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Savannah River Laboratory
Aiken, SC 29808

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ABSTRACT

About 5 kg of ingrown ^{241}Am was recovered from 850 kg of aged plutonium using a process developed specifically for Savannah River River Plant application. The aged plutonium metal was first dissolved in sulfamic acid. Sodium nitrite was added to oxidize the plutonium to Pu(IV) and the residual sulfamate ion was oxidized to nitrogen gas and sulfate. The plutonium and americium were separated by one cycle of solvent extraction. The recovered products were subsequently purified by cation exchange chromatography, precipitated as oxalates, and calcined to the oxides. Plutonium processing was routine. Before cation exchange purification, the aqueous americium solution from solvent extraction was concentrated and stripped of nitric acid. More than 98% of the ^{241}Am was then recovered from the cation exchange column where it was effectively decontaminated from all major impurities except nickel and and chromium. This partially purified product solution was concentrated further by evaporation and then denitrated by reaction with formic acid. Individual batches of americium oxalate were then precipitated, filtered, washed, and calcined. About 98.5% of the americium was recovered. The final product purity averaged 98% $^{241}AmO_2$; residual impurities were primarily lead and nickel.

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INTRODUCTION AND SUMMARY

About 850 kg of plutonium metal, nominally 11.5% ^{240}Pu, was transferred from the Hanford, Washington facility to the Savannah River Plant (SRP). The plutonium was to be separated from ingrown ^{241}Am and converted to PuO_2 for use as fuel in the Fast Flux Test Facility (FFTF) at Hanford. During several years of storage, about 5.1 kg of ^{241}Am had grown into the stored plutonium by the decay of ^{241}Pu. If not separated, the ^{241}Am would greatly increase the radiation exposure of personnel during conversion of the plutonium metal to oxide and during fabrication of reactor fuel elements.

The separated ^{241}Am is in demand for a number of industrial and scientific applications. It is also used extensively as a component of neutron sources in many fields, predominantly petroleum well logging. To satisfy this demand, a large-scale process was developed for separating and purifying it using existing facilities at SRP.

The process, diagrammed in Figure 1, involved the following operations:

- DISSOLUTION (B-Line Dissolvers). The metal was dissolved in 1.67M sulfamic acid in small batches to a concentration of 60 ±10g Pu/L. The PuO_2 coating on the surface of the metal plus the PuH_x (where x = 2.0 to 2.7) produced from the reaction of $H_2(g)$ with plutonium metal formed a sludge that was collected and subsequently dissolved separately with 14M HNO_3 containing 0.2M KF.

- FEED ADJUSTMENT FOR EXTRACTION (Warm Canyon Tanks). Dissolver solution was accumulated and diluted to <6 g Pu/L with 3M HNO_3. Sodium nitrite solution was added to destroy residual sulfamate and oxidize Pu(III) to Pu(IV).

- SOLVENT EXTRACTION (Warm Canyon-Second Plutonium Cycle). Plutonium and americium were separated in a single pass through the mixer-settlers using 30% TBP in n-paraffin for the extraction of plutonium.

- Pu FINISHING (B-Line Ion Exchange, Precipitators, and Calciners). The recovered Pu(III) solution was processed to PuO_2 by conventional ion exchange, oxalate precipitation, and calcination methods.

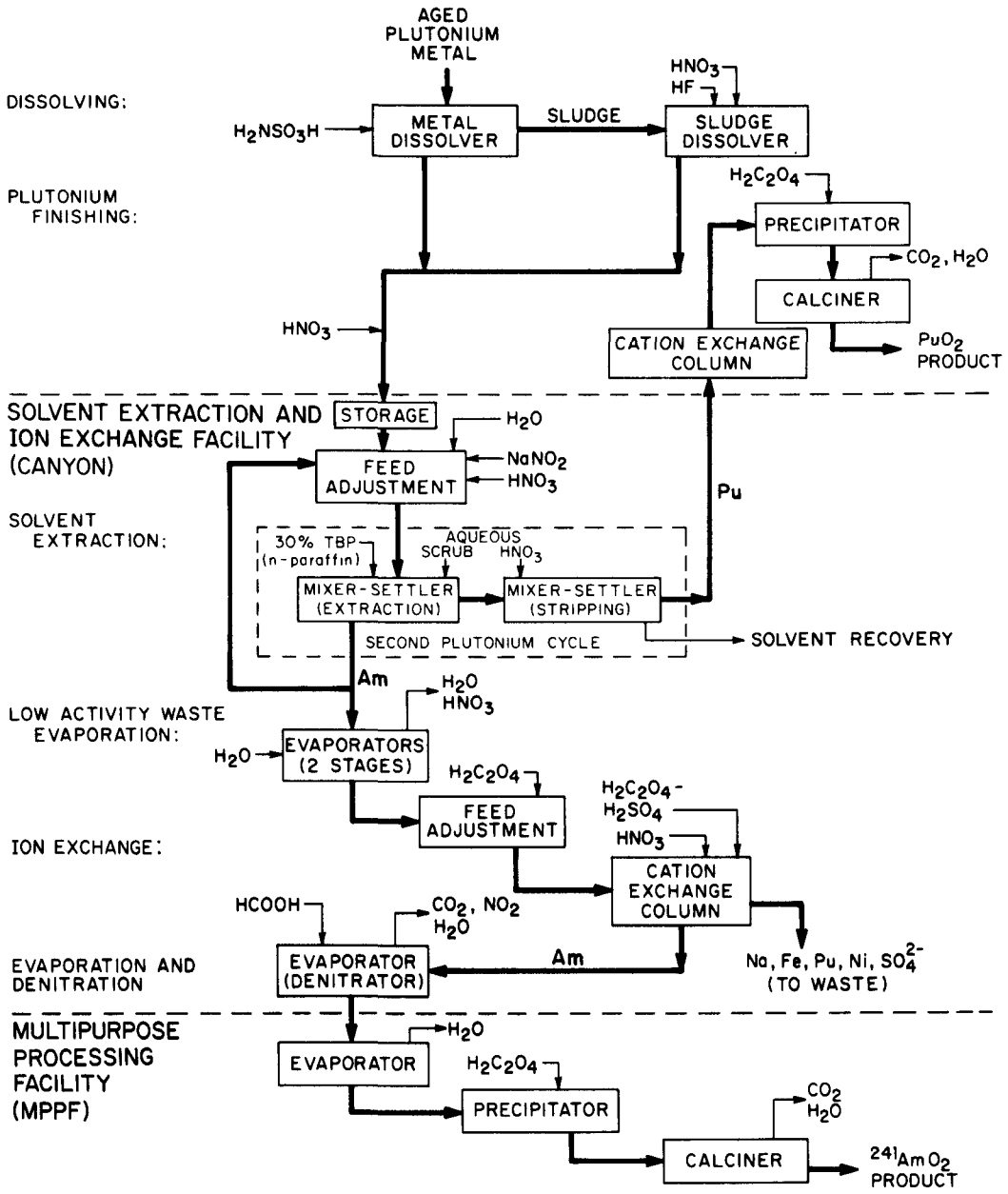

FIGURE 1. Process Flowsheet for Recovery of ^{241}Am from Aged Plutonium Metal

- FEED ADJUSTMENT FOR ION EXCHANGE (Warm Canyon Low-Activity Waste Evaporators). The aqueous, Am-bearing, nitrate solution from solvent extraction was concentrated and acid-stripped to increase the americium concentration and to reduce the acidity to levels acceptable for cation exchange. Oxalic acid was then added to the concentrated feed solution to complex iron and residual plutonium, so they would not be absorbed on the ion exchange column with the americium.

- CATION EXCHANGE (Warm Canyon "II-F Frames" Facility*). Americium was further concentrated and purified by cation exchange chromatography with Dowex^{TM} (registered trademark of Dow Chemical Co., Midland, Michigan) 50WX12 resin. Americium absorbed on the resin column was eluted with 5.5M HNO_3, following two separate decontamination washes (with 0.25M H_2SO_4/0.05M $H_2C_2O_4$ and with 0.2M HNO_3).

- DENITRATION (Hot Canyon - Rerun Evaporator). The acid concentration of the eluted americium solution was reduced to 0.25M HNO_3 by semibatch reaction with formic acid; the denitrated solution was further concentrated, in place, by evaporation to >2g Am/L.

- Am FINISHING (MPPF). The denitrated americium concentrate was transferred to the Multi-Purpose Processing Facility (MPPF) evaporator and was further concentrated (2 to 10 g Am/L), precipitated in small batches (typically 70 to 140 g Am) by the addition of 0.9 M oxalic acid, digested at ambient temperature, filtered, and washed. The americium oxalate was air-dried, calcined at 700°C, and packaged for shipment.

The process used established technology for separation (i.e., solvent extraction) and purification (cation exchange chromatography and oxalate precipitation). However, adaptation of the process to existing facilities required a substantial development effort to control corrosion, to avoid product contamination in process, to keep the volume of process and waste solutions manageable, and to denitrate solutions by reaction with formic acid. The Multi-purpose Processing Facility (MPPF), designed for recovery of transplutonium isotopes, was used for the first time for the

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* This SRP facility is normally used for anion exchange purification of neptunium and plutonium recovered from the first cycle of the Purex process.

precipitation and calcination of americium. Also, for the first time, large-scale formic acid denitration was performed in a canyon vessel. A number of process variables were investigated in both the Savannah River Laboratory (SRL) and in the Separations Technology Laboratory (STL) at SRP. In the course of process design, the procedure was demonstrated on a laboratory scale in STL with actual process solutions.

