MASTER

CHEMISTRY RESEARCH AND DEVELOPMENT PROGRESS REPORT
MAY THROUGH OCTOBER 1978

Frend John Miner

Rockwell International

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Chemical Research – – – – – – – – – – – – – – – – – James D. Navratil

Process Chemistry and Engineering – – – – – – – – – – – Edward D. Ericksen

SUBJECT DESCRIPTORS

Actinides
Adsorption
Air Sparge Mixing
Americium
Americium Oxalate
Americium Recovery
Annular Tanks
Ash Fusion
Calorimeters
Calorimetry
Chemistry
Chromatography
Decontamination
Digesters
Dissolution
Distillation
Enthalpy of Formation
Hydrofluoric Acid
Incinerator Ash
Ion Exchange
Lathe Coolants
Lead
Leaching
Materials Recovery
Magnesium Oxide Crucible
Mixing
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Molten Salts Residues
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Photochemistry
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Plutonium

Plutonium Dissolution
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Zinc

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CHEMICAL RESEARCH

*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 ENGINEERING

Metal alloy consolidation was completed successfully. The induction-heated furnace well was redesigned and installed to correct a corrosion problem and made replacement of the well easier. Preparations have begun to develop the pyroredox process for purifying plutonium metal. (DDS Endeavor 332*)

Zinc, magnesium, and calcium solvent metals were removed from plutonium-americium feed alloy on a regular basis during this report period. Splattering has been controlled, but residue generation has been a problem. (DDS Endeavor 332)

High levels of americium in molten salt extraction salts provide the means for isothermal calorimetry, which can be used to estimate plutonium and americium concentrations in products from pyrochemical processes. (DDS Endeavor 332)

Plutonium peroxide precipitation using ion column eluate as feed is being studied. The existing process in the Plutonium Recovery Facility cannot use eluate as feed with acceptable efficiency. A system was designed for improved continuous plutonium peroxide precipitation. Preliminary test results indicate mixing characteristics and particle flow patterns are greatly improved as compared to the performance of existing production equipment. (PPS*)

The solubility of silica in nitric acid–hydrofluoric acid solutions at room temperature has been studied. Preliminary results indicate the solubility of silica in $12N$ nitric–$0.1N$ hydrofluoric acid to be one gram per liter. (DDS Endeavor 331)

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*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 study comparing the mixing efficiencies of annular and raschig ring—filled
tanks has begun. Results from bench-scale experiments show that mixing in
the annular tank is three to five times faster than mixing in the raschig
ring—filled tank. (DDS Endeavor 331*)

Dissolution experiments were conducted on a plutonium alloy obtained from
pyrochemical processing of salt produced by a molten salt extraction process.
Solutions of hydrochloric acid and of nitric acid—hydrofluoric acid were used;
the best results were obtained with $6N$ HCl and $15.6N$ HNO_3 $-0.1N$ HF.
(DDS Endeavor 331)

Hydrochloric acid solutions were used to leach plutonium and americium from
vacuum melt furnace crucibles. Results indicated that most of the americium
dissolved and remained in the filtrate, while most of the plutonium was
contained in the heel. (DDS Endeavor 331)

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CHEMICAL RESEARCH

James D. Navratil

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 evaluated critically 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 compilation and critical evaluation of the thermodynamic properties of actinide materials initiated several years ago is being continued.

An experimental program utilizing adiabatic and solution calorimetry has been initiated to determine the thermodynamic properties of plutonium and the plutonium-hydrogen system. The basic hardware of silver metal for use in the adiabatic calorimeter was obtained on a loan basis from the National Bureau of Standards, Washington, D.C. Contractual services of Calorimetrics, Inc. were utilized to assist in the construction of the calorimeter. Installation of a glove box to house the existing solution calorimeter was also initiated.

Achievements and Discussion

The design, construction, and installation of the adiabatic calorimeter has been completed. Prelim-

inary experimentation indicated that heat capacity measurements can be made with a precision of 3 parts in 20,000. Actual heat capacity measurements on the empty container for samples will not begin until testing has been finalized and a thorough understanding of the operation is realized.

Installation of the glove box for the solution calorimeter has been completed, and the solution calorimeter has been installed. Preliminary calibration of the solution calorimeter in the glove box indicates that the calorimeter is operating satisfactorily in this environment.

Future Work

Heat capacity measurements on the empty container and on the aluminum oxide standard will be taken over a temperature range of 298 to 800 K in the adiabatic calorimeter. These results will serve to calibrate this instrument.

Calibration of the solution calorimeter will be finalized in the glove box. The enthalpy of plutonium metal in acid will then be determined, followed by the enthalpy of solution of several plutonium hydrides.

Consultation and evaluation of thermodynamic data will continue.

AMERICIUM RECOVERY AND PURIFICATION

Paul G. Hagan, Armen R. Kazanjian, and Milton E. Killion

Objective

The objective of this work is to improve the americium oxalate precipitation process and to

provide technical assistance for its continued operation.

Prior Work

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

Achievements and Discussion

The parameters of the oxalate precipitation process were investigated for efficiency in separating and purifying americium and for finding a method for removing lead, which is a major impurity in the americium product. Results of this study show the process is strongly acid and dependent upon oxalate ion concentration. For maximum efficiency in separation and purification, the acid concentration should be close to 0.3N, and the oxalate concentration should be about 0.04M. In addition, the presence of chloride ion has been found to aid in preventing the coprecipitation of lead. Figure 1 shows the solubility of americium and lead oxalate as a function of nitric acid concentration. An optimal separation of lead with a minimal loss of americium can be achieved when the solution is about 0.3M in hydrogen ion. At this acidity, the solubility of americium is about 6 mg/l and the lead is about 42 mg/l. Using the current conditions of process operations, and the supposition that the solution contains 10% lead in relation to americium, approximately 0.9% of the americium would be lost to the filtrate; however, there would be a 65% reduction of lead in the final americium product.

Oxalate concentration, within the ranges studied, affects the solubility of lead but not the americium. Figure 1 shows that when oxalate is reduced from 0.1M to 0.04M, the solubility of lead is increased to about 65 mg/l, which in most production runs would eliminate most of the lead.

A small amount of chloride in the solution has been found to enhance the separation of lead by forming
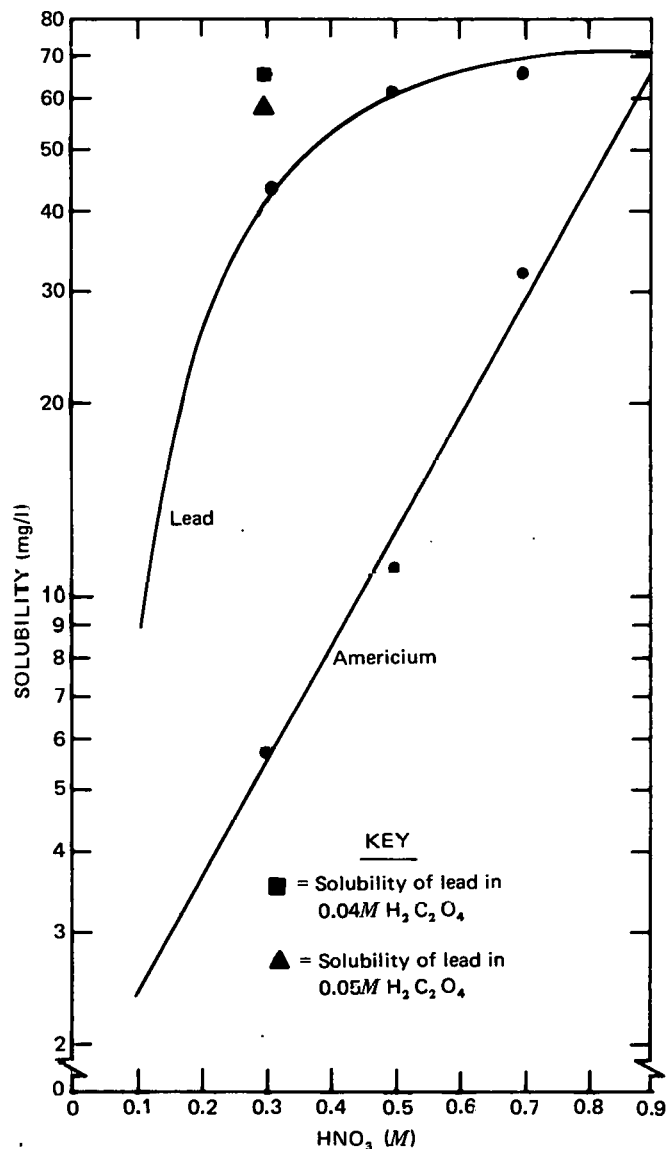
FIGURE 1. Solubility of Americium and Lead in 0.1M H$_2$C$_2$O$_4$ (Oxalic Acid) as a Function of Nitric Acid Concentration

a soluble lead chloride complex. If the solution contains about 2 g/l chloride, the solubility of lead is increased to 81 mg/l. Chloride, however, can have a deleterious effect on the stainless steel equipment used in the process. A study is currently in progress to determined if this slight amount of chloride would cause corrosion problems.

Additional studies have shown the process is not appreciably affected by temperature. Test precipitations at ambient, 40, 50, and 70 °C show only a

slight increase in the solubility of americium and lead. Tests were also made on the effect of digestion time. The results of these tests show the digestion time must be in excess of 30 minutes for completeness of precipitation.

In support of Chemical Operations, studies were also made to determine if plutonium is separated from americium during the oxalate precipitation process. The results show americium and plutonium are insoluble to approximately the same degree and therefore, using the current conditions of precipitation, plutonium would not be separated from the americium.

Future Work

Work is in progress to demonstrate, on a production scale, the americium recovery and purification process using the prescribed parameters found in these studies. Additional work is being planned for finding methods of removing other troublesome contaminants such as plutonium.

