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PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

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ABSTRACT

A process for recovery of Am-Cm residues from high-activity waste concentrates has been developed specifically for application in Savannah River Plant (SRP) canyon tanks. The Am-Cm residues were collected from a campaign to produce plutonium containing high isotopic concentrations of ^{242}Pu. The separation of Am-Cm from the high-activity waste stream, containing about 2M $Al(NO_3)_3$, is necessary to produce an acceptable feed solution for a later pressurized cation exchange chromatography separation and purification step. The new 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 new process generates about one-fourth the waste of the californium solvent extraction process, which it replaced. The new process also produces a cleaner feed solution for the pressurized cation exchange chromatography separation and purification step.

CONTENTS

SEPARATION OF Am-Cm FROM $Al(NO_3)_3$ WASTE SOLUTIONS BY IN-CANYON-TANK PRECIPITATION AS OXALATES

INTRODUCTION AND SUMMARY

Savannah River Laboratory (SRL) and 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 7 kg of Am-Cm from about 600 kg of aluminum nitrate contained in about 14,000 L of high-level waste. 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. The new process generates one-fourth the radioactive waste as the solvent extraction process which it replaced and produced a cleaner solution for downstream processing to separate the Am and Cm before conversion to their respective oxides.

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

- **Dissolution.** Plutonium dioxide - aluminum targets irradiated for the production of >85% ^{242}Pu was dissolved in a solution of 6.5M HNO_3, 0.012M $Hg(NO_3)_2$, and 0.02M KF.

- **Feed Adjustment.** Dissolver solution was treated first with ferrous sulfamate and sodium nitrite to adjust the plutonium valence to Pu(IV). After adjusting this solution with uranium (from dissolved UO_3), a gelatin strike was performed to remove silica and trace amounts of undissolved solids. This yielded a final solution very similar to the normal Purex first cycle feed.

- **Solvent Extraction.** Pu and U were separated from the Am and Cm in a single pass through the Purex first cycle.

- **Pu and U Finishing.** Both U and Pu were finished to final products using the normal Purex and finishing routes.

- **Feed Concentration.** Am, Cm, fission products, and the small amount of Pu and U lost to the waste stream were accumulated and concentrated by evaporation. After concentrating, this material was acid stripped to produce a solution of about 2M $Al(NO_3)_3$ - 1M HNO_3.

