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REMOVAL OF SULFAMIC ACID FROM PLUTONIUM SULFAMATE-SULFAMIC ACID SOLUTION

L. W. GRAY

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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07-2)-1

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REMOVAL OF SULFAMIC ACID FROM PLUTONIUM SULFAMATE-SULFAMIC ACID SOLUTION

by

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ABSTRACT

Plutonium metal can be readily dissolved in aqueous solutions of sulfamic acid. When the plutonium sulfamate-sulfamic acid solutions are added to normal purex process streams, the sulfamate ion is oxidized by addition of sodium nitrite. This generates sodium sulfate which must be stored as radioactive waste. When recovery of ingrown ^{241}Am or storage of the dissolved plutonium must be considered, the sulfamate ion poses major and undesirable precipitation problems in the process streams. The present studies show that 40 to 80% of the sulfamate present in the dissolver solutions can be removed by precipitation as sulfamic acid by the addition of concentrated nitric acid. Addition of 64% nitric acid allows precipitation of 40 to 50% of the sulfamate; addition of 72% nitric acid allows precipitation of 50 to 60% of the sulfamate. If the solutions are chilled, additional sulfamic acid will precipitate. If the solutions are chilled to -10°C, about 70 to 80% of the original sulfamic acid in the dissolver will precipitate. A single, low-volume wash of the sulfamic acid crystals with concentrated nitric acid will decontaminate the crystals to a plutonium content of $<10^5$ dis/(min-gram) (~ 2 μg Pu/g sulfamic acid).

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REMOVAL OF SULFAMIC ACID FROM PLUTONIUM SULFAMATE-SULFAMIC ACID SOLUTION

INTRODUCTION AND SUMMARY

The first step in the chemical reprocessing of alpha-phase plutonium metal at the Savannah River Plant (SRP) is dissolution in a nearly saturated aqueous solution of sulfamic acid.[1-3] Before any downstream processing can occur, the sulfamate ion must be removed, either by hydrolysis to ammonium and sulfate ions (Appendix A), by oxidation to nitrogen gas and sulfate ion (Appendix B), or by precipitation as sulfamic acid. Since about 1962, the preferred method at SRP has been to oxidize the sulfamate ion by adding sodium nitrite to the processing solutions. In the past, the amount of metal-dissolving solution has normally been a minor fraction of the total plutonium-containing solutions for processing. Processing of the waste stream has been limited to evaporation, acid stripping, neutralization, and storage in underground tanks. However, when large amounts of aged plutonium metal are processed, recovery of the ingrown ^{241}Am from the plutonium recovery waste streams becomes a major consideration. The amount of sodium ions in the plutonium waste stream from the oxidation of sulfamic acid by sodium nitrite then becomes the limiting factor in the recovery of the ^{241}Am. Therefore, a method was needed to decrease the amount of sodium in the ^{241}Am-bearing stream.

Four methods hold promise for decreasing the sodium content:

1. Remove the sulfamate from the plutonium metal dissolver solutions by precipitation as sulfamic acid.

2. Hydrolyze the sulfamate ion to ammonium bisulfate by heating the diluted, stored, plutonium solutions just before processing in the solvent extraction cycle.

3. Oxidize the sulfamate by introducing a gaseous oxidizing agent, such as N_2O_4 or NO.

4. Generate an oxidizing agent *in situ* by irradiating the stored plutonium sulfamate - nitric acid solution either with radioactive sources or with ultraviolet light (Appendix C).

This report discusses the first of the four options. The other less-desirable options are discussed in the appendices to this report.

The benefits to be gained are:

1. The waste generated from this process for long-term storage is directly proportional to the amount of sulfamate ion transferred to the canyon. Waste generated will therefore be reduced in a like amount to the percentage of sulfamic acid precipitated.

2. The number of cation exchange runs that must be performed is directly proportional to the amount of sulfamate ion transferred to the canyon. Therefore, precipitation of 50% of the sulfamic acid would reduce the cation exchange runs by 50%; precipitation of more than 75% of the sulfamic acid might allow the cation exchange process to be eliminated.

