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G. A. BURNEY, H. D. HARMON, and M. L. HYDER

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by

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ABSTRACT

A process was developed for recovering ^{241}Am from aged plutonium oxide. The oxide is dissolved with nitric acid and fluoride, the fluoride is complexed with aluminum, and plutonium and americium are separated by one cycle of solvent extraction. Americium is concentrated and purified by cation exchange chromatography and precipitated as oxalate. The process was successfully operated in Savannah River Plant facilities to recover ∿720 g of ^{241}Am from about 60 kg of aged plutonium oxide.

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RECOVERY OF AMERICIUM-241 FROM AGED PLUTONIUM

INTRODUCTION

About 60 kg of highly irradiated plutonium, having a ^{242}Pu content averaging 52%, was purified and stored at the Savannah River Plant (SRP) as PuO_2. In the fall of 1974, after several years of storage, this plutonium was prepared for re-irradiation to increase its ^{242}Pu concentration. During storage, about 750 g of ^{241}Am had grown into the stored plutonium by decay of ^{241}Pu. Because radiation from ^{241}Am would greatly increase radiation exposure to personnel during target fabrication and because ^{241}Am is itself valuable, a procedure was developed for separating and recovering that isotope at SRP using existing facilities for dissolution, solvent extraction, ion exchange, and precipitation. This procedure was completely piloted on the laboratory scale at the Savannah River Laboratory (SRL); the process steps (Figure 1) are as follows:

1. Dissolve PuO_2 in small batches in the JB-Line recovery dissolver (Building 221-F), using nitric acid and minimum fluoride.

2. Complex the fluoride with aluminum, and accumulate the solution in an F-canyon* tank as feed for the second plutonium solvent extraction cycle.

3. Separate americium and plutonium by solvent extraction; plutonium product is recovered as PuO_2 in JB-Line.

4. Evaporate and acid strip the americium-bearing solution from solvent extraction.

5. Concentrate americium by cation exchange in JB-Line; precipitate americium oxalate and calcine to AmO_2.

The process was successfully operated in the plant with the recovery of more than 95% of the americium. The americium oxide contained low levels of metal impurities, despite the relatively large concentrations of aluminum, iron, chromium, and nickel present in the feed to cation exchange. The AmO_2 product was shipped to Oak Ridge National Laboratory for distribution.

* Building 221-F contains the heavily shielded large-scale solvent extraction facilities used to recover plutonium from irradiated uranium. It also contains F-canyon and a facility for recovering plutonium from solution (JB-Line).

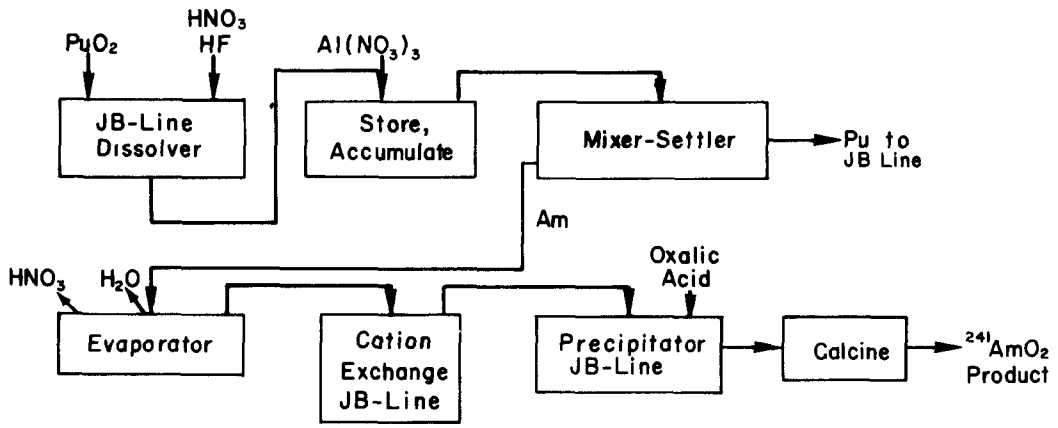

FIGURE 1. Recovery of ^{241}Am from Aged Plutonium

EXPERIMENTAL

Dissolution Procedure

Dissolution experiments were conducted in 125-ml Erlenmeyer flasks equipped with a condenser and modified to facilitate sampling. Weighed quantities of $^{242}PuO_2$ (~4.0 g) were dissolved in 25 or 50 ml of dissolvent at 110 ±5°C. The solution was generally not stirred because the plant operation is conducted in an unstirred vessel. Samples were withdrawn periodically, and percent dissolution was calculated from the initial weight of $^{242}PuO_2$ and gross alpha analysis of the solution. Americium and plutonium were determined by gross alpha counting and alpha pulse height analysis.

