_2$-KCl-$MgCl_2$ SYSTEMS 8

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COMBINED ANION EXCHANGE-BIDENTATE ORGANOPHOSPHOROUS EXTRACTION PROCESS FOR MOLTEN SALT EXTRACTION RESIDUES 8

A combined anion exchange-bidentate organophosphorous solvent extraction process is being tested on a pilot-plant scale for separating plutonium and americium from molten salt extraction (MSE) residues. (DDS Endeavor 333)

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The recovery of actinides from combustible wastes by leaching or fusion methods is being investigated. The information gained will be used by the Department of Energy and by Oak Ridge National Laboratory to help determine the feasibility of partitioning actinides from waste. (ORNL subcontract)

ACTINIDE RECOVERY AND RECYCLE PREPARATION FOR WASTE STREAMS 12

The program was completed for determining the feasibility of removing actinides from secondary aqueous waste streams likely to be produced during reactor fuel fabrication and reprocessing. Methods for the salt waste and wastewater streams and recycle preparation problems were evaluated. (ORNL subcontract)

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1980 Proposed Program for Process Development (NM-01-04) and Related Work, CD 77-4282, December 30, 1977. Production and Production Support programs are identified as PPS.

PROCESSING CHEMISTRY AND ENGINEERING

PROCESSING LECO CRUCIBLE RESIDUES CONTAINING A TIN ACCELERATOR 16

The recovery of plutonium from Leco crucible residues containing tin accelerator was studied. Results show that HCl-HF and HCl-HF-$SnCl_2$ give 98% and 99.5% plutonium dissolution respectively with discardable heels after one contact with the solution. Three contacts were needed to achieve 96% plutonium dissolution with HNO_3-HF; the heels were above the discard limit. (DDS Endeavor 331*)

DISSOLUTION OF REFRACTORY RESIDUES IN HYDROCHLORIC ACID 17

A study was made of the dissolution characteristics of refractory residues in hydrochloric acid solutions. To make hydrochloric acid dissolution feasible and to make the solutions compatible with current production processes, a method of chloride removal is necessary. Several procedures for removal of chloride ion were investigated. (DDS Endeavor 331)

METAL DISTILLATION 20

Two furnaces are used to separate metals from plutonium alloys by distillation. One furnace, which is operational, is used to remove the high-vapor-pressure metals such as zinc, magnesium, and calcium. This step has been successfully demonstrated. The second furnace is designed to separate americium from plutonium-americium alloys. It is being installed. (DDS Endeavor 332)

INDUCTION-HEATED, TILT-POUR FURNACE 21

The induction heated, tilt-pour furnace is being used to demonstrate various pyrochemical processes. During this report period, the furnace was used to recover plutonium and americium from molten salt extraction salt (salt cleanup) and to consolidate metal product, under a molten salt cover, from Step 1 and Step 3 cleanup operations. (DDS Endeavor 332)

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1980 Proposed Program for Process Development (NM-01-04) and Related Work, CD 77-4282, December 30, 1977. Production and Production Support programs are identified as PPS.

PLUTONIUM RECOVERY FROM BACKLOG SALTS 22

The salt cleanup process has been modified, which eliminates two steps. Instead of performing a zinc chloride oxidation and calcium reduction on the Step 1 alloy, the Step 1 zinc-magnesium alloy is being loaded to ~35% in plutonium and americium. The alloy buttons that are produced are being consolidated in the tilt-pour furnace to eliminate salt occulsions. The buttons also are being moved directly to the vacuum melting step. (DDS Endeavor 332*)

PLUTONIUM PEROXIDE PRECIPITATION PROCESS 23

Plutonium peroxide precipitation, using ion column eluate as feed, is being studied. The existing process in the plutonium recovery facility cannot use this material as feed with acceptable efficiency. Process and equipment changes are being evaluated to provide an acceptable process. (PPS)

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1980 Proposed Program for Process Development (NM-01-04) and Related Work, CD 77-4282, December 30, 1977. Production and Production Support programs are identified as PPS.

PREFACE

Previous Chemistry R&D progress reports have included work from all of the groups within Chemistry R&D. Beginning in January 1978, this format was changed. Progress reports are now being published in three sections on the following time schedule:

Chemistry R&D	Date
Product Integrity and Surveillance (plus classified work from Process Chemistry and Engineering)	January and July
Chemical Research, and Process Chemistry and Engineering	May and November
Component Development, Pilot Plant, and Instrumentation and Statistical Systems	June and December

The Product Integrity and Surveillance Report will be the only one classified.

Reports previously issued in this series are as follows:

RFP-1837-A	Period Ending December 31, 1971
RFP-1921-A	Period Ending August 30, 1972
RFP-2004-A	Period Ending December 31, 1972
RFP-2102-A	Period Ending June 30, 1973
RFP-2200-A	Period Ending December 31, 1973
RFP-2276-A	Period Ending June 30, 1974
RFP-2360-A	Period Ending December 31, 1974
RFP-2417-A	Period Ending June 30, 1975
RFP-2464	Period Ending December 31, 1975
RFP-2546	Period Ending June 30, 1976
RFP-2640	Period Ending December 31, 1976
RFP-2680-A	Period Ending June 30, 1977

The reports listed above with an "A" suffix are unclassified. A report containing classified information exists for each comparable time period. The classified reports have the same RFP number but without the "A" suffix.

PUBLICATIONS AND TECHNICAL PRESENTATIONS

C. T. Illsley, R. L. Kochen, and J. D. Navratil. *Removal of Actinides from Contaminated Soil.* RFP-2565. Presented at the American Association for the Advancement of Science meeting in Denver. February 20-25, 1977.

P. G. Hagan and F. J. Miner. *Recovery of Americium and Plutonium from Molten Salts by Carbonate Precipitation.* RFP-2397. Presented at 173rd ACS National Meeting, New Orleans. March 21, 1977.

C. E. Alford and J. D. Navratil. *Evaluation of Extraction Chromatography for Americium Recovery.* RFP-2625. Presented at the Colorado-Wyoming Academy of Sciences meeting, Air Force Academy. April 22, 1977.

J. D. Navratil and C. E. Baldwin. *Recovery Studies for Plutonium Machining Oil Coolant.* RFP-2579. Rockwell International, Rocky Flats Plant. April 27, 1977.

J. D. Navratil, S. G. Proctor, and L. L. Kirkby. *Computerized Mathematical Model for the Anion Exchange Processing of Plutonium(IV).* RFP-2572. Rockwell International, Rocky Flats Plant. May 9, 1977.

J. D. Navratil and H. F. Walton. "Ion Exchange and Liquid Chromatography," *Chemistry* 50:18 (1977).

F. L. Oetting and M. H. Rand. *Thermodynamic Properties of* UO_{2+x}. International Colloquium of Refractory Oxides for High Temperature Energy Sources, Odeillo, France. June 28 to July 1, 1977.

J. D. Navratil. *Evaluation of Anion Exchange Resins for Preanalysis Separations of Actinides.* RFP-2682. Presented at the 19th Annual Conference on Analytical Chemistry, Denver. August 1, 1977.

J. D. Navratil and R. G. Leebl. *Evaluation of Anion Exchange Resins for Processing Plutonium - Neptunium Residues.* RFP-2657. Rockwell International, Rocky Flats Plant. August 20, 1977.

J. D. Navratil, R. E. Sievers, and H. F. Walton. "Open-Pore Polyurethane Columns for Collection and Preconcentration of Polynuclear Aromatic Hydrocarbons from Water." *Anal. Chem.* 49:2260 (1977).

G. H. Thompson, D. L. Cash, E. L. Childs, J. D. Navratil, L. L. Martella, and C. E. Plock. *Waste Management Analysis for the Nuclear Fuel Cycle - Parts I and II, Progress Report for Period Ending March 31, 1977.* RFP-2667. Rockwell International, Rocky Flats Plant. September 21, 1977.

J. D. Navratil and R. E. Sievers. "Chemical Separations With Open-Pore Polyurethane." *Amer. Lab.* October 1977.

K. R. Souply and W. E. Sperry. *Screw Calciner Mechanical Direct Denitration Process for Plutonium Nitrate to Oxide Conversion.* RFP-2601. Rockwell International, Rocky Flats Plant. October 14, 1977.

G. D. Lehmkuhl. *Alternate Fuel Cycle Technologies Nitrate-to-Oxide Conversion Project Progress Report January-June 1977.* RFP-2591. Rockwell International, Rocky Flats Plant. September 2, 1977.

J. S. Vrentas, J. L. Duda, and G. D. Lehmkuhl. "Characteristics of Radial Transport in Solid-Liquid Slug Flow," *Industrial and Engineering Chemistry Fundamentals,* Vol. 17, No. 1, February 1978.

CHEMISTRY RESEARCH AND DEVELOPMENT PROGRESS REPORT FOR JULY 1977 THROUGH APRIL 1978

Frend John Miner

CHEMICAL RESEARCH

James D. Navratil

CALORIMETRY AND THERMODYNAMICS OF NUCLEAR MATERIALS

Franklin L. Oetting

Objective

The primary 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 for use in the design of nuclear reactors.

Prior Work

Experimental high-temperature enthalpy data have been obtained for PuC, Pu_2C_3 and PuO_2. A program for the compilation and critical evaluation of the thermodynamic properties of actinide materials was initiated several years ago and is being continued.

A program that uses adiabatic and solution calorimetry has been initiated to determine the thermodynamic properties of the plutonium-hydrogen system. Rocky Flats obtained the basic hardware for an adiabatic calorimeter from the National Bureau of Standards, Washington, D.C. on a loan basis and initiated the installation in existing facilities of a glove box for the solution calorimeter.

Achievements and Discussion

A thermodynamic analysis was made of the total energy release for the reaction of plutonium metal and two degreasing solvents, carbon tetrachloride and Freon* TF. These energy effects were compared to similar energy releases by the reaction of aluminum and the two solvents. These degreasing solvents evolve comparable heat when formed from their elements and are thus considered stable; however, their reaction with plutonium and aluminum form compounds that are much more stable and evolve much more heat. Thermodynamic analysis gives only the potential energy release. The rate at which the reactions proceed was not considered.

A thermodynamic calculation was made on the hydrofluorination of PuO_2 contaminated with significant amounts of $Pu(SO_4)_2$. Specifically it was concluded that PuF_4 is the only plutonium fluoride formed in the hydrofluorination process. In preference to PuF_4, other fluorides such as PuF_3, PuF_6, and PuOF do not have the stability to exist under the given conditions. Analysis also indicates that PuF_4 is more apt to form at lower temperatures (below 400 ±100 °C). Above this temperature, PuF_4 will not be a product. If the removal of $Pu(SO_4)_2$ is a necessary criterion for increasing the yield of plutonium metal from the hydrofluorination process, removal of the sulfate can only be accomplished by a two-step process: decomposition of the sulfate at temperatures exceeding 650 °C and subsequent hydrofluorination of the decomposition product, PuO_2.