3. Corrosion of the evaporators would be expected to be less than that experienced in the 1977 campaign for ^{241}Am recovery.

The most promising method for introduction into SRP processes is to remove the sulfamate ion by precipitation as sulfamic acid. Depending on the concentration and temperature of the nitric acid added, from 60 to 85% of the sulfamate ion could be removed. The method consists of the following general steps:

1. Add 4 L of chilled, concentrated nitric acid to 2 L of plutonium dissolver solution.

2. Chill the resulting solution (optional).

3. Filter the solution to remove the precipitated sulfamic acid.

4. Wash the crystals with a small volume of chilled, concentrated nitric acid.

5. Dilute the solution to $\leqslant$ 6g Pu/L for canyon storage.

6. Oxidize the remaining sulfamic with sodium nitrite.

7. Dilute the solution to $\leqslant$0.5g Pu/L and adjust the acid to 4M HNO_3 for solvent extraction.

Without the removal of the sulfamic acid, the waste stream can only be concentrated by a factor of about 25 if one expects to recover the ^{241}Am from the waste stream by a cation exchange process.[4] The maximum concentration factor that can be achieved without precipitation problems is about 110 (a factor of 4 dilution is required to adjust the acid before the next step). However, if the sulfamic acid were removed by precipitation, the waste stream could be concentrated by a factor of 200 to 400 before moving to the cation exchange process. Or, the solutions could be concentrated by a factor of 500 to 1000 and perhaps precipitated directly (after acid adjustment).

BACKGROUND

During calendar year 1977, SRP isolated approximately 5.3 kg of ^{241}Am from aged plutonium metal.[4] The plutonium metal was dissolved in 1.67M sulfamic acid to yield solutions containing 50 to 60 g Pu/L, before storage in 3M HNO_3 at a concentration of $\leq$ 6g Pu/L.

After the plutonium valence was adjusted to Pu(IV) by adding sodium nitrite, the plutonium concentration was diluted to $\leq$0.5g/L and the nitric acid concentration was increased to $\sim$4M. Americium and plutonium were then separated by one cycle of solvent extraction with tri-n-butylphosphate (TBP) in a normal paraffin hydrocarbon solvent. The plutonium was stripped from the organic phase with hydroxylamine nitrate in nitric acid and further concentrated by cation exchange before precipitation as the oxalate. The oxalate precipitate was then calcined to plutonium dioxide. The waste stream containing the ^{241}Am from the solvent extraction cycle was concentrated by evaporation, acid stripped, and further concentrated by evaporation. After concentration by a factor of about 100, the concentrate was diluted by a factor of about 4 to adjust the acid concentration to about 0.5M. Oxalic acid was then added to complex any residual plutonium and any ferric ions present from evaporator corrosion. The adjusted solution was fed to a 15-in. diameter cation column, washed first with 0.25M H_2SO_4-0.05M $H_2C_2O_4$, and then washed with 0.25M HNO_3. The combination of prior complexing with oxalic acid and the sulfuric acid-oxalic acid wash removed most of the Pu, Na, and Fe ions and a portion of the Ni ions. The nitric acid wash removed most of the sulfate. The ^{241}Am was then eluted from the column with 5M to 6M HNO_3. This isolated solution of ^{241}Am was then stored for later processing in the multi-purpose processing facility (MPPF).

A number of processing problems occurred during this plant-scale recovery program:

- The dissolution rate was very slow, $\sim$2 kg per dissolver per 24-hr. day.
- Evaporator corrosion was excessive.
- Solids precipitated several times due mainly to the high concentration of sodium sulfate in the ^{241}Am stream.
- An excessive number of cation exchange column runs were necessary due to the high sodium concentration.

As a result of these problems, studies were begun to solve the problems before the next ^{241}Am-Pu separations campaign. These studies include:

- Removal of the sulfamate ion by precipitation instead of oxidation by sodium nitrite.
- Faster dissolution of plutonium metal in sulfamic acid at elevated temperatures.
- Faster dissolution of plutonium metal by using nitric acid - HF as the electrolyte for electrolytic dissolution.