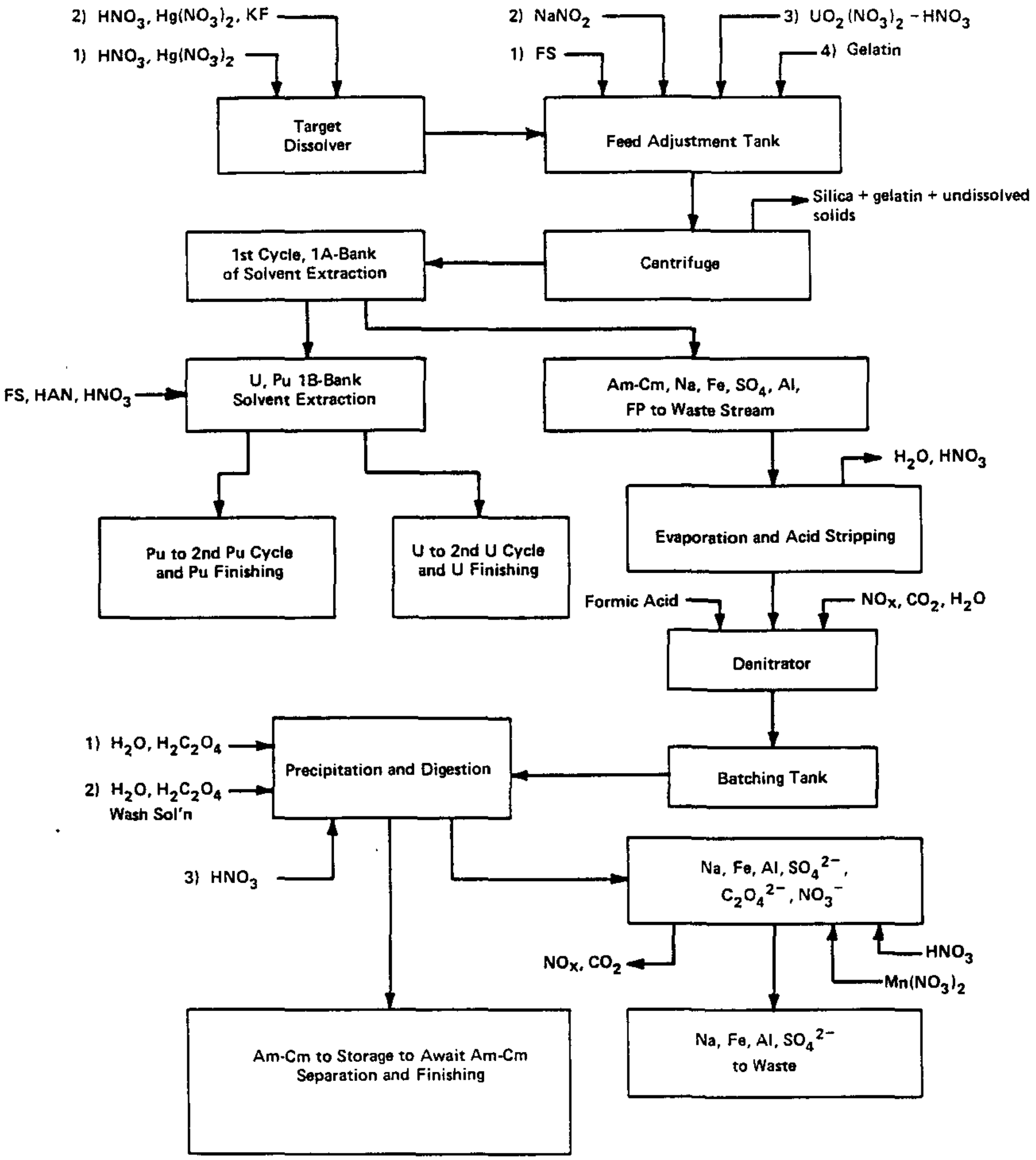

FIGURE 1. Flowsheet for Separation of Am-Cm from $Al(NO_3)_3$ Waste Solutions

Digestion and Settling Procedures

To simulate in-canyon-tank precipitation and settling of the precipitate, a glass tank 5.5 inches in diameter and 32 inches 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 acid 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 ratio. Once the major parameters were defined, off-gas rates were measured by water displacement from a water-sealed reaction train.

RESULTS

Formic Acid Denitration

Simulated solutions were subjected to laboratory formic acid denitrations. Results are shown in Figure 2. As a result of the hydrolysis of the large concentration of Al^{3+}, it is possible to drive this solution to a pH >10. However, free acid concentrations less than about 0.2M need to be avoided when processing actinides because of the possibility of hydrolysis and precipitation of the actinide. The most useful free acid concentration was obtained when a formic acid to free acid ratio of about 1.6 to 1.9 was used.

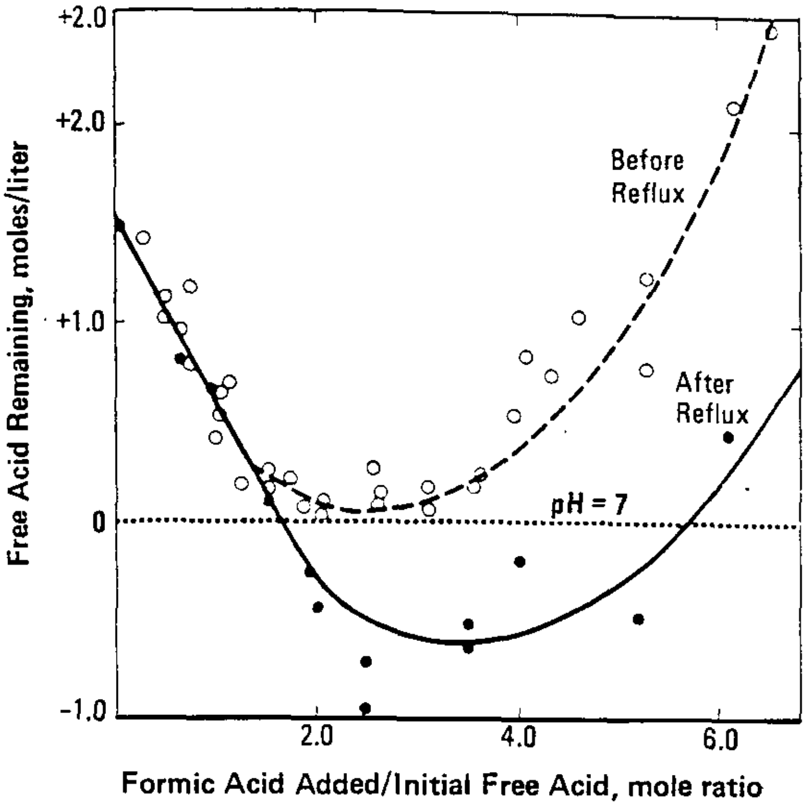

FIGURE 2. Formic Acid Denitration of Simulated Solutions

- **Acid Adjustment.** The acid concentration was further reduced by four batch formic acid denitrations. The four batches were combined before further processing, yielding one solution containing a free acid concentration of about 0.4M.

- **Oxalate Precipitation and Digestion.** Before precipitation, it was necessary to dilute the Al concentration to less than 0.5M. Ten individual batches were diluted with process water and heated to >60°C. Two volumes of 0.9M oxalic acid were then added per volume of Am-Cm solution while maintaining a temperature of about 60°C; no precipitation occurs at this temperature. The solution was then cooled slowly to 40-45°C to initiate slow precipitation and crystal growth. After a 4-hour digestion cycle, the solution was cooled to ≤35°C and allowed to settle for 8 hours.