Cation Exchange Procedure

Cation exchange experiments were conducted in a 25-cm-long by 0.7-cm-diameter column containing 5 to 10 ml of 50 to 100 mesh *Dowex* 50W X-12 resin (registered trademark of Dow Chemical Co.) at a feed rate of 14 ml/(cm^2-min). This resin and feed rate are the same as those used in the plant. Elution was downflow at 0.5 ml/(cm^2-min); in the plant, the direction of flow is reversed for elution. Otherwise, the experiments represented anticipated plant operation.

The capacity of the resin for ^{241}Am was determined by monitoring the location of ^{241}Am on the column and by analyzing the alpha content of the column effluent during feeding. Elution was monitored similarly. The behavior of other cationic impurities was determined by atomic absorption analysis of effluent.

Plutonium was determined by gross alpha counting and alpha pulse height analysis.

Oxalate Precipitation Procedure

Oxalate precipitation tests were conducted in a 150-ml glass beaker using a four-bladed paddle for mixing. 0.9M $H_2C_2O_4$ or 1.8M $K_2C_2O_4$ precipitant was added to the eluate from cation exchange to give ~0.3M excess oxalate, and the slurry was mixed for at least one hour before filtration. The filtrate was analyzed for residual americium by alpha counting. Americium oxalate was dissolved in strong nitric acid, and ^{241}Am and plutonium were determined by gross alpha counting and alpha pulse height analysis; other cationic impurities were determined by emission spectrographic analysis.

RESULTS

Dissolution of $^{242}PuO_2$

Dissolution tests were made to determine the minimum fluoride concentration required for rapid and complete dissolution of $^{242}PuO_2$. Results of these studies are presented in Table 1. A fluoride concentration of 0.025M produced complete dissolution in 2 to 3 hours with 80 g PuO_2/ℓ of dissolvent; at 160 g/ℓ, however, dissolution with 0.025M fluoride was incomplete. Because >150 g PuO_2/ℓ is desired in plant operations, 0.035M is the minimum acceptable fluoride concentration. 0.050M fluoride gives still faster dissolution.

TABLE 1

Dissolution of $^{242}PuO_2$ in 15M HNO_3-KF

Dissolving Time, hr	*PuO_2 Dissolved, %*					
	0.01M KF[a]	*0.025M KF[a]*	*0.025M KF[b]*	*0.035M KF[b]*	*0.050M KF[b,c]*	*0.050M KF[b]*
1	6.0	95.4	6.2	67.5	99.9	96.0
2	8.2	98.2	8.6	93.7	97.9	96.7
3	27.8	99.6	-	102.6	97.8	98.3
4	18.9	102.4	-	103.3	101.1	99.1
5	23.1	100.6	-	-	100.3	98.3
6	26.1	98.4	-	102.0	101.4	-

a. 4 g PuO_2 in 50 ml dissolvent
b. 4 g PuO_2 in 25 ml dissolvent
c. Stirred

Feed Adjustment and Solvent Extraction

As indicated previously, the recovery process separates americium and plutonium by solvent extraction. Valence adjustment chemicals were not used in preparing the feed to solvent extraction because they would add cationic impurities to the ^{241}Am product stream (normally the aqueous waste stream in Purex). Plutonium is normally adjusted to Pu(IV) for first cycle solvent extraction; studies were conducted to determine the Pu(IV) content of unadjusted feed solutions prepared by diluting the raw ^{242}Pu solution to ~4M HNO_3. A solution of 15M HNO_3-0.035M KF containing 160 g Pu/ℓ was analyzed for Pu(IV) content and then diluted to 4M HNO_3. The diluted solution was analyzed periodically for Pu(IV) over a 26-day period. The results (Table 2) indicated ~80% Pu(IV) after the solution had stood for several days. The remainder of the plutonium was assumed to be in the extractable Pu(VI) state expected from the dissolution conditions (high HNO_3 and ~110°C).