This document reports on the precipitation of sulfamic acid from plutonium sulfate-sulfamic acid solutions,

LABORATORY PROCESS DEVELOPMENT

The solubility of sulfamic acid in various concentrations of nitric acid was determined by allowing a known amount of sulfamic acid to come to equilibrium with a known volume of standardized nitric acid solution. After equilibrium was obtained, the remaining crystals were filtered, air-dried, and weighed. Filterability of the proposed precipitate was determined by adding known volumes of standardized nitric acid to known volumes of standardized sulfamic acid. Decontamination of the precipitated sulfamic acid was determined by dissolving plutonium metal in 1.67M sulfamic acid and adding concentrated nitric acid to precipitate the sulfamic acid.

When precipitated from either $NH_2SO_3^-$-NO_3^--H^+ solutions or from Pu^{3+}-$NH_2SO_3^-$-NO_3^--H^+ solutions, the sulfamic acid precipitate was orthorhombic crystals in the mm-size range. When precipitated from Pu^{3+} solutions, all the residual blue Pu^{3+} solution could be removed easily by washing with a small volume of cold, concentrated nitric acid. The resulting washed crystals of sulfamic acid contained less than 10^5 dis/(min-gram) of residual plutonium (∿2 μg Pu/g crystals).

The solubility curve obtained (Figure 1) was used to calculate the sulfamate remaining in solution at about 25°C as various concentrations of nitric acid were added to the dissolver solution. The calculated curves so obtained are given in Figure 2. The minimum solubility occurred when 2 to 2.25 L of concentrated nitric acid was added per liter of dissolver solution. The solubility was about 20% less if 72% HNO_3 (15.7M) was added than when 64% HNO_3 (14.07M) was added.

