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ABSTRACT

A process for the purification of Am-Cm residues was developed specifically for application in Savannah River Plant (SRP) canyon tanks. These Am-Cm residues were collected from several campaigns to produce plutonium containing high isotopic concentrations of ^{240}Pu. An initial purification from Al^{3+} had already been accomplished by a solvent extraction process. The product of this process was contaminated with $NaNO_3$ as a result of entrainment of the solvent extraction $NaNO_3$ scrub solution. To produce an acceptable feed solution for a later pressurized cation exchange chromatography separation and purification step, the bulk of the $NaNO_3$ must be removed. This purification process includes formic acid denitration, adjustment of contaminating cations by evaporation and water dilution, and oxalate precipitation of the actinides and lanthanides. After washing, the precipitate was dissolved in 8M nitric acid, and the oxalate was destroyed by nitric acid oxidation that was catalyzed by manganous ions. This process produces a purer feed solution for downstream processing by pressurized cation exchange chromatography separation and purification step.

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INTRODUCTION

The Savannah River Laboratory (SRL) and the Savannah River Plant (SRP) have been separating actinides for more than 25 years.[1,2] Work continues to upgrade processes and to initiate new processes. This report summarizes work on a precipitation process to recover about 8.3 kg of Am-Cm from about 200 kg of sodium nitrate contained in about 9000 liters of solution. The process, developed specifically for SRP equipment, includes formic acid denitration of the Am-Cm bearing stream for acid adjustment; oxalate precipitation of the Am-Cm; and Mn^{2+} catalyzed oxidation of oxalate in both the decanted supernate and the precipitated actinides.

SUMMARY

The process was developed to purify the Am-Cm stream sufficiently to allow an Am-Cm separation by using high-pressure ion exchange equipment in the Multipurpose Processing Facility (MPPF).

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

- **Formic Acid Denitration.** The acid concentration of the Am-Cm solution was reduced to <0.5M by semibatch reaction with formic acid.

- **Oxalate Precipitation and Digestion.** Before precipitation, it was necessary to dilute the Na^+ concentration to less than 0.5M to minimize the precipitation of sodium oxalate. Two individual batches were diluted with process water and heated to $\geq$60°C. One volume of 0.9M oxalic acid was then added per two volumes of Am-Cm solution while maintaining a temperature of about 60°C; no precipitation occurred at this temperature. The solution was then cooled slowly to 40-45°C to initiate slow precipitation and crystal growth. After a 4-hr digestion cycle, the solution was cooled to $\leq$35°C and allowed to settle for 8 hrs.

- **Decanting.** A low rate jet jumper (25 gpm) with a short dip tube was used for decanting. The jumper left 2500 liters of