After the laboratory demonstrations, pilot cold (nonradioactive) chemical runs of several of the unit operations were performed in both canyon and MPPF equipment. These runs confirmed the operating limits which had been established during the laboratory experiments.

The cation exchange process, however, could not be piloted with cold chemicals. Instead, each separate batch was monitored by multiple sampling and rapid analysis of the raffinate during the loading step. Subsequent column loadings from the batch of ^{241}Am solution were then adjusted according to the loss results of the first column-loading of each batch.

The process operated successfully in the plant. More than 98% of the americium was recovered from the cation exchange column as an acidic nitrate solution. Substantial quantities of sodium, iron, chromium, nickel, sulfate, and phosphate were removed. Decontamination from all impurities was satisfactory although some chromium and small amounts of nickel, iron, and lead remained. The plutonium metal feed stock contained about 5 ppm natural lead which was not removed effectively in the process. Recovery of americium in the finishing process (oxalate precipitation and calcination) averaged 98.5%. Most of the residual chromium contaminant was removed from the oxalate in decanted supernate and washes. The finished oxide product purity exceeded specifications, i.e., >95% $^{241}AmO_2$. By selective blending, impurities in the shipped product, predominantly lead and nickel, were kept below 2%.

EXPERIMENTAL PROCEDURES

Dissolution

Dissolution experiments were conducted in round-bottomed flasks connected through a water-seal to a graduated cylinder (Figure 2). Weighed quantities of plutonium metal with measured surface areas were dissolved in 1.67M NH_2SO_3H at ambient temperature. The volume of hydrogen gas generated was measured by measuring the volume of water expelled from the water seal. Dissolution kinetics were calculated from the initial surface areas and the quantity of hydrogen gas evolved.

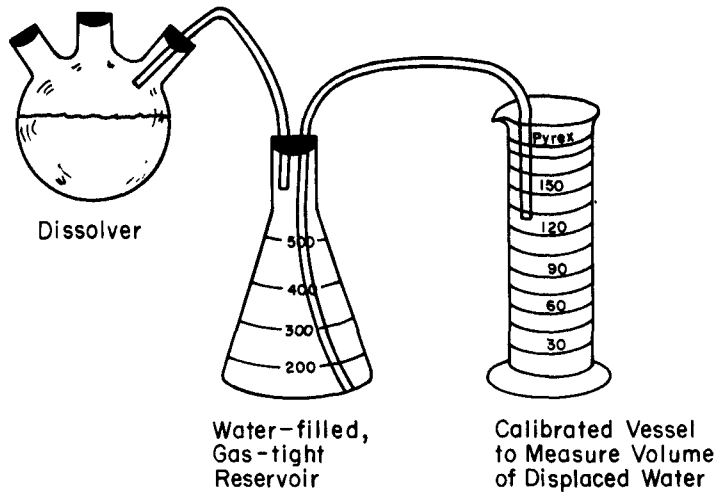

FIGURE 2. Experimental Apparatus for Dissolving Metal Specimens

Dissolver Solution Storage

Simulated storage experiments were conducted in 125-mL Erlenmeyer flasks. Solutions containing 60 g Pu/L as $Pu(NH_2SO_3)_3$ in sulfamic acid were diluted to $\sim$6g Pu/L with either 4M HNO_3 or with 7.5M HNO_3. Samples were withdrawn periodically, and the Pu(IV) concentration was determined by TTA extraction followed by gross alpha counting and alpha spectrometry.

Valence Adjustment

For effective extraction, plutonium must be oxidized from Pu(III) to Pu(IV) or Pu(VI) oxidation states. Four methods of oxidation were investigated: (1) heat, (2) nitrous oxide gas, (3) nitric oxide gas, and (4) sodium nitrite solution. As the major use of the oxidant is to destroy the sulfamate, these experiments were performed only on non-radioactive solutions of sulfamic acid in nitric acid. The solubilities of the reaction products were then determined for downstream processing of the ^{241}Am-containing solution.

Initial Evaporation

To obtain a general indication of corrosion problems and possible precipitation problems, $Pu(NH_2SO_3)_3$ - NH_2SO_2H solutions from a production dissolver were diluted to 6 g Pu/L in 3M HNO_3, and then sodium nitrite was added to adjust the valence from Pu(III) to Pu(IV). The solution was then adjusted to 0.5 g Pu/L and 4M HNO_3, and then extracted three times with 30% TBP in dodecane

which had been pre-equilibrated with 4M HNO_3. The solvent was scrubbed with 1M HNO_3 and stripped with 0.05M hydroxylamine (HAN) - 0.01M HNO_3. The plutonium was returned to the production line. The aqueous scrub solution and the aqueous waste solution from the extraction were combined and evaporated in two steps in stainless-steel beakers. One set of experiments used an evaporation factor of 25 before acid stripping began; the other set used a factor of 50. After the first evaporation step, the solutions were diluted by a factor of four with distilled water and acid stripping begun. Acid stripping continued until the acid concentration was reduced to 2M, and the volume was reduced by a factor of 100.

Corrosion studies were also made using expected concentrations of sulfate ion and nitric acid under simulated processing conditions. After it was determined that larger than expected concentrations of stainless-steel corrosion products (Fe, Cr, and Ni) were in the feeds to the evaporators, additional corrosion studies were made in solutions of varying Cr(VI) and nitric acid concentrations.

Cation Exchange

Cation exchange experiments were conducted in 25-cm-long by 0.7-cm-diameter columns containing 7 mL or 13 mL of 50 to 100 mesh Dowex™ 50WX12 resin or 20 to 50 mesh Dowex™ MP-50 resin at a feed rate of 3 to 4 mL/(cm^2-min). The resins and the feed rate are those considered for the plant flow-sheet. Elution was downflow at 0.5 mL/(cm^2-min), just as in 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 gamma content and the alpha content of the column effluent during feeding. Column washing and elution were monitored similarly. The behavior of other cationic impurities was determined by atomic absorption analysis of the effluent. Plutonium was determinded by extraction with thenoyltrifluoro-acetone (TTA) in xylene, followed by gross alpha counting and alpha pulse height analysis of the TTA extract.

Formic Acid Denitration

Formic acid denitrations were carried out in a 250-mL round-bottomed flask fitted with heating mantle, thermometer, and reflux condenser. After heating to the reaction temperature, formic acid (23.5M) was added through the condenser from a separatory funnel (Figure 3) at a rate $\leq$0.05 moles per min per liter of nitric acid solution.

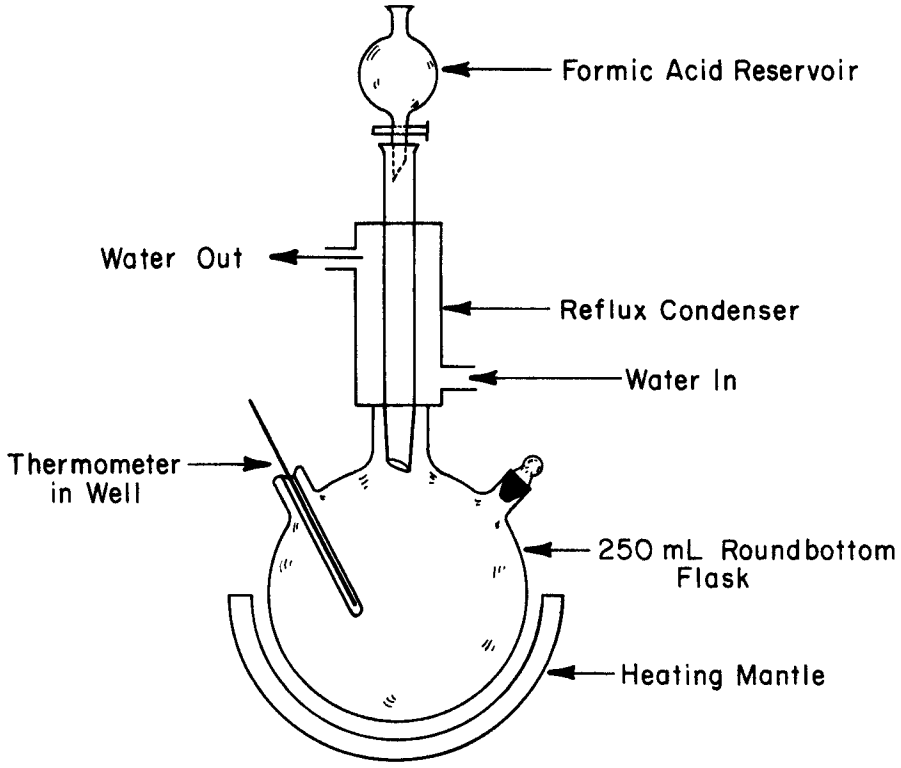

FIGURE 3. Experimental Apparatus for Formic Acid Denitration Experiments

Oxalate Precipitation

Two options were investigated to separate the ^{241}Am from about 40 kg of iron, chromium, and nickel present as corrosion products of process equipment. One option was precipitation of Am(III) oxalate in canyon vessels; the second option was precipitation of the oxalate from 2g ^{241}Am/L in MPPF. Both options were simulated in normal lab glassware with actual plant solutions. Futhermore, the oxalates of the major contaminants were prepared, and their solubilities in simulated solutions were determined.