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

Gary H. Thompson, C. Michael Smith, and Richard H. Schmunk

Objective

The objective is to optimize the cation exchange process used for the recovery of 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, but the process has not been optimized. Work reported previously[1] on the current series of tests included

a. Resin evaluation. Macroporous resin was more efficient than gel-type resin, but actinide recovery was inadequate.

b. Evaluation of a proposed change from the $NaCl-KCl-MgCl_2$ system to the $CaCl_2-KCl-MgCl_2$ system. Actinide loading was reduced to 70% of that attainable from the sodium solution, and 50% of the calcium fed to the column eluted in the plutonium and americium product solution.

No previous work on hydrolytic plutonium formation in this process has been done.

Achievements and Discussion

Resin Evaluation

Plutonium is adsorbed on the resin as Pu(III), then eluted with $7M$ HNO_3 as $Pu(NO_3)_6^{2-}$. Although this anionic complex is not adsorbed on cation exchange resin, it is bulky and has difficulty diffusing out of the resin matrix. The process should be made easier by using a gel-type resin of lower cross-linkage or a more porous macroporous resin.

Five ion exchange tests were made. Waste solution prepared from MSE residues was fed to the column (upflow loading) to breakthrough. The adsorbed actinides were washed with water (upflow), then eluted (downflow) with 4.2 column volumes (CV) of $7M$ HNO_3 (630 ml); 4.2 CV is the average volume required for actinide recovery in production columns. The resins, waste solutions, and actinide recovery are shown in Table 1. Actinide capacity and recovery were best with Bio-Rad AG MP-50 resin, although Duolite C-25D, a macroporous resin with lower cross-linkage, was expected to be better. The difference is attributed to shrinkage of the resin in $7M$ HNO_3. Shrinkage of the matrix narrows pore size and openings within the resin itself, thus inhibiting diffusion.

The overall improvement in americium recovery over that reported previously[1] is attributed to the upflow-downflow mode of column operation.

TABLE 1. Actinide Elution From Cation Exchange Resin

Column volume (CV):	150 ml
Elutriant:	$7M$ HNO_3
Flow rate:	1.84 ml/(min cm^2) or 13 ml/min
Volume of elutriant:	630 ml (4.2 CV)
Temperature:	23 °C

Resin[a]	Type of MSE Waste[b]	Actinide in Feed Pu (g)	Actinide in Feed Am (g)	Actinide Recovery[c] Pu (%)	Actinide Recovery[c] Am (%)
Bio-Rad AG MP-50	Ca-K-Mg	5.21	0.215	95.9	96.8
Bio-Rad AG MP-50	Na-K-Mg	4.71	0.260	95.7	98.0
Dowex 50W-X8	Ca-K-Mg	3.54	0.146	74.5	93.3
Dowex 50W-X8	Na-K-Mg	3.48	0.194	82.0	95.5
Duolite C-25D	Na-K-Mg	3.14	0.173	72.0	86.5

a. Dowex 50W-X8 is a gel-type resin; Bio-Rad AG MP-50 and Duolite C-25D are macroporous resins. The latter was 20-50 mesh, the others were 50-100 mesh.
b. Waste solutions containing K, Mg, and either Na or Ca.
c. Single determination.

TABLE 2. Recovery of Americium by Oxalate Precipitation in the Presence of Calcium

Sample	Amount (g or ℓ)	Component[a] (g) Am	Component[a] (g) Ca	Component[a] (g) Mg	Component[a] (g) Na	Component[a] (g) K
Feed	1 ℓ	0.199	8.97	0.08	0.10	2.29
Run I						
Ca-Am ppt	10.9 g	0.174	7.17	0.01	0.06	0.41
Waste	1.7 ℓ[b]	0.009	1.80	0.07	0.13	1.45
Run II						
Ca-Am ppt[c]	0.2 g	0.150	0.01	---	---	0.01
Ca-Am ppt[d]	5.7 g	0.026	4.28	0.01	0.01	0.13
Waste[e]	1.2 ℓ	0.014	4.68	0.06	0.09	1.46

a. Single determination.
b. Volume: 1 ℓ feed + 0.5 ℓ $1M$ oxalic acid + 0.2 ℓ of $0.1M$ oxalic acid wash.
c. Precipitant: 75 ml of $1M$ oxalic acid.
d. Precipitant: Additional 125 ml of $1M$ oxalic acid.
e. Volume: 1 ℓ feed + 0.075 ℓ $1M$ oxalic acid + 0.125 ℓ $1M$ oxalic acid.

Evaluation of a Proposed Change From the NaCl-KCl-MgCl₂ System to the CaCl₂-KCl-MgCl₂ System

The amount of calcium in the proposed system is greater than the amount of sodium in the current system (69% versus 47%), and divalent calcium adsorbs more effectively than monovalent sodium. As a result, 55% of the calcium in the feed remains on the column, is eluted in the plutonium and americium product fraction, and is in the americium product after the anion exchange recovery of plutonium.

A synthetic nitrate eluate (Table 2) was prepared with the composition of actual column eluate except that plutonium was omitted and H^+ was $0.5M$ rather than ~ $5M$. Two methods for recovering americium as the oxalate were tested. The first was the addition of oxalic acid in excess. The second comprised the addition of oxalic acid in portions and recovering the precipitate by filtration before addition of the next portion. The resulting oxalates were calcined for 2 hours at 600 °C, and samples of the oxide were analyzed. Results are shown in Table 2. Oxide formed by excess oxalic acid con-

tained 2 wt % americium and 66 wt % calcium. Selective precipitation gave a product containing 75 wt % americium and only 5 wt % calcium from the first precipitate; however, americium recovery would still be required from the resulting waste solution, and the process would not be feasible for production.

Column wash tests on resin loaded to breakthrough with the CaCl₂-KCl-MgCl₂ solution showed that a $0.1M$ oxalic acid wash removed 35% of the calcium. The best contaminant removal was accomplished by a $1.5M$ HNO_3 column wash, which removed 85% of the calcium with 8% loss of americium.

Determination of Formation of Hydrolytic Plutonium

The formation of hydrolytic and polymeric species of plutonium upon dilution of plutonium solutions is well known. Water has been used during the MSE cation exchange recovery process to wash the column after loading to breakthrough; after elution, the columns were left filled with water until reconditioned for a subsequent run.

Even though Pu(III and Pu(IV) are strongly adsorbed on the resin, it is possible that some plutonium could diffuse out of the resin matrix into the acid-deficient solution and form hydrolytic species. Such solutions would ordinarily be low level and would be discarded. Recycle is possible, however, if plutonium is above discard level from any mechanism. Hydrolytic species would not adsorb in plutonium partitioning step but would pass with the americium through the column.

A conventional NaCl-KCl-MgCl$_2$ test using Dowex 50W-X8 resin was made. Water was permitted to stand on the resin overnight, then was adjusted to 7M HNO$_3$ and extracted with 30% tributyl phosphate (TBP) in n-dodecane. A second portion was removed after 4 days and extracted. Analyses showed that nonextractable species in the overnight sample comprised only 0.0024 ± 0.0001% (duplicate tests) of the plutonium and only 0.011% (single determination) after 4 days on the column. Consequently this mechanism does not seem probable as a source of plutonium contaminant in the americium product.

At this point, however, Chemical Operations conducted an actinide recovery run using 0.35M HNO$_3$ rather than water in the wash steps. The plutonium in the americium product was reduced by a factor of two. As a result, dilute HNO$_3$ is now used in the process.

Future Work

Resin evaluation. From the viewpoint of capacity and elution, Bio-Rad AG MP-50 is better than Dowex 50W-X8 and Duolite C-25D. Additional resin evaluation will be done. Other parameters to be evaluated include elutriant concentration, wash media, and flow rates.

Effect of CaCl$_2$-KCl-MgCl$_2$ system. Various elutriants and washes will be tested to determine their ability to remove calcium from the loaded cation exchange resin. In particular, the HNO$_3$ washing process will be optimized.

Formation of hydrolytic plutonium. Since dilute nitric wash is now being used in place of water, no additional work is planned.

References

1. Frend John Miner. *Research and Development Semiannual Progress Report for January Through June 1977, Chemistry Research and Development,* RFP-2680A. Rockwell International, Rocky Flats Plant. October 21, 1977.

PHOTOCHEMICAL SEPARATIONS OF ACTINIDES

Armen R. Kazanjian, Larry L. Martella, and James D. Navratil

Objective

The use of photochemistry to effect the separation and purification of plutonium and americium by oxidation-state adjustments is under investigation.

Prior Work

This is a new project.

Achievements and Discussion

The use of photochemistry to recover and purify plutonium and americium from process solutions may be feasible. Recovery and purification would most likely be made by photochemically altering the oxidation state of the actinide element. In particular, americium and plutonium may be recovered and purified using anion exchange techniques and photochemically stabilizing the tetravalent state instead of using chemical reagents.

Initial work has consisted of surveying the photochemical literature and conducting preliminary experiments to photochemically oxidize Am(III) to Am(IV). The experiments consisted of irradiating nitric acid solutions containing HIO$_3$ and KBrO$_3$, and basic solutions of K$_2$CO$_3$ containing either NaOCl or H$_2$O$_2$ with a 100-W tungsten light. The solutions were checked for Am(IV) spectrophotometrically and by adding chloride ion to determine if a precipitate would form. In all cases, no evidence of Am(IV) formation was observed.

Future Work

Photochemical studies will be continued in an attempt to form Am(IV) in HNO_3 and to stabilize Pu(IV) in $7M$ HNO_3 by using an adjustable wavelength light source.

ADVANCED ION EXCHANGE MATERIALS AND TECHNIQUES

Charlotte E. Alford, Larry L. Martella, James D. Navratil, and William F. Santiago

Objective

The objective is to evaluate new ion exchange resins and techniques for plutonium purification.

Prior Work

Anion exchange resins were tested to find a low-cost, high-performing, large-bead resin for the plutonium recovery process. Dowex 11 (20-50 mesh) was found to have the fastest elution and lowest cost of the large-bead resins tested. Small-bead (50-80 mesh) Dowex 1-X4 did have a higher capacity than Dowex 11, but was four times more expensive and it caused column plugging problems.