- **Decanting.** A low rate jet jumper (25 gpm) with a short dip tube was used for decanting. The jumper left 2500 L of slurry (precipitate plus supernate) in the precipitator after decanting. This residual volume provided the jet suction of fluid at least 7 inches 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 oxidized by reaction with nitric acid using manganous ion catalyst in the evaporator. Off-gas rates (nitrogen oxides, carbon dioxide, and water) were 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 previously purified 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.

PROCESSING SUMMARY

A total of 10 batch precipitations were necessary to accumulate the Am-Cm product. Four washes of the precipitate were done to "dilute-out" the aluminum and other polyvalent cation contaminants in the residual supernate.

Overall recovery of product was not as high as expected - only 5 kg Am-Cm was recovered and purified by this method. Losses of product were due to entrainment of solids during the decanting step. Of the 1.6 kg Am-Cm entrained to the waste evaporator, 1.1 kg Am-Cm was retained and is available for recovery via another method; the remainder was transferred to the Waste Tank Farm and therefore was not available for recovery.

EXPERIMENTAL PROCEDURES

Formic Acid Denitration 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 using synthetic solutions, 200 mL of the synthetic solutions were 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-hour 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 using the major contaminants but 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 using flameless atomic absorption.

As a result of the high concentration of nitrate (from aluminum nitrate) the reaction rate is controlled by the formic acid addition rate until the free acid concentration is reduced to about 0.5M. For semi-batch denitrations it appears that a nitric acid concentration of 1 to 2M at the end of each individual denitration in an excellent stop-point. Using 1 to 2M nitric acid as a projected stop-point ensures that there will be no residual formic acid at the end of the reflux and evaporation step. Additional high nitric acid-aluminum nitrate solution 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 evaporated, it is then possible to drive the denitration reaction to a residual free acid concentration of $<0.5M$.

Precipitation of Simulated Solutions

To explore possible precipitation procedures, simulated solutions were prepared using Dy^{3+} as a stand-in for the actinides and lanthanides. The ratio of Al^{3+} to Dy^{3+} was held constant. However, the total ratio of these species to free nitric acid was varied in the stock solutions. Precipitation conditions were simulated by additions of either a half-equal volume or an equal volume of either a 0.9M oxalic acid or a saturated (about 2M) potassium oxalate solution. After precipitation and centrifugation, the residual dysprosium in solution was determined by flameless atomic absorption. The percent dysprosium remaining in solution was then calculated and is shown in Figures 3 and 4.

These tests indicate that to obtain high yields in the precipitation, the aluminum concentration must be $\leq 0.5M$ (Figure 3) and the free acid concentration must be $\leq 0.2M$ (Figure 4). This can best be obtained by evaporating the Am-Cm-Al solution to about 2 to 2.2M $Al(NO_3)_3$ and denitrating this concentrate with formic acid (Figure 2) to about 0.5M nitric acid. Dilution of this solution to an aluminum concentration of $\leq 0.5M$ would yield a feed suitable for oxalate precipitation.

Digestion and Settling Rates

The volume of precipitate and settling rate was also determined by precipitation as 4 L of simulated solution, adjusted to about 0.5M Al^{3+} and about 0.25M HNO_3, by the addition of 2 L of 0.9M oxalic acid. When the precipitation was carried out at room temperature, less than 10% of the precipitate had settled after a 60-hour settling period. When the oxalic acid was added to a 60°C solution and then further held at 40 to 45°C for an additional