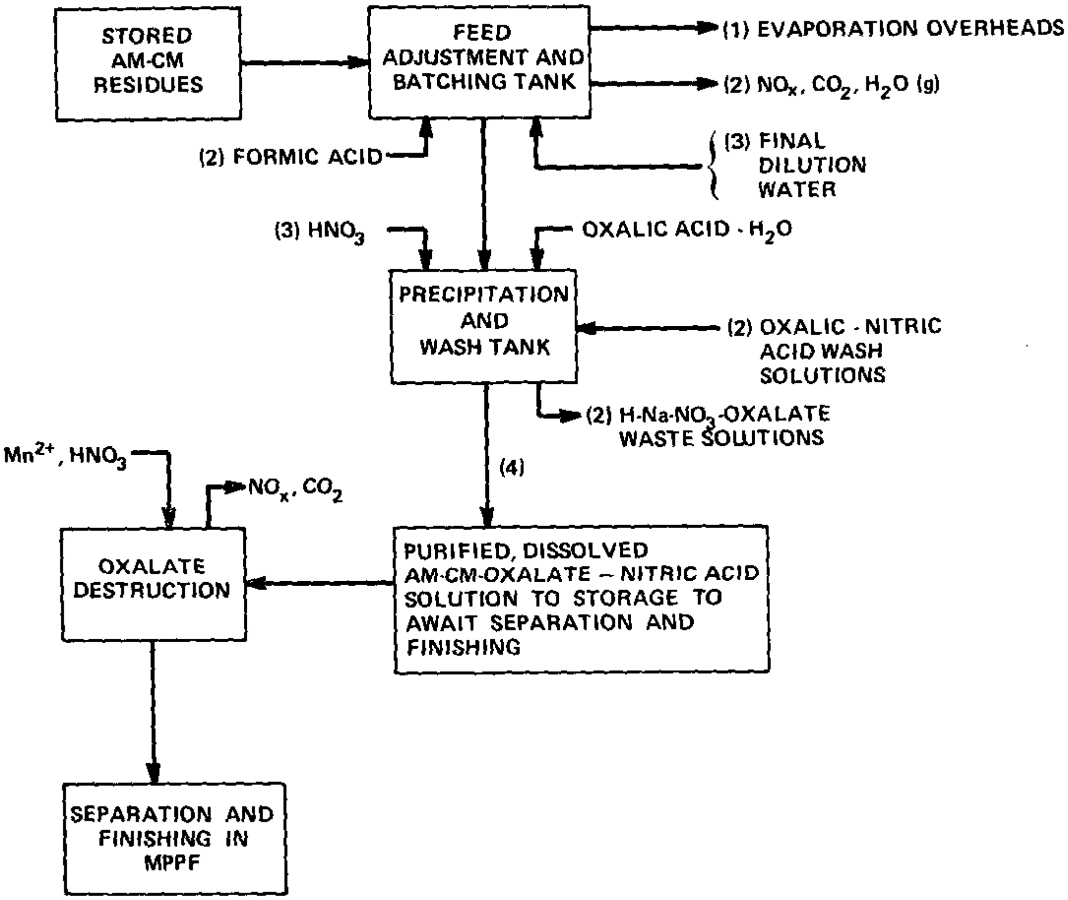

FIGURE 1. Flow Sheet for Separation of Am-Cm from $NaNO_3$ Waste Solutions

slurry (precipitate plus supernate) in the precipitator after decanting. This decanting left at least 7 in. of fluid above the settled precipitate when the total amount of Am-Cm and lanthanide fission products were accumulated in the tank.

- **Washing and Dissolving.** Precipitate accumulated in the tank was washed several times, at <35°C with a solution of approximately 0.2M oxalic acid and 0.5M nitric acid. In each wash, a volume of solution equal to the residual slurry volume was added and agitated. Solids were allowed to settle before decanting the wash supernate. This procedure was repeated until analysis showed acceptably low concentrations of impurities in the wash solution. The washed precipitate was then agitated and dissolved in 8M nitric acid.

- **Oxalate Oxidation.** The decanted supernate and wash solutions were concentrated, and oxalate ion was oxidized by reaction with nitric acid by using manganous ion catalyst in the evaporator. The off-gas rate (nitrogen oxides, carbon dioxide, and water) was controlled by adjusting the concentrations of nitric acid and manganous ion in the evaporator and controlling the transfer rate during supernate addition.

- **Am-Cm Finishing.** The purified Am-Cm solution was combined with Am-Cm solution purified in a subsequent campaign and will be stored until processing can begin in the MPPF. This processing will be a pressurized ion exchange system to separate Am-Cm from fission products and from each other.

EXPERIMENTAL PROCEDURES

The reaction train for the formic acid denitrations was a three-necked roundbottom flask fitted with a water-cooled, open-to-the-atmosphere condenser. Formic acid was metered by gravity-feed through the condenser to the heated simulated or authentic solutions. One neck of the flask was used for temperature measurement; the other neck was used to withdraw samples. The reflux condenser ensured that negligible formic acid and water vapor escaped the reaction zone. No volume corrections were applied to the experimental data because previous studies have shown the equilibrium volume was within 2% of the original nitrate solution volume.

In the experimental procedures with synthetic solutions, 200 mL of the synthetic solutions was heated to >90°C before formic acid addition began. Samples were removed when the reaction initiated and when 1/2, 3/4, and the full-calculated amount of formic acid had been added, again after a two-hr reflux period and again after the solution had been evaporated to 100 mL.

PRECIPITATION PROCEDURES

To define the major chemical parameters of precipitation, simulated solutions were prepared by using the major contaminants but by using dysprosium as a stand-in for the lanthanides and actinides. Precipitations of these simulated solutions were performed in centrifuge cones. This allowed fast separation of the precipitate from the mother liquor. Analyses were performed by using flameless atomic absorption.

DIGESTION AND SETTLING PROCEDURES

To simulate in-canyon-tank precipitation and settling of the precipitate, a glass tank 5.5 in. in diameter and 32 in. high was fabricated. Precipitations were performed with and without elevated temperature digestion steps. The solutions were well agitated to suspend all particles before allowing the precipitate to settle. The settling rate of the precipitate and final volume of slurry were then measured.

DECANTING PROCEDURES

Removal of supernate from over the precipitate was simulated in the same 10-L tank used for precipitation-digestion-settling experiments. To simulate the canyon jet, a vacuum was pulled on a receiving flask before the valve between the vacuum flask and the solution was opened. Transfer rates through the simulated jet could be varied by varying the vacuum in the flask or the transfer tube size.

DISSOLUTION PROCEDURES

Dissolution experiments were performed by heating simulated product slurries in open beakers with various concentrations of nitric acids and manganous nitrate.

OXALATE DESTRUCTION PROCEDURES

Slurries of product and waste solutions were adjusted to various Mn^{2+} and nitric acid concentrations and heated in open beakers to obtain the oxalate oxidation rates. Once the major parameters were defined, off-gas rates were measured by water displacement from a water-sealed reaction train.

RESULTS

Formic Acid Denitration

Results of laboratory formic acid denitrations with simulated solutions are shown in Figure 2. The lowest possible free acid concentration for the simulated solutions was obtained when a formic acid to free acid ratio of about 1.6 to 1.9 was used. This ratio yielded a final free acid of about 0.7 to 0.8M. In the region before a mole ratio of about 1.6 has been added, the final free acid is excess nitric acid. After a mole ratio of about 1.9, the final free acid was excess formic acid.