Achievements and Discussion

The resins were tested for elution behavior and breakthrough capacity at 0.5 g/l plutonium feed concentration. The resins were contained in 1.8-cm bore columns with resin bed heights of 15.0 cm and resin volume of 38.2 ml. A tubing pump was used to deliver the feed through the column at a constant flow rate. Fractions of the column effluents were analyzed for plutonium to determine breakthrough capacity and elution characteristics.

Table 3 summarizes the results of the resins tested. The breakthrough capacities of the 20-50 mesh resins were not significantly different. Elution results show a significant difference in IRA-938 as compared to the other resins tested. Ninety percent of the plutonium on the IRA-938 resin was eluted with approximately 75% less $0.35M$ HNO_3 than the other resins required.

A comparison between IRA-938 and IRA-93 was made for selectively separating plutonium and uranium. The results, shown in Figure 2, show that less HNO_3 is needed to remove the uranium on IRA-938 resin.

The advantages and disadvantages of fluidized-bed versus static-bed ion exchange operations reported in the literature are being analyzed. The advantages

TABLE 3. Properties of Anion Exchange Resins

Property	Dowex 1-X4 20-50 mesh	Dowex 11 20-50 mesh	IRA-938 20-50 mesh	Dowex 1-X4 50-80 mesh
Breakthrough capacity[a]	17.6	22.2	26.6	39.9
Elution[b]	47.26	14.05	3.58	14.0

a. Milligrams of plutonium passed per milliliter of resin bed when the ratio of plutonium concentration in effluent to plutonium concentration in feed reached 0.10. Flow rate = 8.3 ml/min. Average of two determinations.
b. Milliliters of $0.35M$ HNO_3 to elute 90% of the plutonium from 1 ml of resin. Flow rate = 8.3 ml/min. Average of two determination.
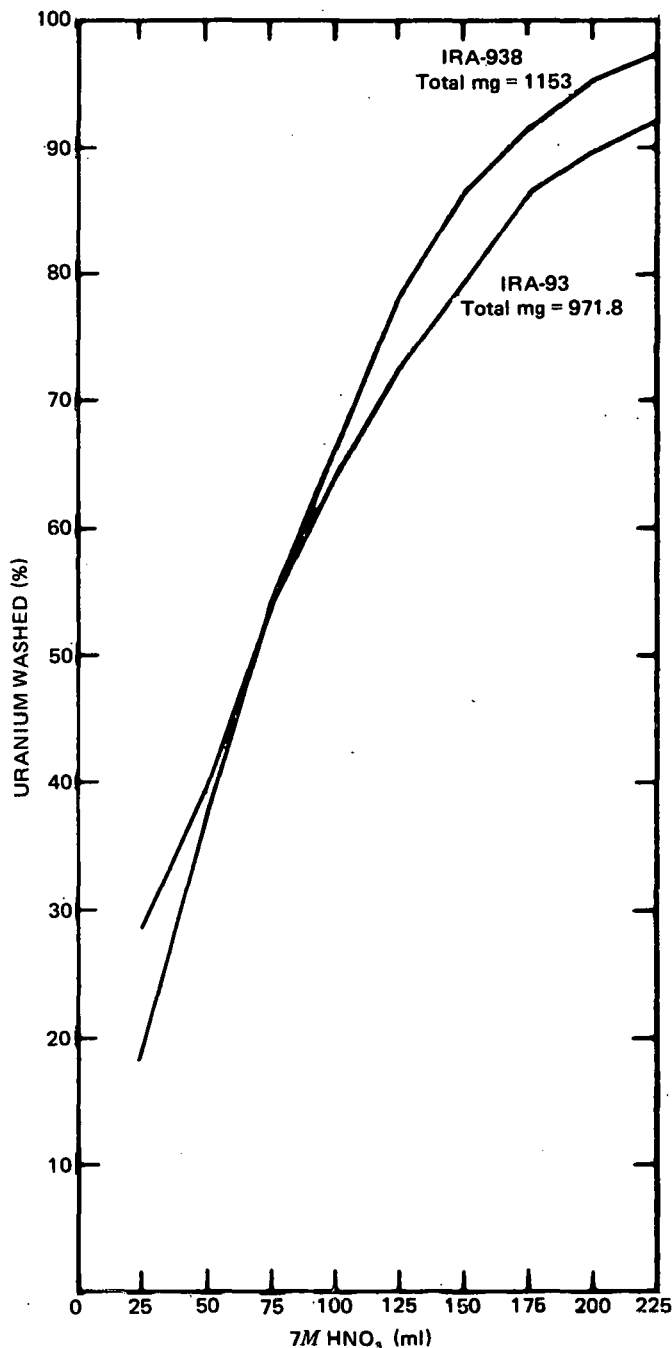
FIGURE 2. Uranium Washing Study

of fluidized-bed operations over static-bed systems appear to warrant an experimental program to evaluate fluidized-bed operations for plutonium purification.

Future Work

Radiation degradation studies will be conducted for the IRA-938 resin, and fluidized-bed ion exchange will be evaluated further.

SECONDARY ACTINIDE RECOVERY

Paul G. Hagan and James D. Navratil

Objective

The objective of this work is to develop solvent extraction processes at Rocky Flats for recovering low-level concentrations of plutonium and americium from acidic process waste streams.

Prior Work

The solvent extraction distribution ratio values have been determined for plutonium, americium, thorium, and uranium using dihexyl-N,N-diethyl-carbamoylmethylenephosphonate (DHDECMP). In investigations with similar extractants, studies were made to determine if the presence of chloride ion aided in partitioning actinides and lanthanides from solution, and to determine the extraction behavior of selected metal ions. The aqueous solubility was determined for five bidentate organophosphorus compounds. Extraction chromatography techniques were also evaluated on a laboratory scale using DHDECMP on various support materials.

Achievements and Discussion

A solvent extraction process was investigated for recovering low-level concentrations of plutonium and americium from ion column effluent waste streams. The solvent extractant DHDECMP was studied in a six-cycle process using an aqueous/organic (A/O) ratio of five. Results show that plutonium was removed during the first cycle by a factor of 50, which reduced the plutonium in the waste stream from 1.9×10^{-4} g/l to 4×10^{-6} g/l. The accuracy of analysis for plutonium in

these solutions is limited to 10^{-6} g/l values; therefore, the ultimate value for which plutonium can be removed in a six-cycle process is unknown. The americium is removed during each cycle by a factor of two. Therefore, in a six-cycle process the americium is reduced in the waste stream from 1.2×10^{-3} g/l to 4.3×10^{-5} g/l.

Since the current goal at Rocky Flats is to recover plutonium and americium values to concentrations less than 10^{-5} g/l, it appears that solvent extraction processing may afford this capability.

Future Work

The secondary actinide recovery process, with DHDECMP extraction chromatography using Amberlite XAD-4 as a support, will be verified on a larger scale to demonstrate plutonium and americium removal from acidic process waste streams.

REMOVAL OF PLUTONIUM FROM LATHE COOLANT OIL

Charlotte E. Alford, Larry L. Martella, James D. Navratil, and Gary H. Thompson

Objective

The objective of the program was to evaluate methods for reducing plutonium in lathe coolant oil to discard level and to determine whether non-filterable plutonium was present as submicron solids or in solution.

Prior Work

Work has been done on removing plutonium from lathe coolant oil and determining the nature of plutonium in the oil.[1] The work showed that the mixtures of spent oil and carbon tetrachloride contained particulate plutonium in addition to plutonium species that was soluble in water or in oil and carbon tetrachloride.

Achievements and Discussion

Lathe machining oil having a carbon tetrachloride diluent and contaminated with plutonium is generated in plutonium machining areas at Rocky Flats. The contaminated oil is passed through filters rated for particulates ≥ 0.2 μm to reduce plutonium content to the discard level $(1.6 \times 10^{-3}$ g/l).

In recent months, two batches of contaminated oil were processed through the filtration system, which comprises six Pall Trinity® filters (≥ 0.2 μm) placed in series. The plutonium concentration remained the same.

Laboratory tests showed that filtration through Millipore® filters (≥ 0.2 μm) failed to remove plutonium. Experiments with adsorbents (silica gel, molecular sieve, and five commercial charcoals) showed that only Calgon® F-300 and F-400 charcoal adequately reduced plutonium contamination (decontamination factors were 50 and 23, respectively). The only charcoal adsorbent available in a Pall Trinity filter that fits the current production filtration system did not remove plutonium.

Analysis of the oil showed water content to be 40 times that of new oil, and acidity to be 6 times that of new oil. This indicated that the troublesome plutonium species probably resulted from solubilization of plutonium in hydrochloric acid, which was formed by hydrolysis of carbon tetrachloride. The addition of small amounts of 10M NaOH to the oil to precipitate plutonium hydroxide caused precipitation of a gelatinous substance, possibly a saponification product.

Because the problem appeared to be a difficult one, probably requiring installation of a second processing line containing adsorbent columns, another method for eliminating the oil was suggested. Henceforth, contaminated oil that cannot be reduced to the plutonium discard level by filtration will be burned in the fluidized bed incinerator. This process will not only reduce waste volume, but will convert the volatile carbon tetrachloride to sodium chloride. This will result through reaction of the carbon tetrachloride with the fluidized incinerator bed medium, sodium carbonate.

Future Work

No future work is planned.

References

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

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 (TBP)–impregnated sorbents for separating uranium and plutonium from mixed actinide residues. These residues are presently processed with a modified Purex solvent extraction process.

Prior Work

Bayer AG Lewatit® OC-1023, a new commercial extraction chromatography support impregnated with TBP, was tested for uranium-plutonium separation using modified Purex processing conditions. Uranium breakthrough and elution behavior were determined for the OC-1023. Plutonium(III) removal by washing was difficult and further laboratory-scale work was warranted.

Achievements and Discussion

Testing of OC-1023 was continued since use of the sorbent would permit processing mixed actinide residues in existing ion exchange column equipment rather than expensive solvent extraction contactor equipment. The problem of poor plutonium(III) washing was caused by the presence of hydrolysis

products of TBP on the support. Washing the OC-1023 with sodium carbonate solution prior to use improved the removal of plutonium(III) during washing.

