168
11/17/79
RFP-2952
October 5, 1979

DR. 291

RFP-2952
October 5, 1979

MASTER

CHEMISTRY RESEARCH AND DEVELOPMENT

PROGRESS REPORT

NOVEMBER 1978 THROUGH APRIL 1979

Frend John Miner

MASTER

Rockwell International

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

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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

Printed
October 5, 1979

RFP-2952
UC-4 Chemistry
TIC-4500-R66

MASTER

CHEMISTRY RESEARCH AND DEVELOPMENT

PROGRESS REPORT

NOVEMBER 1978 THROUGH APRIL 1979

Frend John Miner

Chemical Research -----Gary H. Thompson

Process Chemistry and Engineering -----Edward D. Erickson

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ROCKWELL INTERNATIONAL
ENERGY SYSTEMS GROUP
ROCKY FLATS PLANT
P.O. BOX 464
GOLDEN, COLORADO 80401

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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

SUBJECT DESCRIPTORS

Actinides
Adsorption
Americium
Americium Oxalate
Americium Oxides
Americium Recovery
Calorimeters
Chemistry
Chromatography
Decontamination
Digesters
Dissolution
Enthalpy of Formation
Hydrofluoric Acid
Ion Exchange
Lead
Leaching
Magnesium Oxide Crucibles
Materials Recovery
Mixing
Molten Salt Residues
Plutonium
Plutonium Chloride

Plutonium Dissolution
Plutonium Hydrides
Plutonium Metal
Plutonium Nitrates
Plutonium Peroxide
Plutonium Processing
Plutonium Recovery
Plutonium Residues
Precipitation
Purification
Radioactive Waste Processing
Radioactive Wastes
Raschig Rings
Recovery
Separation Processes
Soils
Solvent Extraction
Specific Heat
Tanks
Thermodynamic Properties
Tilt-Pour Furnace
Waste Management
Waste Processing

CONTENTS

PREFACE	7
---------------	---

PUBLICATIONS AND TECHNICAL PRESENTATIONS	8
--	---

CHEMICAL RESEARCH

CALORIMETRY AND THERMODYNAMICS OF NUCLEAR MATERIALS	9
---	---

Investigations into the thermodynamic properties of plutonium metal and the plutonium-hydrogen system are currently underway. In addition, a compilation of the thermodynamic properties of all actinide materials is in progress. (DDS Endeavor 112*)

AMERICIUM RECOVERY AND PURIFICATION	10
---	----

The acidity of americium solutions presently is reduced by dilution, which increases the volume of aqueous waste. Neutralization is being tested to determine if this method would be more effective, yet have no adverse effect on the AmO_2 product. (DDS Endeavor 113)

OPTIMIZATION OF THE CATION EXCHANGE PROCESS FOR RECOVERING AMERICIUM AND PLUTONIUM FROM MOLTEN SALT EXTRACTION RESIDUES	11
---	----

Two programs are in progress for improving the cation exchange operation. The first is an evaluation of a high-capacity macroporous resin; the second is a study of the selectivity of cation resins for multivalent ions. (DDS Endeavor 113)

EVALUATION AND COMPARISON OF BIDENTATE EXTRACTANTS AND METHODS FOR ACTINIDE RECOVERY	12
---	----

Three organophosphorus bidentates are being evaluated for liquid-liquid extraction and chromatographic extraction of actinides from aqueous solutions. (DDS Endeavor 333)

*All Development and Development Support (DDS) endeavor numbers refer to FY-1981 Proposed Program for Process Development (JM-01-03-04) and Related Work, CD 79-192, February 13, 1979. Production and Production Support programs are identified as PPS.

A COMBINED ANION EXCHANGE - BIDENTATE ORGANOPHOSPHORUS
EXTRACTION PROCESS FOR MOLTEN SALT EXTRACTION RESIDUES13

Pilot-plant-scale testing of a combined anion exchange - bidentate organophosphorus solvent extraction process for separating plutonium and americium from molten salt extraction residues has been completed. (DDS Endeavor 333*)

A COMBINED ANION EXCHANGE - EXTRACTION CHROMATOGRAPHY
TECHNIQUE FOR SECONDARY RECOVERY15

Laboratory-scale testing of the removal of plutonium and americium from ion column effluent by the combined anion exchange - extraction chromatography method is nearing completion. (DDS Endeavor 333)

PLUTONIUM RECOVERY IN THE ADVANCED SIZE REDUCTION
FACILITY16

A sodium nitrate - borax solution was shown to be the best medium for electrodecontamination at Rocky Flats. Plutonium recovery is easier and less waste is generated. (PPS*)

DECONTAMINATION OF ROCKY FLATS SOIL17

The soil decontamination process for Rocky Flats soil is being improved and tested on a pilot-plant scale. (PPS)

SOIL DECONTAMINATION AT OTHER SITES18

Processes are being developed to decontaminate soils from other DOE sites that have been contaminated with actinides. (Other DOE)

*All Development and Development Support (DDS) endeavor numbers refer to FY-1981 Proposed Program for Process Development (JM-01-03-04) and Related Work, CD 79-192, February 13, 1979. Production and Production Support programs are identified as PPS.

PROCESS CHEMISTRY AND ENGINEERINGSEPARATING LEAD AND CALCIUM FROM AMERICIUM BY CHROMATE
AND OXALATE PRECIPITATION20

Two hundred eighty-five grams of impure americium oxide were purified by a chromate and oxalate precipitation process. The calcium concentration in the impure oxide was decreased from 2.8 weight percent to 1600 parts per million, and the lead concentration was decreased from 2.5 weight percent to 4000 parts per million. (PPS*)

A DEMONSTRATION OF THE PYROREDOX PROCESS IN THE
INDUCTION-HEATED, TILT-POUR FURNACE22

The oxidation step of a pyroredox process for purifying plutonium metal has been demonstrated on a production scale. (DDS Endeavor 302*)

PROCESS DEVELOPMENT FOR RECOVERY OF AMERICIUM FROM VACUUM
MELT FURNACE CRUCIBLES24

Hydrochloric acid solutions, containing americium and plutonium from leached ceramic crucibles used in a pyrochemical process, were processed through laboratory-scale processes used in production recovery operations. The impurities in solutions were analyzed before and after ion exchange. (PPS)

PLUTONIUM PEROXIDE PRECIPITATION PROCESS25

A new system was designed for improving the solution mixing performance of the continuous peroxide precipitation process. Evaluations of production data indicate improved product quality, more consistent process operation, and a decrease in the amount of material recycled in the process. (PPS)

*All Development and Development Support (DDS) endeavor numbers refer to FY-1981 Proposed Program for Process Development (JM-01-03-04) and Related Work, CD 79-192, February 13, 1979. Production and Production Support programs are identified as PPS.

A COMPARATIVE STUDY OF ANNULAR AND RASCHIG RING-FILLED
TANKS27

A quantitative study of mixing solutions in annular and raschig ring-filled tanks has been made using exit age distribution theory. The ring-filled tank approaches plug flow mixing behavior and the annular tank approaches stirred tank mixing behavior. The location of solution entry points was also studied. (DDS Endeavor 302*)

*All Development and Development Support (DDS) endeavor numbers refer to FY-1981 Proposed Program for Process Development (JM-01-03-04) and Related Work, CD 79-192, February 13, 1979. Production and Production Support programs are identified as PPS.