LABORATORY RESULTS

Dissolution of Plutonium Metal

Plutonium metal dissolves readily in sulfamic acid (NH_2SO_3H) at ambient temperature according to the reaction

$$Pu^o + 3H^+ \longrightarrow Pu^{3+} + 3/2H_2(g)$$

The rate of dissolution was found to depend on the hydrogen ion concentration and on the surface area of the metal. A short induction period preceded the dissolution. For calculational purposes, a typical dissolving cycle was: 1) a 2.55 kg plutonium metal "button" (171.2 cm^2 surface area) was charged to 3.0 L of 1.67M sulfamic acid; 2) dissolution proceeded for 60 min; 3) 2 L of this solution was displaced with 2 L of fresh 1.67M sulfamic acid; 4) Steps 2 and 3 were repeated until the plutonium metal inventory decreased to 1300 g Pu; 5) another plutonium metal charge was made; 6) Steps 4 and 5 were repeated as long as necessary. Under this procedure, the initial batches of solution from the dissolver averaged about 50 $\pm$ 5 g Pu/L. After charging the second plutonium button, the plutonium concentration increased to about 60 $\pm$ 10 g Pu/L for each batch displaced. A more complete treatment of the dissolving experiments is given elsewhere.[1]

Laboratory experiments indicate that it is possible to increase the dissolution rate by elevation of the temperature to the 60 to 80°C range. These studies have been reported.[2] In general, an increase in the dissolution rate by a factor of four is possible.

Storage of Dissolved Plutonium Solution

Plutonium storage experiments were simulated to answer two questions:

1) Would sufficient radiolysis of the solution occur during storage to oxidize the Pu(III) to Pu(IV)?

2) Would precipitation of plutonium sulfate occur if all the plutonium ions were oxidized to Pu(IV) and if all the sulfamate ions were converted to sulfate ions?

In-growth of Pu(IV) versus time is shown in Figure 4. It was obvious from this curve that valence adjustment by radiolysis would be insignificant for most of the campaign.

The solubility of plutonium (in grams per liter) vs sulfate concentration is shown in Figure 5 for various concentrations of nitric acid. These same data are replotted in Figure 6 as the solubility of plutonium vs nitric acid concentration at various concentration of sulfate. Because the plutonium concentrations in the canyon tanks is kept below 6 g Pu/L for nuclear safety, nitric acid concentrations as high as 6M can be tolerated as all flowsheets dilute the sulfate ion concentration to less than 0.4M.[3]

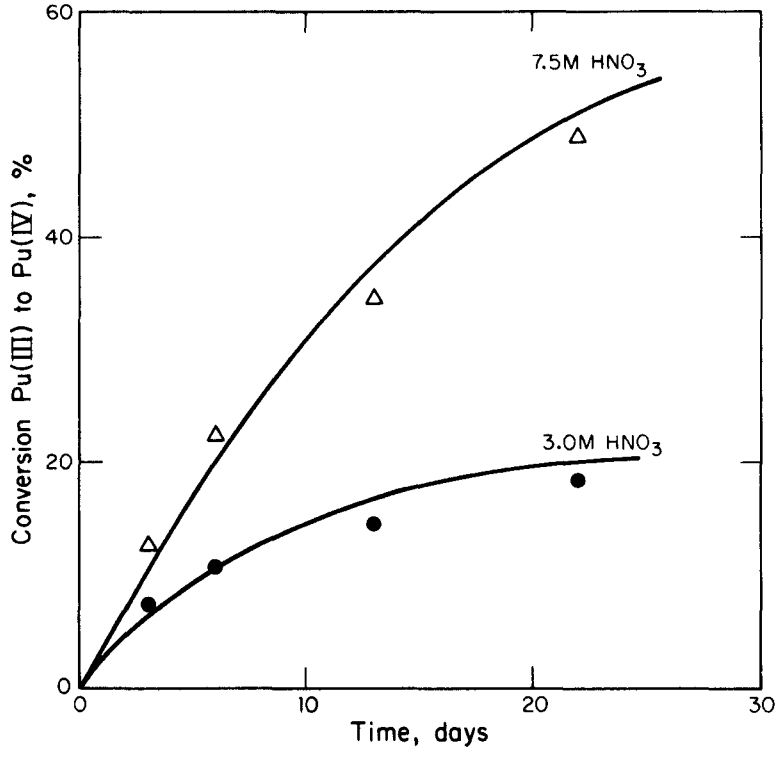

FIGURE 4. Radiolytic Oxidation of Pu(III) to Pu(IV) in Sulfamic - Nitric Acid Solutions

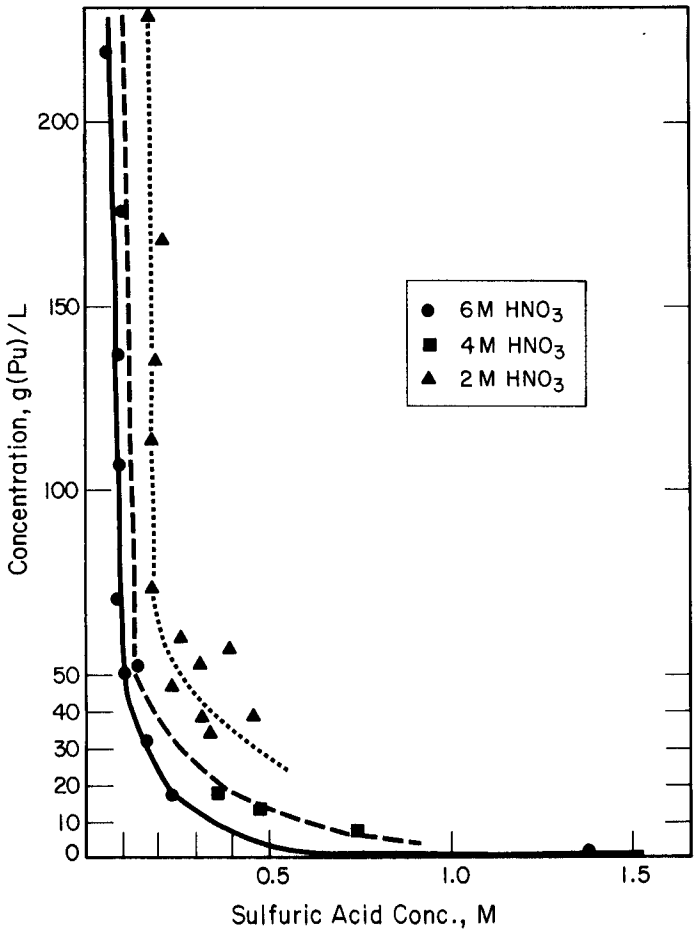

FIGURE 5. Equilibrium Curves of Pu(IV) and Sulfate Ions in Nitric Acid Solutions

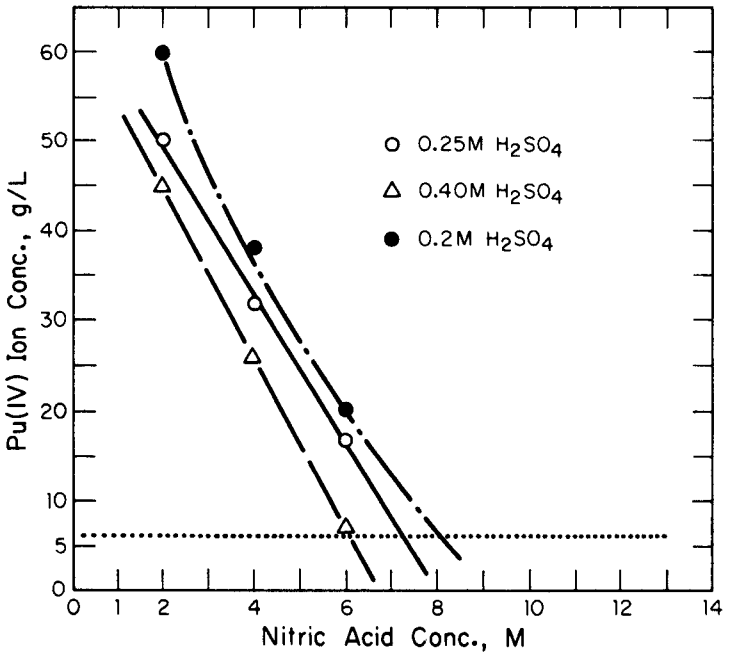

FIGURE 6. Equilibrium Curves of Pu(IV) and Nitrate Ions in Sulfuric Acid Solutions

Feed Adjustment and Solvent Extraction

Four methods of valence adjustment were used in laboratory experiments: (1) heat, (2) nitrous oxide (gas), (3) nitric oxide (gas) and (4) sodium nitrite. All four systems effectively adjust the plutonium valence to the extractable Pu(IV) state. Sodium nitrite was chosen for the plant process as it is the method in routine use for normal Purex processing.

Heat was not used because sulfamate hydrolysis is more rapid than its oxidation by nitric acid[4] and the hydrolysis product, NH_4^+, has a higher affinity for cations exchange resin than Na^+ ion.[5] Therefore, for increased americium loading on the resin, it is better to use sodium nitrite than heat. Ammonium ion also has another drawback. When the waste is neutralized, ammonia is evolved into the canyon vessel vent system, which contains nitric acid vapors. Solid ammonium nitrate then forms and is removed by the vessel vent-filters. For the full campaign, about 1700 kg of ammonium nitrate would have been formed. This amount of ammonium nitrate on the vessel vent-filters is unacceptable. Addition of nitrogen oxide gases was rejected because (at present) a system is not available to add gases to canyon tanks. On a laboratory scale, however, both of the gases effectively oxidize the sulfamate ion when in 3 to 4M HNO_3.