Amberlite® XAD-4 with sorbed TBP was also evaluated for separating plutonium and uranium from mixed actinide residues. The new support was found to have a high capacity for uranium and to effectively separate plutonium and uranium. Amberlite XAD-4 with TBP was comparable to OC-1023 for the process.

Amberlite XAD-4 resins were also tested for removing dissolved TBP from nitric acid effluent. Losses of TBP and its hydrolysis product, dibutyl phosphate (DBP), by solubility can cause problems in subsequent processing or waste treatment steps of the raffinate. Several non-ionic, macroporous resins were tested in laboratory-scale column equipment for removal of dissolved TBP and DBP from nitric acid waste. Amberlite XAD-4 resin gave the best results for effectively removing dissolved TBP and DBP from $5M$ HNO_3.

Future Work

The modified Purex process using Amberlite XAD-4 sorbed with TBP to process mixed actinide residues will be tested on pilot-plant-scale equipment.

PLUTONIUM RECOVERY IN ADVANCED SIZE REDUCTION FACILITY

Armen R. Kazanjian and Milton E. Killion

Objective

The new size reduction facility may include two stages of plutonium decontamination: an initial stage to remove the bulk of the plutonium and a final electropolishing stage. The experiments described in the following paragraphs are part of an effort to establish methods of solution recycle and plutonium recovery from the decontamination solutions.

Prior Work

No previous work has been done in this area.

Achievements and Discussion

Plutonium recovery from the initial decontamination solutions would be simplified if the plutonium were insoluble. Solubility measurements have been made by stirring 0.1 g air-oxidized PuO_2 in 20 ml solution for 6 hours, filtering, and analyzing the filtrate. Some of the results are as follows:

Solution	Solubility (g/l)
Water at 90 °C	1.2×10^{-4}
Oxalic acid (saturated) at room temperature	0.15
Oxalic acid (saturated) at 90 °C	0.89
Alkaline-permanganate at room temperature	0.26
Alkaline-permanganate at 90 °C	0.35
Oakite LSD Caustic at 90 °C	8.2×10^{-4}
Formula A Paint Remover at 90 °C	4.2×10^{-3}
75-3 Paste Stripper PPG at 90 °C	3.5×10^{-3}
ZEP Formula 1365 Paint Stripper at 90 °C	3.1×10^{-2}

Plutonium also has to be recovered from phosphoric acid that may be used as an electropolishing medium. Experiments have determined the solubility of PuO_2 in various concentrations of phosphoric acid at 90 °C and at room temperature. The solubilities at various times have been determined; those attained after one hour of stirring are as follows:

Parameters	Plutonium (g/l)	Amount Dissolved (%)
20% H_3PO_4 at room temperature	0.41	8.1
20% H_3PO_4 at 90 °C	0.70	14
42% H_3PO_4 at 90 °C	1.7	34
75% H_3PO_4 at room temperature	0.35	6.9
75% H_3PO_4 at 90 °C	2.9	58

Phosphoric acid must be recycled in the size reduction facility to separate dissolved stainless steel. Experiments have been made to effect this separation using an ion exchange technique called acid retardation. Results show that Dowex SBR-P resin is somewhat effective, and further experiments with varying parameters are being made to improve the efficiency.

A sodium nitrate—borax solution and a nitric acid—borax solution are also being considered for use as electropolishing media. Experiments also have been made to recover plutonium from these solutions. For example, filtration characteristics of the sodium nitrate solution and ion exchange separation of plutonium from the nitric acid solution have been investigated.

Future Work

These efforts will continue until the final planning stage is reached for the Advanced Size Reduction Facility.

PLUTONIUM PEROXIDE PRECIPITATION

Paul G. Hagan and Armen R. Kazanjian

Objective

The objective of this work is to improve the plutonium peroxide precipitation process and to provide technical assistance for its continued operation.

Prior Work

Work has been done to determine the effects of operational parameters such as temperature, rate

and manner of peroxide mixing, impurities, and acidity. A basic understanding of precipitate formation has been established, and test runs have been made in prototype equipment showing the workability of a newly designed plutonium peroxide precipitation process.

Achievements and Discussion

Investigations have been made for the fundamental understanding of particle formation and precipitation and for support in Chemical Operations processing. Laboratory studies, in which simulated process runs were made, have shown the formation of a desirable crystal structure is related to the hydrogen ion concentration of the solution. As a result of this and other previous work, proposals have been made for certain operational changes. These changes include control of the hydrogen ion and peroxide concentrations and the method and manner in which the peroxide and plutonium solutions are mixed. This work is the impetus for a new design in equipment for precipitate formation and digestion, which is currently being built for installation in the new plutonium recovery facility.

In additional investigations for Chemical Operations, a study was made to determine if trace quantities of thorium are separated from plutonium by the peroxide precipitation. The results, which simulated process conditions on a laboratory scale, show a decontamination factor of two.

Future Work

Plans are being made to study the effects of other ions such as sulfate, phosphate, and fluoride, that are common to the precipitation solution, and to investigate further the basic plutonium peroxy complex mechanisms.

DECONTAMINATION OF ROCKY FLATS SOIL

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

Objective

The object 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, and a conceptual flowsheet for the process was devised. This process, designated the primary process, reduced the volume of contaminated soil by about 65%. Various reagents were tested to aid in dispersing and decontaminating the soil. Cursory secondary process experiments were conducted using ultrasonics, pH adjustment, flotation, heavy liquid separation, calcination, and chemical oxidation treatments.

Achievements and Discussion

Scale-up of the primary process to pilot plant level and experiments to maximize the soil decontamination were done. Seven 1-kg-level runs were performed on one batch of untreated pad soil to determine the reproducibility of the primary process. Additional 1-kg-level tests were made on soil from five other locations under the pad; the effects of elevated pH and ultrasonic agitation were tested.

Separations in these tests were similar to previous results. However, in each case the effluent from the screens contained colloidal suspensions. In previous work no colloidal suspensions were obtained. The difference is attributed to oven drying of the soil in previous work which possibly altered the surface charge on the soil particles. The colloidal suspensions were not higher in plutonium, so decontamination was not enhanced by this phenomenon. Ultrasonification also failed to improve decontamination.

Future Work

Work to improve the scrubbing and sieving techniques, and experiments to establish the optimum working pH are planned. A thorough study of

potential secondary process treatments is also planned.

SOIL DECONTAMINATION AT OTHER DEPARTMENT OF ENERGY SITES

Roger L. Olsen, Doyle L. Mitchell, and John A. Hayden

Objective

The objective of this program is to develop and demonstrate soil decontamination processes for the removal or concentration of plutonium and other actinides from contaminated soil from other sites.

Prior Work

Although work is being done on soil at the Rocky Flats Plant, decontamination of soil from other DOE sites is a new project; no previous work has been done for other sites.

Achievements and Discussion

Work on this project was initiated in June 1978. The initial effort involved planning and work preparation. A tentative budget and manpower allotment were prepared and four main tasks were specified:

1. Preparation for soil characterization.

2. Identification of sites and sample collection.

3. Improve the primary soil decontamination process.

4. Identification of other physical decontamination methods.

Future Work

After soil samples are received at Rocky Flats, chemical and physical characterization studies will be initiated along with separations experiments.

RECOVERY OF ACTINIDES FROM COMBUSTIBLE WASTES

Gary H. Thompson, Everett L. Childs, Robert L. Kochen, C. Michael Smith, and Richard H. Schmunk

Objective

The objective of the program was to evaluate methods for actinide recovery from combustible waste. Current proposals for combustible wastes involve incineration and possible recovery of actinides from the ash. The findings from this laboratory-scale program, which was done under contract for Oak Ridge National Laboratory (ORNL), will be used by DOE and ORNL to assist in determining the feasibility of partitioning actinides from combustible waste.

Prior Work

Preliminary leaching and dissolution tests were done using cold fluidized bed incinerator (FBI) ash and conventional incinerator ash (from combustion of line-generated waste). Fusion in 90 wt % Na_2CO_3 — 10 wt % $NaNO_3$ was found to recover $\geqslant 98\%$ of the plutonium and americium from conventional incinerator ash. This was accomplished if silica was first removed by refluxing with $\geqslant 6M$ NaOH.

Evaluation of a more promising method also was begun. Refluxing ash with $0.1M$ Ce(IV) in $4M$ HNO_3 was found to oxidize the carbon in all incinerator ash to carbon dioxide and to solubilize the actinides. Actinide recovery was approximately 95%. Oak Ridge National Laboratory requested an evaluation of this system exclusively and specified that only conventional incinerator ash be used; consequently, work being done to prepare contaminated FBI ash was terminated.

Achievements and Discussion

The Ce(IV)-HNO_3 system was tested to determine optimum conditions for actinide recovery from conventional incinerator ash. Ceric ion was reduced to cerous by reaction with the carbon in the ash. To reduce cerium salt requirements and avoid

TABLE 4. Comparison of the Ce(IV)-HNO₃ and HF-HNO₃ Systems for Actinide Recovery From Conventional Incinerator Ash

Sample: 1.0-g ash

Temperature: reflux

Initial liquid-to-solid ratio
  Ce(IV)-HNO₃ to ash = 250 ml/g
  HF-HNO₃ to ash = 100 ml/g

| | | 0.1M Ce(IV)-4M HNO₃ | | | 0.1M F⁻-12M HNO₃ | |
| | | Actinide Recovery (wt %)[a] | | | Actinide Recovery (wt %)[b] | |
Contact	Time (hr)	Pu	Am	Time (hr)	Pu	Am
1	5	95.0 ± 0.58	94.0 ± 2.9	2	89.0	89.0
2	7	1.2 ± 0.35	3.4 ± 1.9	2	7.1	9.3
3	7	0.3	0.3	2	2.2	1.9
4	(c)	(c)	(c)	2	<0.6	<0.9
5	(c)	(c)	(c)	2	<0.6	<0.8

a. Mean ± standard deviation for four runs.
b. Single determination.
c. Not determined.

addition of undesirable components (e.g. sulfate or ammonium ion), cerium was added as cerous nitrate, then oxidized electrolytically by a current of one ampere to Ce(IV). Optimum ash dissolution conditions was 0.1M Ce(IV) in refluxing 4M HNO₃.