Significant progress has been made on the design and construction of the adiabatic calorimeter. Construction and installation of the heaters, thermopiles, power supplies and proportional controllers for the adiabatic shield, inner guard, and outer

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*Trademark of DuPont, E. I., de Nemours and Co., Inc., 1007 Market Street, Wilmington, Delaware.

guard have been completed. Work is continuing on (a) completion of the wiring from the heaters and sensors to the power supplies and proportional controllers, (b) design and construction of the calibration heaters, (c) design and construction of the sample container, (d) construction of a new adiabatic shield lid, and (e) design and construction of a power safety shutdown system for the adiabatic calorimeter. The target date for this calorimeter to be operational is Easter 1978.

The installation of a solution calorimeter that will be used to measure the enthalpy of formation of compounds in the plutonium-hydrogen system has been delayed until installation of a glove box.

Future Work

Papers dealing with the thermodynamic properties of the plutonium-carbon system and the plutonium-oxygen system will be prepared and submitted for publication. Thermodynamic properties of plutonium metal and the plutonium-hydrogen system will be measured experimentally. Consultation and evaluation of thermodynamic data will continue.

ACTINIDE RECOVERY AND PURIFICATION

Gary H. Thompson

Objective

The objective is to recover actinides from residues and to decontaminate the recovered actinides so subsequent processing will provide a pure product.

Prior Work

Prior work has been done at Rocky Flats to recover actinides from molten salt extraction (MSE) residues by ion exchange, solvent extraction, and/or precipitation. Previous work also included attempts to remove lead from americium product by oxalate, sulfide, or sulfate precipitation; metal reductor columns; and metathesis of oxalate to hydroxide.

Achievements and Discussion

An investigation was made concerning the recovery of plutonium and americium from MSE residues by precipitation as the formate. The solubility of plutonium(III) formate in various formic acid—formate ion solutions was determined. Plutonium (III) solubility was 53 mg/l in 15*M* formic acid and 15 mg/l in 23.5*M* (concentrated) formic acid. Plutonium(III) solubility was 27 mg/l in $\geqslant 0.2M$ formate ion in $\geqslant 1M$ formic acid. Plutonium and americium recoveries from MSE (magnesium-aluminum) alloys were 96% and 99%, respectively, with decontamination factors* (DFs) of 645 for magnesium and 156 for aluminum. Initial recovery of plutonium and americium from MSE waste salts was only 64% and 91% for plutonium and americium, respectively, but with excellent DFs for potassium (1×10^4), sodium (1×10^4), and magnesium ($>9.2 \times 10^3$), and a fair DF (22) for lead. Postprecipitation increased plutonium recovery to 93.3% and americium recovery to 98.5% but with drastic reduction in decontamination because of occluded contaminants.

There are two serious disadvantages in the use of formic acid and formate ion to recover actinides. The first is the large concentration (relative to oxalic acid) of formic acid or formate ion required to precipitate the actinides. The second is the reaction between formic and nitric acids. This reaction becomes violent if concentrated solutions are mixed; nitrogen oxides are evolved. Although nitric acid is not used in the formate process, formate and nitric acid solutions from current processes would meet during waste processing unless special precautions were taken. No further work on formate is planned.

Future Work

Work is in progress to demonstrate actinide purification, especially americium, by modifying the oxalate precipitation process. Digestion time and acidity may be varied to decontaminate from some species (e.g., lead). Other purification methods to be considered will include ion exchange and special precipitants (e.g., fluoroborate).

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*Decontamination factor (DF) = $\frac{\text{weight of contaminant in feed}}{\text{weight of contaminant in product}}$

OPTIMIZATION OF THE CATION EXCHANGE PROCESS FOR RECOVERING AMERICIUM AND PLUTONIUM FROM MOLTEN SALT EXTRACTION RESIDUES

Gary H. Thompson, David L. Cash,
and C. Michael Smith

Objective

The objective is to optimize the cation exchange process used for recovering americium and plutonium from molten salt extraction (MSE) residues.

Prior Work

Prior work has been done at Rocky Flats to develop the process currently used to recover actinides from MSE residues. This process has not been optimized, however. Although resin evaluation for the anion exchange process has been done, no evaluation of resins for the cation exchange process has been made.

Achievements and Discussion

During the course of evaluating the effect of a proposed change to a $CaCl_2$–KCl–$MgCl_2$ MSE system (reported elsewhere in this report), it was noticed that plutonium elution from Dowex* 50W-X8 resin is slow and incomplete. Americium elutes more rapidly and recovery is better.

Plutonium is adsorbed on the column as Pu(III). It is removed by elution with 7*M* HNO_3, which oxidizes the Pu(III) to Pu(IV) and causes formation of the hexanitrato complex, $Pu(NO_3)_6{}^{2-}$. This complex, being anionic, is not adsorbed on cation exchange resin. Plutonium (Pu^{4+}) is tightly held, however, until $NO_3{}^-$ diffuses into the resin matrix and forms the hexanitrato complex. Once formed, this bulky complex has difficulty diffusing out through the resin matrix. The process should be made easier by using a gel-type resin of lower cross-linkage, or a macroporous resin (in which the porosity decreases the distance to be traveled through the matrix until an open channel is reached).

Seven ion-exchange tests were made on resins of 50-100 mesh particle size. A waste solution prepared from MSE residues was fed to the column until breakthrough. The adsorbed actinides were washed with water and eluted with 4.2 column volumes of 7*M* HNO_3 (630 ml); 4.2 column volumes is the average volume required for actinide recovery in production columns. The resins, waste solutions, and actinide recovery are shown in Table 1 (page 4). Actinide capacity and plutonium recovery were best with Bio-Rad AG MP-50 resin; the reason for poorer americium recovery from this resin is unknown.

Future Work

From the viewpoint of capacity and elution rate, the macroporous resin appears to be the better resin. Additional resin evaluation will be done. Other parameters will be examined to optimize the process. These will include elutriant concentration, flow rates, wash media, and valence adjustment in addition to loading and elution techniques.

DECONTAMINATION OF SOIL

Robert L. Kochen and James D. Navratil

Objective

The objective of this program is to further 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

A process consisting of attrition scrubbing and wet-screening was developed to reduce the volume of Rocky Flats soil contaminated with plutonium and americium. The process reduced the volume of contaminated soil by approximately 65 percent.

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*Trademark of The Dow Chemical Co., Abbott Rd., Midland, Michigan.

TABLE 1. Actinide Elution From Cation Exchange Resin

Column Volume (CV): 150 ml
Elutriant: 7*M* HNO_3
Flow Rate: 0.85 ml/(min cm^2) or
(6 ml/min)

Volume of Elutriant: 630 ml (4.2 CV)
Temperature: 23 °C

Resin[b]	Type of MSE Waste[c]	Actinide in Feed		Actinide Recovery[a]	
		Pu (g)	Am (g)	Pu (%)	Am (%)
Dowex 50 W-X8	Na-K-Mg	4.60	0.220	58.2 ±1.5	94.6 ±0.1
Dowex 50 W-X8	Ca-K-Mg	3.44	0.143	68.8 ±1.1	88.7 ±0.1
Dowex 50 W-X4	Na-K-Mg	2.19	0.105	99.6	99.4
Bio-Rad AG MP-50	Na-K-Mg	5.94	0.284	91.3	66.2
Bio-Rad AG MP-50	Ca-K-Mg	5.21	0.217	93.0	79.8

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[a] Mean percent plus or minus standard deviation on duplicate samples or single determination

[b] Dowex 50W-X8 and -X4 are gel-type resins; AG MP-50 is a macroporous resin.

[c] Waste chloride solutions containing either Na, K, and Mg or Ca, K and Mg.

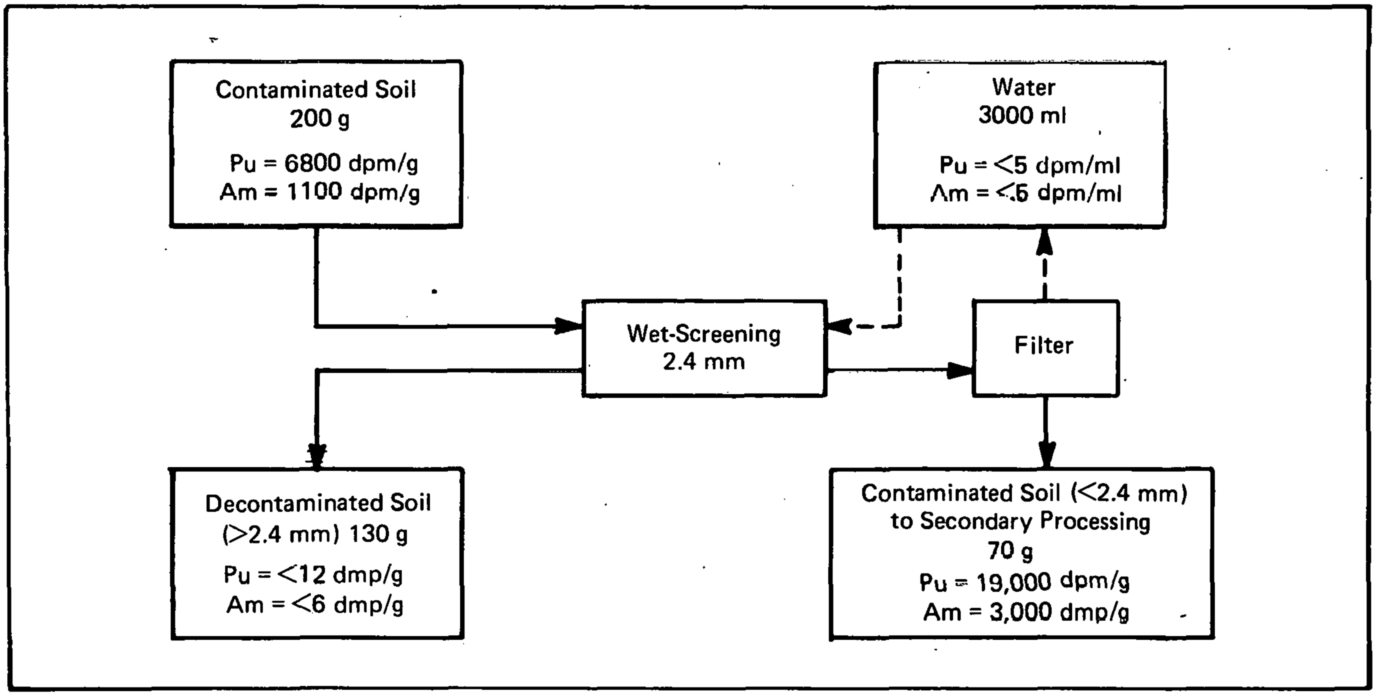

FIGURE 1. Conceptual Primary Process

Various reagents were also tested to aid in dispersing and decontaminating the soil. The reagents that improved the process were solutions of oxalic acid and sodium hexametaphosphate.