Americium Concentration by Batch Extraction

The canyon equipment requires that the volume of the ^{241}Am-bearing 2AW solution be first reduced in one evaporator by a factor 25 to 50. Then, the concentrated solution is transferred to a second evaporator and diluted in place to decrease the nitric acid concentration. The solution is again evaporated ("acid-stripped"). During acid stripping, the volume of solution is also reduced to its final product ^{241}Am concentration.

Four items were important to determine the best operation within these constraints:

(1) The solubility of sodium sulfate.

(2) The solubility of ammonium sulfate.

(3) The solubility of sodium americyl sulfate.

(4) The fate of residual TBP.

The solubilities of sodium sulfate and ammonium sulfate are shown in Figure 7. From a solubility standpoint, it would be better

to hydrolyze the sulfamate ion to ammonium and sulfate ions than to oxidize it with sodium nitrate as the solubility of sodium bisulfate is the limiting factor during the evaporation of the solution. However, downstream processing dictates that oxidation, not hydrolysis, must be the mode of destruction of the sulfamate because the affinity of the resin for NH_4^+ is greater than the affinity of the resin for sodium ion.[5]

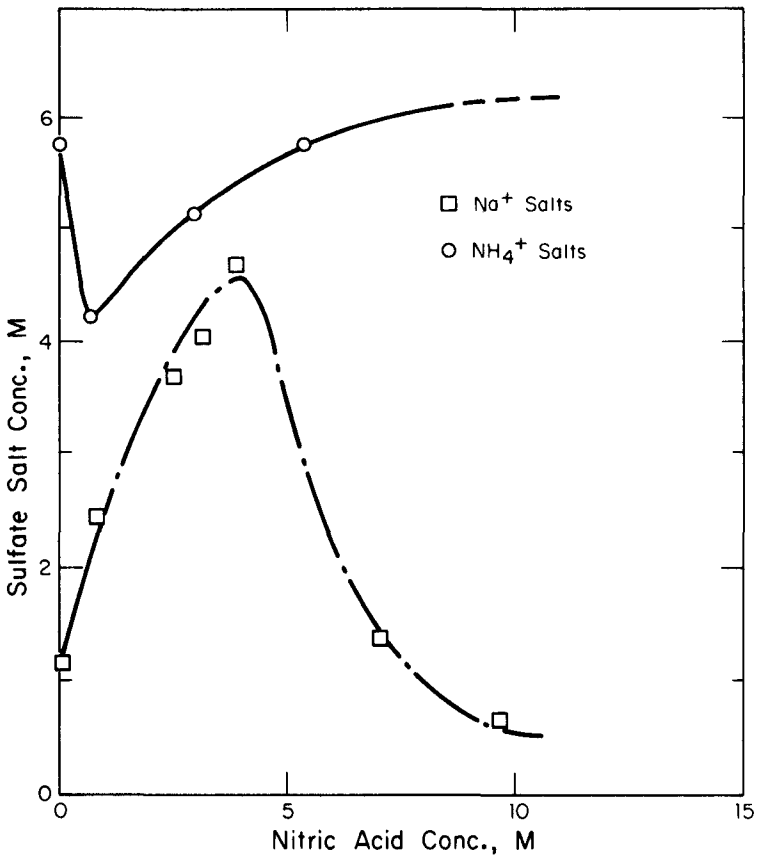

FIGURE 7. Solubility of Sulfate Salts in Nitric Acid

Sodium americyl sulfate is relatively insoluble in nitric acid, and precipitation of this salt may limit evaporation of the 2AW solution. The solubility of sodium americyl sulfate was determined in several nitric acid solutions containing Am^{3+}, Na^{+}, and SO_4^{2-} ions (Table 1). The rate of precipitation is slow, requiring several hours to several days to achieve equilibrium.

TABLE 1

Solubility of Sodium Americyl Sulfate

Composition of Solution[a]

HNO_3, M	Na^{+}, M	SO_4^{2-}, M	Am, g/L in solution (In equilibrium with solid)
0.8	2.1	1.0	0.15
1.4	2.3	1.1	0.25
1.4	3.3	1.5	0.15
4.2	2.1	1.0	0.4
4.2	3.1	1.5	0.2

[a] The feed samples contained 1.5g Fe/L, 0.4 g Cr/L, and 0.2 g Ni/L.

The decomposition of TBP during the evaporation-concentration leads to some precipitation of organic phosphate salts. As shown in Figure 8, TBP is soluble in the aqueous phase[6] and, therefore, TBP and its degradation products are contained in the waste stream. If fully decomposed to the ortho-phosphate ion, there is no solubility problem. There is a solubility problem, however, with the intermediate degradation products.

On the laboratory scale, feed prepared from stored plutonium solution was contacted with 30% TBP to produce a typical ^{241}Am waste solution. One portion of this waste solution was evaporated by a factor of 25; the other portion, by a factor of 50. After acid-stripping, the solutions were evaporated by an overall factor of 100. The maximum nitric acid concentration and temperature were achieved by the initial evaporation factor of 50. No solids were detected in this solution.

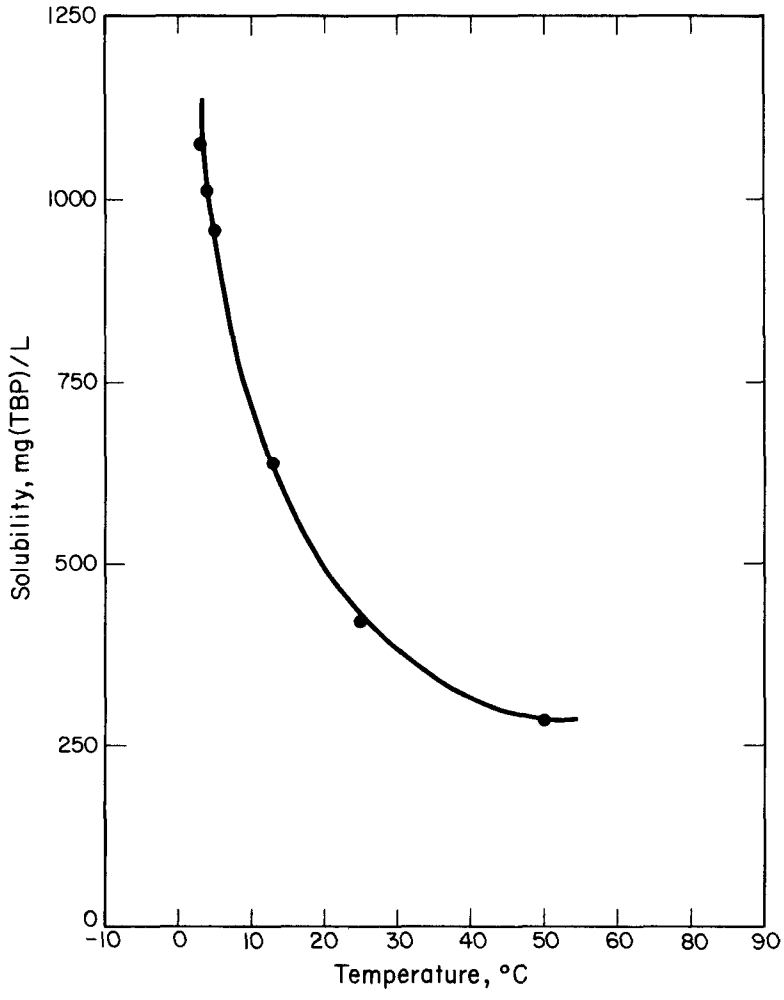

FIGURE 8. Solubility of Tributyl Phosphate (TBP) in Water at 5 to 55°C

However, with the solution only evaporated by an initial factor of 25, sufficient solids were present to plug ion exchange columns. These solids, a white gel, were soluble in water and dilute nitric acid, but much less soluble in 4M HNO_3 than water. Tests indicated the solids contained sodium and sulfate ions and organic phosphates. In addition, the gel carried ^{241}Am. Insufficient solids were obtained for a complete characterization.

Cation Exchange of ^{241}Am Solution

Cation exchange experiments were performed with both gel- and macroporous-type resins and with both simulated and authentic plant solutions. The feed was prepared with and without a masking agent (e.g., oxalic acid) to minimize absorption of ferric ions on the column. In general, gel-type resin was more effective. A masking agent was necessary to obtain adequate column capacity.

The resin capacity for americium is only a few per cent of the theoretical capacity (about 2 equivalents per liter) because the feed contains large amounts of other cations. Initially, the feed had been estimated to contain about 0.4M Na^+, about 0.5M H^+, and 0.07g Am/L based on chemicals added in prior processing; and, about 0.2g Fe/L, about 0.1g Cr/L, and about 0.04g Ni/L based on estimated corrosion rates during evaporation.

Tests are summarized in Table 2 with Dowex™ 50Wx8, 50-to 100 mesh resin. Initial tests with simulated solutions at lower estimated concentrations of iron, chromium, and nickel (Test 1), the resin capacity to one per cent breakthrough of americium was 52 bed-volumes of feed; at higher concentrations of these corrosion products (Test 2), resin capacity for americium was 35 bed-volumes of feed. Resin capacity for americium from these feed compositions is only 1.5% to 2.5% of the resin exchange capacity.