Actinide recovery at four grams of ash per liter of Ce(IV)-HNO₃ solution was 95.0 ± 0.58% plutonium and 94.0 ± 2.9% americium. Subsequent contacts with fresh Ce(IV)-HNO₃ solution gave little additional recovery, as shown in Table 4. This table also compares the recovery of actinide with that attained by the conventional method, i.e., refluxing with 0.1M F⁻ in 12M HNO₃ for two hours. Recovery is similar after two contacts.

Additional testing showed that actinide recovery for a single batch contact with 0.1M Ce(IV) in 4M HNO₃ remains fairly constant (approximately 95%) at ash concentrations up to 30 g/l. Recovery decreases rapidly beyond that concentration; it is 78% at 40 g/l.

At ORNL's request, residue from the Ce(IV)-HNO₃ dissolution was refluxed in varying amounts of 0.1M F⁻ in 12M HNO₃ to determine the liquid-to-solid (L/S) ratio for optimum actinide recovery. Preliminary results show that 80% recovery of the remaining actinide is recovered at L/S = 50 ml/g. Recovery was not improved at L/S = 75 or 100 ml/g.

Subsequent work involved secondary recovery methods. Plutonium recovery was accomplished by reducing Ce(IV) to Ce(III) with solid oxalic acid and extracting plutonium into 30% tributyl phosphate (TBP) in n-dodecane; recovery was 99.99%. Americium was recovered by extraction into 30% dihexyl-N,N-diethylcarbamoylmethylenephosphonate (DHDECMP) in diisopropylbenzene; recovery was 99.7%.

Future Work

The ORNL subcontract terminates at the end of FY 1978 at which time a final report will be submitted. No additional work is contemplated at this time.

PROCESS CHEMISTRY AND ENGINEERING

Edward D. Erickson

INDUCTION-HEATED, TILT-POUR FURNACE

Robert G. Auge, James B. Knighton, 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 in Building 776. The objectives of this 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 furnace and its start-up has been described in the last progress report (RFP-2803, November 8, 1978). The furnace was used to demonstrate that zinc-magnesium alloy (Step I product of the salt cleanup process) could be loaded to 35 wt % in plutonium plus americium. Several Step I and Step III alloy metal product buttons were melted under a salt cover to consolidate the metal into one large button and remove salt occlusions.

Achievements and Discussion

Design modification of the induction-heated furnace well containing the tungsten crucible and graphite susceptor has been completed. A niobium metal liner was installed between the inconel well and the graphite susceptor. This should protect the inconel well from attack by zinc metal. The furnace well is attached to the rest of the furnace by a metal flange. This will make future replacement of the well easier and less costly.

A leak in the furnace well had developed as a result of zinc metal corroding the inconel furnace wall. The zinc came into contact with the wall when one test of a plutonium oxidation reaction was being performed. Zinc chloride, contained in a potassium chloride—calcium chloride salt, reacted too quickly with plutonium metal. This reaction is exothermic and forms zinc metal and plutonium chloride. The reactants foamed up and out of the tungsten crucible, and the zinc metal contacted the inconel furnace wall in a localized area.

Two subsequent tests of this process have been performed without incident. The time required to heat the furnace from 23 °C to 700 °C was changed from forty-five minutes to one hour and fifteen minutes.

The tilt-pour furnace has been run for 600 hours over a period of two and one-half years of total operating time. During that time use of this furnace has demonstrated molten salt extraction, electro-refining, salt cleanup operations, and metal consolidation.

Future Work

The pyroredox process will be developed in the tilt-pour furnace. The process consists of plutonium metal being oxidized by zinc chloride and transferred into a molten potassium chloride—calcium chloride salt phase. The salt phase is then contacted with molten calcium metal to reduce the plutonium back into the metal phase. This process is capable of purifying plutonium metal to approximately the same quality as electrorefined metal. A vacuum melting process will be used to remove any excess calcium metal.

VACUUM MELTING
Ralph O. Wing, Robert F. Fitzpatrick, Greg D. Bird, James B. Knighton, and Ray E. Giebel

Objective

The objective of this process is to remove solvent metals—usually zinc, magnesium, and calcium—from plutonium-americium alloys. This objective involves using the difference in vapor pressures at elevated temperatures and reduced pressures. The purpose of the project is to develop an alternative method to aqueous processing for plutonium and americium recovery from molten salts extraction (MSE) salts.

Prior Work

Feed alloys for this process are produced from the Molten Salt Cleanup project.[1] Vacuum melting is performed in a metal bell jar with an O-ring seal, coupled to a vacuum system. The bell jar contains an induction coil, a tantalum-MgO crucible combination to contain the feed alloy, and a tantalum

condenser assembly. The process is operated between 600 and 900 °C at vacuums of 10^{-3} torr. The feed contains from 50 to 90 wt % solvent metals. One of the problems reported earlier was splattering of the feed material within the MgO crucible.[2]

Achievements and Discussion

During this report period, alloy metal was processed on a regular basis. Seventy-six percent of the product was suitable for subsequent recovery operations; 24% was unsuitable because of contained impurities. Since the inception of the process, 61% of the solvent metals removed as condensate have been discardable, and 39% have been above the discard level in contained plutonium and americium. Condensed solvent metals collected from the condenser and bell jar surfaces are consolidated under a chloride salt cover in MgO ceramic crucibles in a stationary cell.

Splatter during vacuum melting has been controlled by hanging a tantalum splatter shield inside the MgO containment crucible, and just above the feed alloy. Splatter is also controlled by holding the temperature below the melting point of the alloy until most of the solvent metals have vaporized. The rate of vaporization is enhanced by operating the process below the melting point, thereby preserving the maximum surface area for vaporization to occur. Splattered metal has been removed from MgO ceramic crucible material by hydriding to form PuH_2, which falls from the crucible surfaces. The impure hydride that is collected is then oxidized to PuO_2, ZnO, and MgO by burning in air.

The vacuum melting process has generated residues that have been difficult to dispose of because of high americium content and contamination with chloride salts. Residues include sweepings, scrap tantalum, MgO crucible, and chloride salts, in addition to zinc, magnesium, and calcium alloys.

Future Work

A backlog of feed material remains. Also, recycle feed will be generated as a result of removing

impurities from the off-specification, vacuum-melt product. Pyroredox purification (zinc chloride oxidation followed by calcium reduction) will likely be the purification step employed. "Above-discard" solvent metals may also be recycled through vacuum melting to produce a discardable alloy.

References

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2. J. B. Knighton, R. E. Giebel, and J. W. Berry. "Plutonium Recovery From Backlog Salts." *Research and Development Semiannual Progress Report for January through June 1977, Chemistry Research and Development*, RFP-2680-A, p. 51. Rockwell International, Rocky Flats Plant. October 21, 1977.

DETERMINATION OF PLUTONIUM AND AMERICIUM IN SALTS AND ALLOYS BY CALORIMETRY

Ray E. Giebel

Objective

The objective of this effort is to rapidly estimate, by isothermal calorimetry, the plutonium and americium content of non-homogeneous salt and metal alloy products. These products result from pyrochemical recovery processes.

Prior Work

Measuring the plutonium content of plutonium oxide and other plutonium forms by isothermal calorimetry is performed routinely at Rocky Flats.[1]

Achievements and Discussion

The power output (in watts) of more than 70 pyro-chemical recovery products has been measured by isothermal calorimetry. Each measurement required 24-hr residence time in a calorimeter. The americium content of the products were not known; however, empirical approach described in this report was used to estimate plutonium and americium content from measured wattages.

Plutonium and americium were assumed to be the only contributors to power output. It was also assumed there were no chemical reactions, such as oxidation, contributing heat. Many of the products measured were alloys from a vacuum melting process used to remove zinc, magnesium, and calcium. The alloy that was produced contained principally plutonium and americium. The content of plutonium plus americium in these alloys was estimated to be

$$0.91N = G \tag{1}$$

where   N = weight of a metal alloy button

   G = grams plutonium + grams americium

The factor 0.91 was determined by averaging analytical results from typical alloys. The specific power for plutonium of isotopic composition used at Rocky Flats was assumed to be 0.002293 W/g. The specific power for americium-241 is 0.11423 W/g. Plutonium and americium contents of the alloys are calculated by algebraically solving Equation (1) and Equations (2) and (3), which are as follows:

$$0.002293 \text{ Pu} + 0.11423 \text{ Am} = W \tag{2}$$

where   Pu = grams plutonium

   Am = grams americium

   W = total wattage

and $$\text{Pu} + \text{Am} = G \tag{3}$$

The specific power of americium is 50 times the specific power of plutonium. If the americium content of an alloy product is understated, wattage interpretation will result in more plutonium plus americium present than the total net weight. If the americium is overstated, the plutonium plus americium content of the alloy decreases by 50 g

for every gram that the americium is overstated. Using this method, the americium content of vacuum melt alloy products is determined to within ±3%.

Data from alloy determination by calorimetry were used to determine a "stream average" for the ratio of grams americium to grams plutonium. This average ratio was then applied to heat outputs of intermediate salt products and residues to calculate approximate plutonium and americium contents.

Future Work

This method will be used to guide the development and testing of future pyrochemical processes. This work will include an evaluation of the estimates obtained versus analytical results.

References

1. F. L. Oetting and R. G. White. *An Eight Unit Isothermal Calorimeter for Routine Plutonium Analysis,"* RFP-1401. The Dow Chemical Company, Rocky Flats Division. November 14, 1969.

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 process in the 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

Characterization studies of the production process and testing of production equipment in the Process Engineering cold test laboratory were reported in the previous progress report (RFP-2803, November 8, 1978). These studies led to the following conclusions:

1.   As a result of poor mixing in the digesters, some feed was bypassing the digesters and going through the system with little residence time.