Achievements and Discussion

A conceptual flow sheet for the primary soil decontamination process is shown in Figure 1. This

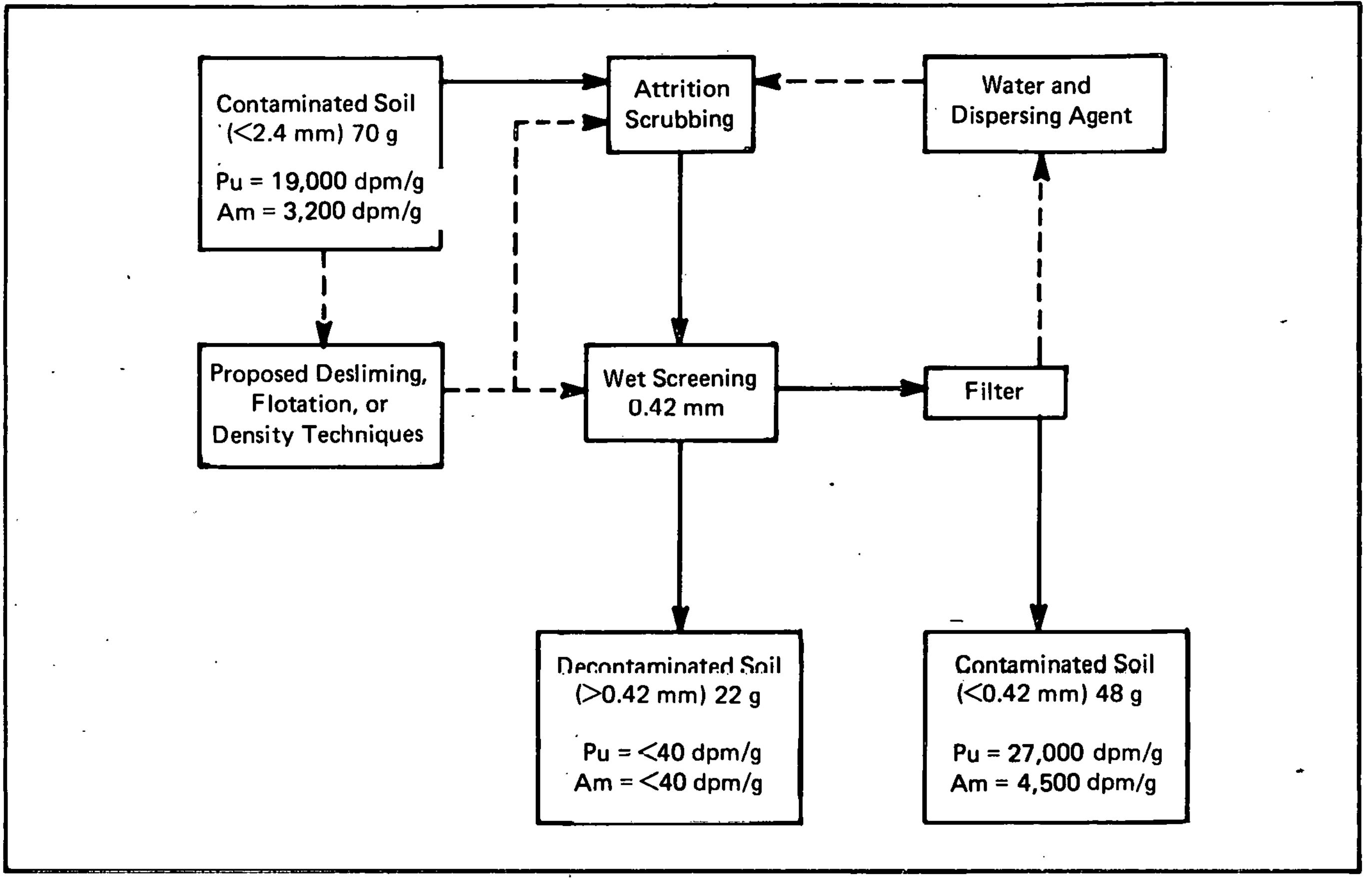

FIGURE 2. Candidate Secondary Processes

proposed process appears to be the most efficient and simplest method for volume reduction of Rocky Flats soil. The process, verified on a laboratory scale, decontaminated 65 wt % of the soil to below proposed limits (<40 dpm/g). Solids were easily removed from the process water by filtration with Whatman 42 filter paper. The plutonium and americium concentrations were both <5 dpm/ml in the filtered water; this degree of concentration is acceptable for process reuse.

Further volume reduction of contaminated soil fractions from the primary process could be accomplished using the secondary treatment methods shown in Figure 2. The attrition scrubbing and wet screening, using a dispersing agent of either oxalic acid or sodium hexametaphosphate, gave further volume reduction of the contaminated fraction. Preliminary experiments using desliming operations, separation with high-density liquids, and flotation techniques gave inconclusive results.

Future Work

Verification of the primary process on a larger scale is planned. Secondary methods planned for further evaluation include foam flotation, density separation, and improved scrubbing-sieving techniques.

SECONDARY ACTINIDE RECOVERY

Charlotte E. Alford, Paul G. Hagan,
and James D. Navratil

Objective

The objective is to develop a process for recovering low-level concentrations of plutonium and americium from acidic process waste streams.

TABLE 2. DHDECMP and Americium Capacities of Supports

Support	DHDECMP Capacity (g DHDECMP/ml dried support)	Am Capacity[a] (μg Am/ml support)
Amberlite® XAD-4	0.34	1.0
Amberlite XAD-7	0.32	0.02
Poly M Phenyl Ether[b]	0.29	2.1
Amberlite XAD-1	0.24	0.01
Bio-Rad® SM-2	0.24	0.01
Amberlyst® A-26	0.24	0.004
Amberlite XAD-2	0.22	0.02
Amberlite IRA-93	0.22	0.01

a. Capacity when americium concentration ratio of effluent-to-feed is 0.1.

b. 80 to 100 mesh beads; all others 20 to 50 mesh.

Prior Work

The bidentate organophosphorous extractant, DHDECMP (dihexyl-N,N-diethylcarbamoylmethylene 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 could be used rather than the more expensive solvent extraction equipment.

Over 30 support materials were evaluated for DHDECMP capacity. Amberlite* XAD-4, a macroreticular sorbent, was chosen as a means of determining americium capacity and elution behavior. This sorbent was selected because of its relatively high DHDECMP capacity and low extractant losses. Preliminary results, however, indicated the americium capacity and elution behavior of the DHDECMP-loaded XAD-4 was too unfavorable for large-scale use.

Achievements and Discussion

Support materials with the highest DHDECMP loading, as determined from previous studies, were tested for americium breakthrough capacity. The results are shown in Table 2.

The supports tested gave orders-of-magnitude lower americium capacity than theoretically possible with DHDECMP by itself. Apparently the DHDECMP is sterically hindered when attached to the support materials, and this prevents effective coordination with americium. Extraction chromatography techniques using DHDECMP do not appear feasible for large-scale, secondary actinide recovery processing because of the low americium capacity. The technique would certainly be useful, however, for analytical chemistry separations.

The use of DHDECMP by itself, using extraction contactor equipment, is a feasible method for secondary actinide recovery. Previous results were verified, on a laboratory scale, by using a different batch of impure DHDECMP (63%) to remove plutonium and americium from acidic process waste. Results of that test show that for each extraction cycle, the plutonium concentration is lowered by a factor of 5, and the americium concentration is lowered by a factor of 2. Since the current goal is a reduction of actinide loss to the process waste stream to levels of 10^{-5} g/l, it appears the use of DHDECMP extractant would accomplish this goal.

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*Trademark of Rohm and Haas Co., Independence Mall West, Philadelphia, Pennsylvania.

TABLE 3. Results of Plutonium-Uranium Separations Using Lewatit OC-1023

Flow Rate: 2 ml/(cm² min)

Feed U(g/l)	Composition Pu(g/l)	Column Dimensions dia × height(cm)	Uranium Breakthrough Capacity[b]	Effluent U/Pu (μg/g)	Pu on Column (% of total)[a] Before Wash	After Wash	Uranium Elution[c]
0.07	11	1.2 × 15	2	180	45	41	17
2.4	24	1.2 × 20	41	2100	10	8	15

a. Thirteen column volumes of wash solution passed.
b. Grams of uranium fed to one liter of support when the ratio of the uranium concentration in the effluent to feed reached 0.05.
c. Column volumes of 1*M* $(NH_4)_2SO_4$ to elute 100% of uranium from the support.

Future Work

The secondary actinide recovery process for removing plutonium and americium from acidic process waste streams will be verified on a larger scale.

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 are presently processed by a modified Purex solvent extraction technique.

Prior Work

Bayer AG Lewatit® OC-1023, which is a new commercial extraction chromatography support impregnated with tributyl phosphate (TBP), was tested for uranium-plutonium separation using modified Purex processing conditions. Uranium breakthrough capacity and elution behavior were determined for the OC-1023. Results of uranium breakthrough capacity indicated that the support had a high capacity for 10 g/l uranium feed. The total uranium capacity of the support was determined to be ~65% of the theoretical TBP capacity.

Achievements and Discussion

Extensive washing and elution studies were performed on the Lewatit OC-1023. For the washing determinations, the OC-1023 was loaded into laboratory-scale ion exchange columns. The support was first conditioned with 5*M* HNO_3 - 0.1*M* $Fe(SO_3NH_2)_2$. Synthetic feeds containing plutonium-uranium in 5*M* HNO_3 - 0.1*M* $Fe(SO_3NH_2)_2$ were fed to the columns. The residual plutonium on the support was removed by washing with 0.35*M* HNO_3 - 0.1*M* $Fe(SO_3NH_2)_2$. The uranium sorbed on the support was then eluted with 1*M* $(NH_4)_2SO_4$. Fractions of the effluent, wash, and eluate were collected and analyzed for uranium and plutonium.

Representative results of uranium capacity, washing, and elution tests using Lewatit OC-1023 are shown in Table 3. The results show that the support has a high capacity for 25 g/l plutonium - 2.5 g/l uranium feeds. The total uranium capacity of the support under these conditions was determined to be ~53% of the theoretical TBP capacity. The uranium breakthrough capacity decreased substantially in the runs with 10 g/l plutonium - 0.1 g/l uranium feeds. This was apparently caused by low uranium concentration in the feed. The uranium content of the effluent was below required limits.

The washing results, shown in Table 3, show that all of the plutonium cannot be washed from the column. The presence of dibutyl phosphate on the OC-1023 apparently prevented complete plutonium removal.

The uranium elution results, also shown in Table 3, show that the uranium can be eluted with a minimum of eluant; however, the plutonium-uranium ratio of the eluted uranium exceeds the maximum allowable limits. This apparently was caused by insufficient washing and the presence of dibutyl phosphate, which retains the plutonium.