PREFACE

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
RFP-2803	Period Ending April 30, 1978
RFP-2870	Period Ending October 31, 1978

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

J. D. Navratil, L. L. Martella, C. M. Smith, G. H. Thompson, D. L. Cash, E. L. Childs, and L. J. Meile. Waste Management Analysis for the Nuclear Fuel Cycle - Part I and II. Progress Report for April 1 to September 30, 1977. RFP-2749. Rockwell International, Rocky Flats Plant. October 23, 1978.

F. L. Oetting. "The Chemical Thermodynamics of Nuclear Materials. III. Plutonium Mononitride." J. Chem. Thermodynamics, 10, 941 (1978).

J. A. Hayden. "Size Fractionation Methods: Measuring Plutonium in Respirable Dust." Science, 202, 753 (1978)

J. D. Navratil, G. H. Thompson, and R. L. Kochen. "Waste Management of Actinide Contaminated Soil." RFP-2856. Presented at the Symposium on Science Underlying Waste Management, Boston, Massachusetts. November 27 - December 1, 1978.

J. D. Navratil, L. L. Martella, and G. H. Thompson. "Americium Recovery at Rocky Flats." RFP-2886. Presented at the ACS/CSJ Congress, Honolulu, Hawaii. April 1 - 6, 1979.

J. D. Navratil and G. H. Thompson. "Removal of Actinides from Selected Nuclear Fuel Reprocessing Wastes." Nuclear Technology, 43, 135 (1979).

P. G. Hagan and F. J. Miner. "Plutonium Peroxide Precipitation: Review and Current Research." RFP-2848. Presented at the ACS/CSJ Congress, Honolulu, Hawaii, April 1 - 6, 1979.

R. M. Greinert and D. H. Neal. Plutonium (IV) Oxalate Precipitation and Calcination Process for Plutonium Nitrate to Oxide Conversion. RFP-2602. Rockwell International, Rocky Flats Plant. July 26, 1978.

K. R. Soupy and W. E. Sperry. Batch Direct Denitration Process for Plutonium Nitrate to Oxide Conversion. RFP-2704. Rockwell International, Rocky Flats Plant. January 20, 1978.

J. B. Knighton and C. E. Baldwin. "Pyrochemical Co-Processing of UO_2 - PuO_2 LMFBR Fuel by the Salt Transport Method." Presented at ACS/CSJ Congress, Honolulu, Hawaii. April 1 - 6, 1979.

CHEMISTRY RESEARCH AND DEVELOPMENT PROGRESS REPORT
NOVEMBER 1978 THROUGH APRIL 1979

Frend John Miner

CHEMICAL RESEARCH

Gary H. Thompson

CALORIMETRY AND THERMODYNAMICS OF
NUCLEAR MATERIALS

Franklin L. Oetting
and
C. Michael Smith

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.

Prior Work

Experimental high-temperature enthalpy data have been obtained for $\text{PuO}_2(\text{c})$. A program for compilation and critical evaluation of the thermodynamic properties of actinide materials initiated several years ago is being continued.

An experimental program was initiated to determine the thermodynamic properties of plutonium and the plutonium-hydrogen system. Utilized in the program were adiabatic calorimetry for high-temperature heat capacity measurements and solution calorimetry for enthalpy of formation

measurements. Both of these calorimeters were made operational.

Achievements and Discussion

Two complete sets of heat capacity measurements were made on the empty container. These measurements were made over the temperature range of 298 to 750 K in the adiabatic calorimeter utilizing two different modes of heating. The measurements provided considerable insight into the peculiarities of this calorimeter and were helpful in the understanding and operation of this instrument.

Numerous problems were encountered and solved. The most serious problem, continual shorting of the adiabatic shield heater, required complete dismantling of the calorimeter and minor changes in its design. The calorimeter is now operating satisfactorily.

The precision and accuracy of the results obtained on the solution calorimeter were determined by measuring the enthalpy of neutralization of NBS SRM 724 [tris-(hydroxymethyl) aminomethane] in excess of 0.1M HCl. The average value of five runs, $-7111.7 \pm 5.4 \text{ cal mol}^{-1}$, was in good agreement with the standard value of $-7108 \pm 8 \text{ cal mol}^{-1}$ (See Reference 1).

Seven calorimetric experiments involving the enthalpy of solution were performed with alpha plutonium in 6M HCl. The enthalpy of solution of Pu metal going to $\text{Pu}^{3+}(\text{aq})$ was $-141.74 \pm 0.19 \text{ kcal mol}^{-1}$. This value is in excellent agreement with that reported

by Akhachinskij² although there is a wide variation in this number in the literature.³

Several experiments involving the enthalpy of solution of delta plutonium metal and $\text{PuH}_{2.7}(\text{c})$ in 6M HCl were also completed. The preliminary results appear consistent; final results are pending, awaiting complete analysis of impurities.

Future Work

Heat capacity measurements on the empty container in the adiabatic calorimeter will be completed. The measurements on molybdenum (standard), alpha plutonium, delta plutonium, and several of the plutonium hydrides will follow.

Work on the enthalpy of solution of delta plutonium and $\text{PuH}_{2.7}(\text{c})$ will be completed. Other hydrides will be synthesized and their enthalpies of solution will be determined.

References

1. J. D. Navratil and F. L. Oetting, The Exothermic Enthalpy of Tris with 0.1M Hydrochloric Acid - Standard Reaction for Solution Calorimetry. RFP 1976. Dow Chemical U.S.A., Rocky Flats Division. March 12, 1973.
2. V. V. Akhachinskij, "The Heat of Solution of Plutonium in Hydrochloric Acid." Thermodynamic's. Proc. Symp. on Thermodynamics, 2, 561 (1966). International Atomic Energy Agency. Vienna, Austria.
3. J. Fuger and F. L. Oetting, "The Aqueous Actinide Ions." The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2. International Atomic

Energy Agency. Vienna, Austria 1976.

AMERICIUM RECOVERY AND PURIFICATION

Paul G. Hagan
and
Richard H. Schmunk

Objective

The objective of this work is to improve the americium recovery and purification process and to provide technical assistance for its continued operation.

Prior Work

Processes have been developed at Rocky Flats to recover actinides from molten salt extraction residues by ion exchange, solvent extraction, and precipitation techniques. More recently, studies have been made to optimize the recovery of americium by oxalate precipitation and for removing lead, a major impurity in the americium product.

Achievements and Discussion

A study is in progress to improve the americium recovery operation by neutralizing the feed solution in place of the current dilution method. Neutralization reduces the loss of americium product and reduces exposure to personnel by decreasing process time. Preliminary results show no basic structural changes in the americium oxide product when the feed solution is neutralized. The oxide has a cubic structure and is isomorphous with PuO_2 , UO_3 , and ThO_2 .

In support of Chemical Operations, a study was also made of the thermal decomposition of americium oxalate

$[\text{Am}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}]$. Americium oxalate loses water of hydration as it is heated to 300 °C. At that temperature, the oxalate begins to decompose; the conversion to americium oxide (AmO_2) is complete at about 450 °C.

Future Work

Work is in progress, on both a laboratory and production scale, to demonstrate the utility of a neutralization step in the americium recovery process operation.