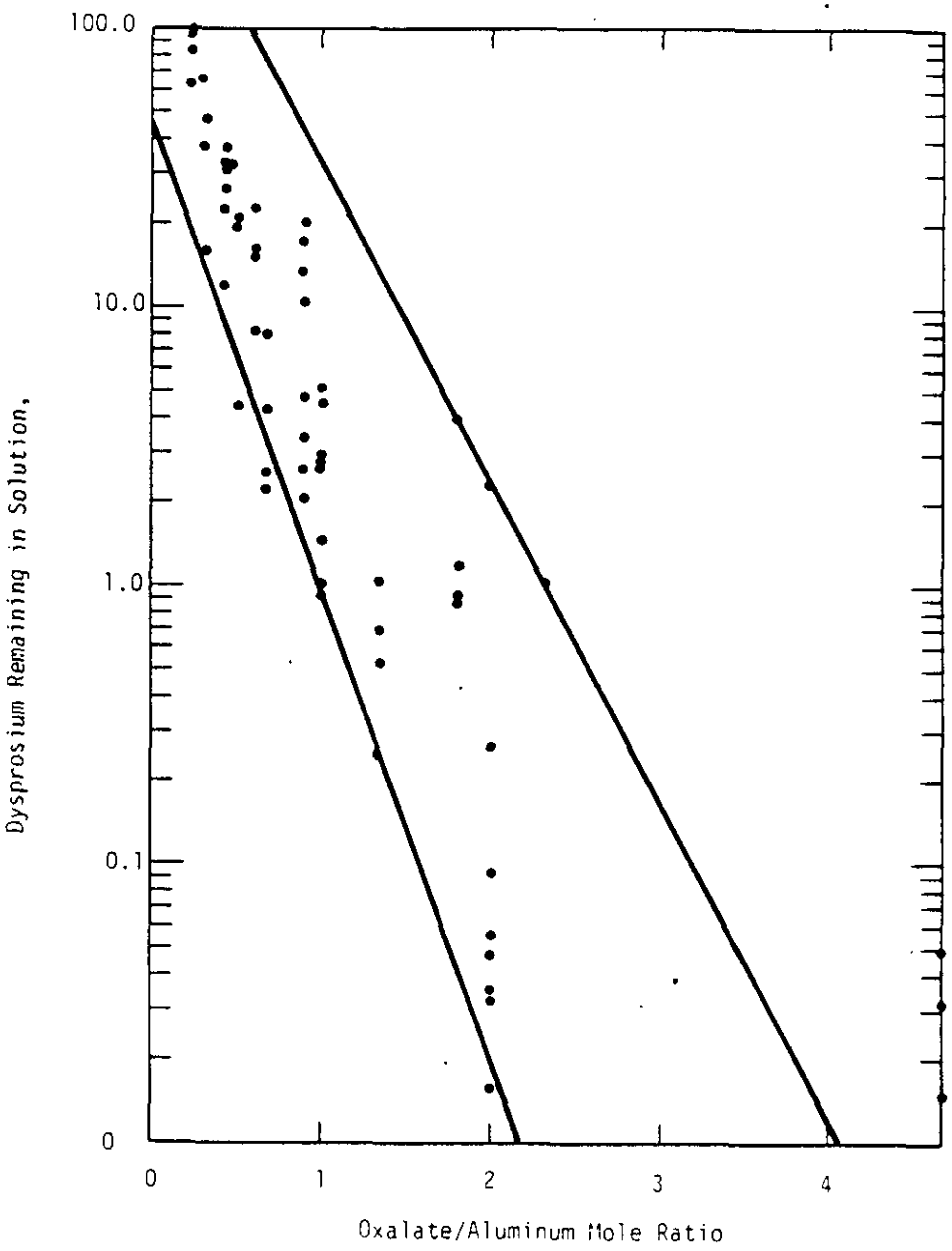

FIGURE 3. Precipitation of Dysprosium from Simulated Waste as a Function of Oxalate Ion Concentration

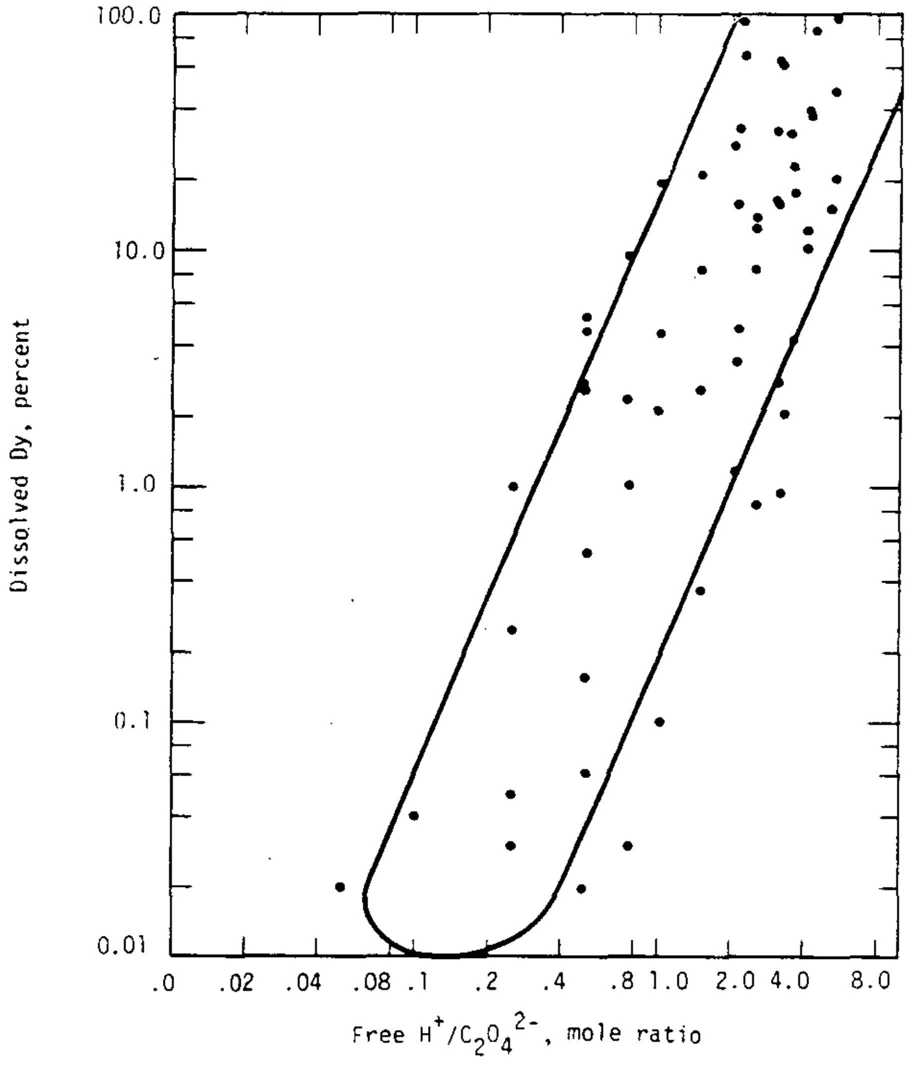

FIGURE 4. Precipitation of Dysprosium from Simulated Waste as a Function of Free Acid

2 hours, the settling rate and final volume of precipitate were very similar to the previous Am-Cm material containing $NaNO_3$.