2.   Stagnant layers of cubic-crystal precipitate were observed in the bottom of the digesters.

Achievements and Discussion

The first step toward improving the process was changing the design of the digesters. A new agitator impeller system was designed using pitched-blade turbine impellers to replace the existing flat-blade impellers. This system not only mixes the solution more efficiently, it also does less damage to the precipitate crystals and prevents layers of precipitate from building up in the bottom of the digesters. In addition to the impellers, an inner agitation tube was designed. This tube provides a torturous path for the feed (down through the tube, up to the outer annulus, and then to the overflow). The new digester design satisfies the requirements of adequate digestion time and continuous precipitate particle flow through the system.

Tests using nonradioactive materials to simulate the precipitate have been run on the existing and the new systems for comparison and for prediction of how the changes will affect the process.

An anion exchange resin (200-400 mesh) was used to simulate plutonium peroxide in settling velocity experiments. The settling velocities of this resin and of the precipitate particles were evaluate by the equation

$$U_{sv} = \frac{(\rho_s - \rho_e) \, g \, D_s^2}{18 \, \mu_m}$$

where U_{sv} = settling velocity

ρ_s = solid particle density
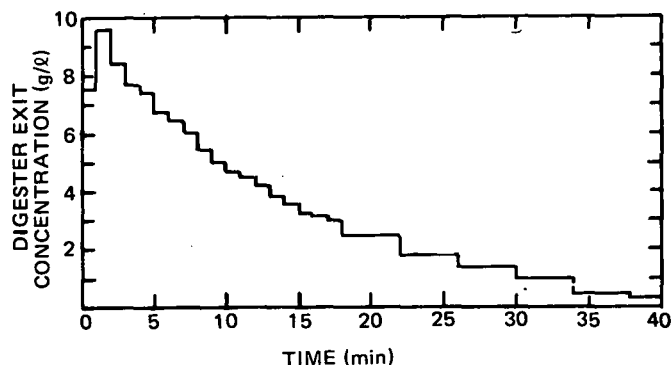
FIGURE 3.   Residence Time Distribution for Existing Digester System. (Simulation using fine mesh resin.)
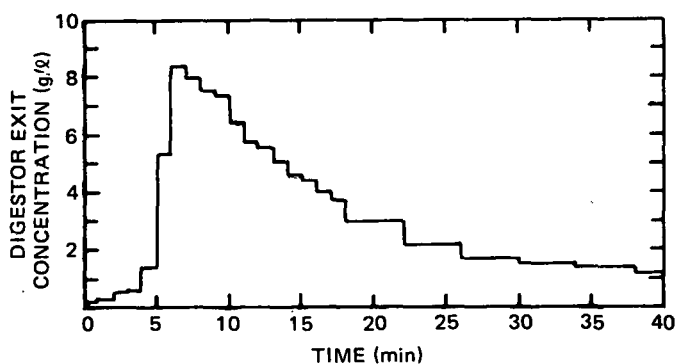
FIGURE 4.   Residence Time Distribution for Proposed Digester System. (Simulation using fine mesh resin.)

ρ_e = liquid density

g = gravity

D_s = solid particle diameter

μ_m = mixture viscosity

Using the physical properties for the new and the existing systems, and also the particle size distributions shown in photomicrographs of the resin and the precipitate, settling velocity distribution curves were prepared. The average settling velocities were determined by finding the centroid of each graph. Centroids of 0.112 ft/min for the precipitate and 0.124 ft/min for the resin particles were calculated. These averages show that the resin is acceptable to use as a stand-in for plutonium peroxide precipitate.

The simulations have produced a residence-time distribution for each design, as a measure of their efficiency as digesters. (See Figures 3 and 4.)

These distribution curves of particle concentration versus time indicate the amount of digestion time for crystal growth in each digester. The average residence times, found by the centroid of each graph, were 11 minutes for the existing system and 16 minutes for the new system. From these results, we can expect a 40-50% increase in the residence time when the new system is in operation.

Future Work

After testing is complete and final changes are made, the new equipment will be installed in the production line. Characterization studies of the plutonium peroxide precipitate formed will be conducted to evaluate the effectiveness of the process. The basic design of the digester assembly has been established. Process design in the following areas will be established with the support of the Chemical Research group:

1. Direct strike addition of peroxide to the plutonium nitrate feed.

2. The use of a static mixer for the first contact of peroxide with plutonium nitrate feed.

3. Addition of nitric acid to the peroxide reagent before contact with the plutonium nitrate feed.

4. Optimum nitric acid concentration in the plutonium nitrate feed.

5. The need for sulfate ion addition to the plutonium nitrate feed solution.

6. The effect of the oxidation state of plutonium in the plutonium nitrate feed.

A mass flow meter has been purchased and will be evaluated for use in measuring the flow of plutonium nitrate feed and reagents used in the plutonium peroxide precipitation process.

SILICA REMOVAL STUDY

Ian M. Edwards

Objective

The objective of this study is to find a feasible method of removing silica from acidic process solutions. The method must be simple and must not cause any adverse effects on production operations.

Prior Work

No prior work has been done on this project.

Achievements and Discussion

The first step in the process used at Rocky Flats to recover plutonium from various residues involves dissolution in nitric acid (HNO_3)-hydrofluoric acid (HF) mixtures. Some of these residues, such as incinerator ash, MgO crucible material, and MgO sand, contain silica (SiO_2), which dissolves along with plutonium. When a significant amount of silica is present in the feed, formation of colloidal silica occurs. This silica reacts with HF to form fluosilicates, which in turn crystallize in condensers and in off-gas piping to the fume scrubber. These problems prompted a study to determine the following: (a) the chemistry of SiO_2 in HNO_3-HF solutions and (b) what can be done to alleviate the problem.

A literature search was conducted that included a computer search of available literature. As a result of this search, it was found that extensive work has been done on silica in water systems, but very limited work in HNO_3-HF solutions has been conducted. A previous attempt by Groh[1] to remove silica from solutions of nuclear fuels resulted in a gelatin being used as a flocculant. Other studies were concerned with less useful objectives; however, a great deal of silica chemistry and behavior, along with a wealth of other references, has been found in References 2, 3, and 4.

Because of the lack of published data on the chemistry of SiO_2 in HNO_3-HF solutions, a study

to determine the solubility of silica in acid solutions has begun. Initially, four weighed amounts of silica were placed in 50 ml of $0.1N$ HF (0.13 g, 0.23 g, 0.5 g, and 0.32 g of SiO_2 were used). These solutions were placed in polyethylene beakers (250 ml) at room temperature for 115 hr to establish equilibrium, and then filtered to remove any undissolved solids. The solids were then dried and weighed. The results showed the solubility of SiO_2 to be ~ 1.2 g/l in $0.10N$ HF. At this point, 200 ml of $12N$ HNO_3 was added to each beaker to see if the solubility would decrease, but no visible effect was observed. To further study the effect of HNO_3 on SiO_2 solubility, four solutions containing $12N$ HNO_3 and $0.1N$ HF were contacted with 0.6 g of SiO_2 for ~ 40 hr. The solubility of SiO_2 under these conditions was determined to be 800 mg/l. Test results indicated that the solubility of silica is greater in HF solutions than in HNO_3-HF solutions.

The effect of HF concentration on the solubility of SiO_2 has been studied as follows: 0.9 g of SiO_2 was added to solutions of $12N$ HNO_3, which were $0.05N$, $0.1N$, $0.25N$, $0.5N$, $1.0N$, $3.5N$, and $6.0N$ HF. These 250-ml solutions were allowed to stand at room temperature for two weeks to observe polymerization and emulsion tendencies. No polymerization or emulsions occurred in this period; however, a white crust formed on the cover glasses and varied in thickness in proportion to the HF concentration. Lab analysis showed this crust to be a fluosilicate. The study to determine the effect of HF concentration on SiO_2 solubility is still in progress.

The method used for analyzing SiO_2 content was done by weight difference. It was found that there were unexplained discrepancies in the results obtained from atomic absorption methods. Work is in progress to resolve this problem.

Future Work

Reproducibility of data will be studied along with other methods of determining the amount of silica in solution. Other items to be studied include temperature effects on silica behavior, precipitation of silica via various methods, the possibility of utilizing gelatin as a flocculant,[1] the ability of substances to reduce silica solubility in HF solutions, identifying a method to scrub out undesirable fluosilicates, and identifying a method for finding mechanisms involved in SiO_2 dissolution.

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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 efficiencies of both annular and raschig ring—filled tanks. The ultimate goal is to determine if, on a full scale, an annular tank is faster than a raschig ring—filled tank in its capability for mixing a nonhomogeneous solution while maintaining the surface-to-volume requirements of nuclear safety.

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

Prior Work

No prior work has been done on this project.

Achievements and Discussion

At the present time, raschig ring—filled tanks are
used to mix and store solutions containing various
concentrations of plutonium. The ability to
completely mix the solutions in these tanks
and obtain uniform concentration is important to
process operations. Solutions and reagents are
mixed in 250-ℓ tanks in preparation for plutonium
peroxide precipitation. In turn, several of these
batches are combined in a 1000-ℓ tank. The
efficiency of the continuous precipitation process
depends on all of these tanks being uniformly mixed

The vessels operate safely, but there are several
problems associated with maintaining raschig ring—
filled tanks. First, periodic inspections of the tanks
are necessary to check for sludge accumulation.
The rings also need to be changed because sludge
causes them to foul, and they tend to break during
mixing operations. Hence, Chemical Operations is
interested in replacing existing raschig ring—filled
tanks with annular tanks. It is the purpose of
this study to compare the mixing and sludge-
removal characteristics of annular tanks with
raschig ring—filled tanks.

The bench scale annular tank (Figure 5) used in
this study is 14.6-cm o.d. X 46.4-cm tall with a
2.54-cm annulus. The raschig ring—filled tank
is 15.2-cm i.d. X 30.5-cm tall and is filled to 26.7
cm with 8- X 8-mm raschig rings. Each tank has a
void volume of three liters. A literature search
was conducted but revealed no rigorous, theoretical
techniques to study mixing in annular tanks. Hence,
all results presented here are empirical in nature.