Comparison of the dynamic samples with the samples after refluxing gives important information for semibatch denitrations that can be expected for 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 was, however, oxidized during the refluxing of the solution after the addition of the formic acid. For the semibatch denitrations, it appears that a nitric acid concentration of about 2M at the end of each individual denitration was 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 step. Additional high nitric acid solutions can then be added to the evaporated-denitrated solution without autoinitiation 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 0.8M.

Addition of formic acid beyond this point simply accumulates in the tank and therefore increases the free acid concentration.

Precipitation of Simulated Solutions

As with an earlier ^{241}Am campaign, acceptable losses ($<$1%) of transplutonium elements were achieved by using 0.3M oxalic acid in the final slurry and a free nitric acid of $\leq$0.7M. These conditions can be achieved by adjusting the free nitric acid

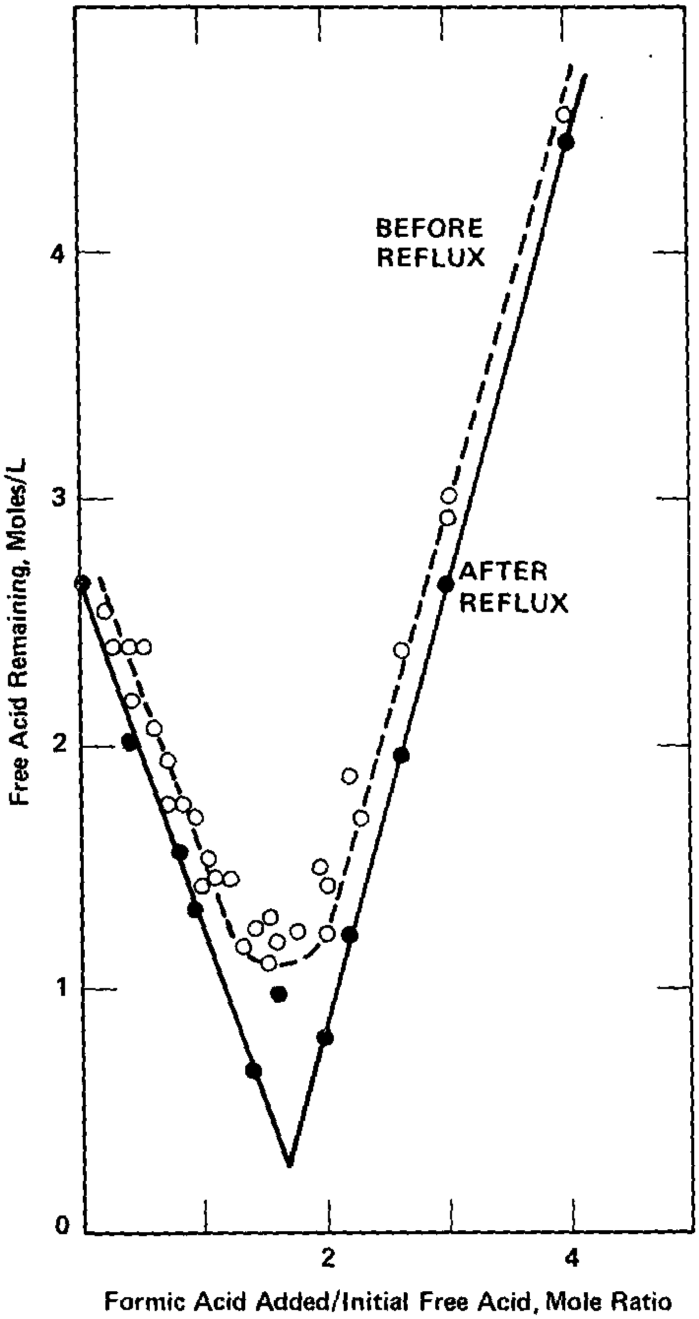

FIGURE 2. Formic Acid Denitration of Tank 17.1 Simulated Solution

concentration of the feed to $\leq 1.0M$ and adding one volume of 0.9M oxalic acid to two volumes of adjusted feed.

Digestion and Settling Rates of the Precipitate

To design the proper short suction leg jet, it was necessary to know the volume of slurry to be expected in the tank, the rate of settling, and the minimum distance above the slurry the jet must be to prevent movement of the slurry.

The volume of precipitate and settling rate was determined by precipitation of 4 L of simulated solution adjusted to 1M HNO_3 by the addition of 2 L of 0.9M oxalic acid. The settling rate (Figure 3) for the major portion of the precipitate was about 1.25 in. per min. Fines, however, settled at about 0.8 in. per min. The volume of precipitate-slurry was determined to be about 3.6 L per mole of dysprosium in the simulated solution.

Projecting these data to a $12.5M^3$ tank indicated an approximate 2-hr settling time for the major portion of the precipitate and perhaps 4 to 6 hrs for the remainder of the fines to settle.

Digestion of the precipitate at about 40°C for about 2 to 4 hrs, however, eliminates the fines.