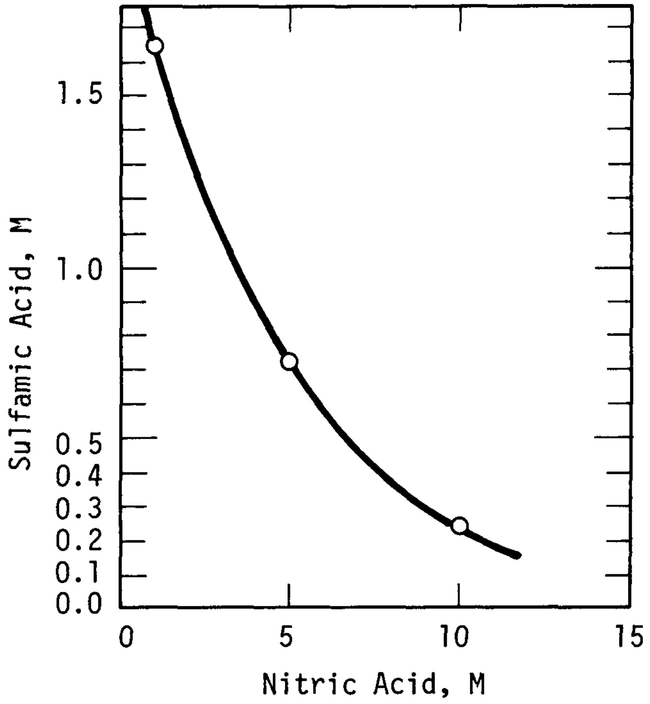

FIGURE 1. Effect of Nitric Acid Concentration on the Solubility of Sulfamic Acid

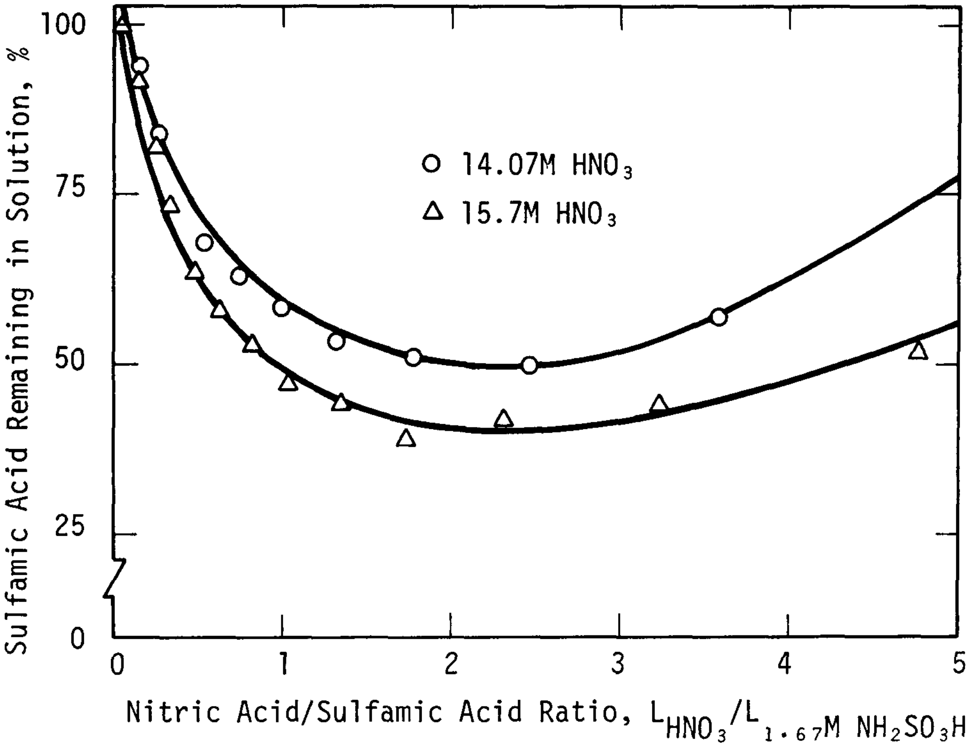

FIGURE 2. Precipitation of Sulfamic Acid from Concentrated Nitric Acid Solutions

SOLUBILITY OF SULFAMIC ACID

Sulfamic acid is moderately soluble in water: 14.68 g dissolve in 100 g of water at 0°C; and 47.08 g dissolve at 80°C. All sulfamates except the basic mercury salt are very soluble. Lead, ammonium, sodium, and magnesium sulfamates are more soluble than the corresponding nitrates, sulfates, chlorides, and acetates (Table 1).[5]

TABLE 1

Solubility of Pertinent Inorganic Salts[a]

Cation	*Anion* *Sulfamate*	*Nitrate*	*Acetate*	*Chloride*	*Sulfate*
Ammonium	216	214.2	234	39.3	76.7
Sodium	125	91	50	36	28
Magnesium	112	75.4	65.5	56.7	26.8
Calcium	79	138	34.2	90	0.208
Barium	29	10.4	77.3	37	0.00026
Zinc	115	126	44.5	425	57.9
Lead	218	58	55	1.08	0.004

---

a. Solubility in grams of salt/100 grams of water at 25°C.

Because of the low relative solubility of acceptable barium salts, barium ions cannot be added to precipitate the sulfamate. The least soluble sulfamate salt is $Ba(NH_2SO_3)_2$; 29 g (0.088M) dissolve per 100 g of water at 25°C.[5] The only common barium salts of sufficient solubility are the chloride and the acetate; but neither of these is compatible with downstream processing.

Any attempt to remove the sulfamate ion from plutonium metal dissolving solutions, then, must depend upon its removal as sulfamic acid. Because the acid is moderately soluble, the volume of solution at the point of precipitation must be kept to a minimum. Also, because the solubility of the acid[5] is temperature dependent (Figure 3), the temperature should be reduced as much as practical to insure maximum removal of the sulfamate.