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

Paul G. Hagan
and
Richard H. Schmunk

Objective

The objective of this work is to improve the cation exchange process used for recovering plutonium and americium from molten salt extraction (MSE) waste salts.

Prior Work

The cation exchange process was developed at Rocky Flats for separating plutonium and americium from MSE waste salts and for converting the anionic chloride medium to a nitrate medium. Since that time studies have been made to determine the effectiveness of cation exchange for separating plutonium and americium from cations other than those which are common to the MSE salt process, and to evaluate different types of resin for cation exchange improvement. In addition, operating conditions have been investigated for process improvement

through column loading, elution, and washing techniques.

Achievements and Discussion

Two current programs show promise for major process improvement. The first is a study of a cationic macroporous resin, BioRad* AG MP-50. The results of comparative tests with this resin show 30 to 50% more capacity than the resin currently being used by Chemical Operations, Dowex† 50W-X8. The resin also shows better sorption and elution kinetics, and more selectivity for actinide ions.

The second program is a study of the selectivity of cation exchange resin for trivalent, divalent, and monovalent cations. These tests have been made with both the BioRad AG MP-50 resin and the Dowex 50W-X8 resin. The interaction for selective separation is affected by several factors; most important are valence, ionic medium, and ionic strength. Laboratory investigations of these factors show greater separation of the actinides can be achieved through (1) dilution of the MSE salt feed stream, and (2) by lowering the concentration of the chloride medium.

Future Work

Additional work needs to be done on the BioRad AG MP-50 resin to determine chemical and radiolytic stability and differences which may exist in selective separation and elution kinetics. The program to improve the cation exchange process through operational procedures needs to be

*Trademark of BioRad Laboratories, Richmond, California

†Trademark of Dow Chemical, Abbott Rd., Midland, Michigan

continued to (1) determine practical ionic strength values for column loading and (2) pursue other process improvement features such as new techniques for selective elution and washing.

EVALUATION AND COMPARISON OF BIDENTATE EXTRACTANTS AND METHODS FOR ACTINIDE RECOVERY

Larry L. Martella

Objective

The objective is to evaluate three organophosphorus bidentates for recovery of plutonium and americium from process streams. An additional objective is the comparison of the liquid-liquid solvent extraction and extraction chromatography methods with the three bidentates, dihexyl-N,N-diethylcarbamoylmethylenephosphonate (DHDECMP); dibutyl-N,N-diethylcarbamoylmethylenephosphonate (DBDECMP); and dibutyl-N,N-diethylcarbamoylphosphonate (DBDECP).

Prior Work

Prior work has shown that organophosphorous bidentates are effective in recovery plutonium and americium from high-acid solutions containing common contaminants. Laboratory evaluation of the liquid-liquid extraction and chromatographic extraction techniques have been done, and pilot-scale testing is in progress.

Achievements and Discussion

Americium breakthrough capacities (50%) were determined for DHDECMP, DBDECMP, and DBDECP adsorbed on

Amberlite* XAD-4 resin; 50% breakthrough is defined as the volume fed to the column when the americium concentration in the column effluent is 50% of the feed concentration. The capacities were determined for a solution containing 1.0×10^{-3} g Am/l in 7.0M HNO_3 . The 50% breakthrough results for a 0.9-cm-dia column containing 15 ml of adsorbent fed at 1.7 ml/min were DHDECMP, 695 ± 36 ml; DBDECMP, 287 ± 39 ml; and DBDECP, 125 ± 5 ml (mean $\pm$ standard deviation for duplicate runs). DHDECMP is therefore the most effective extractant for americium recovery.

Two similar tests were made for 0.1 g Pu/l in 7M HNO_3 using DHDECMP. Fifty percent breakthrough was not attained after 1300 ml of feed was passed through the column, so the tests were terminated at this point.

The capacity of DHDECMP for americium and plutonium was determined for both the liquid-liquid and chromatographic extraction methods. Ten milliliters of Amberlite XAD-4 resin containing 0.34 g DHDECMP/ml was contacted for 30 minutes with 50 ml of feed containing 8.7×10^{-4} g Am/l or 0.1265 g Pu/l in 7M HNO_3 . Five milliliters of 80 vol % DHDECMP (highest purity material presently available at Rocky Flats) was also contacted with each feed for 30 minutes. Table 1 gives the analytical results for each actinide and system. Results show that more plutonium or americium can be loaded per gram of DHDECMP when the latter is sorbed on Amberlite XAD-4 resin.

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

TABLE 1. Actinide Capacity of DHDECMP in Liquid-Liquid and Chromatographic Extraction Methods

Pu Feed: 0.1265 g/l DHDECMP Purity: 80 vol %
 Am Feed: 8.7×10^{-4} g/l Contact Time: 30 min

Extraction Method	Actinide Capacity, mg/g DHDECMP*	
	Pu	Am
Chromatographic	1.86 ± 0.0	$(9.52 \pm 0.0) \times 10^{-3}$
Liquid-Liquid	0.116 ± 0.0	$(7.71 \pm 0.0) \times 10^{-4}$

*Mean $\pm$ standard deviation for duplicate tests.

Future Work

Breakthrough capacities (50%) for the three bidentates sorbed on Amberlite XAD-4 resin will be determined using solutions with higher plutonium concentrations. Actinide capacity tests for the two remaining bidentates (DBDECMP and DBDECP) will also be completed.

A COMBINED ANION EXCHANGE - BIDENTATE ORGANOPHOSPHORUS EXTRACTION PROCESS FOR MOLTEN SALT EXTRACTION RESIDUES

Larry L. Martella, James D. Navratil,*
 Francis L. Kingman,[†] Pat McHugh,[†]
 James F. McLachlan,[†] and
 Arlyn D. Mills[†]

Objective

The objective is to test a combined anion exchange - bidentate organophosphorus extraction process for separating and purifying plutonium and

americium from an aluminum-magnesium alloy on a pilot-plant scale. A second objective is to adapt the bidentate organophosphorus extractant to a chromatographic technique on both a laboratory and a pilot-plant scale.

Prior Work

The combined anion exchange - bidentate organophosphorus solvent extraction process was first investigated on a laboratory scale for separating and purifying plutonium and americium. Results of these demonstration runs on MSE (molten salt extraction) residues showed effective separation of plutonium and americium from each other and from impurity elements.

Achievements and Discussion

The conceptual flow sheet for the recovery of actinides by the bidentate organophosphorus process is shown in Figure 1. After dissolution, plutonium is recovered and purified by the anion exchange process using Dowex* 1-X4 (50-80 mesh) resin in 7M HNO₃. Americium in the ion column effluent is extracted from high acid (e.g. 7M HNO₃) solutions with 30 vol % dihexyl-N,N-diethylcarbamoylmethylene-phosphonate (DHDECMP) in diisopropylbenzene (DIPB); DHDECMP extracts actinides and lanthanides but not common contaminants.

For the pilot-plant liquid-liquid extraction, 2.5l of feed was contacted with fresh batches of bidentate at an aqueous-to-organic (A/O) ratio of 5 for 15 minutes until the americium concentration was $< 1.9 \times 10^{-2}$ g/l; three contacts were required.

*On leave to IAEA, Vienna, Austria.