JETTING OF WASTE SUPERNATE FROM OVER THE PRECIPITATED SLURRY

To simulate jetting of the waste supernate, solutions were transferred by vacuum from the simulated canyon tank to a second tank through a 1/4-in.-I.D. tube. At linear velocities through the tube of about 315 linear ft per min, solution could be transferred at about 1-1/2 in. above the slurry without moving precipitate. Movement of the transfer-tube closer than 1 in. resulted in the movement of precipitate into the tube.

The Purex canyon normally uses two standard transfer jets; one at 75 gal per min, the other at 25 gal per min. The face velocity of the 75 gpm jet is about 460 linear ft per min; the 25 gpm jet is about 155 linear ft per min. Simulations indicate the 25 gpm jet could be used 6 in. above the slurry without excessive transfer of precipitate.

WASHING THE PRECIPITATED OXALATES

The optimum precipitation concentrations exceeded the solubilities of sodium oxalate and sodium oxalate monohydrate. Residual

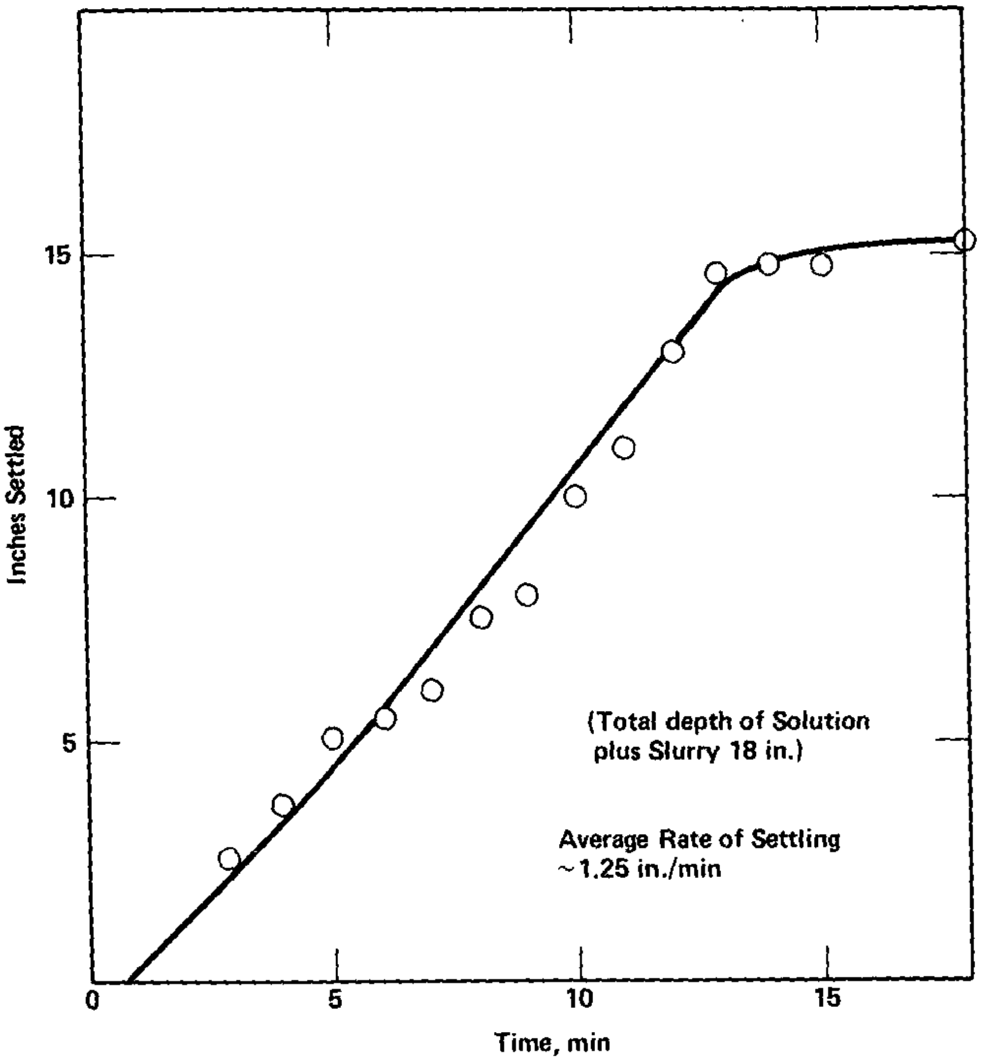

FIGURE 3. Settling Rate of Typical Mark 40 Simulated Oxalate Precipitate

sodium, therefore, must be both dissolved as well as diluted out of the residual slurry left behind when the supernate is removed from the tank.

DISSOLUTION OF WASHED PRECIPITATE

Downstream processing of the Am-Cm product requires that the precipitate be dissolved, the oxalate ion removed from the solution, and the acid adjusted to $\leq 1M$. Attempts were made to dissolve the precipitate at various nitric acid concentrations. Dissolution in 1 to 5M nitric acid was successful only if Mn^{2+} was added to catalyze the oxidation of oxalate ion. At a concentration of 8M nitric acid, the precipitate could be dissolved at temperatures of 60 to 80°C. Because downstream processing requires that the extraneous polyvalent cation to lanthanide - actinide ratio must be less than 0.14, addition of Mn^{2+} must be kept to a minimum. Because the precipitate can be dissolved in 8M HNO_3 this should be used to dissolve the precipitate.