The extractability of the plutonium was confirmed by distribution tests. The 4M HNO_3-^{242}Pu solution was diluted again to 2 g Pu/ℓ in 4M HNO_3 (the feed concentrations proposed by SRP) and was extracted with 30% tributyl phosphate. A plutonium distribution coefficient of 18.4 was measured; calculations of 1A bank mixer-settler operation based on the measured distribution coefficient indicated 99.9% plutonium recovery. It was therefore concluded that satisfactory plutonium extractability could be achieved by dilution and by allowing the solution to stand for several days.

TABLE 2

Pu(IV) Concentration in Dissolver Solution Diluted to 4M HNO_3[a]

Time, days	*% Pu in Pu(IV) State*
0	65.5
3	81.2
5	81.2
9	82.1
12	79.3
19	84.4
26	94.3

a. Original solution was nominally 15M HNO_3-0.035M KF containing 160 g Pu/ℓ.

Cation Exchange of ^{241}Am

Initial laboratory experiments were made with simulated solutions containing Al^{3+}, Am^{3+}, and F^- in nitric acid. When the process steps preceding cation exchange were completed in the plant, the feed to cation exchange was found to contain significant amounts of iron, chromium, and nickel; therefore, cation exchange and oxalate precipitation were also demonstrated in the laboratory with the plant solution. A summary of the data for the cation exchange studies is in Table 3.

TABLE 3

Summary of Cation Exchange Studies

Feed Composition	*Simulated Feed*	*Plant Feed No. 1*	*Plant Feed No. 2*
HNO_3, M	0.35	0.5	0.5
Al^{3+}, g/ℓ	0.45	0.089	0.089
F^-, M	0.0033	-	0.001
^{241}Am, g/ℓ	0.12	0.074	0.074
Feed volume, bed volumes	50	130	100
Americium sorbed, %	>99.9	95	>99.8
Aluminum breakthrough, bed volumes	20	~40	~20
Aluminum sorbed, %	~60	~50	~25
Wash Composition			
HNO_3, M	0.35	-	-
KF, M	0.002	-	-
$(NH_4)_2SO_4$, M	-	0.25	-
H_2SO_4, M	-	0.01	0.25
Wash volume, bed volumes	25	10	25
Americium removed in wash, %	0.5	~7	<0.1
Aluminum removed in wash, %	15	50-75	10-20
Plutonium removed in wash, %	-	>90	~80
Elutriant Composition			
HNO_3, M	4.7	5	5
Sulfamic Acid, M	0.3	-	-
Eluate volume, bed volumes	2.9	2.9	2.9
Americium in eluate, %	~70	~65	~70
Aluminum in eluate, %	15	~10	~10

Simulated Solution

The compositions of the cation exchange feed, wash, and elutriant are given in Table 3. Fluoride was required to accelerate the rate of dissolution of PuO_2; aluminum is required by technical standards to complex fluorides to limit the corrosion rate of stainless steel equipment in the canyon. A volume of 500 ml of this solution was fed to the column; >99.9% of the americium was sorbed. Scanning with a radiation detector showed americium in the top 65% of the column.

Although the capacity of the 10 ml of resin was sufficient to sorb aluminum from ~400 ml of feed, aluminum was found in the column effluent after only 200 ml of feed. Fluoride and acid decrease the aluminum distribution coefficient into the resin. After 400 ml of feed, aluminum concentration in the effluent equaled that in the feed.

Americium was detected in the top 80% of the column length following the wash.

A volume of 29 ml of eluate was collected; this eluate contained ∿70% of the americium (∿42 mg) and about 15% of the total aluminum (∿35 mg). This elution was considered satisfactory, especially because the plant column is not completely eluted in normal operation but leaves a heel to be processed in the next cycle of sorption and elution.