TABLE 2

Capacity Ion Exchange Resin for Americium

	Feed Composition[a]				
Test	Fe, g/L	Cr, g/L	Ni, g/L	Oxalic Acid, M	Capacity of Resin,[b] Bed-Volumes
1	0.1	0.05	0.02	-	52
2	0.3	0.15	0.05	-	35
3	0.1	0.05	0.02	0.005	70
4	1.5	0.4	0.2	0.05	40
5	3.5	1.3	0.7	0.1	12
6	1.7	0.6	0.35	0.05	55

a. Feeds for Tests 1 through 5 were 0.5M H^+, 0.4M Na^+, 0.25M SO_4^{2-}, and 0.07 g Am/L. Feed for Test 6 was 0.25M H^+, 0.2M Na^+, 0.125M SO_4^{2-}, and 0.035 g Am/L.

b. Dowex™ 50WX8 gel-type, 50 to 100 mesh, ion exchange resin; Dow Chemical Co., Midland, Michigan.

The capacity of resin for americium was increased by adding one to two moles of oxalic acid per mole of iron to the feed. A complex, singly-charged iron cation $(FeC_2O_4)^+$ was formed, which is weakly retained by the resin. Feed for Test 3 was the same feed as for Test 1, except that 0.005M oxalic acid was included and the resin capacity at 1% americium breakthrough increased from 52 to 70 bed-volumes. Less than 10% of the iron was retained by the resin at the completion of sorption when oxalic acid was in the feed. When the resin was washed with 15 to 20 bed-volumes of dilute oxalic acid following sorption, only about 1% of the iron was retained by the resin.

Iron is quite effectively separated if oxalic acid is omitted in the feed and used as wash; however, lower resin capacity for americium results because the iron is sorbed during feeding. Addition of oxalic acid to feed and wash solutions also removes >98% of the trace zirconium, niobium, and plutonium.

Cation exchange runs were also made with simulated and authentic feed solutions that contained a wide-range of corrosion product concentrations. At an approximately 15-fold increase in corrosion products (Test 4), and with 0.05M oxalic acid in the feed, capacity to one per cent breakthrough was 40 bed-volumes. When corrosion products were increased to 5.5 g/L (Test 5), the capacity was only 12 bed-volumes. Dilution of Test 5 feed with an equal volume of water (Test 6) doubled the column capacity for americium; however, this was not an attractive plant option because processing time would be increased.

Oxalic acid in the feed did not affect the sorption behavior of chromium and nickel on the cation resin. However, about 75% of the Ni(II) was in the sorption and wash effluents because resin affinity for divalent nickel was lower than the resin affinity for trivalent chromium and americium.

More than 99% of the sodium was separated when two sodium-free acid washes were made after sorption. The first wash was about 15 bed-volumes of 0.2M H_2SO_4 - 0.05M $H_2C_2O_4$; the second wash about 5 bed-volumes of 0.25M HNO_3. These washes removed residual sodium ion, and also flushed sulfate and oxalate ions from the resin bed.

Elution with 5M HNO_3 at 0.5 mL/(min-cm^2) removed about 87% of the americium in four bed-volumes, and >99% in eight bed-volumes.

Dowex macroporous resin had much lower americium capacity and required much more 5M nitric acid for americium elution.

Corrosion Control During Product Evaporation

High corrosion rates (>0.02 inch per month) of stainless-steel equipment were indicated by chemical analyses during the concentration of the low-activity waste (LAW) stream in the plant evaporator. As it was shown that Cr(VI) in boiling nitric acid could accelerate corrosion of the equipment, and tens of kilograms of chromium were being recovered along with the americium, laboratory tests were run on stainless-steel samples in nitric acid with various chromium concentrations.

The first set of tests used both an annealed sample and a sensitized sample in boiling column eluate containing ^{241}Am. Corrosion of the samples exceeded the acceptable levels of 0.002 inches/month.

Additional tests were run on simulated solutions using 65% nitric acid plus 0.002, 0.004, 0.010, and 0.100 wt% chromium ion added as sodium dichromate. Two temperatures, 80°C and boiling, were used for the corrosion experiments. The stainless-steel test samples were from the same heat (production batch) of material that had a 0.001 ipm corrosion rate from the original (non-chromium containing) Huey test.

Corrosion test data showed Cr(VI) concentrations of 0.004 wt% (1.15×10^{-3}M) in boiling 65 wt% HNO_3 will cause unacceptably high corrosion of stainless steel (i.e., greater than 0.002 inches month). However, at 80°C, corrosion rates for solutions containing less than 0.1 wt% Cr(VI) were acceptable (see Table 3 and (Figure 9). In general, results of the corrosion tests were:

1. Solutions containing less than 0.1% Cr(VI) and not exceeding 80°C will not cause accelerated corrosion.

2. Solutions containing more than 0.002% Cr(VI) and held at the boiling point will yield a corrosion rate of 2 to 12 times greater than the Huey test acceptance level of 0.002 inches per month (ipm).

3. The corrosion rates of samples in 80°C solutions are greater during earlier exposures and decrease with the increasing time.

4. In boiling solutions, the corrosion mechanism is intergranular attack with the higher calculated corrosion rates in the latter stages being due to complete grain drop-out.

TABLE 3

Corrosion of Stainless-Steel Test Coupons

Sample Condition	Chromium (VI) Added, wt%	Accumulative Corrosion Rates, ipm* 46 hrs.	122 hrs.	170 hrs.	266 hrs.	477 hrs.
A. Temperature = 80°C						
Annealed	0.002	0.0001	0.0003	0.0002	0.0002	0.0002
Annealed	0.004	0.0002	0.0002	0.0002	0.0002	0.0001
Annealed	0.010	0.0004	0.0004	0.0003	0.0002	0.0001
Annealed	0.100	0.0044**	0.0021**	0.0015	0.0010	0.0006
Sensitized	0.002	0.0002	0.0003	0.0002	0.0002	0.0002
Sensitized	0.004	0.0003	0.0004	0.0003	0.0003	0.0002
Sensitized	0.010	0.0005	0.0003	0.0003	0.0002	0.0002
Sensitized	0.100	0.0053**	0.0022**	0.0017	0.0011	0.0007
B. At boiling temperature						
Annealed	0.002	0.0011	0.0014	0.0015	0.0018	0.0065**
Annealed	0.004	0.0011	0.0013	0.0014	0.0033**	0.0094**
Annealed	0.010	0.0012	0.0010	0.0011	0.0013	0.0029**
Annealed	0.100	0.0133**	0.0072**	0.0070**	0.0080**	0.0118**
Sensitized	0.002	0.0012	0.0011	0.0011	0.0012	0.0025**
Sensitized	0.004	0.0015	0.0012	0.0013	0.0016	0.0049**
Sensitized	0.010	0.0032**	0.0075**	0.0088**	0.0149**	0.0278**
Sensitized	0.100	0.0115**	0.0090**	0.0100**	0.0127**	0.0243**

* ipm = inches per month.
** Exceeds Huey test acceptance level of 0.002 ipm (See Note 4).

NOTES:
1. All solutions contained 65% HNO_3 with the indicated amounts of chromium.
2. The sensitized samples were heat-treated at 650°C for 1 hour.
3. Each sample had approximately 5 square inches of surface area and was placed in 275 mL of test solution. The test solutions were not changed.
4. The Huey test requires samples to be boiled in 65% HNO_3 for 240 hours and to have a corrosion rate of less than 0.002 ipm.

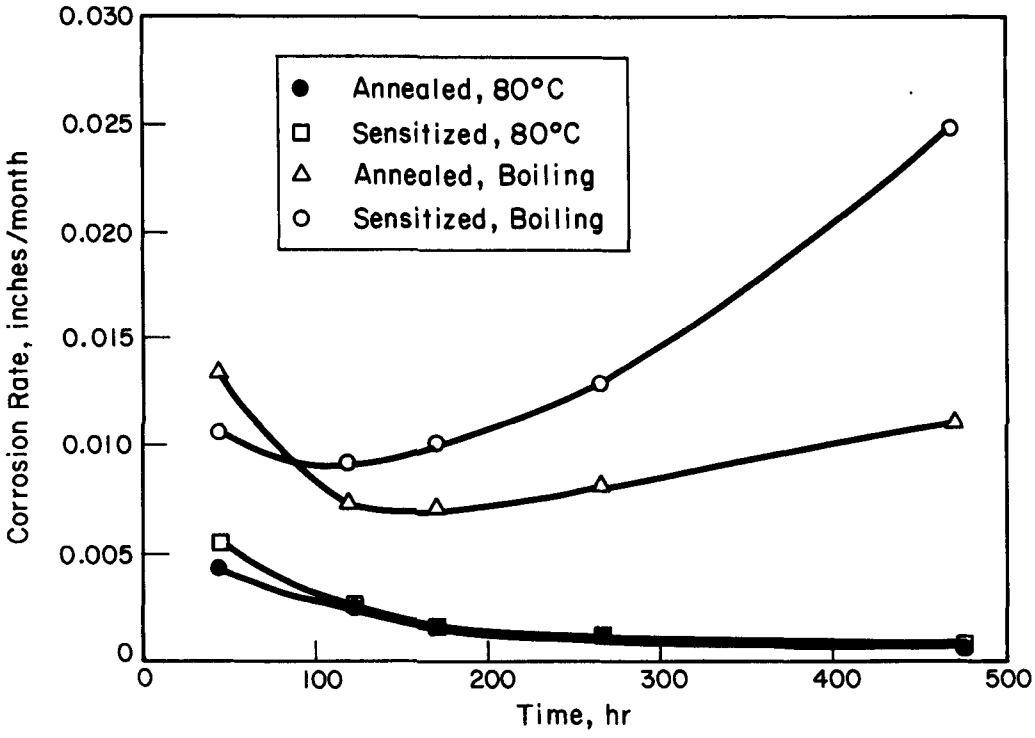

FIGURE 9. Corrosion Rates of Stainles-Steel Specimens in 65% Nitric Acid Containing 0.10% Cr(VI) Ions

As a result of these data, the simmering temperature of the ^{241}Am solution eluate was maintained below 80°C. A plant test confirmed the laboratory findings. The process tank was periodically cooled, samples taken, and iron concentrations were determined.