[†]Special Recovery Group, Chemical Operations.

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

FIGURE 1. Conceptual Flow Sheet for Processing Molten Salt Extraction Residues

Residual impurities were then removed by washing with 7M HNO_3 at an A/O of 0.2; three to five washes were done. The americium was back-extracted with water (A/O of 0.2) in five to seven contacts. The recovered americium was precipitated with oxalic acid, and the americium oxalate was calcined to AmO_2 .

Table 2 shows feed and product concentrations of actinides and major impurities. Aluminum and magnesium decontamination was good with decontamination factors (DF) of 77 and 510, respectively. (DF is the ratio of impurity in the feed to impurity in the product.) Table 3 shows the impurities in the americium oxide product.

TABLE 2. Results of Pilot Scale Recovery of Americium From Dissolved Aluminum-Magnesium Alloy

Stream	Concentration* (g/l)			
	Am	Pu	Al	Mg
Feed	0.15	8.17×10^{-3}	0.385	1.02
Product	0.14	7.5×10^{-4}	0.005	0.002

*Single determination.

TABLE 3. Impurities in Americium Oxide Product*

Impurity Concentrations** (ppm)		
Pu	Al	Mg
3240	< 100	< 50

*Specifications require > 95% AmO₂ with less than 1% of any individual impurity and less than 0.5% Pu.

**Single determination.

Since Rocky Flats is not equipped to do plant-scale liquid-liquid extraction, an extraction chromatography technique is also being investigated. This technique uses DHDECMP-impregnated solid support (Amberlite⁺ XAD-4 resin) in a column. Preliminary testing has shown the actinide capacity to be variable, increasing with the actinide concentration in the feed. An americium capacity of 6.5 g/l was attained from an aluminum-magnesium solution containing 2.5 g/l.

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

Pilot-plant testing of the chromatographic technique is in progress. One test in which 55l of 0.6 g Am/l feed was passed through two 4-in.-dia X 24-in.-long columns has been completed. Americium breakthrough was not detected prior to feed shutdown. Analysis of the strip (back-extracted) product is in progress.

Future Work

Development of the liquid-liquid and chromatographic extraction techniques will be completed and the two methods will be compared.

A COMBINED ANION EXCHANGE - EXTRACTION CHROMATOGRAPHY TECHNIQUE FOR SECONDARY RECOVERY

Larry L. Martella

Objective

The objective is to test the combined anion exchange - extraction chromatography method for the removal of low concentration plutonium and americium from the ion column effluent. This effluent is produced during the plutonium recovery and purification process. A concentration of $< 1.0 \times 10^{-5}$ g/l for both plutonium and americium has been set as the standard.

Prior Work

Dihexyl-N,N-diethylcarbamoyl-methylenephosphonate (DHDECMP) in diisopropylbenzene (DIPB) has been tested for liquid-liquid extraction of low levels of actinide from secondary waste streams. A combined anion exchange - extraction chromatography process has been tested for the recovery of americium and plutonium from aluminum-magnesium molten salt extraction residues.

Achievements and Discussion

Ion column effluent having a plutonium concentration of 2.67×10^{-4} g/l and an americium concentration of 9.53×10^{-4} g/l was passed through three columns (1.9-cm dia X 30 cm) of Dowex* 1-X4 (50-100 mesh) resin for plutonium removal. The plutonium and americium concentrations were reduced to 4.07×10^{-5} g/l and 9.14×10^{-4} g/l, respectively.

This solution became the feed for three runs using a 1.8-cm-dia column containing 15 ml of DHDECMP-loaded Amberlite XAD-4 resin. Feed was passed through the column until 50% breakthrough was obtained. Because of its lower distribution coefficient (ratio of actinide in organic to that in aqueous solution), americium breakthrough occurred first. After column washing with 7M HNO_3 , the column was eluted with 0.4M hydroxylamine nitrate in 0.35M HNO_3 .

Analysis of the runs showed that plutonium was reduced to $< 1.0 \times 10^{-5}$ g/l for feed volumes up to 600 ml. Americium results showed a decrease in americium capacity during each consecutive run. This has since been attributed to incomplete elution of plutonium in the runs, reducing americium capacity since plutonium is more strongly extracted and retained than is americium.

Future Work

Additional testing will be done to improve plutonium removal. The elutriant will be 0.05M HNO_3 ; this decrease in acidity is expected to enhance plutonium elution.

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

PLUTONIUM RECOVERY IN ADVANCED SIZE REDUCTION FACILITY

Armen R. Kazanjian
and
Milton E. Killion

Objective

Plutonium decontamination methods are being investigated for the Advanced Size Reduction Facility. The success of these methods depends on the ease of plutonium recovery and solution recycle. The object of this work is to evaluate plutonium recovery and solution recycle for the various decontamination solutions being investigated.

Prior Work

The solubility of air-oxidized plutonium dioxide in phosphoric acid, oxalic acid, and alkaline permanganate solutions was measured.

Achievements and Discussion

A sodium nitrate - borax solution was shown to be the best medium for electrodecontamination at Rocky Flats. Plutonium recovery is easier and less waste is generated. The only disadvantage is that chromium does not precipitate in this neutral solution as do the other component elements of stainless steel. Therefore, chromium must be periodically removed to maintain electrolytic efficiency. Chromium can be precipitated as lead chromate by the addition of lead nitrate. Alternate methods of chromium removal were also investigated. The addition of ferrous sulfate was found to be effective in reducing chromium and precipitating chromous hydroxide. Caustic solution must be

added to restore neutrality. Chromic ion was also reduced by the addition of hydroxylamine nitrate and hydrogen peroxide; these reagents were only partially effective.

Phosphoric acid is no longer being considered as an electrodecontaminant because the acid can not be recycled. A special ion exchange resin was obtained from Battelle-Hanford and used in experiments to purify phosphoric acid by a method called acid retardation. Variables examined were phosphoric acid concentration, flow rate, and flow direction. There was no evidence of impurity separation, so testing was discontinued.

A nitric acid - borax solution was tested as an electrodecontaminant. The disadvantage of this system is the generation of large volumes of liquid waste that must be transferred for processing. The sodium nitrate - borax solution leaves only a small volume of solids to be processed.

The usual anion exchange technique was used to recover plutonium from spent sodium nitrate - borax and nitric acid - borax solutions. Separation of the plutonium from the impurities using Dowex 11 anion exchange resin gave a plutonium product with < 0.01 g/l impurities.

Initial decontamination in the Advanced Size Reduction Facility may be accomplished with pressurized steam. Plutonium dioxide, the usual contaminant form, is insoluble in water and should be readily filtered. The filterability was determined by decontaminating a piece of plutonium-contaminated stainless steel with boiling water and filtering the solution through filters rated for 0.1- μ m or 5- μ m particles. The 0.1- μ m filter was necessary to remove 97% of the plutonium-containing particulates.

Future Work

No further work is planned.

DECONTAMINATION OF ROCKY FLATS SOIL

Charlotte E. Alford, John A. Hayden, Robert L. Kochen, Roger L. Olsen, and John R. Stevens

Objective

The objective of this program is to further develop, improve, and scale-up the soil decontamination process for plutonium, americium, and uranium. The process will be used to decontaminate approximately three acres of Rocky Flats soil presently covered by an asphalt pad.