Plant Solution

The 2AW solution from solvent extraction was evaporated and acid stripped in the plant equipment to yield ~2500 ℓ of 1.8M HNO_3 containing ~775 g of americium, cationic impurities (Table 4), ~6 g of plutonium, and ~0.5 Ci of fission-product gamma activity. This solution was diluted to ~10,400 ℓ of 0.5M HNO_3 with slightly acidic water. About 1.5 ℓ of the diluted feed was transferred to SRL to pilot cation exchange and oxalate precipitation steps.

Experimental conditions for feed sorption and washing were the same as in the test with simulated feed. No valence adjustment was required for plutonium because Pu(IV) and Pu(VI) are removed from the column with the sulfate wash.

With no fluoride addition (Test 1), sorption of americium was effective for ~100 bed volumes (Table 3). The loaded resin was washed with $(NH_4)_2SO_4$-H_2SO_4 solution to remove plutonium and other cation impurities. Aluminum, chromium, iron, and nickel were retained for 40 to 60 bed volumes, after which they all

rapidly reached a feed-to-effluent concentration ratio (c/co) of about 1. From 50 to 75% of the aluminum, chromium, iron, and nickel and more than 90% of the plutonium were eluted by the sulfate wash.

TABLE 4

Plant Feed to Cation Exchange
(10,400 ℓ containing 0.5M HNO_3)

Element	*Concentration, g/ℓ*
Americium	0.074
Plutonium	7.8×10^{-4}
Aluminum	0.089
Iron	0.11
Chromium	0.051
Nickel	0.015
Calcium	<0.005
Magnesium	<0.005
Manganese	<0.005
Silicon	<0.004
Phosphorus	<0.025
Fluorine	0.031 (Calculated)

Elution conditions and results of americium elution were similar to those with simulated solution.

In Test 2, KF was added to the feed at a ratio of 1 mole to 5 moles of Al + Fe. This additional fluoride was added because after the solution had been evaporated and stripped with steam to remove acid, analyses showed much lower fluoride content than expected from fluoride additions during dissolution. An apparent increase in column capacity of 10 to 20% was obtained compared to Test 1. The major effect of the fluoride addition was earlier breakthrough of aluminum, at ~20 bed volumes compared to 40 bed volumes in Test 1. Breakthrough of iron, chromium, and nickel was not appreciably different from Test 1. After loading, the resin was washed with dilute sulfuric acid to remove plutonium. The overall DF for plutonium was ~5. From 10 to 20% of the aluminum, chromium, iron, and nickel were removed from the resin by the sulfate wash.

Elution conditions and results were again similar to the test with simulated solution.

Precipitation of ^{241}Am

Laboratory precipitations were made with americium from both the simulated and plant solutions.

Simulated Solution

Prior to precipitation of americium, the cation exchange eluate was diluted with 1.2 volumes of water to reduce its acidity (originally 2.9M HNO_3). Two test precipitations were conducted on portions of the resulting solution; one used oxalic acid, and the other used potassium oxalate as precipitant. Nearly quantitative recovery of americium was obtained in each case (~99%), and most of the aluminum remained in the supernate. Several other precipitations were made with simulated solutions at increased nitric acid or aluminum concentrations; the tests are summarized in Table 5.

TABLE 5

Americium Oxalate Precipitated from Simulated Solutions

Solution Composition	*Americium Lost to Filtrate, %*
1.5M HNO_3-0.03M Al (Eluate)[a]	<1
1.5M HNO_3-0.03M Al (Eluate)	1
1.4M HNO_3-0.1M Al	2
1.4M HNO_3-0.2M Al	3
2.7M HNO_3-0.1M Al	4

a. Precipitant was 1.8M $K_2C_2O_4$; other tests used 0.9M $H_2C_2O_4$

Precipitation did not occur immediately. Oxalic acid was added over a period of about 15 minutes, and precipitation was observed after ~15 minutes of digesting the resulting solution. The total digestion period was 60 minutes. Separation from aluminum was excellent with <0.1 wt % aluminum in the AmO_2 product.