Future Work

Tests will be run in which the Lewatit OC-1023 is treated to remove any dibutyl phosphate that might retain plutonium. Another support containing TBP will also be evaluated to obtain extraction chromatography data for comparison with the solvent extraction process.

COMPARISON OF CATION EXCHANGE RECOVERY OF ACTINIDES FROM THE $NaCl$-KCl-$MgCl_2$ AND $CaCl_2$-KCl-$MgCl_2$ SYSTEMS

Gary H. Thompson, David L. Cash,
Everett L. Childs, and C. Michael Smith

Objective

The objective of the program is to evaluate the effect of changing from a $NaCl$-KCl-$MgCl_2$ system currently used in pyrochemical purification of plutonium metal to a proposed $CaCl_2$-KCl-$MgCl_2$ system. A higher mole percent of $CaCl_2$ is required compared to that of NaCl, and divalent calcium competes more effectively for ion exchange sites than monovalent sodium. For these reasons, an appreciable amount of calcium is expected to follow americium through the process and contaminate the final AmO_2 product.

Prior Work

A large amount of work has been done at Rocky Flats on pyrochemical purification of plutonium and on recovering plutonium and americium from molten salt extraction (MSE) waste salts. Previous MSE salt containing $CaCl_2$ used less $CaCl_2$, however, than is now proposed (45 vs 80 mole percent), and no evaluation of the difficulties this proposed increase could cause for actinide recovery has been made.

Achievements and Discussion

Solutions obtained by solubilizing $NaCl$-KCl-$MgCl_2$ and $CaCl_2$-KCl-$MgCl_2$ MSE residues were used for two cation exchange tests each. The ion exchange resin used was Dowex* 50W-X8, the type used by the Chemical Operations Group. Actinide loading on the ion exchange column from the calcium solution was reduced to 70% of that attainable from the sodium solution. Approximately 50% of the calcium fed to the column was adsorbed and eluted in the plutonium and americium product fraction when the column was stripped with 7*M* HNO_3. Table 4 shows cation exchange test results for actinide recovery and decontamination involving the two types of residues. The presence of calcium will not interfere with the anion exchange recovery of plutonium, but calcium will precipitate as the oxalate with americium.

Future Work

Additional work is being done to determine the amount of calcium that will precipitate as the oxalate with americium. Another program is in progress to determine the oxalate precipitation conditions needed to eliminate contaminants (e.g., lead). The results of this work will be applied to the calcium problem.

COMBINED ANION EXCHANGE-BIDENTATE ORGANOPHOSPHOROUS EXTRACTION PROCESS FOR MOLTEN SALT EXTRACTION RESIDUES

Larry L. Martella and James D. Navratil

Objective

The objective is to test a combined anion exchange-bidentate organophosphorous extraction process for separating plutonium and americium from an aluminum-magnesium alloy on a pilot-plant scale.

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*Trademark of the Dow Chemical Company, Abbott Road, Midland, Michigan.

TABLE 4. Actinide Recovery and Decontamination From $NaCl-KCl-MgCl_2$ and $CaCl_2-KCl-MgCl_2$ MSE Residues

Element	$NaCl-KCl-MgCl_2$ System[a] Feed (g)	Product (g)	DF[b]	$CaCl_2-KCl-MgCl_2$ System[a] Feed (g)	Product (g)	DF[b]
Pu	4.8 ±0.16	2.8 ±0.13[c]	--	3.4 ±0.00	2.7 ±0.13[d]	--
Am	0.22 ±0.00	0.21 ±0.00	--	0.14 ±0.00	0.13 ±0.01	--
Ca	--	--	--	5.9 ±0.58	3.3 ±0.18	1.8
K	18 ±0.07	2.8 ±0.13	6.2	2.1 ±0.07	1.4 ±0.19	1.5
Na	13 ±1.3	1.3 ±0.12	10	0.19 ±0.13	0.05 ±0.01	3.8
Mg	1.6 ±0.4	0.24 ±0.03	6.7	0.22 ±0.03	0.05 ±0.01	4.4

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a. Mean percent plus or minus standard deviation for duplicate tests.

b. Decontamination factor (DF) = $\frac{\text{weight of contaminant in feed}}{\text{weight of contaminant in product}}$

c. Plutonium recovery was low because only 4.2 column volumes (630 ml) of 7*M* HNO_3 elutriant was used; the remainder was recovered by 6*M* HCl strip.

d. Plutonium recovery was low after 6.7 column volumes (1 liter) of 7*M* HNO_3 elutriant used; the remainder was recovered by 6*M* HCl strip.

Prior Work

An anion exchange-30 vol % DHDECMP (dihexyl-N,N-diethylcarbamoylmethylene phosphonate)-CCl_4 (carbon tetrachloride) process was evaluated for separating and purifying plutonium and americium from MSE (molten salt extraction) residues. The residues consist of 8 mol % magnesium chloride, equal molar mixtures of potassium and sodium chlorides, and aluminum-magnesium and zinc-magnesium alloys. Results of these demonstration runs for each MSE residue showed americium and plutonium to be effectively separated from the impurity elements.

Achievements and Discussion

The process is outlined in Figure 3 (page 10). After dissolution in nitric acid, filtration, and adjustments in acidity and valence, the feed is processed by anion exchange to remove plutonium. The feed and wash solutions from anion exchange processing are then processed by solvent extraction. The bidentate extractant removes essentially all of the americium, thus leaving the impurities in the effluent.

For the solvent extraction step, diisopropylbenzene (DIPB) was tested as a diluent to replace carbon tetrachloride. Extraction coefficients for plutonium and americium were determined as a function of HNO_3 concentration using several combinations of DIPB and DHDECMP. Extraction coefficient is defined as the concentration of solute in the organic phase divided by the concentration of solute in the aqueous phase at equilibrium.

Table 5 (see page 10) shows the extraction coefficient (D) values for the mixed extractants tested. These values are an average of two determinations. Results indicate that 30% DHDECMP-70% DIPB would be the best extraction system. Americium extracts from 7*M* HNO_3 but back-extracts with water. Plutonium remains in the organic phase.

Future Work

Setup of pilot-plant equipment for the process will be completed. The process will then be demonstrated on a large enough scale to produce gram quantities of purified AmO_2 for process evaluation.

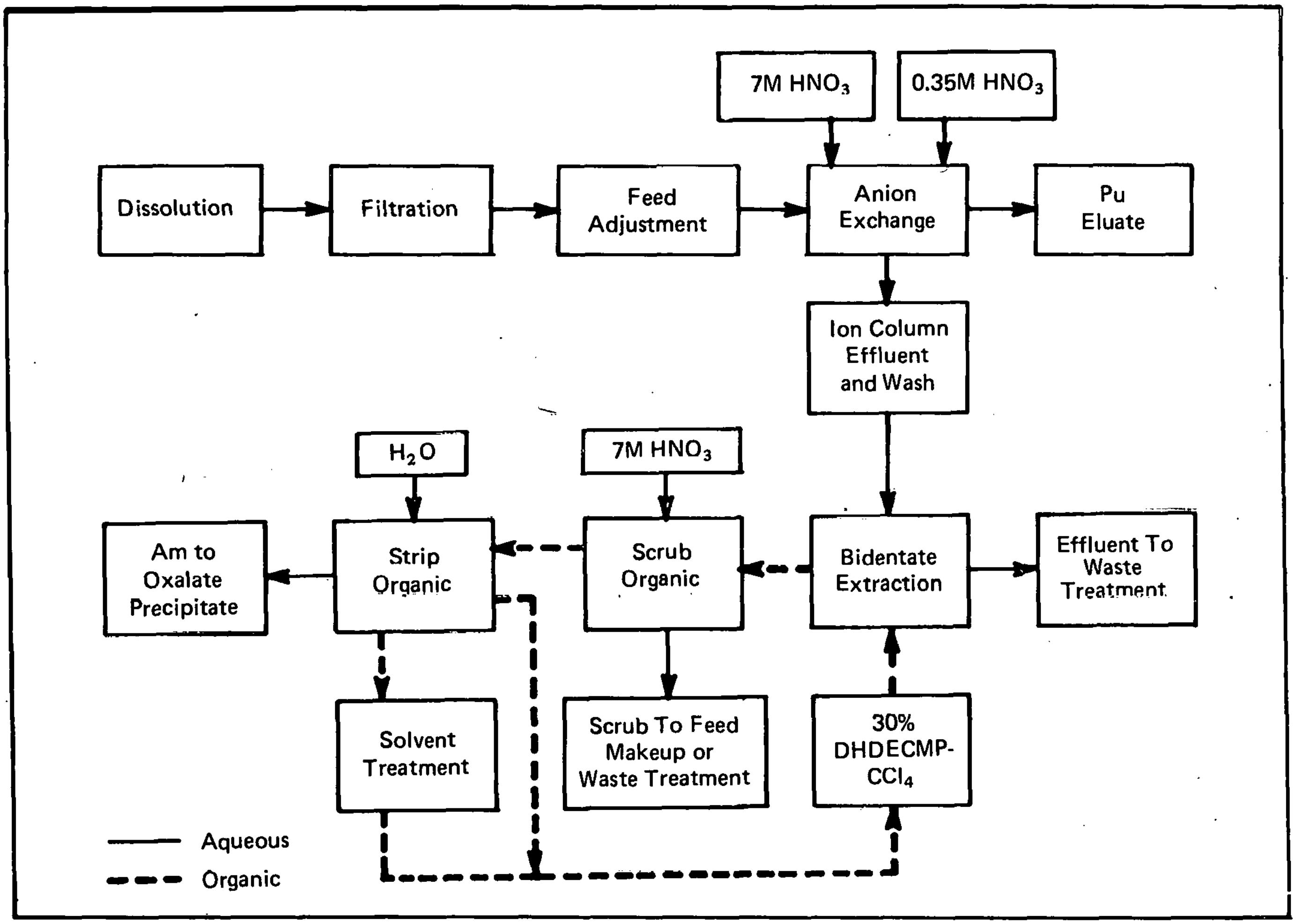

FIGURE 3. Conceptual Flow Sheet for Processing Molten Salt Extraction Residues

TABLE 5. Extraction Coefficient Values for Plutonium and Americium in DHDECMP-DIPB

Feed = 0.01 g/l Pu + 0.01 g/l Am
Temperature = 22-24 °C
Aqueous-to-Organic Ratio = 1

DHDECMP (vol %)	DIPB (vol %)	HNO_3 (*M*)	D* Americium	D* Plutonium
10	90	1	0.075	2.3
10	90	7	0.13	6.9
20	80	1	0.25	4.0
20	80	7	0.83	17
30	70	1	0.71	17
30	70	7	2.9	–
40	60	1	1.1	–
40	60	7	6.2	–

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*D = Concentration of solute in the organic phase divided by the concentration of solute in the aqueous phase at equilibrium.