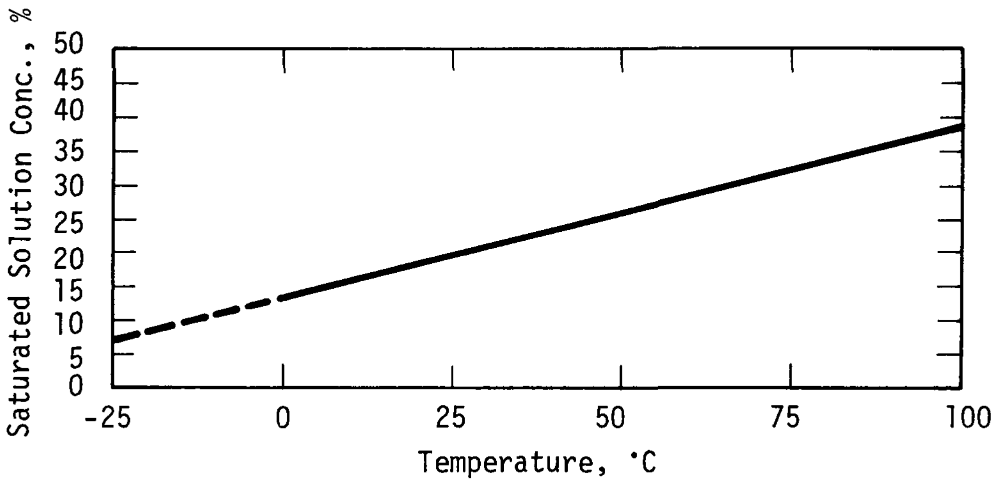

FIGURE 3. Effect of Temperature on the Solubility of Sulfamic Acid in Water

APPLICATION TO PLANT PROCESS LINE (JB-LINE)

For this system to operate, one of the present 2-L tanks in the present JB-Line recovery system would have to be replaced by a 6-L tank. The conceptual process tankage and piping then would be as given in Figure 4. Dissolver solution (2L) would be displaced from the dissolver into a catch-tank and then filtered to a second tank to remove any entrained dissolver sludge. Chilled, concentrated (72%) nitric acid (4L) would then be added to precipitate the sulfamic acid. After allowing about 20 to 30 minutes for complete precipitation, the solution would again be filtered, sampled for accountability, diluted to $\leq$ 6 g Pu/L and transferred to storage to await further processing.

The use of this system could be expected to reduce the sulfamate transferred to the solvent extraction cycle to about 40 to 60% of that from the previous campaign. As a result, the sodium nitrite addition required for oxidizing the sulfamate ions would also be reduced by about a factor of two. This reduction would allow an additional factor of two for evaporation of the waste stream without precipitation problems. Also, the volume of feed for the cation column would be only one-half the volume for the previous campaign for the same overall cation concentration. Processing time in this system would therefore be reduced by about a factor of two.