Plant Solution

Two americium oxalate precipitations were made using the eluates from cation exchange. Both eluates were diluted with an equal volume of water to ~1.5M HNO_3 before precipitation, and 0.9M $H_2C_2O_4$ precipitant was used. Cationic impurities in the two eluates varied considerably because different feed and wash compositions were used in cation exchange. Cationic impurities (mg/ℓ) above the detectable limit by emission spectrographic analysis in the two eluates were chromium (300, 2000), iron (350, 1500), nickel (20, 60), aluminum (200, 150), and calcium (40, 100). The americium was ~3 g/ℓ in both solutions. Of these impurities, only calcium was detectable in the AmO_2 product.

Americium oxalate precipitated slowly, and the slurry was digested 60 minutes after oxalic acid addition was complete; americium loss to the filtrate was ~3% in each test.

SUMMARY OF SRP PROCESSING

The process steps for dissolution of ^{242}Pu oxide in JB-Line, solvent extraction separation of ^{242}Pu and ^{241}Am in the second plutonium cycle, and recovery of both americium and plutonium as oxides in JB-Line are shown in Figure 1. Extensive flushing of tanks and equipment in JB-Line and F-canyon was necessary to assure minimum cross-contamination of both products by fission products and other plutonium isotopes. All process steps were successfully performed in the plant. Approximately 60 kg of plutonium as oxide was delivered for billet fabrication, and approximately 720 g of americium oxide was shipped to Oak Ridge National Laboratory.

Dissolution of PuO_2

Dissolution in the JB-Line dissolver in 14M HNO_3-0.05M HF at 110 to 115°C was as predicted by laboratory tests. The oxide dissolved to 220 g Pu/ℓ in 3 hours with no agitation. When a draft tube was installed to provide agitation and keep much of the undissolved PuO_2 suspended, the dissolution rate was increased; 220 g Pu/ℓ was attained in 1.5 hours and 265 g Pu/ℓ was attained in 3 hours.

Solvent Extraction

The dissolver solution was collected in Tank 9.6 in 221-F canyon, and was found to contain ~63 kg of plutonium (52.3% ^{242}Pu) and ∿775 g of ^{241}Am in ∿11,000 ℓ (Table 6). When all of the dissolver solution was collected in Tank 9.6, fluoride was complexed with aluminum (2 moles Al/mole F) to minimize corrosion of canyon equipment.

Plutonium valence adjustment was not required. Water and 64% nitric acid were added to adjust the solution to 2 g Pu/ℓ and 4.5M HNO_3; total volume was ~28,000 ℓ. This solution was processed through the second plutonium cycle to separate plutonium and americium. After all feed (2AF) had entered the 2A mixer-settler, ~6800 ℓ of 22.5% HNO_3 was fed to flush plutonium and americium through the banks. Second cycle operations (Table 7) for the campaign were slightly different from those normally used for Purex. The higher plutonium concentration in 2AF and the slower feed rate minimized the volume of aqueous waste (2AW) produced. The extractant (2AX)-to-feed flow ratio was increased to provide more extraction capacity and the B-bank aqueous strip (2BX)-to-2AX flow ratio was increased to minimize the plutonium concentration and thus the alpha activity in the aqueous product (2BP). The aqueous scrub (2AS) flow was adjusted to maintain a similar 2AS-to-2AX ratio. The 2BP was washed by contacting it with 100 gallons of n-paraffin diluent in Tank 9.5 to remove entrained TBP and thereby prevent formation of plutonium-organic phosphate solids. This wash was very effective because no solids were observed despite more than two weeks of storage with the alpha activity ~14 times that of normal Purex 2BP.

Plutonium losses included 0.3 g of plutonium retained in 2BW (stripped solvent) and ~2 g of plutonium lost to 2AW. Approximately 20 g of plutonium and ~0.6 g of americium remained in the second plutonium cycle after flushing. Isotopic purity of the plutonium was maintained; about 0.1 Ci of fission product activity went into the americium-bearing 2AW stream during processing.

Evaporation and Steam Stripping

The 2AW was diluted to 6 to 8% HNO_3, evaporated, and steam stripped to recover acid. The resulting solution (2630 ℓ of 2M HNO_3) contained ∿775 g of americium, 6.5 g of plutonium, and 0.5 Ci fission products.