OXALATE DESTRUCTION IN PRODUCT STREAM

As the Am-Cm will be separated by an ion exchange process, it is necessary to remove all of the oxalate ion. If the separated solution is to be stored for an extended period of time before separation, self-radiolysis of the solution will of course destroy a portion of the oxalate. Mousty, Toussaint, and Godfrin[3] have shown that extended boiling of a 10M HNO_3 oxidized sufficient oxalate to render a suitable solution for separation. However, the extended boiling of 10M HNO_3 solutions in stainless steel can lead to excess corrosion of the equipment and, therefore, the introduction of polyvalent cations (Fe, Cr, Ni) to the process solution. Koltunov[4] has shown that manganous ion (Mn^{2+}) will catalyze the oxidation of oxalate in nitric acid solutions. Low concentrations of manganous ion were, therefore, used in an attempt to catalyze the oxidation of oxalate in the precipitated slurries.

Figure 4 shows the destruction of oxalate in the precipitated slurry in 8M nitric acid. A manganous ion concentration of 0.045M Mn^{2+} in 8M HNO_3 will oxidize the oxalate in the slurry in about one-half the time required for a concentration of 0.011M Mn^{2+}.

Because Mn^{2+} is a polyvalent cation, its concentration in the final solution fed to the cation columns should be kept below 0.05M to avoid excess competition for resin sites. For the overall process, it is better to use the longer oxidation times than to use higher Mn^{2+} concentrations. Catalyzed oxidation should not be performed until the volume of solution is reduced to the minimum possible volume.

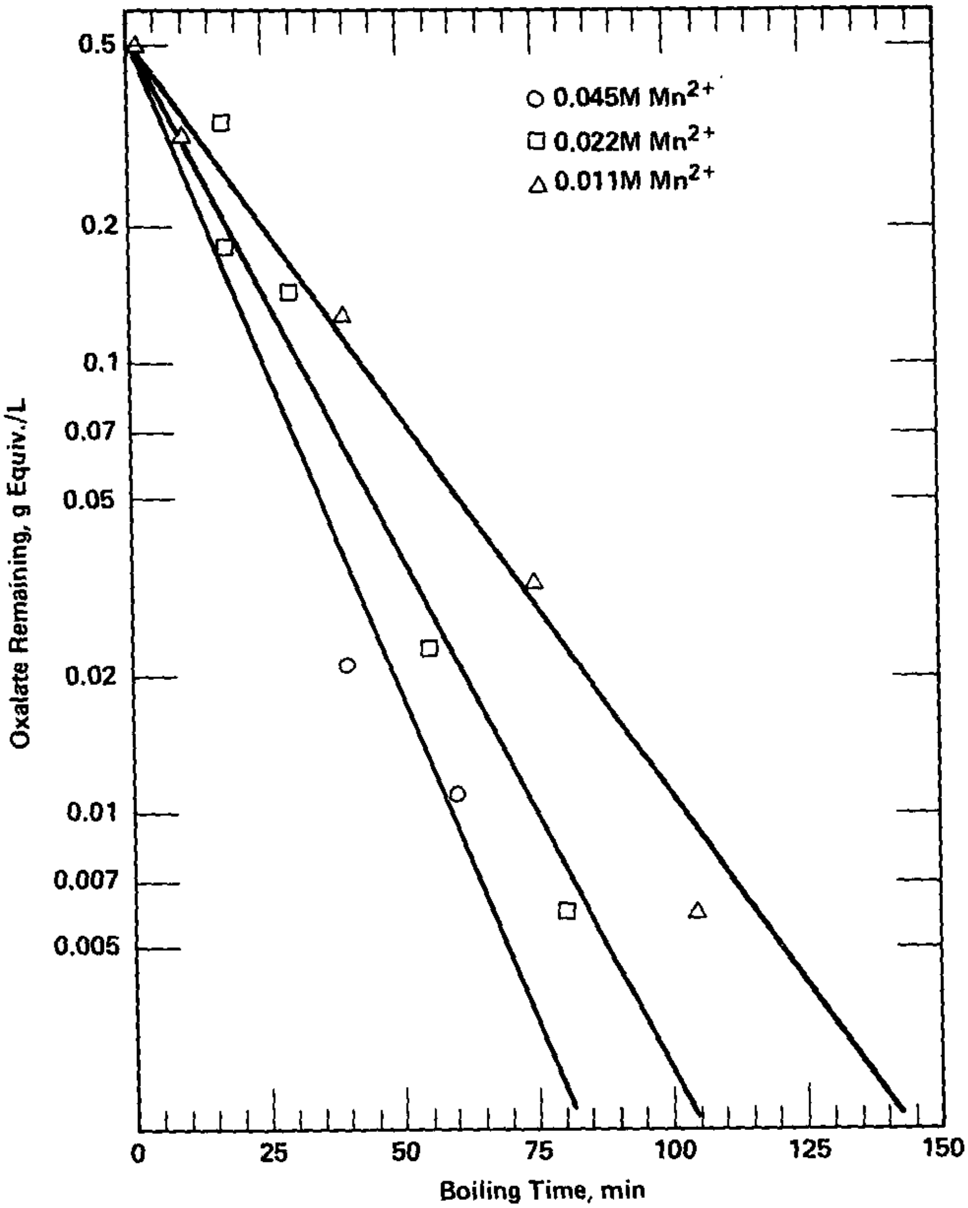

FIGURE 4. Oxidation of Oxalate Ion with 8M Nitric Acid Catalyzed by Manganous Ion