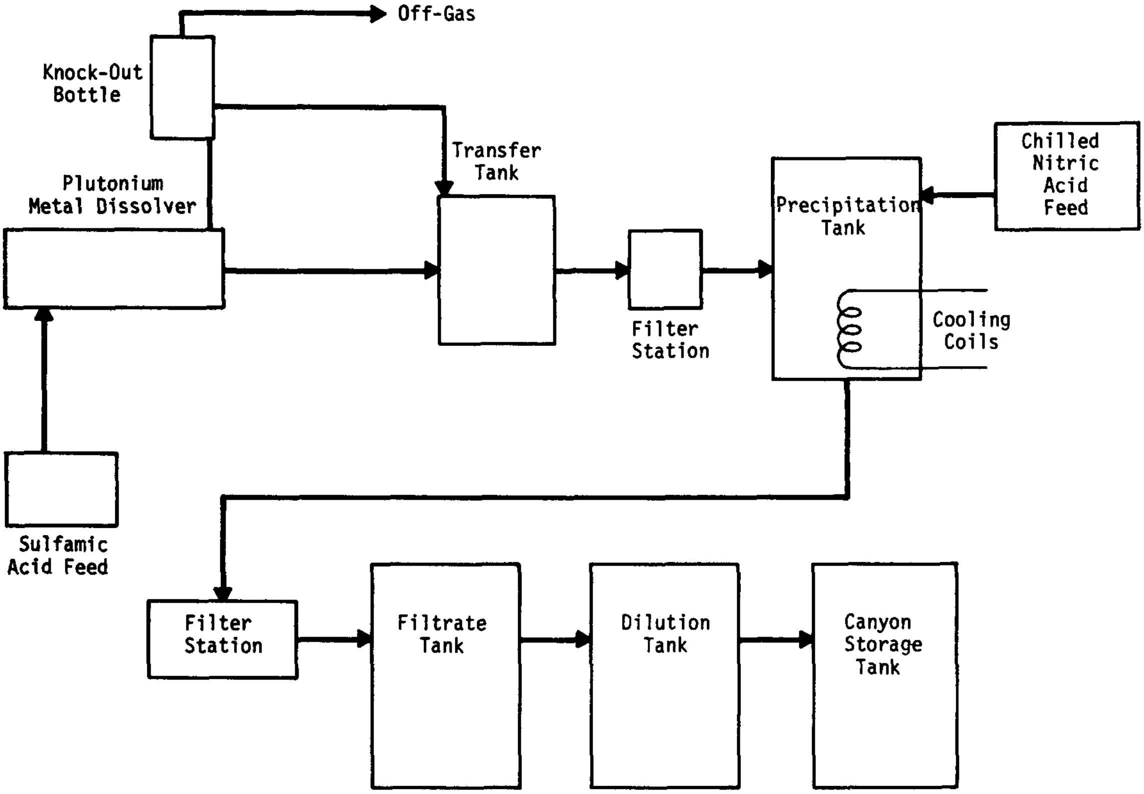

FIGURE 4. Conceptual Process for Removing Sulfamic Acid from Plutonium Sulfamate - Sulfamic Acid Solutions

Additional sulfamate could be removed if the plutonium sulfamate-sulfamic acid-nitric acid solution were chilled before the sulfamic acid crystals were filtered off. The amount of additional sulfamic acid removed would depend upon how low the refrigeration unit would bring the temperature within the available time in the processing cycle. Up to a maximum of an additional 60% of the sulfamic acid could be removed without freezing the solution. Chilling the solution should reduce the amount of sulfamate ion in the final solution by 70 to 80% from that in the original solution (see Tables 2 and 3).

The downstream benefit of using the combination of precipitation with concentrated nitric acid and chilling would be an overall concentration factor of about four over that experienced in the 1977 campaign. This also would reduce the processing time in the cation exchange process by a factor of about four.

TABLE 2

Precipitation of Sulfamic Acid by the Addition of 64% (14.07M) Nitric Acid

Vol. of 14.07M HNO_3 Added, mL	*Final HNO_3 Conc., M*	*Sulfamate Remaining in Solution, %*[a]		
		25°C	*0°C*	*-10°C*
76.51	1.0	100.00	67.95	55.13
165.7	2.0	94.23	64.03	51.95
271.0	3.0	83.83	56.96	46.21
397.2	4.0	76.13	51.73	41.97
551.0	5.0	67.71	46.01	37.33
743.5	6.0	63.16	42.92	34.82
990.1	7.0	58.34	39.64	32.16
1318.0	8.0	54.13	36.78	29.32
1775.1	9.0	53.18	36.14	29.32
2457.0	10.0	49.70	33.77	27.40
3583.1	11.0	57.63	39.17	31.77
5797.1	12.0	69.19	47.01	38.14
12149.5	13.0	100.00	67.95	55.13

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a. Initial volume of 1.67M sulfamic acid equaled 1000 mL in each instance.

TABLE 3

Precipitation of Sulfamic Acid by the Addition of 72% (15.7M) Nitric Acid

Vol. of 15.7M HNO_3 Added, mL	*Final HNO_3 Conc., M*	*Sulfamate Remaining in Solution, %*[a]		
		25°C	*0°C*	*-10°C*
68.0	1.0	100.00	67.95	55.13
146.0	2.0	92.64	62.95	51.07
236.2	3.0	82.53	56.08	45.50
341.9	4.0	73.52	49.96	40.53
467.3	5.0	64.05	43.52	35.31
618.6	6.0	58.15	39.51	32.06
804.6	7.0	52.95	35.98	29.19
1039.0	8.0	47.62	32.36	26.25
1343.3	9.0	44.90	30.51	24.75
1754.4	10.0	39.42	26.79	21.73
2340.4	11.0	42.00	28.54	23.15
3243.2	12.0	44.47	30.22	24.51
4814.8	13.0	52.23	35.49	28.79
8235.3	14.0	74.00	50.28	55.13

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a. Initial volume of 1.67M sulfamic acid equaled 1000 mL in each instance.