TABLE 6. Actinide Recovery From Fluidized Bed Incinerator Ash by Fusion and 4*M* HNO_3 Recovery

Flux: Solid Ratio of 10:1
Time: 2 hours

Sample: Mixture of Am-traced PuO_2 (2.27×10^{-4} g Am/g Pu) fired at 925 °C to constant weight and FBI ash. 90 wt % ash - 10 wt % oxide

Flux	Temperature (°C)	Actinide Recovery* (%) Pu	Am
90 wt % Na_2CO_3 - 10 wt % $NaNO_3$	900	8.2 ±6.1	28 ±22
Na_2CO_3	900	15	15
90 wt % Na_2CO_3 - 10 wt % Na_2SO_4	900	10	24
$K_2S_2O_7$	500	97	94
$KHSO_4$	500	94	93
NaOH	500	2.4 ±0.44	15 ±5.8

*Results of single determination, except for carbonate, nitrate, and NaOH (mean percent plus or minus standard deviation for duplicate samples).

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. The findings from this laboratory-scale program, which is being done under contract for Oak Ridge National Laboratory (ORNL), will be used by the Department of Energy (DOE) and ORNL to assist in determining the feasibility of partitioning actinides from combustible waste.

Prior Work

Preliminary leaching and dissolution tests were completed using cold ash from the pilot plant-scale fluidized bed incinerator (FBI) at Rocky Flats. In these experiments, recovery method efficiency was measured by determining the percent of ash solubilized. Digestion in 95% H_2SO_4-5% HNO_3 or fusion in Na_2O_2 gave the best results.

In subsequent testing, ^{241}Am-traced high-fired PuO_2 was used in place of cold FBI ash. The 95% H_2SO_4-5% HNO_3 digestion solubilized the oxide but lengthy refluxing was required. Fusion resulted in Na_2O_2 severely attacking the crucibles. A new and better flux, 90 wt % Na_2CO_3-10 wt % $NaNO_3$, was discovered that recovered ≥99% of the plutonium and americium in the oxide.

Achievements and Discussion

Mixtures of cold FBI ash (90 wt %) and actinide oxide (10 wt %) were treated with the same fluxes used previously. (The concentrated HNO_3 and acid digestion methods were not investigated further.) Results are shown in Table 6. Basic fluxes gave poor recovery, and acidic fluxes gave essentially

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*Pilot Plant Development Group, Chemistry R&D.

the same recovery as before. The reason for this is solubilization of silica in ash by the basic flux. Upon acidification, polysilicic acid (silica gel) is formed. The silica gel makes filtration extremely difficult and also adsorbs the solubilized actinides; plutonium is scavenged more effectively than americium

Fusion in basic fluxes cannot be used unless silica is first removed. This was done by refluxing ash in $\geqslant 6M$ NaOH; the solubilized silica can then be removed (as silicate) by filtration or centrifugation. Once this is done, actinide recoveries approach those reported previously for actinide oxide dissolution.

Another method is now being evaluated. This method uses Ce(IV) in $4M$ HNO_3 to oxidize the carbon in all incinerator ash to carbon dioxide and to solubilize the actinides. The Ce(IV) is rapidly reduced to Ce(III) as carbon is oxidized; Ce(IV) is regenerated *in situ* by electrolysis of the solution. Preliminary results (three tests) gave an actinide recovery of 97.8 ±0.35% (mean percent plus or minus standard deviation) from conventional Rocky Flats incinerator ash, so the method appears promising. It is a more attractive method than the high-temperature carbonate-nitrate fusion process.

The laboratory-scale quartz FBI unit to be used in preparation of contaminated ash has been completed and the system is now being checked out.

Future Work

Evaluation of the Ce(IV)-HNO_3 system will be continued. (ORNL has requested evaluation of this system exclusively, unless it is demonstrated that the system is not feasible. In that case, the carbonate-nitrate fusion process will then be optimized.) Optimum operating conditions will be determined by varying such parameters as Ce(IV) concentration, rate of electrolysis, and solution temperature and time. Contaminated waste will be burned in the laboratory-scale FBI unit. Recovery methods can then be evaluated using contaminated ash produced by combustion rather than by adding actinide oxide to cold ash.

ACTINIDE RECOVERY AND RECYCLE PREPARATION FOR WASTE STREAMS

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

Objective

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

Prior Work

During the last reporting period, a program plan was written, a preliminary literature search was made, and waste streams were defined. The testing of a bidentate organophosphorus solvent extractant for determining the feasibility of removing actinides from salt waste streams was initiated. Conceptual flow sheets were constructed for purifying wastewater by reverse osmosis.

Salt Waste Processing

Prior work with a bidentate organophosphorus extractant, impure DHDECMP (dihexyl-N,N-diethylcarbamoylmethylene phosphonate), showed high uranium distribution ratios (D) in dilute nitric acid. These earlier determinations were repeated using a different batch of purified DHDECMP (Table 7) and an improved uranium analytical method. Figure 4 shows D values of uranium(VI) with DHDECMP versus nitric acid (HNO_3) concentration. The results show lower uranium D values at low acidities than the values obtained previously. This indicates less uranium stripping problems.

Plutonium and americium extraction from acidified salt waste solutions was investigated. The acidified

TABLE 7. Gas Chromatography - Mass Spectroscopy Analysis of Impure and Purified DHDECMP

Component	Impure[a] (%)	Purified[a] (%)	Component	Impure[a] (%)	Purified[a] (%)
diethylamine	0.1	0	hexylchloride	2.5	0.7
decane	0.3	0	chloro-N,N-diethylacetamide	3.0	0.5
undecane	0.3	0	dihexylphosphite	4.1	0
dichloro-N,N-diethylacetamide	0.7	0.3	dihexylmethylphosphite	7.8	7.5
α, diethylamino-N,N-diethylacetamide	2.4	0.2	trihexylphosphate	27.9	26.0
unidentified components	2.5	1.8	dihexyl-N,N-diethylcarbamoylmethylene phosphonate	47.0	63.0

NOTE: DHDECMP purified by Amberlyst® A-26 resin treatment.

a. Relative peak area of gas chromatography and mass spectroscopy.

FIGURE 4. Uranium D Values Versus HNO_3 Concentration for 30 Vol % DHDECMP-CCl_4

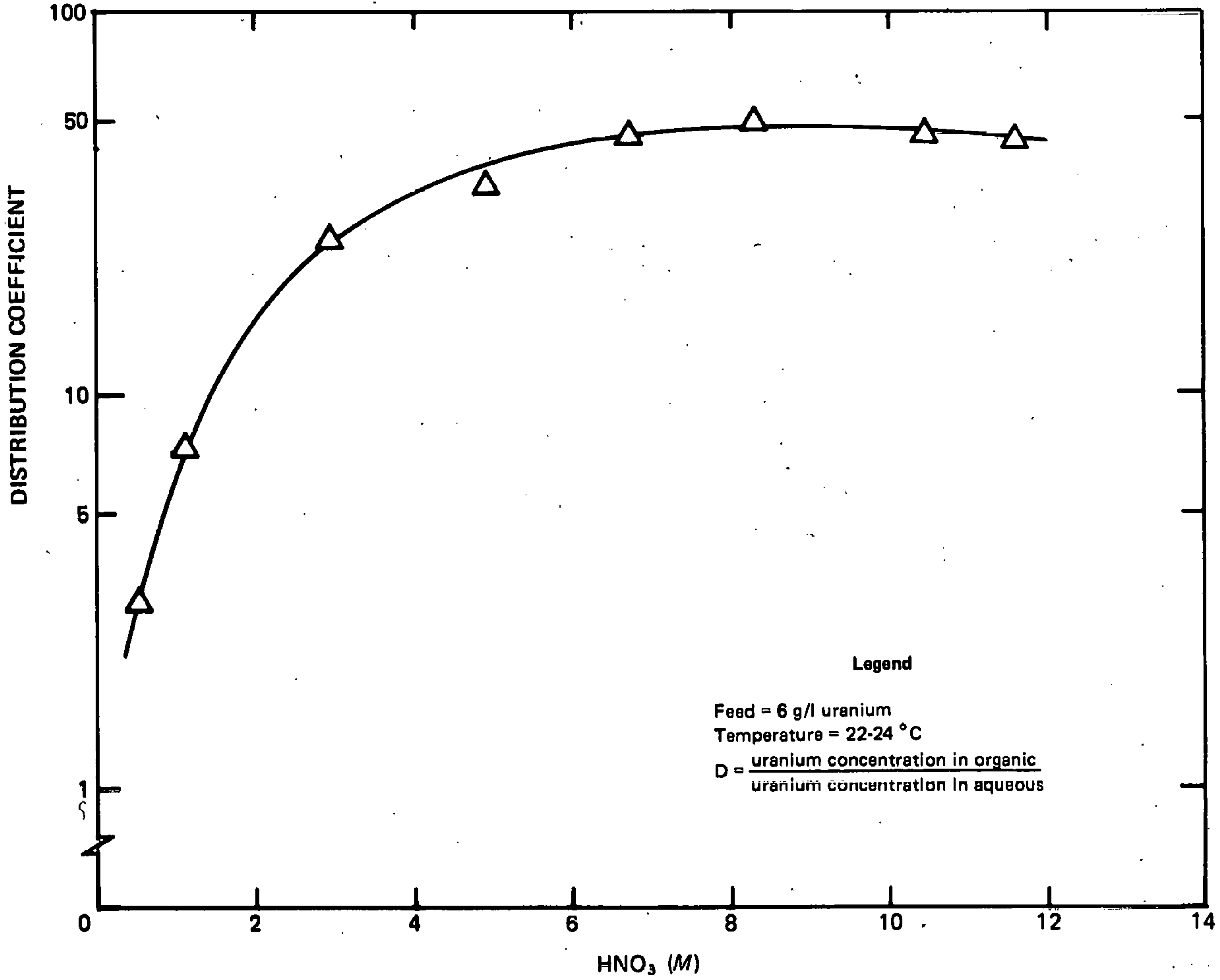

TABLE 8. Actinide Removal From Acidified Salt Waste After Consecutive Contacts With a Bidentate Extractant

Number of Contacts[a]	Percent Pu Removed[b]	Percent Am Removed[c]
2	99.89	90.90
4	99.96	98.91
6	99.97	99.60
8	99.98	99.91

a. Aqueous-to-organic ratio of five.

b. 20 vol % DHDECMP (dihexyl-N,N-diethylcarbamoylmethylene phosphonate) - 80 vol % DIPB (diisopropyl benzene).

c. 50 vol % DHDECMP - 50 vol % DIPB.

salt waste solution was equilibrated eight times with DHDECMP-DIPB (diisopropyl benzene). Results of the plutonium and americium analyses are shown in Table 8. The results show that >99.98% plutonium and >99.91% americium can be removed from the salt waste.