Formic Acid Denitration of Product Solution

Both simulated and authentic ^{241}Am solutions were subjected to formic acid denitration. Results for the simulated solutions are shown in Figure 10.

In general, the solutions were heated above 90°C, and 23.5M formic acid was added through the reflux condenser. Reddish-brown fumes of NO_x began to collect above the solution about 45 sec to 5 min after formic acid addition began. Vigorous reaction began within 5 min. The induction period depended upon both the temperature of solution and the formic acid addition rate. The vigorous reaction started at about the time the formic acid concentration reached 0.06M.

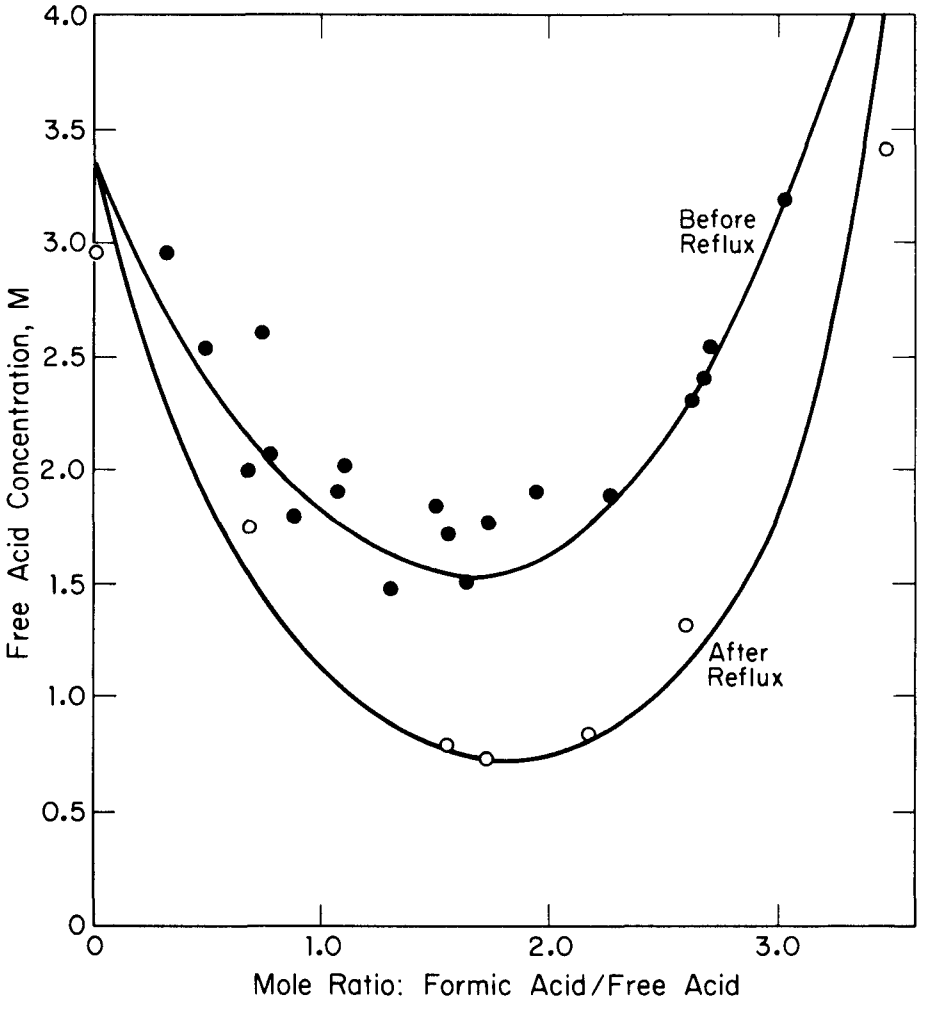

FIGURE 10. Formic Acid Denitration of Americium Product Solutions

The lowest possible free acid concentration for the simulated solutions was obtained when a formic acid to free nitric acid mole-ratio of about 1.6 to 1.9 was used. This ratio yielded a final free acid of about 0.7 to 0.8M. At a mole ratio of about 1.5, the final free acid is excess nitric acid. At a mole ratio of about 1.9, the final free acid is excess formic acid.

Comparison of the dynamic samples with the samples after refluxing yields important observations of the behavior of semi-batch denitrations for in-plant recovery processes. In the region where nitric acid is less than about 3M, formic acid begins to accumulate in the solution, i.e., the reaction rate appears to be controlled by nitric acid concentration instead of formic acid addition rate. This accumulated formic acid is, however, oxidized during the refluxing of the solution after the addition of the formic acid. For the semi-batch denitration, it appears that a nitric acid concentration of about 2M at the end of each individual denitration is an excellent stop-point. Using 2M HNO_3 as a projected stop-point assures that there will be no residual formic acid at the end of the reflux and evaporation steps. Additional high nitric acid solutions can then be added to the evaporated-denitrated solution without auto-initiation of a formic acid-nitric acid reaction.

After all the solution has been transferred to the denitration evaporator and denitrated, it is then possible to drive the denitration reaction to a residual free-acid concentration of about 0.5 to 0.8M.

Formic acid added beyond this point simply accumulates in the tank and, therefore, increases the free-acid concentration.

Precipitation of ^{241}Am Oxalate

Americium is separated from iron, chromium, nickel, and other impurities by oxalate precipitation. The ^{241}Am feed solution for precipitation in the MPPF (after formic acid denitration and volume reduction) was approximately 2 g Am/L, 14 g Cr/L, 1.2 g Fe/L, and 0.8 g Ni/L in one molar nitric acid. Further concentration of the feed solution to greater than 2 g Am/L necessitates evaporation at less than 85°C, because of the potential corrosion of the stainless-steel evaporator resulting from the presence of Cr(VI) ions in hot, strong, nitric acid. A precipitation test with plant solution adjusted to 2 g Am/L yielded americium oxide that met purity guidelines (Table 4). Emission spectrographic analyses showed 0.25 wt % Pb, 0.15 wt % Ni, 0.14 wt % Cr, and 0.1 wt % Fe. All other impurities were <0.1 wt %, and the total impurities were 0.8 wt %. Another test with the plant solution yielded americium oxide with 1.6 wt % total impurities, and with nickel and chromium each about 0.5 wt %.

TABLE 4

Purity Guidelines for $^{241}AmO_2$ Product

Component	Quantity, wt%
Americium Dioxide[a]	$\geq$95
Plutonium	$\leq$0.5
Lead	$\leq$0.5
Other Elements[b]	$\leq$0.5

a. Calorimetry as the assay method.
b. Determined by emission spectrographic analyses.

As an alternative to formic acid denitration, neutralization of the nitric acid with sodium hydroxide was also considered. This suggested procedure consisted of the following steps:

1. Evaporation of the solution at a temperature $\leq$80°C to the minimum volume (preferable $\leq$5400 L).
2. Add 2000 L 50% NaOH (19M).
3. Add 1800 L of 0.9M oxalic acid.
4. Evaporate to $\leq$7000 L total volume.
5. Adjust acid to within 0.1 to $\leq$0.2M (H^+) by addition of 50% NaOH.
6. Allow to settle overnight.
7. Jet-out solution using a special jet to a heel of 3000 L.
8. Add 9000 L of 0.005M oxalic acid; agitate.
9. Jet-out solution to a heel of 3000 L.
10. Add 9000 L of 0.01M HNO_3; agitate.
11. Jet-out solution to a heel of 3000 L.
12. Add 1200 L of 14M (64%) HNO_3; agitate to dissolve precipitate.
13. Feed solution to Evaporator 17.3E to evaporate and acid strip.

These steps would be necessary to hold dissolved losses to less than 3%, and to reduce the residual oxalate sufficiently to allow the precipitate to be dissolved. Continued corrosion of the tank was however, deemed unacceptable and eliminated this procedure from consideration.

PRELIMINARY PLANT TESTS

Full-scale simulation of the canyon ^{241}Am processes were carried out in plant equipment before processing the actual ^{241}Am-bearing stream. The first experiments were formic acid denitration of an aqueous nitric acid solution. The second was the oxalate precipitation of rare earths (simulating americium).

Denitration of Nitric Acid

All denitration in the plant was performed in Evaporator 16.1E (Figure 11). The volume of solution required to cover the coils in this evaporator is 2270 L. The evaporator holds 8830 L at 10 in. from overflow. The evaporator has a design boiling rate of about 1800 kg/hr (4000 lbs/hr). The condensate could be returned to the pot (reflux) or diverted to another vessel (e.g., Vessel 16.2). The evaporator is instrumented to read out pressure differential between the pot and the condenser outlet. The liquid level, pot contents temperature, condensate temperature, and the specific gravity of the pot contents are also measured and recorded. The evaporator does not contain an agitator.

Three tests were run using only nitric acid solutions. In the first test, 7000 lbs of 5.5M nitric acid was denitrated by reaction with formic acid in an 11-hr test. The reaction initiated promptly and proceeded smoothly. Initiation was confirmed by a rising temperature that occurred within 15 minutes after the formic acid feed started, by a declining specific gravity, and by red nitric oxide fumes issuing from the vessel vent. The peak reaction rate, evidenced by peak temperature and off-gas color, occurred 25 minutes after the feed started. The final acidity was 2.5M nitric acid.