An additional benefit might also be gained by using this combination for removing the sulfamic acid from the dissolver solution. In the 1977 campaign, precipitation of materials carrying a portion of the ^{241}Am was experienced at an overall concentration factor of about 120. These precipitates were a result of incomplete degradation of the tri-butylphosphate (TBP) which is dissolved in the waste stream from the solvent extraction cycle. The greater evaporation factors allowed if the sulfamate is removed would more completely degrade the TBP and perhaps allow an even greater maximum concentration factor without precipitation in the evaporator. This then might allow a maximum concentration factor of 7500. This magnitude of evaporation would concentrate the ^{241}Am solution near the point where direct precipitation by oxalic acid is possible.

Direct in-tank precipitation would allow major decontamination of sodium, sulfate, and phosphate ions (from the process) and of iron, chromium, and nickel ions (introduced by stainless steel corrosion) from the product stream. This possible process is presently under investigation and will be the subject of a later report.

CONCLUSIONS

Future processing of aged plutonium metal from which ingrown ^{241}Am is to be recovered should have the sulfamate removed by precipitation in the JB-Line recovery cabinets. These solutions should be chilled for maximum removal of the sulfamic acid.

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APPENDIX A: Hydrolysis of Sulfamate Ions by Heating the Process Solutions

At room temperature, dilute aqueous sulfamic acid solutions are stable for many months, but at higher temperatures hydrolysis is relatively rapid. Upon hydrolysis, the acid forms ammonium hydrogen sulfate. The rate of hydrolysis is a function of concentration, temperature, and pH. Because the nitric acid solutions of interest to purex processing are in the pH range of 0 to 1, the hydrolysis half-life at elevated temperatures is very short ($t_{1/2} < 0.5$ hr).

Hydrolysis, however, produces the following major processing problems:

1. Ammonium ions have a higher affinity than sodium ions for *Dowex*® 50W ion exchange resin. This makes the ion exchange process more difficult than if sodium nitrite were used to oxidize the sulfamate ion.

2. Process waste streams must be neutralized before transfer to the waste farm. When neutralized, the ammonium hydrogen sulfate generated by hydrolysis would be converted to ammonia gas and sodium sulfate. The ammonia gas reacts with the nitric acid vapors in the process vessel vent system to yield ammonium nitrate which collects on the vessel vent filters. This poses its own set of processing problems.

Hydrolysis, therefore, is not a viable processing option.

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APPENDIX B: Oxidization of Sulfamate Ions by Gaseous Oxidizing Agents

Gaseous oxidizing agents, such as N_2O_4 or NO, could be used to oxidize the sulfamate ions to nitrogen gas and sulfate ions. However, the use of such reagents would not reduce the amount of sodium sulfate to be stored as waste, nor would the sulfate corrosion of the equipment be eliminated. The use of gaseous oxidizing agents would reduce the amount of sodium or ammonium ions that would be fed to the cation exchange column. This would, of course, solve a portion of the problems associated with ^{241}Am recovery.

APPENDIX C: *In Situ* Generation of Oxidizing Agents with Ultraviolet Light

Nitric acid is reduced to nitrous acid in the presence of ultra-violet light (<350 nm). This process is more efficient at higher nitric acid concentrations and at temperatures equal to or greater than 25°C. The introduction of sufficient photons of light to a canyon tank, perhaps with a mercury vapor lamp, may be difficult. However, if the sulfamic acid were precipitated from the plutonium metal dissolver solution, and irradiated in small batches with a mercury vapor lamp, sufficient nitrous acid could possibly be generated to oxidize most of the residual sulfamic acid.

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