Settling 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-inch ID tube. At linear velocities through the tube of about 315 linear feet per minute, solution could be transferred at about 1-1/2 inches above the slurry without moving precipitate. Movement of the transfer-tube closer than 1 inch resulted in the movement of precipitate into the tube.

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

Washing the Precipitated Oxalates

As a result of the 2500 L of slurry left in the precipitation tank, the product slurry will contain about 9 moles of Fe^{3+}, 790 moles Al^{3+}, 30 moles Na^{+}, and 18 moles SO_4^{2-}. To yield an acceptable product for downstream processing in MPPF, these ions must be diluted away from the product. Five equal-volume washes of the slurry are calculated to reduce the non-lanthanide impurity concentrations to 0.3 mole Fe^{3+}, 25 moles Al^{3+}, 0.9 mole Na^{+}, and 0.6 mole SO_4^{2-}. This should yield a product of sufficient purity for downstream processing in MPPF.

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 $<1M$. Attempts were made to dissolve the precipitate at various nitric acid concentrations. Dissolution in 1 to 5M nitric acid were 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 without the addition of Mn^{2+}, 8M HNO_3 should be used to dissolve the precipitate.

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

Koltunov's equation was applied to two cases. The first case considered the maximum off-gas rate under proposed operating conditions. It was assumed that the oxidation started at 97°C with 5000-liter 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 were in good agreement with the off-gas rate predicted by Koltunov's equation. Under plant operating conditions, then, 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.

FLOWSHEET

A generalized flowsheet for the separation procedure is given in Figure 6. The flowsheet provides for evaporation and denitration of the high activity waste stream to adjust the acid concentration followed by dilution to adjust the Al^{3+} concentration. A total of 10 precipitation and digestion steps were necessary with accumulation of the precipitated slurry in the precipitation tank. After five washes of the precipitate slurry to remove Na^+, Al^{3+}, Fe^{3+}, and SO_4^{2-} in the slurry heel, the product is dissolved by adjusting the acid concentration to 8M and heating the solution. The product is then stored until the 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 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 5 moles of Mn^{2+} in the MPPF evaporator. After evaporation the acid must be adjusted to MPPF requirements by formic acid denitration.