These and previously reported results indicate the following conclusions: A combined tributyl phosphate (TBP)-DHDECMP extraction system would be the best system for removing actinides from salt waste unless purified DHDECMP (99%) alone would permit efficient uranium back-extraction. The DHDECMP extraction system will remove >99.98% of the plutonium and >99.91% of the americium from the acidified salt waste.

Wastewater Processing

The evaluation of various adsorbents to remove organics and anions from wastewater was completed. Six types of granular adsorbents were evaluated: Anasorb coconut carbon, Calgon bituminous coal, Amoco carbon, Amberlite XAD-4 neutral adsorption resin, Amberlite IRA-93 anionic weak base exchange resin, and Amberlite IRA-900 anionic strong base exchange resin. An *in situ* formed, open-pore-polyurethane (OPP), nongranular adsorbent also was evaluated.

All adsorbents were dry-sieved to obtain a particle size between 40 and 50 mesh. A weighed portion of adsorbent was poured into columns with inner diameters of 0.6 cm, to give a bed height of 10 cm. Bed volume for all granular columns was 2.8 cm^3.

A 2.5 g/l Pierce laundry detergent solution, adjusted to pH 5.0, was prepared for use as the synthetic waste stream. One-liter quantities of the detergent solution were pumped through each column at an average flow rate of 5.0 ±0.3 ml/min. Forty-five fractions of 20 ml each were collected with an SMI* drop-counting fraction collector. A selected number of fractions was analyzed for TOC (total organic carbon) and chloride ion to determine breakthrough capacities.

The elution behavior of the materials was determined by pumping methanol through the columns at a flow rate of 1.5 ml/min. Fractions of the eluate were collected and analyzed to determine the elution behavior.

Results of the detergent and chloride breakthrough capacities and the elution behavior of the adsorbents are shown in Table 9. Amberlite XAD-4 has the highest capacity for detergent, but no ionic capacity. Amberlite IRA-900 resin and OPP have the highest capacity for chloride, but the first material would be best since the second material elutes the detergent poorly. Amberlite XAD-4 eluted the detergent the fastest. These results suggest the use of XAD-4 and IRA-900 (mixed or in separate columns) should accomplish the best removal of organics and anions from wastewater.

Figure 5 is a conceptual flow sheet for removing organics and anions from wastewater by employing the two suggested resin schemes. The material balance is based on the assumption that the resins selectively remove the organics and anions, and that the actinides follow the effluents. These assumptions need verification by testing wastewater containing actinide ions.

Future Work

This program was not funded for FY-1978. If it is continued later, the best methods for both waste streams will be tested further to obtain process information for flow sheet analysis.

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*Scientific Manufacturing Industries

TABLE 9. Breakthrough and Elution Data on Adsorbent Materials

Adsorbent Materials	Breakthrough Capacity[a] (ml det./g mat.)[b]	Breakthrough Capacity[a] (mg Cl^-/g mat.)[c]	Elution (ml CH_3OH/g mat.)[d]
Anasorb	225	7	--
Amoco GX-31	240	--	>12
Calgon F 400	215	--	--
Amberlite XAD-4	250	--	1
Amberlite IRA-93	16	9	--
Amberlite IRA-900	11	47	--
OPP[e]	100	48	8

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a. Breakthrough defined as concentration of solute in effluent divided by concentration of solute in feed.

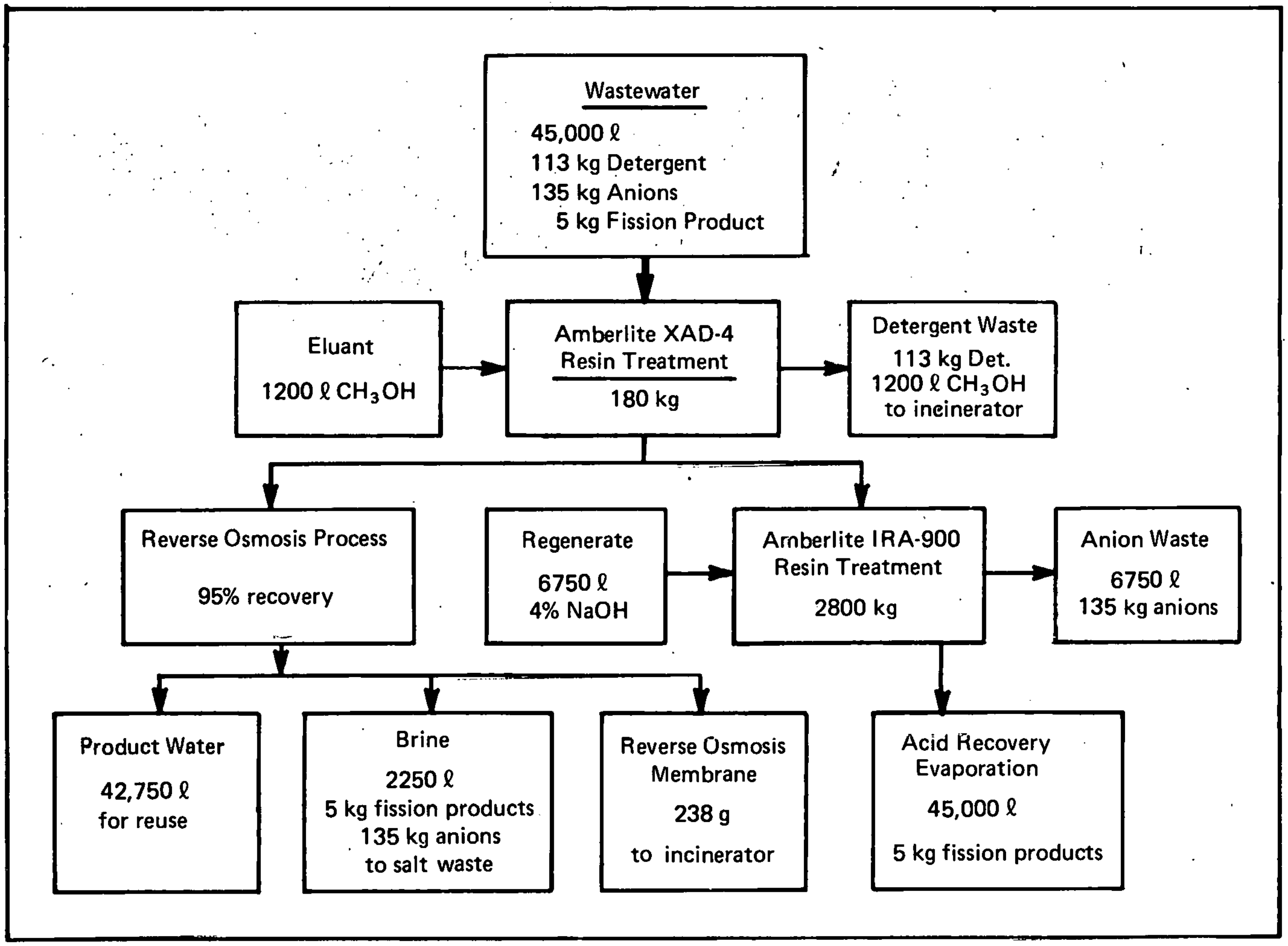
b. Milliliter of detergent passed per gram of adsorbent at breakthrough of 30% total organic carbon (TOC) in effluent. Feed = 89 mg/l TOC

c. Milligrams of chloride passed per gram of adsorbent at breakthrough of 0.30. Feed = 1 mg/l Cl^-.

d. Milliliters of methanol passed per gram of adsorbent at 30% TOC eluted.

e. OPP = Open pore polyurethane.

FIGURE 5. Conceptual Flow Sheet for Wastewater Treatment



PROCESSING CHEMISTRY AND ENGINEERING

Edward D. Erickson

PROCESSING LECO CRUCIBLE RESIDUES CONTAINING A TIN ACCELERATOR

Kay K. Kunert

Objective

The objective of this project is to evaluate possible methods of recovering plutonium from Leco crucible residues that contain tin as the accelerator. Dissolution methods found suitable in prior work with the iron- and copper-contaminated Leco crucible residues are to be studied.

Prior Work

Prior work has been done on Leco crucible residues containing iron and copper as the accelerator.

Achievements and Discussion

Leco crucible residues are generated by the Analytical Laboratory during analyses for carbon in plutonium metal. The residue consists of an aluminum-silicate crucible containing plutonium metal along with an accelerator that ensures complete combustion of the sample.

Three different metals have been used as accelerators: tin, iron, and copper. Residues containing the tin accelerator are the only one discussed in this progress report.

The central material from one of the crucibles was sampled for element identification and found to contain a metal core of β-tin surrounded by residue. The residue was mainly plutonium oxide (PuO_2) with stannous oxide (SnO_2). The presence of the metal core was due to incomplete combustion of the accelerator during the Leco process; the core was not present in all the crucibles.

In preparation for dissolution, the material was crushed in a jaw crusher, then ground to less than 30 mesh using a laboratory jar mill. The ground material was contacted with the following solutions to determine plutonium dissolution rates:

1. $12M$ HNO_3
2. $12M$ HNO_3 - $0.5M$ HF
3. $12M$ HNO_3 - $0.5M$ HF with a $10M$ NaOH - $0.1M$ F preleach
4. $6M$ HCl
5. $6M$ HCl - $0.5M$ HF
6. $6M$ HCl - $0.5M$ HF - $0.2M$ $SnCl_2$

Dissolution tests were conducted using a solid-to-liquid ratio of 1:10. Initial solutions were boiled for 3 hours with samples taken at 0.5-hour intervals. These preliminary tests indicated that maximum plutonium dissolution occurs after 1 hour of boiling. By boiling the solution an additional hour, however, approximately 50% of the initially dissolved tin reprecipitated from HNO_3 solutions, and ~70% reprecipitated in HNO_3 - HF solutions. Because of these results, the remainder of the dissolution tests were conducted using a 2-hour residue time.

Dissolution of plutonium in $6M$ HCl - $0.5M$ HF was 98% complete after one 2-hour contact. This was increased to 99.4% with an additional 2-hour contact with fresh acid. With the $6M$ HCl - $0.5M$ HF - $0.2M$ $SnCl_2$ system, a 99.5% plutonium dissolution was achieved after only one contact. Using $12M$ HNO_3 - $0.5M$ HF, at least 3 contacts were necessary to achieve 96% plutonium dissolution. Heels from the HCl-HF and HCl-HF-$SnCl_2$ dissolutions were below the discard limit for Leco crucible residues. The plutonium content in the heel from the HNO_3-HF dissolution was above the discard limit after 3 contacts.

The tin concentration in solutions from the HNO_3-HF dissolution after 3 passes was 0.030 g Sn/l. This low concentration should not cause problems in production during the ion exchange process. The tin concentration in the solutions from HCl-HF dissolutions was higher but could be removed, or lowered to acceptable levels, during conversion of the plutonium from a chloride to nitrate system.

Table 10 summarizes results from the various dissolution systems investigated.