Prior Work

A method consisting of attrition scrubbing and wet-screening was developed to reduce the volume of contaminated Rocky Flats soil. In addition, a conceptual flowsheet for the process was devised. This process, designated the primary process, reduced the volume of contaminated soil by about 65%. Work was started on the development and testing of alternate procedures to enhance the removal of plutonium from the soil. Construction of the pilot-plant-scale decontamination laboratory was begun.

Achievements and Discussion

Work on alternate procedures to enhance the removal of plutonium from soil was primarily in four areas:

1. Testing polar/non-polar separation media
2. Testing surfactants with acid scrubbing solutions

3. Testing surfactants with basic scrubbing solutions
4. Use of a large magnet to remove ferromagnetic particles from soil

The polar/non-polar separation scheme proved to be very effective in laboratory-scale tests. As much as 99.9% of the activity was removed from 82 wt % of the soil. However, because this process has not been investigated as thoroughly as the wet-screening and attrition scrubbing method, and because we do not have time to do so and meet our schedule, this separation scheme was rejected in favor of the primary scrubbing and screening process. (Design data for the RFP soil decontamination facility is due Oct. 1, 1979; we do not have adequate data to justify incorporating the polar/non-polar separation scheme into a proposed flowsheet.)

Approximately 40 reagents were tested as additives to the scrubbing solutions. The most effective decontaminant was a solution of 2 vol % HNO_3 , 2 vol % pine oil, 0.2 vol % HF, and 5 wt % Calgon in water. This decontaminant consistently decontaminated 80 to 85 wt % of the soil to < 30 dpm/g. However, use of the solution has been discontinued pending completion of corrosion tests on equipment materials.

A 5 wt % Calgon solution adjusted to pH 11-12 was selected for the initial pilot-plant-scale runs. This solution has also proven to be effective on laboratory-scale tests (about 99% of the activity removed from 78 wt % of the soil). This solution is amenable to recycle and is expected to be less corrosive than the acid solution.

The pilot plant laboratory has been completed. Some modifications were necessary and they have been made.

The equipment has been set in place and is now undergoing testing by Pilot Plant Development Group personnel; cold soil is being used for these tests. The Operational Safety Analysis (OSA) of the pilot plant laboratory is in the final review stage.

During laboratory-scale decontamination tests, it was noted that some particles were magnetic (e.g. magnetite) and contained higher levels of activity that were not removed by attrition scrubbing. In some, but not all cases, a better soil product was obtained by incorporating a final magnetic polishing step into the separation scheme.

Future Work

Decontamination of hot soil in the pilot plant laboratory will commence upon final approval of the OSA. Lab support for Pilot Plant personnel will be necessary to optimize operating conditions, maintain water quality for recycle purposes, and to provide some analyses. Data from the pilot plant will be used to establish final design criteria for full-scale operation.

SOIL DECONTAMINATION AT OTHER SITES

Charlotte E. Alford, John A. Hayden, Doyle L. Mitchell*, Robert L. Kochen, Roger L. Olsen, and John R. Stevens

Objective

The objective of this program is to develop and demonstrate soil decontamination processes for the removal

*Pilot Plant Development Group, Chemistry R&D.

or concentration of plutonium and other actinides from contaminated soils from other DOE sites.

Prior Work

Work on this project was initiated in June 1978. Budget and manpower allotments were specified for four main tasks:

1. Preparation for soil characterization
2. Identification of sites and sample collection
3. Improvement of the primary soil decontamination process
4. Identification of other physical decontamination methods

Achievements and Discussion

Soil characterization procedures were designed and written. A representative from the analytical laboratory is being trained to conduct these procedures.

Five sites were identified and arrangements were made to collect, analyze, and ship soil samples to the Rocky Flats Plant for testing. The five sites are Hanford, Idaho (INEL), Los Alamos, Mound, and Oak Ridge. The Hanford soil has been received at Rocky Flats and is undergoing the extensive analysis required by Health, Safety, and Environmental regulations before decontamination testing can begin. Analysis of the INEL soil (at INEL) is complete and the soil sample is ready for shipment to Rocky Flats. Winter weather has delayed sampling of soils at the other three sites.

Direct use of the Rocky Flats primary soil decontamination process is not expected to be applicable to soils from all five of the other DOE sites.

Preliminary tests on other decontamination schemes have been done using Rocky Flats soil.

A proposal has been submitted to the Transuranic Waste Systems Office for the design, construction, and utilization of a mobile soil decontamination laboratory. This facility would permit on-site sampling and characterization of soils. On-site work would allow more efficient sampling of contaminated soils from different locations at a given site and provide more representative samples. Soils do vary widely in such things as composition, even in the same general area. A mobile facility would also solve problems inherent in the transportation and processing of contaminated materials.

Future Work

Soil characterization and actinide separation tests will begin after each soil has been received, analyzed, and approved by Health, Safety and Environmental personnel. If funding is received for the mobile facility, work will proceed as described in that proposal.

PROCESSING CHEMISTRY AND ENGINEERING

Edward D. Erickson

SEPARATING LEAD AND CALCIUM FROM AMERICIUM BY CHROMATE AND OXALATE PRECIPITATION

Donald L. Baaso*
and
Warren I. Yamada

Objectives

The objectives of this project were to develop a purification scheme for removing lead and calcium from americium oxide (AmO_2) and to purify 285 g of the impure oxide.

Prior Work

Calcium has been successfully removed from americium by the addition of ammonium ion (NH_4^+) as a complexing agent in the oxalate precipitation process.¹ Recent work shows that lead can also be separated from americium by oxalate precipitation.

Achievements and Discussion

The process recently developed for removing lead from americium by using oxalate precipitation was limited to dilute solutions of lead (not exceeding 80 mg/l) because of the limited solubility of lead oxalate (PbC_2O_4). The equipment used to process the impure AmO_2 have small volumes; therefore the solutions produced during processing would be highly concentrated in americium as well as impurities. Consequently, a

search was made for methods usable to separate calcium and lead from concentrated solutions.

The characteristics of the lead ion (Pb^{2+}) and the solubilities of various lead compounds were investigated. It was found that lead chromate (PbCrO_4) is insoluble in dilute solutions of strong acids.^{2,3} Laboratory-scale experiments were conducted to determine whether PbCrO_4 could be precipitated from slightly acidic solutions by the addition of chromic acid (CrO_3). One experiment was conducted without americium present; two other experiments had americium present.

The experiment without americium present resulted in a decrease of 99.7 wt % of the original lead present. The lead in the solution was decreased from 2.0 g/l to 0.0063 g/l by the addition of CrO_3 at a Cr:Pb molar ratio of 4 and at a pH of 4.

The starting AmO_2 for the two experiments with americium present contained 2.8 wt % lead. This was decreased to 107 ppm using a Cr:Pb ratio of 2, and to 50 ppm by using a Cr:Pb ratio of 4. Both starting solutions were at pH 5. The americium was then precipitated as the oxalate. The filtrates contained 7.9 and 1.2 mg/l lead, respectively. This indicates a > 99.0% removal of lead by the chromate precipitation step. The calcium decontamination during the oxalate precipitation step was also significant. The calcium was decreased from 2.0 wt % in the starting AmO_2 to 1257 and 1969 ppm respectively for the two tests. Calcium concentration in the oxalate filtrates were 420 and 460 mg/l.