OXALATE DESTRUCTION IN WASTE STREAM

Although the reactions are more rapid at 8M HNO_3, manganous ion catalyzes the oxidation of oxalate at lower acidities. Approximately 1M HNO_3 does seem to be required. As the major solids producing reagent in the waste stream is oxalic acid, it is much cheaper to oxidize the oxalic acid to CO_2 gas than to store it as radioactive solids containing waste. Waste streams are, therefore, acidified with nitric acid, $Mn(NO_3)_2$ is added, and the solutions are evaporated. During the evaporation, the oxalate ion will be oxidized to CO_2 gas.

Koltunov[4] has shown that the rate of catalytic oxalic acid oxidation with low concentrations of nitric acid ($\leq$6M) is given by the equation:

$$\frac{-d(H_2C_2O_4)}{dt} = \frac{k_1\ (H_2C_2O_4)(Mn^{2+})}{(H^+)^{0.73}}$$

where k = 3.29 $\pm$0.04 liter$^{0.27}$ at mole$^{-0.27}$ at m = 3.1 and 95°C. The overall reaction is given by the equation:

$$3H_2C_2O_4 + 2HNO_3 \rightarrow 6CO_2(g) + 2NO(g) + 4H_2O$$

Koltunov's equation was applied to two cases. The first considered the maximum off-gas rate under proposed operating conditions. It was assumed that the oxidation started at 95°C with 5000-L volume of 0.02M Mn^{2+}, 5M HNO_3, 0.9M $H_2C_2O_4$, and 0.25M $NaNO_3$. The second case assumed the waste was concentrated by evaporation before adding Mn^{2+} ion.

In the first case, an off-gas rate of 193 cfm was calculated by Koltunov's equation. In the second case, an off-gas rate of 603 cfm was calculated. Laboratory experiments for both conditions agreed with the off-gas rate predicted by Koltunov's equation. Under plant operating conditions, a maximum off-gas rate is estimated to be less than 10% of the 6000 cfm venting capabilities of the evaporator proposed as the reaction vessel. No foaming problems were observed during the laboratory experiments.

FLOW SHEET

A generalized flow sheet for the separation procedure is given in Figure 5. The flow sheet provides for acid adjustment by formic acid denitration followed by two precipitation batches with the precipitate slurry accumulated in the tank. After three washes of