TABLE 10. Results of Various Dissolution Systems Tested

System	Residence Time	Pu Dissolved (%)	Pu in Heel (g/g)	Sn Dissolved (%)	Sn in Solution (g/g)
$12M$ HNO_3	1 pass, 2 hours	38.0	2.41×10^{-2}	1.4	0.003
$12M$ HNO_3 - $0.5M$ HF	1 pass, 2 hours	75.5	1.77×10^{-2}	6.35	0.05
$12M$ HNO_3 - $0.5M$ HF	2 passes, 2 hours each	88.3	1.23×10^{-2}	5.0	0.035
$12M$ HNO_3 - $0.5M$ HF	3 passes, 2 hours each	95.7	6.01×10^{-3}	10.9	0.030
$12M$ HNO_3 - $0.5M$ HF with preleach*	1 pass, 2 hours	57.0	4.83×10^{-2}	1.6	0.012
$6M$ HCl	1 pass, 2 hours	61.4	6.82×10^{-2}	52.0	0.98
$6M$ HCl	3 passes, 2 hours each	58.0	2.51×10^{-2}	55.0	0.98
$6M$ HCl - $0.5M$ HF	1 pass, 2 hours	98.0	2.03×10^{-3}	42.0	1.2
$6M$ HCl - $0.5M$ HF	2 passes, 2 hours each	99.4	7.5×10^{-4}	46.0	0.49
$6M$ HCl - $0.5M$ HF - $0.2M$ $SnCl_2$	1 pass, 2 hours	99.5	7.29×10^{-4}	--	--
$6M$ HCl - $0.5M$ HF - $0.2M$ $SnCl_2$	2 passes, 2 hours each	99.9	1.45×10^{-4}	--	--

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*The residue was boiled 2 hours in a preleach of $10M$ NaOH - $0.1M$ F^- prior to dissolution in HNO_3 - HF.

Future Work

Future work will be conducted on the conversion of chloride systems to a nitrate system.

DISSOLUTION OF REFRACTORY RESIDUES IN HYDROCHLORIC ACID

Kay K. Kunert, Larry L. Martella, and Charles R. Forrey

Objective

The objective of this project was (1) to develop dissolution parameters for dissolving refractory materials in hydrochloric acid solutions and (2) to develop a process to remove the chloride ion from the plutonium solution. These processes are being developed as production processes for use by the Plutonium Recovery group.

Prior Work

Prior work with hydrochloric (HCl) dissolution has been done while studying the recovery of plutonium from Leco crucible residues and incinerator ash.* During the incinerator ash study, ion exchange was investigated as a method of removing the chloride ion.*

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*See p. 45 ff of earlier progress report: RFP-2680-A dated October 21, 1977.

TABLE 11. Results of Dissolution Tests With Various Solvents

	One Contact One hour		One Contact Two hours		Two Contacts Two hours each	
Solvent	Pu dissolved (%)	g/g in heel*	Pu dissolved (%)	g/g in heel*	Pu dissolved (%)	g/g in heel*
6*M* HCl	--	--	24.3	1.04×10^{-1}	25.0	1.02×10^{-1}
6*M* HCl - 0.5*M* HF	99.1	8.43×10^{-4}	98.7	2.35×10^{-3}	98.9	2.55×10^{-3}
6*M* HCl - 0.5*M* HF - 0.2*M* $SnCl_2$	99.6	7.39×10^{-4}	99.8	4.25×10^{-4}	99.8	2.84×10^{-4}
6*M* HCl - 0.2*M* $SnCl_2$	--	--	92.7	1.16×10^{-2}	95.0	8.14×10^{-3}
6*M* HCl - 0.2*M* $FeCl_2$ - 0.5*M* HF	98.9	4.26×10^{-4}	99.6	1.01×10^{-3}	99.8	6.98×10^{-4}
6*M* HCl - 0.2*M* $FeCl_2$	--	--	36.5	8.81×10^{-2}	99.1	1.47×10^{-3}
6*M* HCl - 0.2*M* $CuCl_2$ - 0.5*M* HF	98.2	4.03×10^{-3}	99.8	5.04×10^{-4}	99.7	6.8×10^{-4}
6*M* HCl - 0.2*M* $CuCl_2$**	46.9	7.96×10^{-2}	92.0	1.32×10^{-2}	94.3	9.07×10^{-3}

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*Discard limit of Leco heels is 8.7×10^{-3} g/g.

**Results of the different runs varied widely.

Achievements and Discussion

Previous work with hydrochloric acid solutions indicated that a stannous chloride reducing agent is required to obtain adequate dissolution. Experience has shown that tin has a limited solubility in nitrate solutions, and it forms residues that plug the ion columns. Therefore, a suitable replacement for the stannous chloride is desired.

Leco crucible residues with an iron accelerator were used for this study. These residues have become refractory because the high operating temperature during the Leco process fuses the reactants with silica from the crucible. This produces a residue that is a combination of high-fired oxides of plutonium, iron, and silicon.

The material was prepared for dissolution by crushing it in a jaw crusher, and magnetically separating the plutonium-rich residue or kernel from the crucible. The kernel was ground to less than 35 mesh in a laboratory jar mill.

The dissolution characteristics of eight solutions were investigated; each solution was 6*M* HCl and included a combination of reducing agents. (See Table 11 for the exact composition of each solution and the results of the dissolution tests.) The highest dissolution of 99.6% was achieved with a one-hour contact with the 6*M* HCl - 0.5*M* HF - 0.2*M* $SnCl_2$ solution; however, three other solutions also produced high dissolutions: 6*M* HCl - 0.5*M* HF (99.1%), 6*M* HC - 0.5 HF - 0.2*M* $FeCl_2$ (98.9%), and 6*M* HCl - 0.5*M* HF - 0.2*M* $CuCl_2$ (98.2%). The insoluble heels from the four dissolutions were below the economic discard limit for Leco heels.

To use hydrochloric acid dissolution and to be compatible with the present nitric acid based production processes, a process must be available for converting from a chloride to a nitrate system. Anion and cation exchange, oxalate and carbonate precipitations, and solvent extraction were investigated as possible methods for this conversion. Solutions generated in the dissolution studies were used for the feed solution in these studies.

In the anion exchange process, the feed solution was made 7.8*M* in the nitrate ion, and the plutonium was loaded on Dowex 1-X4 nitrate form resin. The solution was then washed with 8 to 10 column volumes of 7.2*M* HNO_3 to reduce the chloride content to less than 1 g Cl^-/ℓ. The plutonium was then eluted with 0.35*M* HNO_3 containing hydroxylamine nitrate ($NH_2OH \cdot HNO_3$) to enhance the elution.

TABLE 12. Purification Results of Anion Exchange

Element	Effluent (%)	Wash (%)	Eluate (%)	Decontamination Factor
Pu	0.2	0.2	99.6	--
Cl	49.6	49.1	1.3	345
Sn	0.5	98.7	0.8	310
Fe	3.4	96.1	0.5	328
Cu	94.7	4.6	0.7	133

TABLE 13. Purification Results of Cation Exchange

Element	Effluent (%)	Wash (%)	Eluate (%)	Decontamination Factor
Pu	1.3	0.3	98.4	--
Cl	93.3	6.5	0.2	1,200
Sn	82.5	11.4	6.1	17
Fe	1.3	0.1	98.6	--
Cu	0.5	0.3	99.2	--

The percentages and decontamination factors for elements found in effluent wash and eluate from the anion exchange test are listed in Table 12.

In the cation exchange process, the feed solution was made 0.5*M* in H^+ and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$). Two column volumes of water were used to wash the chloride from the resin, and the plutonium was eluted from the Dowex 50-X8 resin with 7.5*M* HNO_3. High concentrations of iron in the feed solution caused severe gassing when the 7.5*M* HNO_3 was added; sodium nitrite was used to oxidize the iron prior to loading. The chloride concentration was reduced to 1 g Cl^-/ℓ and 98% of the plutonium was recovered, but no reduction in iron and copper was observed. Table 13 shows the results for the cation exchange tests.

Oxalic acid was added to feed solution, which was adjusted to 0.75 *M* HCl. This gave 1 g oxalic acid per gram of plutonium, and it produced a 0.1*M* oxalate solution. One gram of asorbic acid per gram of plutonium was added to stabilize the plutonium in the Pu(III) oxidation state and thus ensure complete precipitation. Following precipitation, the plutonium oxalate was calcined to oxide. Results of the oxalate precipitation test show that 96% of the plutonium can be recovered with no chloride contamination in the oxide. A decrease in tin and iron contamination was achieved but there was no decrease in copper contamination. The major problem with the oxalate precipitation process was that the plutonium concentration in the filtrate was above the discard limit.

Approximately 100% of the plutonium was recovered by carbonate precipitation, and the filtrate averaged 4.5×10^{-4} g Pu/ℓ. The nitric acid solutions, which were formed from dissolution of the precipitate, contained from 0.2 to 1 g Cl^-/ℓ. There was significant purification from tin, iron, and copper. The major problem encountered with the carbonate precipitation process was the formation of a yellowish-white precipitate in the HNO_3 solution. This required an additional filtration step. This precipitate was identified, tentatively, as the mineral varlamoffite, which is made up of Sn, Fe (O, OH).

In solvent extraction, the feed solution was adjusted to 7.2*M* in hydrogen ion with concentrated (15.6*M*) HNO_3. It was then contacted with 30 vol % tributylphosphate - 70 vol % dodecane (conditioned with 7.2*M* HNO_3) in a separatory funnel at an aqueous-to-organic ratio of 5:1. The feed was contacted with six aliquots of extractants for one minute each until the plutonium concentration in the aqueous phase was below 1×10^{-3} g/ℓ. The organic phase was washed with six contacts of 7.2*M* HNO_3 using an aqueous-to-organic ratio of 1:5 to remove residual amounts of extracted impurities. The plutonium was then stripped from the organic phase with 0.35*M* HNO_3 - 0.1*M* $NH_2OH \cdot HNO_3$ with nine one-minute contacts, using an aqueous-to-organic ratio of 1:5. Results in Table 14 show that plutonium is effectively extracted and that the major impurities are not present in significant quantities in the final strip product.

TABLE 14. Results of Solvent Extraction Process

Element	Aqueous After Contact (%)	Wash (%)	Product (%)	Remaining in Organic (%)	Decontamination Factor
Pu	0.3	~0	98.6	1.1	--
Cl	88.2	11.8	~0	--	2,524
Sn	95.2	4.8	~0	--	2,624
Fe	62.0	38.0	~0	--	1,461
Cu	99.5	0.5	~0	--	3,160

Future Work

Future work will involve setting up a production prototype dissolution system capable of dissolving refractory materials in hydrochloric acid. In addition, any further work required to select a process for converting from a chloride to a nitrate media will be completed, and production prototype equipment will be developed.

METAL DISTILLATION

James W. Berry, James B. Knighton, and Ralph O. Wing

Objective

The objective is to develop processes that will separate various metals from plutonium alloys by using the difference in the vapor pressures of these metals and alloys at molten temperatures.