In the second test, a full denitrator volume (4500 L) of clean 6M nitric acid was reacted with formic acid. The nitric acid solution in the evaporator was heated to boiling on total reflux, formic acid feed was started, and then the steam supply to the evaporator was shut off. The reaction initiated within three minutes after formic acid feed was introduced; denitration was confirmed by the sustained differential pressure, and the sustained temperature of the evaporator contents. The reaction proceeded smoothly until completion.

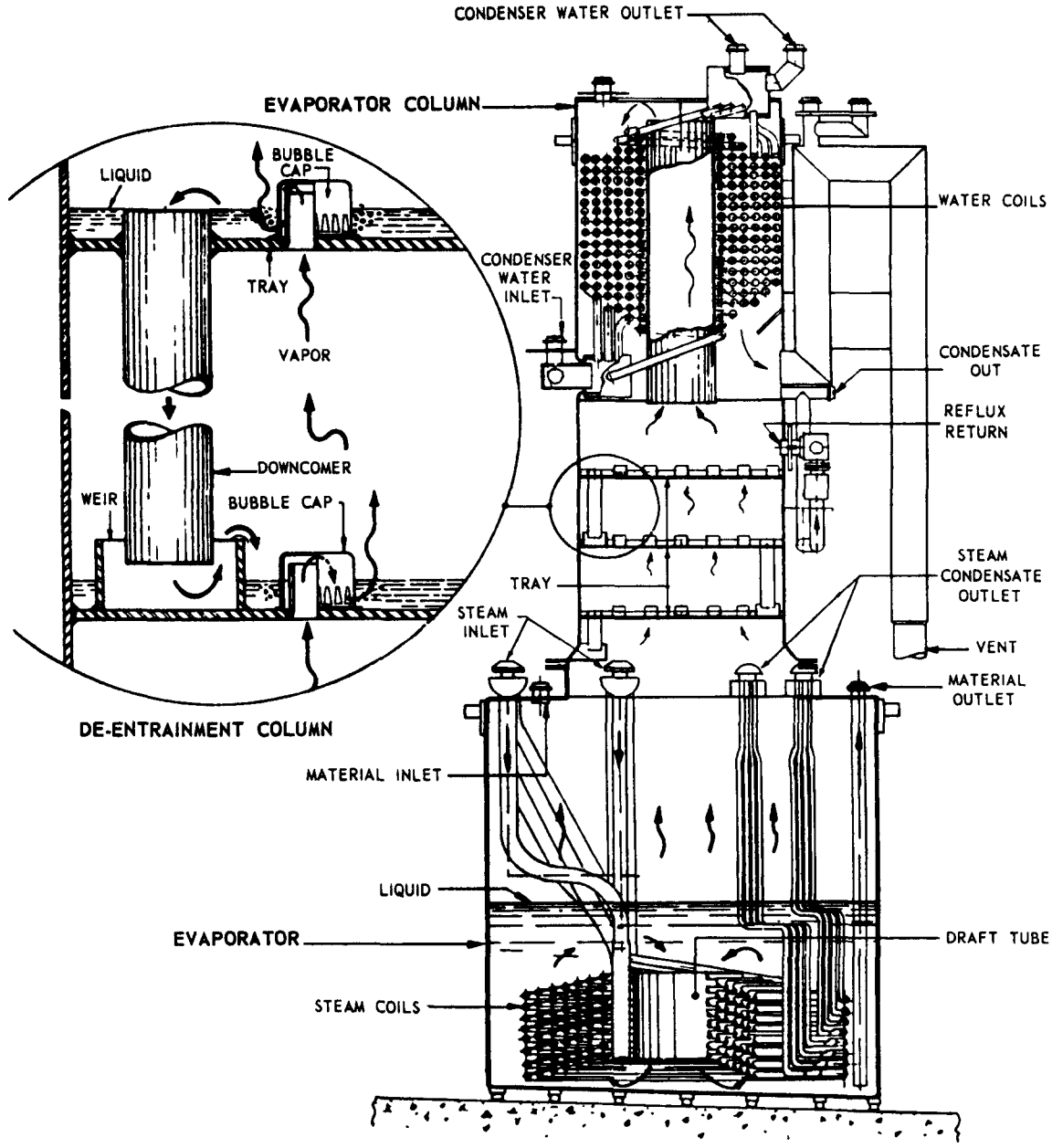

FIGURE 11. Process Evaporator and Condensing Column Apparatus

At the end of this test, the denitrated material was evaporated to about 2500 L and clean nitric acid was added to obtain an 8M nitric acid full-volume batch. In the third test, initiation was prompt and clearly evident by an increase in differential pressure about 8 minutes after formic acid feed began. Manipulating the steam flow proved to be a very reliable means of initiating and controlling the reaction. The rapid drop in column differential pressure, which follows the interruption of steam flow, is abruptly halted and then reversed when the reaction off-gas flow begins. At the end of formic acid feed, the material was refluxed for 2 hr and then evaporated to produce about 2500 L of 4M nitric acid. A final formic acid denitration then reduced the final acidity to less than one molar nitric acid.

Oxalate Precipitation of Simulated Process Solutions

Two precipitation conditions were investigated using dysprosium or samarium as stand-ins for ^{241}Am. Both conditions were based on physical limitations on the volumes in tanks to be used in the ^{241}Am solution processing. The denitrated product solution could be concentrated in Evaporator 16.3E; if so, the volume of solution required to just cover the steam coils in this evaporator, nearly 2500 L, would be the minimum volume. Hence, one condition assumed the solution was evaporated to 2500 L, which would give 2 g Am/L. The second condition was set by the maximum volume of MPPF Evaporator 17.3E; i.e., 1850 L. Hence, the second condition assumed the solution was further evaporated in Evaporator 17.3E to 1800 L, which would give 2.8 g Am/L. Trial runs in MPPF were made with concentrations of simulated contaminant that would be found at both 1800 L and 2500 L. These trial runs in MPPF equipment confirmed that conditions assuming 2500 L would yield an acceptably pure product, whereas a volume of 1800 L might yield a marginally pure product.

Later laboratory demonstrations using authentic solutions, however, showed that acceptably pure americium product could be precipitated from a 4 or 6 g Am/L solution, the equivalent of evaporating the solution to about 900 L. Emission spectrographic analyses showed the total impurities of the americium product from both the 4 and 6 g/L solutions to be about 1.5 wt %.

PLANT PROCESSING

Prior to beginning actual processing in Building 221-F equipment, it was necessary to flush all tanks and pipes extensively to avoid contamination of the plutonium and the americium products with plutonium of a different isotopic composition, or with fission products, or with other impurities. Processing began only after analyses of the flush solutions confirmed that product contamination would be acceptably low.

Plutonium Dissolution

Plutonium metal was dissolved in 1.67M sulfamic acid at an average rate of 1.81 kg per day per dissolver. Sludge and plutonium oxides generated from metal oxidation were dissolved in HNO_3-HF solutions. This plutonium concentrate ($\sim$60 g Pu/L) was diluted to 5 to 6 g Pu/L before transfer to Building 221-F canyon storage tanks to meet the nuclear safety requirements of the canyon.

Solvent Extraction

Feed for the second plutonium cycle was prepared by first oxidizing the Pu(III) to Pu(IV), and the sulfamate ion to nitrogen gas and sulfate ion with sodium nitrite. The plutonium was diluted to about 0.5 g/L to meet the nuclear safety requirements of the second plutonium cycle. Nitric acid was adjusted to 3.8M to 4.0M to meet the salting requirements of the solvent extraction separation process.

Americium and plutonium were separated by one cycle of solvent extraction using 30% TBP (tri-n-butyl phosphate) in a normal paraffin hydrocarbon diluent. Plutonium was extracted, while americium was diverted to the aqueous waste stream (2AW).

Plutonium was stripped from the solvent with hydroxylamine, concentrated further by cation exchange, precipitated as plutonium oxalate, and calcined to the oxide.

Evaporation and Steam Stripping

The aqueous waste stream (2AW) containing the ^{241}Am was concentrated and stripped of acid using two batch evaporators in the Low-Activity Waste (LAW) system. The first concentration step was performed in the first LAW batch evaporator; acid stripping with water and additional evaporation was performed in the second LAW batch evaporator. The average concentration of the ^{241}Am entering this two-step evaporation process was 3.4×10^{-3} g/L. After the first step, the ^{241}Am concentration was 0.08 to 0.15 g/L. After the second step, the ^{241}Am concentration was 0.2 to 0.3 g/L, and the nitric acid concentration was 2.0 to 2.5M.

Cation Exchange

Feed adjustment consisted of diluting the solution with water such that the concentration of hydrogen ions plus sodium ions was less than or equal to one molar, and adding oxalic acid (0.03M to 0.05M) solution to serve as a complexing agent to facilitate rejection of Fe, ^{95}Zr, ^{95}Nb, and Pu ions.

The adjusted solution was fed to a 15-in.-diameter cation exchange column filled with 42 L of Dowex 50Wx12 (50 to 100 mesh) resin. After feeding, the column was washed first with 0.25M H_2SO_4 to further remove Na, ^{95}Zr, ^{95}Nb, Pu, and Fe ions. Next, the column was washed with 0.25M HNO_3 to remove sulfate ions. Americium was then eluted with 5M HNO_3, and the resin was conditioned with dilute acid for the next run. A summary of typical column operations is given in Table 5.