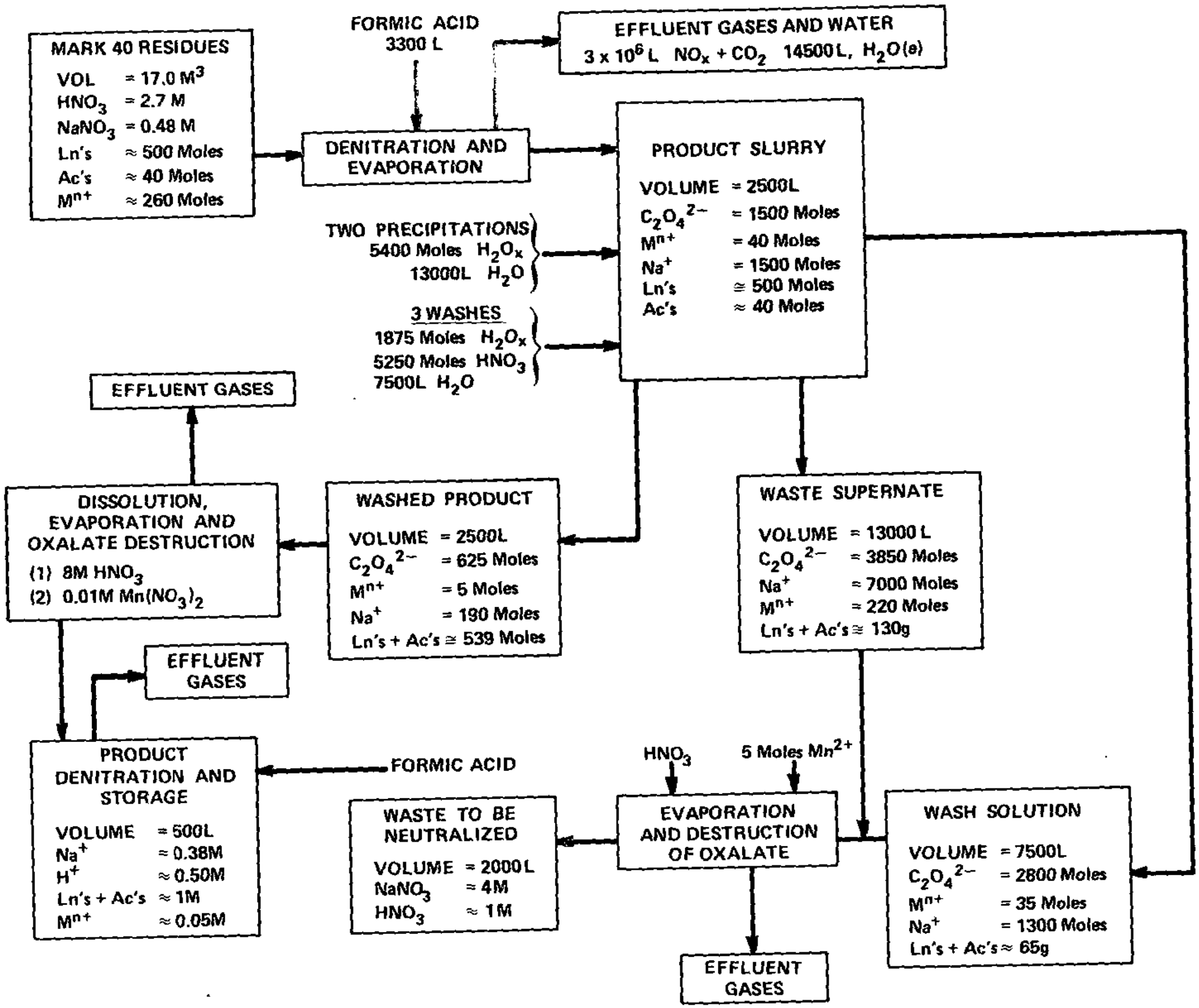

FIGURE 5. Flow Sheet for Mark 40 Residue Purification

the precipitated slurry to remove sodium and polyvalent cations, the product is dissolved by adjusting the acid concentration to 8M and heating the solution. The product is then stored until the Multipurpose Processing Facility (MPPF) is ready to process the material. The supernates are transferred to an evaporator containing boiling 5M HNO_3 and 0.02M Mn^{2+}. The solution is transferred at a rate to maintain approximately a constant volume in the evaporator. Sufficient acid is added at the end of each batch to oxidize the oxalate to be transferred in the next batch. All material is accumulated in the evaporator.

When MPPF processing begins, the product solution must be evaporated from the about 8000-L storage volume to about 600 L. If the oxalate has survived both the initial heating steps and the high radiation field during storage, it must be oxidized during the evaporation step. Sufficient Mn^{2+} should be added to give approximately 5M Mn^{2+} in the MPPF evaporator.

After evaporation, the acid must be adjusted to MPPF requirements by formic acid denitration.

SUMMARY OF PLANT PROCESSING

Approximately 8 kg of combined Am-Cm was recovered from stored waste from the processing of plutonium targets. An overall recovery of 94.75% (0.25% dissolved losses, 5.0% entrained losses) of the transplutonium isotopes was achieved while rejecting approximately 99.5% of the Na, 95% of the sulfate, and 85% of the Fe contained in the original solution.

Operating performance was excellent. There were no personnel injuries or exposures to formic acid above the TLV, no operating incidents, and no unexpected releases to the environment. All oxidation-reduction reactions initiated promptly and proceeded smoothly.

Some minor mechanical problems and an ineffective evaporator flush caused minor delays in the program.

The movements of reactants and products in the plant is shown in Figure 6.

CHARACTERIZATION OF ACTUAL SOLUTION

Because the stored solution was a combination of four different campaigns, a characterization of the solution was necessary. A variety of techniques, including radiometric, spark source mass spectrographic, colorimetric, atomic absorption, ion chromatographic and other wet chemical techniques, was used to obtain the characterization given in Table 1.

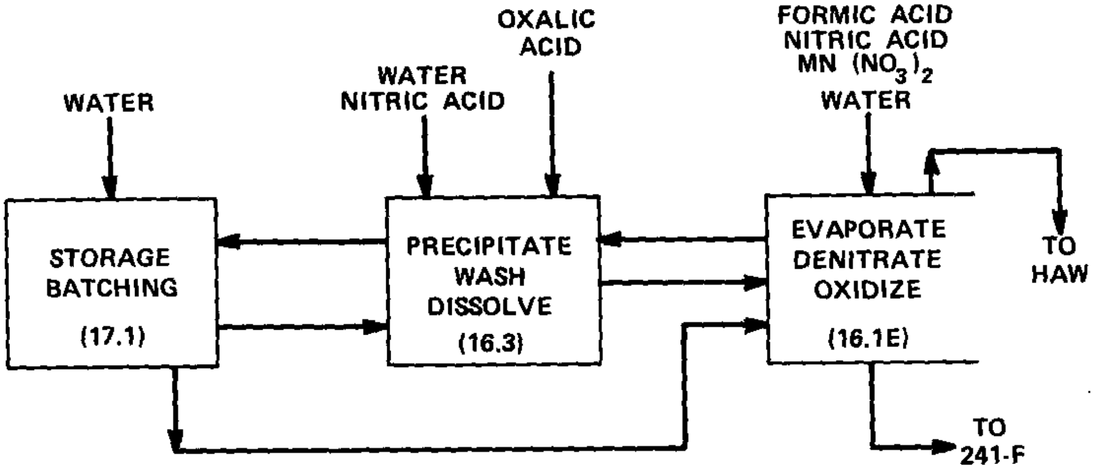

FIGURE 6. Am-Cm Purification Process Flow

EVAPORATION

Between the time of the characterization and actual processing, the solution was allowed to evaporate naturally. To obtain low losses, however, it was necessary to further evaporate the solution. After evaporation, the volume of solution was $3.75M^3$ with a final nitric acid concentration of 5.9M.