Prior Work

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

Achievements and Discussion

Vacuum melting is defined as a distillation process used to remove high-vapor-pressure metals such as zinc, magnesium, and calcium from plutonium alloys of these metals. These alloys are produced during the molten salt cleanup project.* The process is operated at temperatures between 600 and 900 °C and at vacuums of 10^{-3} torr. Feed alloys contain 5 to 40 weight percent plutonium plus americium. The zinc, magnesium, and calcium metals that are distilled from the plutonium condense into metal ingots weighing 2000-2500 grams. These ingots, which are discardable, contain up to 1×10^{-3} grams of plutonium per gram of alloy and 1×10^{-4} grams of americium per gram of alloy.

All of the demonstration work has been performed in an experimental furnace† in which 69 kilograms of alloy have been successfully processed. A production prototype furnace is being designed to perform the vacuum melting operation on a production basis.

Vacuum distillation is defined as a distillation process for separating low-vapor-pressure metals such as americium from plutonium. The process is operated between 1150 and 1300 °C and at vacuums of 10^{-6} torr. Feed material, which is the product from the vacuum melting process, contains approximately 80 percent plutonium and 7 percent americium. Nineteen kilograms of feed alloy is available to begin development tests in the distillation furnace.

Start-up operations of the distillation furnace system have progressed to the point of reaching the lower operating temperature of 1150 °C and a vacuum of 10^{-5} torr.

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*See "Plutonium Recovery From Backlog Salts" in this report.

†See p. 51 ff. of earlier progress report RFP-2680-A dated October 21, 1977.

Special ytrria (Y_2O_3) crucibles are being developed for use in the vacuum distillation process. The initial crucibles were formed by isostatic pressing at 100,000 psi, machining the outside surfaces, and firing at 1750 °C. These crucibles have shown stress cracking after firing. Slip-cast yttria crucibles produced by Los Alamos Scientific Laboratory have been thermal-cycled from room temperature to 1000 °C without damage. These will be used for the first demonstration tests.

Future Work

Vacuum melting will continue on a production basis until the molten salt cleanup work is finished. Vacuum distillation will be started up and developed to a production level process. The product of vacuum melting will be processed through vacuum distillation. Handling techniques will be developed to minimize radiation exposure.

INDUCTION-HEATED, TILT-POUR FURNACE

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

Objective

Induction-heated, tilt-pour furnaces will be used in the new Plutonium Recovery Facility (Building 371) at Rocky Flats. A prototype tilt-pour furnace has been installed (Building 776). The objectives of the development program are to develop a basic tool for the 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 will 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. Numerous electrorefining tests have also been reported (RFP-2680-A, October 21, 1977).

The automatic sequence panel for controlling tilt-pour furnace operations has required extensive electronic modification. These modifications have been made, and the panel has now been interfaced with the furnace and is being used routinely. The pyroredox process was demonstrated in a tilt-pour furnace, but the product metal was high in aluminum, carbon, tantalum, and tungsten. It was concluded that the same furnace should not be used for both oxidation and reduction reactions. The first three steps of the salt cleanup operation (See "Plutonium Recovery From Backlog Salts" elsewhere in this report) have also been demonstrated. Problems again were experienced in performing oxidation and reduction reactions in the same furnace.

Achievements and Discussion

The tilt-pour furnace was used to demonstrate that the zinc-magnesium alloy (Step I product of the salt cleanup process) could be loaded to 35% in plutonium plus americium. This alloy could then be moved directly to the vacuum melting step for removal of zinc magnesium solvent metals. Steps II and III (zinc chloride oxidation and calcium reduction) could be bypassed.

The furnace is currently being used to consolidate, under a molten salt cover, Step I and Step III alloy metal products that have been backlogged from the salt cleanup operation. Metal consolidation has been proven necessary to remove salt pockets and occlusions that have interfered with vacuum melting of the metal alloy.

Future Work

After all of the backlogged salt cleanup alloys have been consolidated, the tilt-pour furnace will be shut down for a design modification. The induction-heated furnace well containing the tungsten crucible and graphite susceptor developed a leak and required repair. There is evidence that another leak is developing in the Inconel* furnace well, and corrosion is occurring on the inside Inconel surface. In the new design, the furnace well will be joined to the body of the furnace using a flange to accommodate replacement. Also, a niobium liner has been designed and will be incorporated as a part of the furnace well. This liner will protect the inner Inconel surface.

PLUTONIUM RECOVERY FROM BACKLOG SALTS

Ray E. Giebel and James B. Knighton

Objective

At Rocky Flats, americium is separated from plutonium metal using a molten salt extraction process. The product salt from this extraction process has been fed to an aqueous process for recovery of plutonium and americium; however, a backlog of salt has been accumulated awaiting aqueous processing. The objective of this project is to develop, demonstrate, and lend technical support to pyrochemical methods for recovering plutonium and americium from these salts on a production basis.

Prior Work

The first three steps in the pyrochemical process for recovering plutonium and americium from backlog salts are concentration and purification steps; they have been performed on a production basis in stationary furnaces. The three steps are identified as Step I, zinc-magnesium reduction; Step II, zinc chloride oxidation; and Step III, calcium reduction. StepIV, vacuum melting [for removal of volatile solvent metals (zinc, magnesium, and calcium)], is now in operation. The final step, separation of americium from plutonium by vacuum distillation, has been demonstrated at Oak Ridge National Laboratory. Equipment for vacuum distillation is being installed at Rocky Flats.

Achievements and Discussion

Steps II and III (zinc chloride oxidation followed by calcium reduction) have been eliminated from the pyrochemical recovery process. The concentration of plutonium and americium in the Step I alloy product has been increased from about 10 to about 35%. This alloy has been a satisfactory feed to the vacuum melting step. The increased concentration of plutonium and americium in the Step I alloy product has been accomplished first by utilizing calcium as the reducing agent rather than magnesium, and second by contacting the metal alloy with multiple batches of feed salt. Magnesium is necessary in the system for the metals to remain as liquids at operating temperature (~750-800 °C). It is formed during the salt-metal equilibration by the reaction of calcium with magnesium chloride present in the feed salt: $Ca + MgCl_2 \rightarrow CaCl_2 + Mg$. Removing magnesium chloride from the salt phase is necessary for a minimum value of the distribution coefficient for plutonium and americium partitioning between the salt and metal phases. Multiple contacts with fresh feed salt using mass action assists in building up the concentration in the metal phase.

Numerous small metal alloy buttons from Step I reductions or Step III calcium reductions are consolidated into one salt-free button in the tilt-pour furnace. The tilt-pour furnace has proven to be ideal equipment for this operation. The product from consolidation is satisfactory feed for the vacuum melting step. Consolidation has become necessary because the smaller buttons contained salt occlusions that have interferred with the vacuum melting step.

Future Work

The plutonium-americium alloy product from the vacuum melting step will continue to be stored. It

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*Trademark of Huntington Alloys, Inc., Huntington, West Virginia.

will be used as feed for the vacuum distillation step, in which plutonium and americium will be separated as soon as the equipment is operational.

PLUTONIUM PEROXIDE PRECIPITATION PROCESS

Clyde C. Perry and Dennis R. Schlepp

Objective

The objective of this project is to determine optimum precipitation conditions using only ion exchange column eluate. Changes in equipment design and process parameters will be recommended to improve the existing Plutonium Recovery Facility (Building 771). The plutonium peroxide product will be characterized to determine the most favorable type for efficient calcination and hydrofluorination.

Prior Work

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

Achievements and Discussions

The plutonium recovery process must be able to handle different feedstocks with equal efficiency. Problems have been encountered recently in processing ion exchange column feed as the evaporated feed. The precipitate product was either colloidal and unfilterable or calcination and hydrofluorination of the precipitate produced plutonium tetrafluoride, which gave poor yields when reduced to metal. Using similar precipitation conditions, reductions of plutonium tetrafluoride produced from the eluate-only feed had 60-70% yields of metallic plutonium compared to 95-98% yields from feed materials containing eluate combined with dissolved PuO_2. Also, high filtrate losses (40-50%) were observed with both types of feed. A study is being made of the process parameters that could be affecting the efficiencies and giving low reduction yields for the eluate-only stream. Results of this study will be applicable not only in the current plutonium recovery facility but also to the new facility (Building 371) in which eluate will be the only feed material available.

Information from work done in the Alternate Fuel Cycle Technology (AFCT) program was used to design production-scale equipment for start-up of the continuous precipitation using eluate-only feed. This feed contains 15 kg of plutonium. Satisfactory plutonium peroxide could be produced only by doubling the precipitation and digestion times. This situation is not suitable for production purposes because of the reduced flow rates that are required.

The following observations were made during this demonstration run:

1. Many operating factors depend on whether the peroxide crystal structure is hexagonal or cubic. Indications are that hexagonal crystal structure is necessary for high recovery yields. In particular, cubic crystals form small, round particles that tend to solidify in the digesters and to form a hard filter cake, thus preventing wash solutions from penetrating the cake. Hexagonal crystals have an open branched structure that allows easier filtration and washing.
2. The method of start-up affects the nature of the precipitate. Presently plutonium nitrate is fed to an excess of hydrogen peroxide (reverse-strike), favoring the formation of cubic crystals. Changing this procedure by adding hydrogen peroxide to excess plutonium nitrate (direct-strike) will favor hexagonal crystal formation and improve the precipitation.
3. Eluate feed requires twice as long to precipitate the plutonium peroxide as compared to mixed feed. More digester residence time is therefore needed.
4. Little vertical mixing occurs in the digester. The slurry flows along the top of the digesters so the full capacity of the digesters is not utilized. To precipitate column eluate feed in the present equipment, the feed rate was lowered to 25% of normal process flow rates. This would be impractical for actual production runs.

5. Stagnant layers of hexagonal plutonium peroxide in the bottoms of the digesters begin to turn to cubic plutonium peroxide after two hours.

6. Precipitates form faster during direct-strike start-up than during continuous reverse-strike operation.

A basis for evaluation of the quality of the plutonium peroxide produced was established when conditions of calcination and hydrofluorination were stabilized. Acceptable plutonium metal with reduction yields of 95 weight percent was produced using the mixed feed of eluate and dissolved plutonium oxide. Using only ion exchange column eluate as feed, there were no satisfactory reduction yields during the entire period of observation. This narrowed the problem to the precipitation reaction.

Future Work

Several process improvements are planned for future production runs. This includes improved agitation in the digesters and achieving simultaneous addition of reactants in a static mixer in front of the digester. Both of these changes should help the peroxide precipitation and improve yields using the eluate feed. Development work for these changes will be done as a small-scale precipitation process now being designed. Design work is also proceeding on equipment to replace those pieces known to be inadequate.

Work will be continued to determine the effect of nitric acid concentration in the plutonium nitrate feed and the effect of hydrogen peroxide on the plutonium feed ratio.