Several dye tracer experiments have been conducted
as part of the qualitative study of the tanks. For
these experiments, the recirculation rates were
between 11.5 and 32.0 ml/sec. A typical experi-
ment, for either of the tanks, consisted of injecting
5 ml of tracer into the vessel, observing the flow
patterns, and determining the time required to
reach equilibrium. For the annular tank, the
following flow systems were studied: fluid re-
circulation out through the top with entry through
the bottom of the tank (with and without a fluid
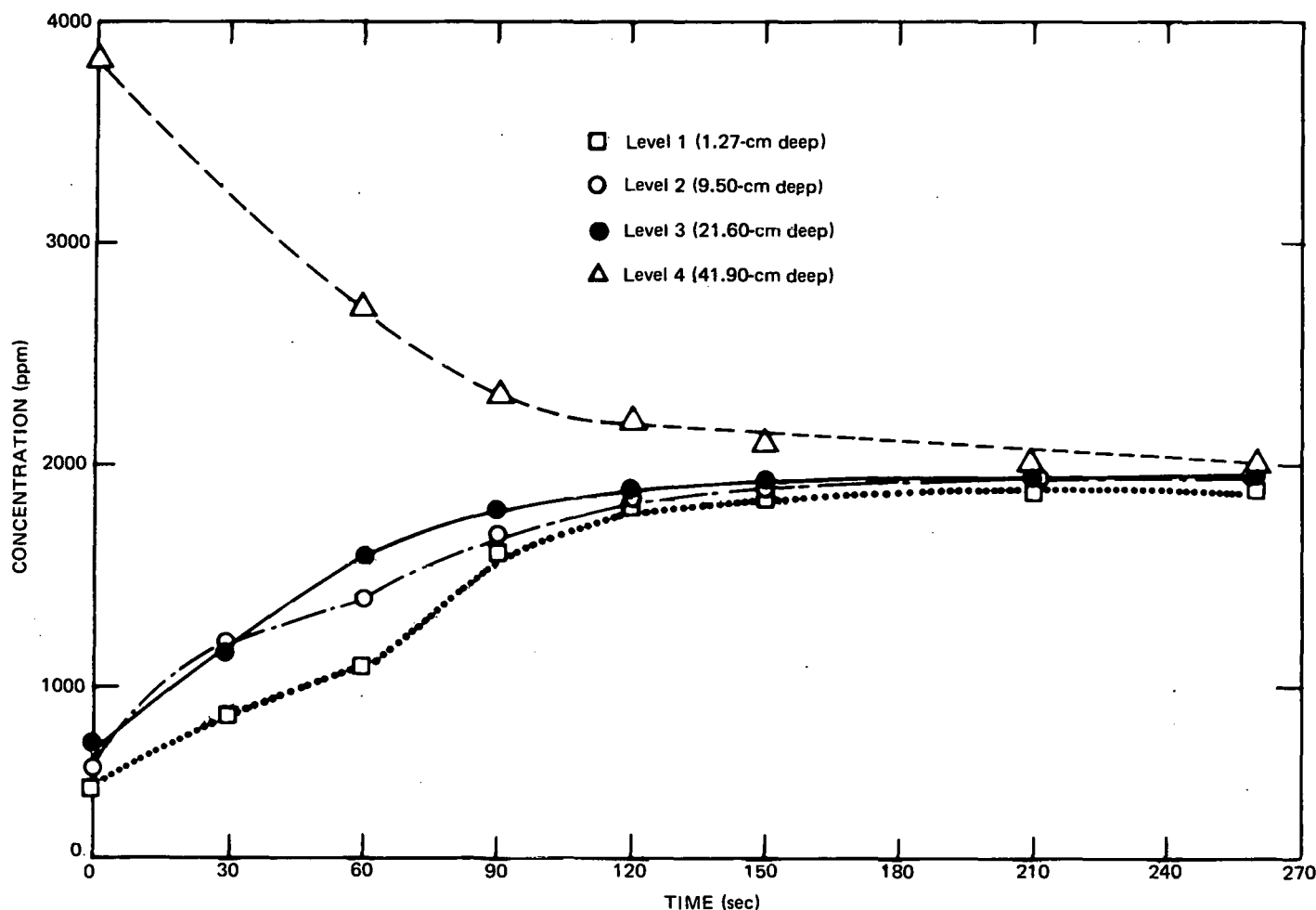
FIGURE 5. Annular Tank
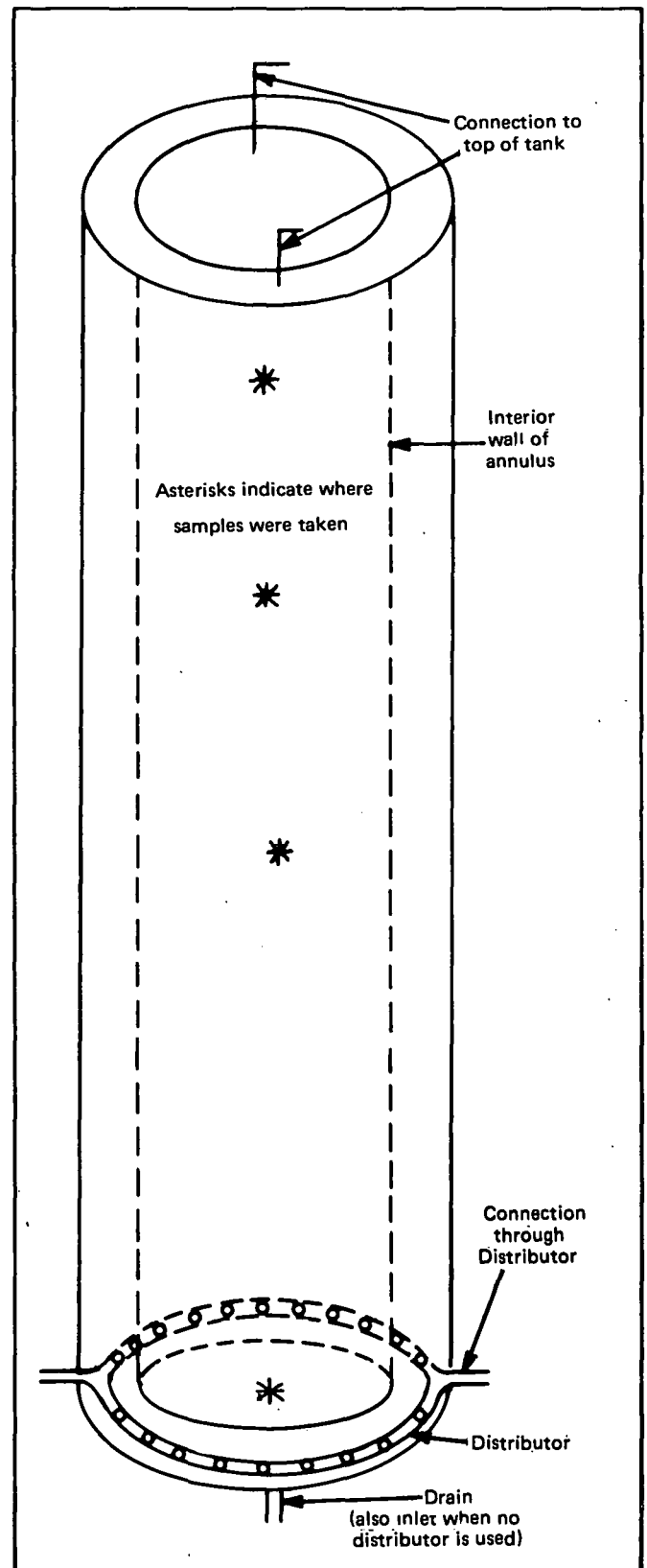
FIGURE 6. Concentration Versus Time Profile for Annular Tank (Stratified Layer Mixing)

distributor), air sparge mixing, and the mixing of stratified salt layers. For the raschig ring—filled tank, air sparge mixing and fluid recirculation (entry through the top, exit through the bottom) were studied.

Based on these experiments, it was concluded that air sparge mixing is more efficient than mixing by recirculation, and mixing occurs in annular tanks at least three to five times faster than in raschig ring—filled tanks.

Conductivity testing has been the source of quantitative concentration-versus-time data for each of the tanks. The technique used to study the annular tank consisted of placing 1000 ml of 3% lithium chloride (LiCl) solution in the bottom of the annular tank. An aqueous layer was then formed above the salt solution by adding 2000 ml of tap water dyed red. For the experiment shown in Figure 6, solution in the vessel was recirculated through the tank by pumping fluid in through the bottom, without a fluid distributor, and out through the top of the tank at 11.5 ml/sec for 10 to 30 sec (sometimes longer). The recirculation was then stopped and samples were taken from different depths (1.27, 9.50, 21.60, and 41.90 cm) for analysis in a Devon Products conductivity cell. The pump was then restarted and the sampling procedure repeated at 10- to 30-sec intervals, as previously discussed, until the tank reached equilibrium. This procedure has shown that visual determinations of equilibrium times are unreliable. In this experiment, the tank appeared uniformly red (and therefore, homogeneous) after 70 sec of recirculation. As shown in Figure 6, 270 sec was

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required to completely mix the tank. The discrepancy between these numbers is due to the eye's inability to perceive small differences in color.

The curves generated for most of the experiments have characteristics similar to those shown in Figure 6. The region at the top of the tank responded to concentration changes in a sigmoidal fashion; the bottom responded with smooth exponential decay.

To study mixing in a raschig ring—filled tank, a conductivity cell was buried under the rings. Between some runs the conductivity cell was relocated; between others, it was maintained in the same position while the rings were repacked around it. Even when the rings were simply repacked without moving the probe, it proved impossible to obtain repeatable data. Two trials were conducted in which the only difference between the experiments was that the rings were repacked. The two experiments differed by 30% in the time required to reach equilibrium. The primary reason for this discrepancy is that the channeling characteristics of the rings were changed by repacking.