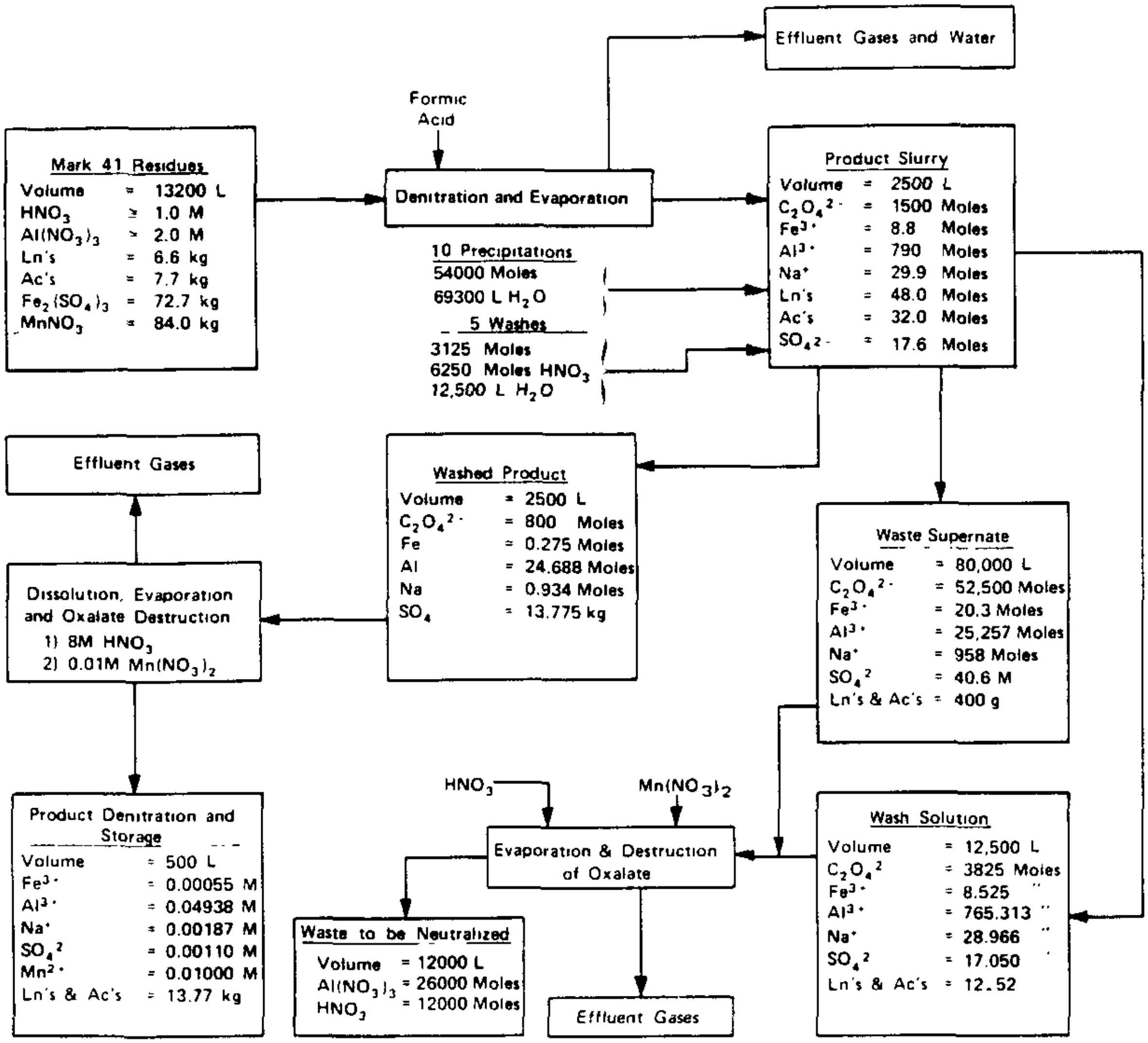

FIGURE 6. Flowsheet for Purification of Am-Cm-Al Residues

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 destroy a portion of the oxalate. Mousty, Toussaint, and Godfrin[3] have shown that extended boiling of a 10M HNO_3 solution oxidized sufficient oxalate to render a suitable solution for separation. However, extended boiling of $\geq$10M HNO_3 solutions in stainless steel can lead to excess corrosion of the equipment and, hence, 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 5 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.

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; at least about 1M HNO_3 was 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 waste. Waste streams are therefore acidified with nitric acid, $Mn(NO_3)_2$ added and the solutions 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 $k_1 = 3.29 \pm 0.04$ liter$^{0.27}$ mole$^{-0.27}$ at an ionic strength of 3.1 and a temperature of 97°C. The overall reaction is given by the equation:

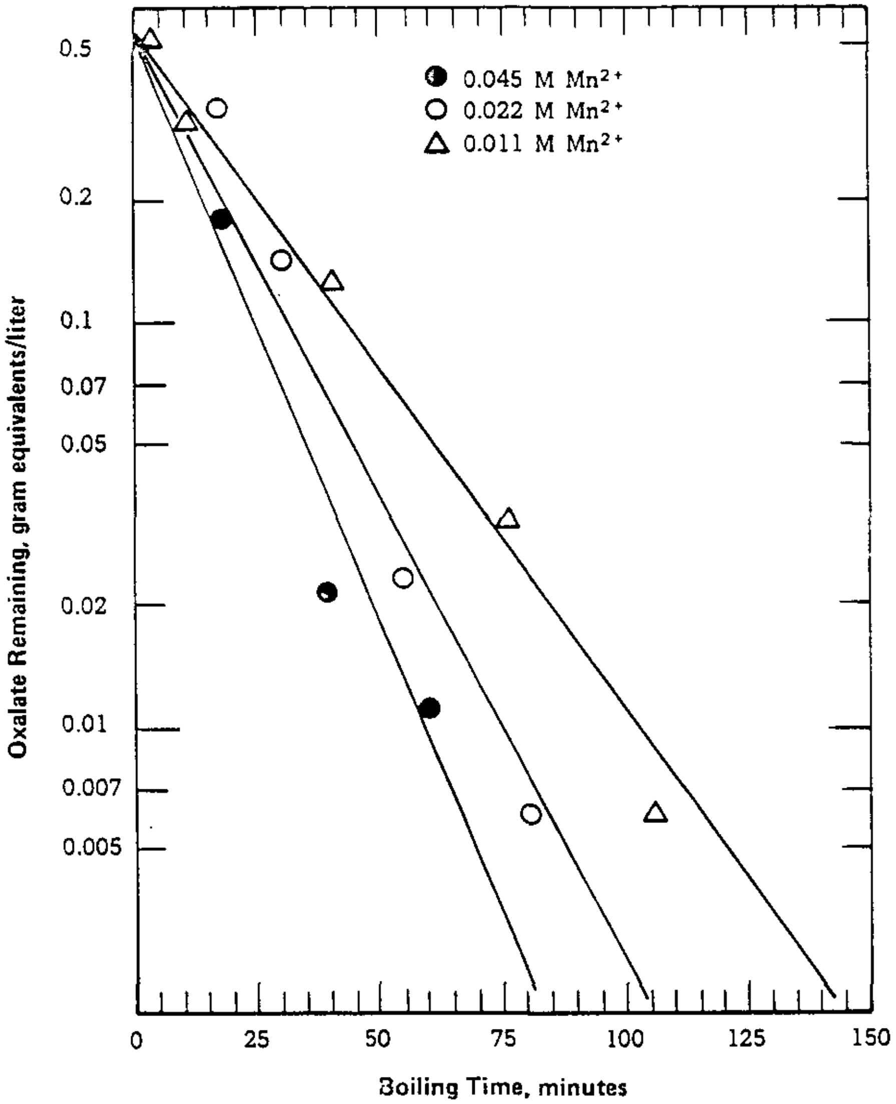

FIGURE 5. Oxidation of Oxalate Ion with 8M Nitric Acid Catalyzed by Manganous Ion

to keep off-gas rates less than 100 cfm. The final oxalate concentration of the waste was <0.02M which indicates >99.8% of the oxalate was oxidized to CO_2 and water.

In all, 43 batches of 9500 L of 0.6M $H_2C_2O_4$, approximately 20 tons, were oxidized in the evaporator operating in a combination of continuous and reflux modes. The reaction time per batch was nominally 12 hours.

The general procedure was to charge the evaporator with 4000 L of 4M HNO_3 containing 0.01M Mn^{2+}. Oxalic acid solution was then added while the evaporator was operated in the evaporative mode at 105 to 110°C. In many cases, the boiloff rate (2000 lb/hr) was equal to the addition rate; thus the operation was continuous without a volume change in the evaporator. Ten hours were normally required for the addition. After 10 hours, the evaporator was operated in the reflux mode for two hours to ensure complete reaction. The final $H_2C_2O_4$ concentration in the evaporator bottoms was normally <0.02M indicating greater than 99% destruction of the $H_2C_2O_4$. The final Fe^{3+} and Al^{3+} concentrations were 0.01M and 1.9M, respectively.

Data concerning volumes and acid concentrations for six of the runs are given in Table 3. Analysis of these data suggests that the two most important oxidation reactions are those producing NO_2 and NO. This conclusion is based on the calculated values for $\Delta HNO_3/\Delta C_2O_4^=$ (column nine of Table 3) for five of six runs. These values were calculated assuming that 60% of the H^+ in the condensate of the evaporator resulted from distillation of HNO_3. The remainder resulted from reaction of NO_2 or NO with O_2 and water vapor to produce H^+ along with NO_3^- or NO_2^- in the condensate. All the values are greater than 1.0 except that for Run 7. A value of greater than 0.67 indicates that the reaction producing NO_2 is also occurring. Reason for the low value in Run 7 is not known unless the analysis of the evaporator charge is in error. The average value for $\Delta HNO_3/\Delta C_2O_4^=$ for the other five runs is 1.4 ±0.3. Based on this number, the overall reaction involves 45% from the reaction producing NO, and 55% from that producing NO_2.

Kinetic data for the six runs in F-Canyon are in Table 4. From the feed times, the reflux times, and the initial and final $H_2C_2O_4$ concentrations, the average rate constant for the six F-Canyon runs was 0.014 ±0.001 min^{-1}.

The rate constant from the F-Canyon data was calculated for a two step process; $H_2C_2O_4$ addition during evaporation followed by refluxing. During $H_2C_2O_4$ addition, the feed rate to the evaporator was assumed equal to the boiloff rate from the evaporator. Thus,

TABLE 3

Reaction Data for Oxidation of $H_2C_2O_4$ by HNO_3-Mn in an F-Canyon Evaporator at About 105°C

Run	Evaporator Charge		Feed	Condensate		Evaporator Bottoms		
No.	Volume, L	HNO_3	Volume, L	Volume, L	H^+	Volume, L	H^+	$\Delta HNO_3/\Delta C_2O_4^{=}$
5	3809	4.2	9500	12330	0.52	2431	2.5	1.1
6	3425	3.9	9500	11517	0.54	2469	0.44	1.5
7	4058	2.6	9500	12618	0.41	2631	1.8	0.5
8	4031	4.9	9500	11028	0.88	3202	1.9	1.4
9	4642	4.8	9500	11997	0.59	2651	3.1	1.7
10	4080	3.7	9500	11300	0.62	3075	1.5	1.1

TABLE 4

Kinetic Data for Oxidation of $H_2C_2O_4$ by HNO_3 - Mn in an F-Canyon Evaporator at About 105°C

Run No.	Feed Time, hr	Reflux Time, hr	Rate Constant, min^{-1}
5	7.3	1.6	0.013
6	8.0	1.3	0.014
7	9.3	1.2	0.014
8	8.2	0.58	0.015
9	8.8	1.5	0.014
10	6.9	0.5	0.015

SUMMARY OF PLANT PROCESSING

Approximately 5 kg of combined Am-Cm was recovered from stored waste from the processing of plutonium targets. An overall recovery of about 75% (about 1.5% dissolved losses; remainder entrained losses) of the transplutonium isotopes was achieved. Of the 25% lost to the waste stream, about 18% is stored for future recovery; about 7% was actually lost to the waste tanks. The major contaminants of the purified Am-Cm product are Fe, Al, and Na.