TABLE 5

Typical Column Run Data

Constituent	Feed	Recovery, %	Product
Am,g	40 to 60	>98	39.2 to 58.8
Pu,g	0.3 to 0.6	<2	<0.01
Na,g	7000 to 14000	∿0.3	∿25
$SO_4^=$,g	14000 to 2800	∿1	∿300
Fe,g	1000 to 3000	∿1	∿30
Cr,g	300 to 900	>99	300 to 900
Ni,g	150 to 450	∿20	15 to 100
Vol., L	1500	---	325
$[H^+]$, M	0.4 to 0.6	---	5 to 6
Fission Products, Ci	0.7 to 2	∿10	0.1 to 0.2

Slow evaporation (70 to 80°C) was begun to allow storage of all the product in one tank. This slow evaporation was successful in controlling the corrosion of process equipment caused by chromium in the product solution.

The isolation system recovered greater than 98% of the ^{241}Am, and concentrated the product by a factor of 125 over

its most dilute point as 2AW, while rejecting greater than 96% of the Na^+, SO_4^{2-}, Fe^{3+}, Pu, and fission products. However, the process solution retained 11.2% of the nickel and >99% of the chromium contaminants.

Formic Acid Denitration

After the evaporation, approximately 36% of the ^{241}Am solution was moved to a denitration evaporator. After dilution from its approximately 11M to 8M nitric acid, the acidity of the solution was further reduced by reaction with formic acid to an estimated 3M nitric acid. After refluxing to assure total destruction of the formic acid, the volume of the denitrated solution was reduced in the evaporator to about 55% of its original volume. A second transfer of ^{241}Am solution from storage to the denitrated solution was made.

The denitration, refluxing, and evaporation steps were repeated. Four additional transfers, denitrations, refluxings, and evaporations were necessary to move and concentrate all the solution to about 2500 L. Finally the entire batch was denitrated. All denitrations proceeded smoothly to completion.

Analysis of the final solution indicated no appreciable corrosion of the evaporator during the denitration procedure. The final acidity was lower than that obtained in the laboratory scale experiments, 0.25M versus 0.7M, respectively.

The lower acidity obtained in the plant-scale run resulted in the precipitation of a small amount of the iron, probably as the phosphate. The precipitate was shown to dissolve, in the laboratory, in 0.5M nitric acid at 50°C. Therefore, after moving the solution from the evaporator, the evaporator was flushed with 1M nitric acid. This flush raised the acid concentration of the prepared solution to about 0.37M, and raised the volume to 2700 L.

Precipitation as Oxalate

Approximately 1500 L of solution were then transferred into the smaller MPPF evaporator. About 150 L of this solution was then transferred into MPPF as feed for the first four precipitator batches. The remaining 1350 L were simmered to reduce the volume to 500 L. Additional transfers were made to combine all the feed as well as flush the canyon tanks of all ^{241}Am products. Simmering at 85°C was continued so that the process evaporator could contain all the solution.

Precipitations were made by adding sufficient 0.9M oxalic acid to bring the final oxalate concentration to 0.3M. After a digestion period, the filtrate was decanted. The oxalate precipitate was washed four times with 0.2M $H_2C_2O_4$-0.7M HNO_3 and once with 0.2M $(NH_4)_2C_2O_4$. On the initial runs, the runs, the washed oxalate precipitate was calcined to a carbonate intermediate to allow easier acid dissolution if impurity analysis indicated recycle was required. As all product batches exceeded the purity guidelines, the low-temperature calcination step to the carbonate was eliminated, and all products were calcined at 700°C.

Results for the first 11 runs, all at ∿2 g ^{241}Am/L, are summarized in Table 6. $^{241}AmO_2$ purity was very good (approximately 98% versus 95% minimum to meet guideline), and all impurities were insignificant except lead, which averaged 0.44% (guideline <0.5%), and weight loss, which averaged 0.59%.

Laboratory tests showed that the apparent high weight loss was due to the sorption of water from the air during handling of the calcined powder.

IN-PROCESS IMPROVEMENTS FOR CANYON PROCESSING

As the result of a number of processing limitations, several changes were made in the process flowsheet. Use of the ^{241}Am-bearing waste stream from the solvent extraction cycle as dilution volume in the feed preparation step allowed a decrease in the amount of ^{241}Am solution to be evaporated from 2.2 million to 1.5 million liters. This volume reduction decreased the evaporator time necessary and, hence, decreased the introduction of stainless-steel corrosion products to the solution.

A decrease in the salting acid (nitric acid) of the feed from 4.0 to 3.8M allowed a lower concentration of nitric acid to be used to adjust tbe nitric acid concentration of the feed. This resulted in reduced amounts of corrosion products (Fe, Cr, Ni) being introduced from the feed adjustment step.

Since the 2 g ^{241}Am/L finishing flowsheet in MPPF was giving a product which far exceeded the purity guidelines, an attempt was made to run either a 4 g/L or a 6 g/L flowsheet. Piloting of the more concentrated flowsheet was performed in the laboratory with actual process solution with favorable results. Excellent product was then obtained with production equipment with both the 4 and 6 g/L flowsheets. The high chromium concentration of the feed, however, gave precipitation and line pluggage problems prior to the precipitator when the 6 g/L flowsheet was used.

TABLE 6

Summary Data Table for ^{241}Am Recovery Operations

Run Number	7AM-1	7AM-2	7AM-1&2	7AM-3	7AM-4	7AM-5	7AM-6	8AM-7	8AM-8	8AM-9	8AM-10	8AM-11
Precipitator	10-5-1	10-5-5	-	10-5-1	10-5-5	10-5-1	10-5-5	10-5-1	10-5-5	10-5-1	10-5-5	10-5-1
^{241}Am batched to PPTR, g	69.4	65.3	-	67.7	64.0	71.0	71.8	71.0	71.0	72.5	72.5	152.7
^{241}Am to waste, g	0.8	0.9	-	1.0	1.4	1.0	1.0	1.0	1.0	1.3	1.3	1.2
Product												
Gross product, g	27.0	56.6	77.7	94.0	65.7	52.2	72.3	92.7	79.8	51.4	86.0	155.1
^{241}Am, g	22.6	49.4	66.4	81.2	56.1	45.6	63.2	80.2	69.0	44.7	74.8	134.2
^{241}Am, %	83.5	87.3	85.5	86.4	86.7	87.3	87.0	86.5	86.4	86.8	87.0	86.5
$^{241}AmO_2$, g	25.5	56.0	75.2	92.0	63.6	51.6	71.6	90.8	78.1	50.6	84.7	152.0
$^{241}AmO_2$, %	94.5	98.9	96.9	97.8	98.2	98.9	98.5	98.0	97.8	98.3	98.5	98.0
Impurities												
Cr, %	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.04	0.04	0.01	0.01	
Fe, %	0.05	0.05	0.06	0.04	0.06	0.07	0.03	0.05	0.06	0.05	0.05	
Ni, %	0.05	0.04	0.03	0.20	0.10	0.10	0.02	0.01	0.07	0.06	0.07	
Pb, %	0.40	0.40	0.25	0.50	0.40	0.50	0.40	0.35	(0.80)	0.20	0.20	
C, ppm	222	<100	<100	213	344	313	302	110	260	ASR[a]	ASR[a]	
Weight Loss, %	0.45	0.39	0.66	0.72	0.63	0.72	0.70	0.54	0.64	0.48	0.56	

RECOMMENDATIONS FOR FUTURE PROCESSING

A number of processing problems and limitations were identified during this plant-scale recovery program:

- The dissolution rate of plutonium metal was very slow: 2 kg per dissolver per 24-hour day.
- Evaporator corrosion was excessive due to the high sulfate concentrations in the ^{241}Am stream.
- Solids precipitated several times because the sodium sulfate concentration was high in the ^{241}Am stream.
- An excessive number of cation exchange column runs were necessary because high sodium concentrations limited loading the columns with the americium solution.
- Finishing operations for the americium product were excessively slow due to high stainless-steel corrosion-product impurities in the feed stock.

Laboratory studies were begun to obtain methods to minimize the above problems before the next campaign begins.

The dissolution rate of plutonium metal can be increased by increasing the dissolution temperature to 70°C and by increasing the sulfamic acid concentration to 3.34M.[2,3] This results in a four-fold increase in the dissolution rate and in more complete utilization of the sulfamic acid. This more effective use of sulfamic acid results in a two-fold decrease in the sulfamate-to-plutonium ratio in the dissolver solution; hence, a 50% decrease in the sodium sulfate-to-americium ratio in the americium recovery system was achieved. The sulfamate-to-plutonium ratio can be further reduced by precipitating sulfamic acid from solution by adding concentrated nitric acid to plutonium dissolver solutions.[7]

The combination of these two changes can reduce the sulfamate-to-plutonium mole ratio from 6.7/1 in this campaign to about 0.16/1. This reduction in sulfamate ion reduces the amount of sodium nitrite necessary in the valence adjustment step [Pu(IV) $\longrightarrow$ Pu(III)] by the same ratio.

An additional set of experiments[3] has shown that the residual sulfamate can be oxidized by generating nitrous acid *in situ* with ultraviolet irradiation. A combination of these three innovations could reduce the sulfate in the americium solution by about 85 to 90%, and reduce the sodium by about 98%.

The above innovations should therefore be introduced into the plutonium dissolving operations to minimize the amount of sulfamate ion transferred to the solvent extraction system.

ACKNOWLEDGMENTS

Corrosion tests were made by F. H. Brown and R. B. Groome of the Equipment Engineering Department of SRP. Most of the analytical determinations were performed either by Laboratories Department of SRP or the Analytical Chemistry Division of SRL.

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