A procedure was written for a full-scale production process based on the experimental runs. During four such

*Special Recovery Group, Chemical Operations

runs, 248 g of AmO_2 of acceptable purity was produced. This material met all specifications for shipment to the ORNL isotope pool. Although the lead contamination was within specifications, it was significantly higher than the values obtained during the laboratory-scale experiments. The lead removed by the PbCrO_4 precipitation step ranged from 20 to 71% of the lead in the starting material. The remainder of the lead decontamination was achieved during the oxalate precipitation step. The AmO_2 products ranged from 908- to 7319-ppm lead. Chromium contamination in the product was insignificant, ranging from < 10 to 127 ppm. Data from these runs are shown in Table 4. Run 1 contained high calcium contamination which was decreased from 2.8 wt % to 1561 ppm by the oxalate precipitation. This corresponds to a 94% decrease.

TABLE 4. Lead Decontamination From Americium During Production Scale Runs

	Run Number			
	1	2	3	4
Pb in AmO_2 feed	2.0 wt %	4.0 wt %	1.3 wt %	1.0 wt %
Pb in AmO_2 product	1858 ppm	7319 ppm	4229 ppm	908 ppm
Pb removed by PbCrO_4 ppt*	71 %	20 %	24 %	56 %
Pb removed by C_2O_4 ppt*	22 %	64 %	46 %	33 %
Cr in product	< 10 ppm	< 97 ppm	127 ppm	41 ppm

*Based on amount of lead in starting oxide.

The oxalate filtrate contained 1.176 g/l calcium.

The performance of the PbCrO_4 precipitation was less than expected during the production-scale runs. This was probably the result of an equilibrium shift in the chromate ion. The production-scale runs were precipitated at a pH of 2 compared with pH 5 for the lab-scale test with americium. This pH difference could have caused an equilibrium condition favoring the dicromate ion ($\text{Cr}_2\text{O}_7^{2-}$) over the chromate ion (CrO_4^{2-}).

Future Work

The chromate-oxalate precipitation technique appears to be a viable process for the removal of lead and calcium from americium. However, control of the pH appears to be of critical importance. Optimum conditions for large-scale runs need to be further defined. A fifth run is planned.

References

1. W. V. Conner and S. G. Proctor, "Americium Recovery From Reduction Residues," U.S. Pat. 3,781,404, December 23, 1973.
2. E. J. Slowinski and W. L. Masterston, Qualitative Analysis and the Properties of Ions in Aqueous Solution, W. B. Saunders Company, 1971.
3. A. Seidell and W. F. Linke, Solubilities of Inorganic and Metal Organic Compounds, Vol. II, American Chemical Society, 1965.

A DEMONSTRATION OF THE PYROREDOX PROCESS IN THE INDUCTION-HEATED, TILT-POUR FURNACE

Robert G. Auge, Greg D. Bird,
and
James B. Knighton

Objective

Ten induction-heated, tilt-pour furnaces will be used to purify plutonium metal in the new Plutonium Recovery Facility at Rocky Flats. A prototype tilt-pour furnace has been installed in an existing facility for testing and development purposes. The objective of this work is to develop an improved basic tool to accomplish pyrochemical processes such as molten salt extraction for removing americium from plutonium. Electrorefining and pyroredox processes for making high-purity plutonium metal will also be demonstrated in the furnace on a production scale. The tilt-pour furnace is being developed to provide improved operating conditions such as the elimination of ceramic crucibles and faster operating cycles than can be accomplished in the present stationary production furnaces.

Prior Work

Previous semiannual reports describe the furnace and its startup.* The use of the furnace for recovering plutonium and americium from waste molten salt extraction residues has been reported.

*RFP-2360-A, February 24, 1975;
RFP-2417-A, August 29, 1975;
RFP-2546, February 14, 1977;
RFP-2870, August 30, 1979.

Achievements and Discussion

The pyroredox process is a three-step pyrochemical process for purifying plutonium metal. (See Figure 2.) The first step is accomplished by the oxidation of plutonium metal to plutonium chloride by the use of zinc chloride. The reactants are contained in a molten eutectic salt of calcium chloride and potassium chloride. All metal impurities less reactive than plutonium are contained in the resulting zinc metal button that is produced. During the second process step, the salt containing plutonium, potassium, and calcium chloride is contacted with calcium metal to reduce the plutonium chloride to metal and reform the calcium chloride - potassium chloride salt. The third and last step is to remove excess calcium metal by distilling the calcium away from the plutonium in a vacuum furnace operated at 700 °C and 10^{-3} torr.*

The oxidation and reduction steps should be conducted in separate, dedicated furnaces to avoid cross-contamination by impurities between the two process steps. Because only one tilt-pour furnace is available, separate tungsten crucibles, stirrers, and tantalum molds were prepared. One set was used for the oxidation step and the second set will be used for the reduction step. Several batches of plutonium have been processed through the oxidation step. The crucible, stirrer, and mold will be changed and the furnace will be calibrated and programmed to prepare it for the reduction step. The first four oxidation runs were completed successfully. Small temperature and pressure excursions were observed during the initial heat-up and mixing part of the run program.

*RFP-2870, August 30, 1979.

FIGURE 2. Pyroredox Process

These small changes did not cause any operational problems and may be minimized by controlling the purity of reagents, decreasing the rate of temperature rise, diluting the reagents with inert salts, and changing the rate of mixing.

The oxidation step product salt has an intense blue-green color typical of trivalent plutonium. Preliminary analytical results for the zinc product buttons indicate that the plutonium content is below the discard level (0.0106 grams of plutonium per gram of zinc alloy metal).

The total feed to the first four runs, consisting of impure plutonium, potassium chloride and calcium chloride salts (KCl-CaCl₂), zinc chloride (ZnCl₂), and products (PuCl₃-KCl-CaCl₂, and zinc alloy) are given in Table 5.

The difference of 10 g between the materials in the feed and the product is accounted for by material coating the stirrer blade and crucible that was not completely removed during cleaning.

TABLE 5. Feed and Products for First Four Runs

<u>Feed</u>	
Pu	7,008 g
KCl-CaCl ₂	5,452 g
ZnCl ₂	6,205 g
Total	18,665 g
<u>Product</u>	
PuCl ₃ -KCl-CaCl ₂	16,690 g
Zn alloy	1,758 g
Miscellaneous cleanings	207 g
Total	18,655 g

Future Work

The tilt-pour furnace has been set up and calibrated to perform the reduction step tests. The plutonium chloride (PuCl₃) in the salts from the four oxidation runs will be reduced by calcium. The plutonium alloy produced will be vacuum distilled to remove zinc and calcium metal. Complete material and plutonium balances will

be made around the oxidation and reduction steps. The purity of the product metal will be compared to the purity of the feed metal to evaluate the process.

PROCESS DEVELOPMENT FOR RECOVERY OF AMERICIUM FROM VACUUM MELT FURNACE CRUCIBLES

Roy E. Dawson

Objective

The objective of this study is to develop a process that permits the recovery of plutonium and americium from vacuum melt furnace crucibles.

Prior Work

A method for dissolving plutonium and americium from broken magnesium oxide crucible pieces was developed.