Dye tracer experiments have also been used to study the channeling characteristics of the raschig ring—filled tank. These tests have shown that channeling in the tank can be altered by simply draining and refilling the vessel as well as by repacking the rings. Any process that alters the rings' positions in the tank will alter the flow characteristics of the tank, and an attempt to construct an empirical model capable of predicting the performance of the tank would be fruitless.

Future Work

The present annular tank is in the process of being modified so conductivity cells can be placed inside the annulus, thereby permitting continuous measurements to be taken. This will allow velocity profiles within the tank to develop completely. It also will eliminate the error induced by diffusional mixing, which occurs when recirculation is stopped for the taking of samples. The cells that will be used in this work are now on order from Beckman

Instruments, and will be of much higher quality than those used to date.

The new tank also will have a bottom that is sloped 20-30° so that preliminary sludge removal tests may be run. After completion of the tests mentioned, mixing experiments will be conducted in full-scale tanks. The correlation between the bench-scale experiments and the full-scale experiments will then be made, and the final results will be published.

RECOVERY OF PLUTONIUM AND AMERICIUM FROM A SALT CLEANUP ALLOY

Roy E. Dawson and Robert L. Smith

Objective

The objective of the experimental work was to develop a process for dissolution of a plutonium (Pu)-americium (Am) salt cleanup alloy. A second objective was to determine if the resulting solution could be introduced as feed material to the existing production processes, for recovery of the Pu and Am.

Prior Work

No prior work has been done.

Achievements and Discussion

A molten salt extraction (MSE) process is used at Rocky Flats to remove Am from Pu metal. In addition to Am, the salt fraction also extracts a small amount of Pu, thus producing an Am, Pu, and $KCl-NaCl_2-MgCl_2$ salt residue. This residue requires further processing to recover and separate the Pu and Am.

This recovery has, in the past, been accomplished with an aqueous process consisting of dissolution in HCl, cation exchange to remove the corrosive chloride ion, and anion exchange for separation of Pu and Am. However, a pyrochemical process is being developed as a possible replacement for the

TABLE 5. Dissolution Results

Form	Sample Size (g)			
	25.5	18.8	18.8	23.1
Form	metal oxide	metal	metal	metal
Temperature	reflux	reflux	room	room
Acid Concentration	$15.6N$ HNO_3 $-0.1N$ HF	$3N$ HNO_3 $-0.1N$ HF	$3N$ HNO_3 $-0.1N$ HF	$6N$ HCl
Filter heel weight (after calcining) in grams	5.4	9.3	4.8	0.7
Dissolution (%)	78.8	50.5	74.5	97.0

wet chemistry operation. A vacuum melting step in the pyrochemical procedure produces a metal alloy, which contains Pu and Am. This study has been undertaken to develop a process for dissolving this metal alloy, and determining if the resulting solution could be introduced as feed material to the production processes. Dissolution tests were conducted using HNO_3, HF, and HCl and solutions with metal alloy, and metal alloy that had been burned to oxide.

A sample of the metal alloy was divided into four pieces weighing from 18.8 to 25.5 g. Each piece was then dissolved under various conditions. The first piece of metal alloy was burned to oxide and dissolved in $15.6N$ HNO_3 $-0.1N$ HF at reflux temperature. Two pieces of metal alloy were dissolved in $3N$ HNO_3 $-0.1N$ HF, with one at room temperature and the other at reflux temperature. The last piece of metal alloy was dissolved in $6N$ HCl at room temperature. Resulting solutions were then filtered through number 541 "Whatman" filter paper using a buchner funnel, and the filter heels were calcined at 625 °C for one hour. The solids and solutions were analyzed for Pu-Am content by radio assay, and impurities were identified by emission spectroscopy.

A summary of the results obtained from the dissolution tests is presented in Table 5. Dissolution in $6N$ HCl resulted in 97% of the metal being dissolved; the highest result obtained for all experiments.

Dissolution of metal alloy in $3N$ HNO_3 $-0.1N$ HF at room temperature was 24% more effective than dissolution of metal alloy in $3N$ HNO_3 $-0.1N$ HF at reflux temperature, and 4.3% less effective than dissolution of oxidized metal in $15.6N$ HNO_3 $-0.1N$ HF at a reflux temperature. Analysis of impurities by emission spectroscopy has not been fully completed; however, initial results revealed four elements (Ca, Mg, Pb, and Fe) that are difficult for present production processes to remove in large quantities. In addition, support laboratories have encountered problems in identifying other impurities. First, a sample of filter heel proved difficult to dissolve for analysis by emission spectroscopy. Secondly, a sample of metal oxide submitted for thermal gravimetric analysis contained unknown impurities that were still oxidizing at 970 °C.

In conclusion, the dissolution of metal alloy in $6N$ HCl at room temperature, and the dissolution of metal oxide in $15.6N$ HNO_3 $-0.1N$ HF, at reflux temperature, provided the best results. Laboratory analysis of the type and amount of impurities in the alloy is still in progress. However, initial results show that the alloy contains several impurities (Ca, Mg, Pb, and Fe) that may interfere with current production processes.

Future Work

Future work will involve the dissolution of metal oxide in HCl, HF, and HNO_3 solutions (dissolution

of metal oxide is preferred as a production process). In addition, the presence of identified and, as yet unidentified, impurities may require further laboratory-scale tests to determine the compatibility of the alloy with current production processes.

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 (Pu) and americium (Am) from vacuum melt furnace crucibles.

Prior Work

This is the first investigation directed at process development for this residue.

Achievements and Discussion

A molten salt extraction (MSE) process is used at Rocky Flats to remove Am from Pu metal. In addition to the Am, the salt fraction also extracts a small amount of Pu, producing an Am, Pu, and $KCl-NaCl-MgCl_2$ salt residue. This residue requires further processing to recover and separate the Pu and Am. This recovery has been accomplished with an aqueous process consisting of dissolution in HCl, cation exchange to remove the corrosive chloride ion, and anion exchange for separation of Pu and Am. However, a pyrochemical process is now being developed as a possible replacement for the wet chemistry operation. Vacuum melting, a step in the pyrochemical process, requires magnesium oxide (MgO) crucibles that contain a Pu-Am residue after use. This study was undertaken to (1) develop a method of leaching the Pu-Am residue from the MgO crucibles, and (2) determine if the resulting solutions can be

introduced into the aqueous salt residue recovery process as feed material.

Eight samples of crucibles, ranging in size from 30 to 1500 g were selected for process development studies. The crucibles had been broken before they were received, and some pieces had been pretreated with a hydriding process in an attempt to remove most of the Pu and Am. Gamma counting of the crucible pieces was used to follow the progress of the development work. For small samples (300 g or less), each crucible piece was counted before and after processing. For large samples (greater than 300 g), 30 pieces of crucible were selected for gamma counting. The mean and standard deviation of the gamma counts for each sample were calculated before and after treatment. Gamma counting was accomplished with a "Victoreen" survey meter through a 30-mil lead-lined glove.

The method investigated consisted of leaching each sample in a $0.5N$ solution of HCl (at a gram-of-crucible-per-milliliter-of-acid ratio of 1:1) for 30 min at room temperature. The crucible pieces were rinsed at the same gram-per-milliliter ratio with process water, and were allowed to dry before final gamma counting. The combined HCl solution and rinse water was filtered through number 541 "Whatman" filter paper by means of a buchner funnel. The filter heel was calcined at 600 °C for 60 min. The heel, plus samples of filtrate, were analyzed by radioassay for Pu-Am content, and by emission spectroscopy for identification of impurities.

A summary of the results obtained from gamma radiation counting is presented in Table 6. A minimum 76% reduction of gamma radiation was obtained for both hydrided and non-hydrided crucibles. Radioassay results indicated an average of 3.58×10^{-2} g/l of Pu in the filtrate and 0.3288 g/g of Pu in the filter heel. Americium averaged 0.266 g/l in the filtrate and 3.97×10^{-3} g/g in the heel. Analysis of impurities by emission spectroscopy revealed four elements (Ca, Mg, Pb, and Fe) that could interfere with production processes or product purity.

TABLE 6. Gamma Radiation Rates on
Crucibles Before and After Treatment

	Mean (mrem/hr)		Standard Deviation (%)		Reduction (%)
	Before	After	Before	After	
Hydrided	119.9	27	79.3	12.75	76.7
Non-Hydrided	147.7	32.8	84.9	10.12	77.8

Determination of gamma radiation rates, before
and after treatment, provided a qualitative indicator
for verifying adequate processing. Care should be
exercised in applying this information quantita-
tively because various conditions that may have
altered the data may not have been corrected for
in the results. This includes (1) background gamma
radiation rates in the glove box, which ranged from
18-44 mrem/hr depending on the proximity of
crucible containers to the survey meter, (2) portions
of the larger samples selected for gamma counting
not being statistically random, and (3) counting
through a lead-lined glove that reduced the average
radiation reading by as much as 20 mrem/hr over
counting through a polyvinyl chloride bag.

Radioassay analyses of filtrate, heel, and leached
crucible confirmed that Pu and Am were removed
from the crucibles. Most of the Am dissolved and
remained in the filtrate, while most of the Pu was
contained in the heel. One problem encountered
during this development work was formation of
a polymer suspension in some of the combined
leach-wash solutions.

Polymer formation in nitric acid solutions is
favored by lowering the acid concentration.[1] The
addition of rinse water to the filtrate may have
promoted the same reaction in the HCl solutions.
Polymer suspensions were precipitated by restoring
the acid normality to 0.5 and heating to increase
the particle size.[2]

Initial results indicated the process is effective in
removing Pu and Am from MgO crucible pieces.
However, before the crucibles can be processed in
production equipment, it must be determined if
(1) concentrations of Ca, Mg, Pb, and Fe are low
enough not to affect production processes or
product purity, and (2) if leaching with higher acid
normalities will prevent polymer formation.

Future Work

Future work will involve leaching with $1N$ HCl
solutions to eliminate Pu polymer formation.
In addition, analysis will be conducted to deter-
mine if crucibles are discardable, and to verify
that concentrations of Ca, Mg, Pb, and Fe are below
acceptable levels for effective removal by produc-
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