Characterization of Waste Concentrate

The analysis of high activity waste concentrate from the processing of the plutonium targets is given in Table 1.

Table 1

Characterization of Am-Cm Solution

Density	1.305 g/cc
Nitric Acid	1.67M
Fission Product Gamma Activity	5.07 x 10^{10} d/m/mL
Aluminum	42.0 g/L
Iron	1.2 g/L
Uranium	1.0 g/L

Formic Acid Denitration

The Am-Cm-Al solution was denitrated in a series of four batches. Residual nitric acid concentrations are shown in Table 2.

Table 2

Residual Acid After Denitration

Batch No.	Residual Nitric Acid Conc. M
1	0.75
2	0.10
3	0.38
4	not determined
Blended material	0.20

The reactions initiated promptly and proceeded smoothly. Foaming was a continuing problem due to the high salt content; this extended both the denitration runs and the evaporation period during the acid adjustment step before denitration.

Precipitation, Digestion, Washing, and Decanting

Approximately 10% of the denitrated Am-Cm concentrate was transferred into the precipitation vessel, diluted with process water, heated to about 60°C, lanthanum nitrate added as a carrier, and then oxalic acid solution was added to adjust the oxalate concentration. The solution was cooled to 40 to 45°C and digested with agitation for 4 hours to promote crystal growth. The precipitated Am-Cm oxalate was settled for 8 hours before the supernate was decanted.

Additional Am-Cm concentrate was then transferred to the precipitation vessel and the precipitation, digestion, settling cycles repeated until all the Am-Cm oxalate precipitate was accumulated in the tank. A total of 10 batches were required. The accumulated oxalate precipitate was washed four times to "dilute out" contaminating cations.

Decanting losses were much higher than anticipated. In an attempt to minimize losses, the chemical composition of the precipitation batches was varied to increase the oxalate/aluminum ratio. These variables had little effect on product losses because the solubility losses were very low (<15% of the actual loss). Apparently, Am-Cm oxalate solids are being disturbed prior to and during decanting and a portion of the disturbed precipitate was decanted. A new decant jet, which had a plate welded across the bottom and holes drilled around the pipe above the plate to provide horizontal rather than vertical suction, was fabricated and installed after the fifth batch. Losses, however, remained unchanged.

A total of about 20% of the product (about 1600 g Am-Cm) was entrained to the waste evaporator with decanted supernate. Most of the oxidized supernate concentrate containing 1150 g Am-Cm was retained and is available for recovery by another method; the remainder was discarded.

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 the reaction volume was constant. During this time, the rate of change of the $H_2C_2O_4$ concentration is given by

$$V \frac{dC}{dt} = \mu C_o - VkC$$

where C = oxalic acid concentration in the evaporator at time t

V = solution volume in the evaporator (assumed constant and equal to charge volume)

k = 1st order constant for oxidation

C_o = concentration of oxalic acid in the feed

μ = feed rate

Integration gives

$$C = \frac{\mu C_o}{Vk} \left[1-\left\{\exp\left(-kt\right)\right\}\right]$$

If t_f is the feed time and t_r is the reflux time, then the final concentration of $H_2C_2O_4$ (C_F) is given by

$$C_F = \frac{\mu C_o}{Vk} \left[1-\left\{\exp\left(-kt_f\right)\exp\left(-kt_r\right)\right\}\right]$$

This equation was then solved for k by successive approximations for each of the six runs (Tables 3 and 4) using data taken during plant operations. The average result for the six runs was 0.014 min^{-1}.

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. A comparison of the major impurities before and after the oxalate precipitation step is given in Table 5. This solution has been combined with Am-Cm residues purified in another campaign[5] and await processing by high pressure ion exchange in the MPPF.

TABLE 5

Composition of Al^{3+}-Am^{3+}-Cm^{3+}-NO_3^- Solutions

	Storage Condition Before Purification	MPPF Feed Requirements	Actual Final Solution
Volume, L	13,200	620 L	
HNO_3, M/L	1.0	<0.5	
Moles, total	13,200	<310	
$Al(NO_3)_3$, M/L	2.0	<0.05*	
Moles, total	26,400	<31*	50
$NaNO_3$, M/L	0.07	<1.00**	
Moles, total	925	<620**	75
KF, M/L	0.12		
Moles, total	1584		
$Hg(NO_3)_2$, M/L	0.023		
Moles, total	304		
$Fe(NO_3)_3$, M/L	0.023		
Moles, total	304		
H_2SO_4, M/L	0.046		
Moles, total	607		
Ln's + Ac's, M/L	0.006		
Moles, total	80		

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* This is the feed requirement for the sum of all polyvalent cations (Al^{3+} + Fe^{3+} + Hg^{2+} + all others).

** This is the feed requirement for the sum of all monovalent cations excluding H^+ (Na^+ + K^+ + any others).

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