Achievements and Discussion

A molten salt extraction (MSE) process is used at Rocky Flats to remove americium from plutonium metal. A small amount of plutonium is also extracted giving a KCL-NaCl-MgCl₂ salt residue containing americium and² plutonium. This americium and plutonium must be removed before the salt can be discarded. This has been accomplished in the past using an aqueous process. However, a pyrochemical process is being developed as a replacement for the aqueous process. This pyrochemical process will require the use of magnesium oxide crucibles. After use, these crucibles will contain plutonium-americium residue. A process is required that will remove the plutonium and americium from the crucibles in a form that will permit separation and recovery of the two elements, either in the current aqueous salt recovery process or in a

pyrochemical process. In addition, the MgO crucible material must be decontaminated to a throwaway level or lower.

Previous work has shown that low-normality hydrochloric acid solution is effective in removing plutonium and americium from the crucible pieces.* However, a plutonium polymer suspension formed when leach solutions were combined with rinse water. Polymer formation was prevented by rinsing the crucibles pieces with low-normality hydrochloric acid instead of water.

Laboratory-scale experiments were conducted on the leach solutions to determine if the solutions could be introduced to the aqueous process as feed material. Laboratory analysis of impurities by atomic adsorption was accomplished after each step. Results for solutions that contain americium are presented in Table 6. Concentrations of some impurities in the anion effluent were above or near the acceptable 1% level. However, a recommendation whether or not to introduce the solutions into the aqueous salt recovery process is pending until a complete analysis of the AmO₂ product is available.

An alternative method of recovering the plutonium and americium from these crucibles is being investigated. Americium and plutonium is removed from the leach solutions by precipitation with oxalic acid, filtration, and calcination to an oxide. Tests have been conducted with two liters of solution. Results should indicate if the oxide can be returned to the pyrochemical process stream, thus eliminating the need for cation and anion exchange.

*RFP-2870, August 30, 1979

TABLE 6. Analysis of Impurities
for Solutions Containing Americium

(Results expressed in grams of impurity per gram of Americium)

Element	Process		
	After Leaching	After Cation Exchange	After Anion Exchange
Al	< 0.14 0.053	0.0499 0.0551	0.0141 0.0268
Ca	2.74 1.44	1.81 1.60	1.413 0.710
Cr	0.014 0.0030	0.0063 0.0022	0.0020 < 0.001
Fe	0.047 0.0124	0.0485 0.0155	0.0161 0.0069
Mg	19.33 7.30	3.703 2.886	3.59 1.60
Ni	0.026 0.0064	0.0050 0.0024	0.0055 0.0018
Pb	< 0.01 0.010	0.0014 0.0036	< 0.004 < 0.002
Si	0.048 0.018	0.0041 0.0036	--- < 0.009

Three batches of leached crucible pieces, each weighing approximately one kilogram, were placed in a high-resolution radiometric counter to determine the amount of plutonium and americium remaining after treatment. Results indicated plutonium assays from 1.27×10^{-4} to 5.20×10^{-4} g/g and americium assays from 1.9×10^{-5} to 8.5×10^{-5} g/g. An economic discard limit for americium has yet to be determined. However, the plutonium concentrations are below the 5.0×10^{-3} g/g discard limit.

In summary, leaching and rinsing with low-normality hydrochloric acid provided a satisfactory method of removing plutonium and americium from the crucible pieces. The resulting solutions may be suitable as feed material for the aqueous salt recovery

process pending further analysis of the AmO_2 product for impurities.

Laboratory analysis is also in progress on the product from oxalate precipitation of leach solutions that have not been subjected to treatment with ion exchange. The remaining crucible pieces have been radio-metrically counted and can be discarded in terms of plutonium content.

Future Work

Future work will involve determining an americium discard limit for crucible pieces and completion of laboratory analysis of the americium oxide products.

PLUTONIUM PEROXIDE PRECIPITATION PROCESS

Dennis R. Schlepp
and
Clyde C. Perry

Objective

The objective of this work is to improve the peroxide precipitation process and thus produce consistent high-quality material for processing to plutonium metal. The ability to use ion column eluate as feed is a prime consideration in the design of process improvements.

Prior Work

The precipitation digesters were redesigned to incorporate modifications for improved mixing and for increased residence time. Preliminary testing was carried out to determine residence time distributions and to estimate the performance of the units when installed. These results were

reported in previous progress reports (RFP-2803, November 8, 1978; and RFP-2870, August 30, 1979).

Achievements and Discussion

The system of redesigned digesters was installed and started up in January 1979. Process parameters have been monitored in all production runs since that time. Results of this study have produced the following results:

1. The system is operating on two digesters; three digesters were required previously. This is directly related to improved flow characteristics and the increased residence time provided by the new design.
2. There were fewer production interruptions due to filtering problems. This resulted from the system's ability to consistently produce good-quality precipitate.
3. Desirable product characteristics such as filterability and reactivity are dependent on particle-size distributions. Previously established standards for "good" product have been met consistently. (See Figure 3.)
4. Distributions of particle-size plutonium oxide are directly related to fluorination efficiency and parameters such as losses of fine plutonium particles to scrubbers and filters. The size distributions of oxide particles show a marked improvement, with the distribution shifting from large amounts of small particles to more consistent makeup of large particles. (See Figure 4.)

FIGURE 3. Distribution of Particle-Size Plutonium Peroxide

FIGURE 4. Distribution of Particle-Size Plutonium Oxide

FIGURE 5. Plutonium Metal Reduction Yields

5. Metal reduction yields have remained high throughout the latest runs, as compared to historical data. (See Figure 5.)
6. Levels of recycled plutonium nitrate have been cut from the range of 17-20%, to less than 10%. This has reduced the load on the ion exchange columns and has allowed processing of more backlog material.
7. Elimination of errors in measuring levels in the feed tanks has allowed accurate material balances on the process. The previous methods accounted for errors of 8.6% in calculating plutonium feed amounts.

Because of production schedules, there was no opportunity to make an eluate-only run on production equipment. However, such runs are planned for evaluating the process and its ability to handle the eluate.

Future Work

The objectives of this project are to provide process modifications to produce high-quality product for metal production and to provide the ability to use eluate as feed. In light of these objectives, work will be going on in several areas:

1. Process Control - This area includes plans to install an accurate flowmeter on the feed stream and a look at automating the process with a programmable controller.
2. Process Chemistry - Evaluations will be made of the effect of direct-strike peroxide addition. This involves use of split-stream addition and mixing of feed and peroxide in a static mixer. This area is critical to future operations using only eluate as a feed material.
3. Parameter Studies - Studies will be made of parameters such as oxide crystal surface area (relating to fluorination ability, sulfate ion concentration, effects of other catalysts (e.g., fluoride ion), and decontamination factors (iron, nickel, and beryllium).

A COMPARATIVE STUDY OF ANNULAR AND RASCHIG RING-FILLED TANKS

Mark A. Fredrickson

Objective

The primary objective of this program is to study the mixing characteristics of both annular and raschig ring-filled tanks. Ultimately, it is to be determined whether a full-scale annular tank is capable of mixing a nonhomogeneous solution more rapidly than a raschig ring-filled tank, while maintaining the surface-to-volume requirements of nuclear safety.