FORMIC ACID DENITRATION

Formic acid denitration of the solution reduced the free acid concentration to 0.9M. The reaction initiated promptly and proceeded smoothly without incident. After denitration, the solution was transferred from the evaporator to a holding tank and diluted to $6M^3$ with process water. The feed prepared for precipitation contained the approximate concentrations given in Table 2.

An ineffective flush of the solution from the evaporator resulted in complications in the final precipitation because this same evaporator was used to receive the supernates from the precipitation steps. As a result, after the initial precipitations, the waste solution containing about 0.4 kg of product was subjected to formic acid denitration and reprepared for the precipitation step.

TABLE 1

Analysis of Am-Cm Residues Generated by the Californium Flow Sheet

Element/Compound	Concentration M/L	g/L
HNO_3	2.72	171.39
$NaNO_3$	≤ 0.48	≤ 41.00
H_2O		903.25
Al		0.03
Fe		0.62
Hg	0.001	
$PO_4{}^{3-}$		0.75
U		0.042
Am		0.384
Cm		0.153
Pu		0.0356
Lanthanides		1.70
Calc. Density	$\leq$1.119 g/cc	
Measured Density	1.116 g/cc	
Volume	19,200 Liters	

TABLE 2

Calculated Precipitator Feed Concentrations

Element/Compound	Concentration M/L	g/L
HNO_3	0.55	34.66
$NaNO_3$	1.54	130.56
Al		0.10
Fe		1.98
Hg		0.003
$PO_4{}^{3-}$		2.40
U		0.13
Am		1.01
Cm		0.36
Pu		0.13
Lanthanides		5.40

PRECIPITATION

To minimize the precipitation of the two sodium oxalate salts and to obtain a lower nitric acid concentration to minimize the solubility of actinide oxalates, the formic acid denitrated solution had been diluted with water. This increase in volume required a semibatch precipitation. Approximately 75% of the feed was transferred to the precipitation tank and heated to 60-65°C before the addition of sufficient 0.9M oxalic acid to make 0.6M oxalate, 0.18M free nitric acid, and 0.5M sodium nitrate final concentration. After slowly cooling to about 45°C, the slurry was digested at 40-45°C to promote large crystal growth. Then, after cooling to 35°C, the precipitate was allowed to settle for eight hrs before decanting the supernate.

After decanting, the remainder of the solution was added to the above remaining slurry, and the process was repeated.

A third precipitation was preformed as a result of the ineffective flush of the original evaporator.

SETTLING RATES AND DECANTING

At the end of the digestion cycle, the precipitate was allowed to settle for eight hrs. Samples were pulled every two hrs during the settling period. (The samples were at the same level in the tank as the jet to decant the supernate.) Analysis of the dissolved portion of the sample showed an average 0.9 ±0.1 mg actinide/L of solution. The amount of solids picked up in the sample vial did not decrease until after 6 hrs. These analyses indicate only 19.5 g or 0.25% of the total transplutonium content was lost to waste as dissolved material. The remainder of the loss of material to waste was the result of entrained solids.

RECYCLE

As a result of the ineffective flush of the evaporator, the material left behind in the evaporator plus the decanted supernates from the first two precipitations was recycled through the process. A slightly lower final nitric acid concentration was achieved during the formic acid denitration of the recycled material.

DESTRUCTION OF OXALATE IN WASTE STREAM

Before supernate or wash solution was added, 5M nitric acid containing 0.02M Mn^{2+} was brought to boiling in the evaporator to ensure prompt and rapid oxidation of the oxalate. Transfer rates of either supernate and wash solution or additional nitric acid needed to ensure complete destruction of the oxalate were limited to keep off-gas rates less than 100 cfm. The final oxalate concentration of the waste was <0.2M, which indicates >99.8% of the oxalate was oxidized to CO_2 and H_2O.

DISSOLUTION AND CHARACTERIZATION OF FINAL PRODUCT

The washed product slurry was adjusted to 8M nitric acid and raised to a simmer of about 40°C to dissolve the oxalate precipitate. This solution will be stored to await processing in MPPF.

A comparison of the major impurities before and after the oxalate precipitation purification step is given in Table 3.

TABLE 3

Americium-Curium Purification Process Performance

		Before Processing	After Processing
Impurity:	Sodium	24	0.08
	Iron	2	0.3
	Sulfate	12	0.6

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