TABLE 6

Composition of ^{242}Pu-^{241}Am Solution (Tank 9.6)

Volume, ℓ	11,000
Specific gravity	1.11
HNO_3, M	3.65
Plutonium, kg	62.9
^{241}Am, kg	0.78
Gross alpha, 10^9 dis/(min-ml)	4.20
Plutonium alpha, 10^9 dis/(min-ml)	3.14
^{241}Am alpha, 10^8 dis/(min-ml)	4.87
Plutonium isotope, %	
238	1.31
239	3.63
240	31.84
241	10.90
242	52.32
Plutonium specific activity, 10^{11} dis/(min-g)	6.76
Pu(IV), % of plutonium	100
F, M	0.0016
Al, M	0.0031
Fission product gamma, 10^3 dis/(min-ml)	
^{95}Nb	6.3
^{95}Zr	6.3
^{137}Cs	4.0
Other	0.1
Total	16.7

TABLE 7

Comparison of Second Plutonium Cycle Flow Rates with Purex Rates (All Rates in ℓ/min)

	2AF	*2AX*	*2AS*	*2AW*	*2BX*
Pu-Am campaign	13.2	11.1	6.1	19.3	5.2
Purex	23.8	11.9	7.1	30.9	4.8

Cation Exchange

The americium solution was transferred from the evaporator to Tank 9.8 and diluted to 10,400 ℓ of 0.5M HNO_3; 11 moles of HF were added. This solution (Table 4) was processed in eight regular (~100 g of americium in each) and two clean-up absorption-desorption operations. Plutonium was maintained in the Pu(IV) or Pu(VI) valence states which are more readily washed from the resin by sulfate. After sorption, the columns were washed with ~15 bed volumes of 0.25M H_2SO_4 to remove plutonium and other impurities. Decontamination factors of ~4 for plutonium, 11 for fission products, 5 for aluminum, and 2 for iron were obtained.

No problems were encountered in cation exchange. Losses from sorption and decontamination washes were 2.2% of americium processed; overall losses from cation exchange were 2.3%, including filter and tank flushes.

Americium Oxalate Precipitation

Americium oxalate was precipitated from each batch of undiluted cation exchange eluate. 0.8M $H_2C_2O_4$ was added to the eluate (~3 g Am/ℓ) over a period of ~30 minutes, and the mixture was digested for one hour after addition. Americium oxalate was accumulated in the precipitator and consolidated into two batches for calcination to the oxide to avoid radiation exposure and to simplify handling.

The americium oxalate was accumulated in the precipitator instead of a filter boat by decanting the supernate through the precipitator dip tube after settling of the oxalate. Precipitations were repeated until about half the americium had accumulated in the precipitator; then the dip tube was lowered, and the slurry was transferred, with agitation, to the filter boat. In this manner, any americium oxalate that decomposed in the precipitator between runs was re-precipitated with the following charge.

Filtrate losses were 2.1% of the throughput. Americium oxalate was air-dried and calcined in oxygen for 3 hours at 150°C, followed by 3 hours at 600°C.

The americium was separated from most cationic impurities, except plutonium, by the oxalate precipitation. About 7 g of plutonium were added to the americium from residues in tanks and the precipitator. Other impurities, except calcium, were below the detectable limits of the emission spectrographic method used to analyze the samples. The oxide quality is summarized in Table 8.

TABLE 8

JB-Line ^{241}Am Oxide Quality

	Batch 1	*Batch 2*
Americium weight, grams	355	366
Americium assay,[a] wt %	86.6	86.8
Loss on ignition at 800°C	0.37	0.52
Impurities, wt % Am		
Plutonium	1.73	1.36
Aluminum	<0.05	<0.05
Iron	<0.05	<0.05
Chromium	<0.05	<0.05
Nickel	<0.05	<0.05
Calcium	0.04	0.05
Others[b]	<0.94	<0.93
Americium oxide radiation,[c] mrem/hr	210	160

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a. $88.28 \times \left(1 - \frac{\text{wt loss}}{100}\right)$ - sum of detected impurities, i.e., wt fraction of "crude" product)

b. Includes Ag, B, Ba, Be, Bi, Co, Mg, Cu, Li, Mn, Mo, Pb, Sn, Zn, Na, Nb, P, Sb, Si, Ti.

c. Measured at 3 inches through side of shipping container.

Acknowledgment

Processing data were supplied by the Separations Technology Department of the Savannah River Plant.