A secondary objective of this research is to determine a design for annular tanks that will allow safe and efficient sludge removal.

Prior Work

A qualitative study of mixing in bench-scale annular and raschig ring-filled tanks was completed.*

Achievements and Discussion

A quantitative study of mixing in annular and raschig ring-filled tanks was begun. In this study, a stimulus-response technique based on exit age distribution theory was used. This technique converts concentration versus time data into dimensionless exit age versus dimensionless time information. Once the data is in dimensionless form, it is plotted. In graphic form, the data may be easily compared with theoretical ideals (perfect mixing and no mixing). The data may also be compared with information gathered from any other vessel of any size on the same coordinate system.

The same general procedure was used to study mixing in both bench-scale annular and raschig ring-filled tanks. Only the flow rate or mode of fluid entry into the vessel was changed between experiments. For the annular tank with tangential entry, experiments were performed in which fluid entered above the drain as well as at points located 90°, 180°, and 270° clockwise from the drain. For the annular tank with nontangential entry, mixing was studied with fluid entering directly above the drain as well as 180° opposite it. Mixing in the ring-filled tank was studied with fluid entering through a 0.375-in.-i.d. by 1-in.-long pipe, a Bete Fog nozzle distributor, and an ordinary hole in the lid.

Once the fluid entry point of the vessel under investigation was selected, the vessel was filled with water. The flow of water was then

adjusted to a predetermined rate (between 12 and 30 ml/sec). A constant volume was maintained in the tank by adjusting the drain valve. At time zero, 5 ml of tracer (4500 ppm KCl) was rapidly injected into the feed line. Samples were taken near the point through which fluid left the vessel every 60 sec for flow rates between 12 and 15 ml/sec, and every 30 sec for flow rates greater than 15 ml/sec. After collection, samples were analyzed in a Devon products conductivity meter.

For pilot-scale experiments, a similar procedure was used. Flow rates ranged between 2.5 and 12.0 l/min. The tracer volume was increased to 50 ml (concentrated KCl) so a measurable response could be found at the vessel's drain.

The procedure for investigating both tangential and nontangential entry in the pilot-scale annular tank was the same. At time zero, 50 ml of tracer was injected into the tank. Continuous specific conductivity versus time data were then obtained at the vessel's drain.

Exit age curves for the bench-scale raschig ring-filled tank are shown in Figure 6. These curves were obtained from three separate experiments, all of which were carried out at different flow rates. The curve represented by the solid line was the result of an experiment in which fluid entered the ring-filled tank through an off-center hole in the lid, with no distributor, at 16.2 ml/sec. Visual observations during the experiment determined that channeling occurred down the wall of the vessel as well as through the rings. The curve represented by the dashes was for a case in which fluid entered the tank at 13.8 ml/sec through a pipe in the center of the lid. Very little channeling down the wall of the vessels was observed, but channeling through the rings was seen. The curve represented by the

*RFP-2870, August 30, 1979

FIGURE 6. Exit Age Distribution Curves for Raschig Ring-Filled Tank

dots was for an experiment in which fluid entered through a Bete Fog nozzle distributor in the center of the lid at 24.6 ml/sec. Again, very little channeling down the wall was observed, but channeling down the rings was seen.

Upon inspection of the curves, the following conclusions can be reached. First, since each curve has only one peak, fluid bypassing is not a problem. In other words, fluid passes through in one bulk mass, not two or three. Second, dead space does not exist in the vessel. Curves repre-

sented vessels having dead space have tails extending past θ equals 10. However, although problems such as dead space and bypassing are not associated with the ring-filled tank, the situation is not good. Each curve resembles a Gaussian distribution and has a high maximum point {function of reduced time $[E(\theta)]$ of ~ 1.55 }. The axis of symmetry for each curve is near θ equals 1. When the shape of the curves are compared with the plug flow case, it is evident that fluid flowing through a raschig ring-filled tank approaches plug flow behavior (no mixing) as an ideal.

FIGURE 7. Exit Age Distribution Curves for Bench Scale Annular Tank With Nontangential Entry.

Also evident from inspecting the distribution curves is the fact that flow rate has little bearing on mixing performance. In all cases investigated, regardless of flow rate, with or without a distribution mechanism, the ring-filled tank approached plug flow behavior.

Figure 7 presents some exit age distribution curves for the bench-scale annular tank with nontangential entry. Analysis of the curves yields the following conclusions. First, dead space and bypassing are not problems. Second, the curves approach perfect mixing (continuous stirred tank reaction) as an ideal. The difference in height between the two curves is not significant as far as mixing efficiency is concerned. The same type of experiments was performed for several flow rates higher than the flow rate in Figure 7 (12 ml/sec) and

yielded the same type of results. Hence, for the bench-scale annular tank with nontangential entry, it was concluded that the position of the inlet does not affect the vessel's performance.

Figure 8 shows the exit age distributions for the bench-scale annular tank with tangential entry. The flow rate used in the experiments that generated this family of curves was 30 ml/sec, which resulted in a mean residence time of 2.09 min. As seen in Figure 8, the inlet position had no significant effect on the shape of the curve.

On comparing tangential versus nontangential entry at the bench scale, it was concluded that for both cases the annular tank approaches perfect mixing behavior. Also, the

FIGURE 8. Exit Age Distribution Curves for Annular Tank With Tangential Entry

FIGURE 9. Exit Age Curve for Pilot-Scale Annular Tank With Nontangential Entry

mode of fluid entry, at the flow rates considered, had little bearing on the performance of the bench-scale annular tank.

Figure 9 presents the results from a pilot-scale experiment on an annular tank in which nontangential entry was used. Inspection of the curve shows a rapid, high peak followed by a long

tail. The curve as a whole does not approach either of the ideals discussed earlier. Its interpretation is therefore more difficult, but it may be understood as follows: First, a significant fraction of the total area is contained under the first peak. This indicates that a large fraction of the tracer particles passed through the tank in a short time. Hence, when nontangential entry is used in the

FIGURE 10. Exit Age Curves for Pilot Scale Annular Tank With Tangential Entry

pilot-scale tank, channeling develops which enables some of the fluid to pass through the tank without being well mixed. As the bulk of the impulse travels through the vessel, the outermost layer of molecules tends to be washed away by convective forces. In addition, a large concentration gradient exists between the pulse and the water in the tank. Hence, diffusional forces tend to draw molecules from the pulse. The tail on the exit age curve corresponds to the tracer particles which left the pulse and remained in the tank a long time.

When tangential entry was used in the pilot-scale annular tank, major problems such as fluid bypassing and channeling were eliminated. Figure 10 presents the results from two typical experiments. The solid curve is for a case in which the inlet was opposite the drain. There is one minor peak, which indicates a small degree of bypassing. However, the area under

the small peak that corresponds to the fraction of particles involved in bypassing is insignificant compared to the total area under the curve. Bypassing is not a major problem. When the entrance is placed above the drain, it is more difficult for any bypassing to develop since the particles are required to traverse a longer distance to reach the drain. The optimum position for the tangential inlet is directly above the drain. Even when a less optimum position is used, however, the mixing is still good.

Future Work

Experiments concerning mixing in full-scale annular tanks will be performed as soon as the vessels are available. Sludge removal from annular tanks will also be studied.

RFP-2952