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SOLVENT EXTRACTION OF IRRADIATED NEPTUNIUM TARGETS
II. FLOWSHEET DEVELOPMENT

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ABSTRACT

This report describes development of a solvent extraction flowsheet for processing ^{237}Np and ^{238}Pu at the Savannah River Plant as a possible replacement for anion exchange processing. The major difficulty in solvent extraction processing is maintaining neptunium in the extractable M(IV) or M(VI) valence states prior to extraction. Miniature mixer-settler tests with 7.5 vol % TBP showed that a sidestream of ferrous sulfamate to reduce Np(V) to Np(IV) in the first bank of mixer-settler contactors greatly decreased loss of neptunium to waste. A nitrite sidestream to catalytically oxidize Np(V) to Np(VI) did not prevent high losses of neptunium.

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SOLVENT EXTRACTION OF IRRADIATED NEPTUNIUM TARGETS.
II. FLOWSHEET DEVELOPMENT

INTRODUCTION

Studies have been conducted at the Savannah River Laboratory (SRL) to design a solvent extraction flowsheet for the recovery, decontamination, and partitioning of ^{237}Np and ^{238}Pu from irradiated neptunium targets. Replacing anion exchange processing of these targets by solvent extraction in Savannah River Plant (SRP) operations would reduce cost and waste volume, and would increase the production rate of ^{238}Pu. The valence of neptunium and plutonium must be adjusted to provide species of both elements that are extractable with tri-n-butyl phosphate (TBP) and may thereby be removed from inextractable fission products. The arrangement of plant equipment necessitates that the two elements be extracted in a single bank of mixer-settler contactors. The extractability of neptunium and plutonium valence states into TBP decreases in the order: $Pu(IV) > Np(VI) > Np(IV) \approx Pu(VI) >> Np(V) \approx Pu(III)$. Np(V) and Pu(III) are relatively inextractable. Stabilization of extractable valences is difficult because of the high specific activity of ^{238}Pu and the chemical effects of plant dissolver solution (2 g/L ^{237}Np, 0.4 g/L ^{238}Pu, 1.2M Al^{3+}, 4.6M NO_3^-, 1M H^+, and fission products). In a previous study, the thermodynamic stabilities of the valence states in the neptunium-plutonium system were calculated, and stabilization of extractable states was attempted; inextractable Np(V) is the stable valence state for neptunium in dissolver solution, and nitrite-scavenging agents do not stabilize extractable valence states.[1]

This report describes (1) development of a solvent extraction flowsheet including valence adjustment, and (2) coextraction, decontamination, and partitioning of neptunium and plutonium with 7.5 vol % TBP. Miniature mixer-settler tests were conducted with sidestreams of ferrous sulfamate (FeSA) and of nitrite (NO_2^-). Other tests without sidestreams examined processing of the Np(IV)-Pu(IV) and Np(VI)-Pu(VI) systems with and without NO_2^- scavenging agents. Plant dissolver solutions were used to demonstrate two alternative solvent extraction flowsheets.

FIRST-CYCLE SOLVENT EXTRACTION FLOWSHEET

The generalized flowsheet (Figure 1) summarizes the streams and conditions tested in miniature mixer-settlers. The most effective process tested includes head-end removal of iodine by *in situ* precipitation of MnO_2, which oxidizes both neptunium and plutonium to M(VI). A FeSA sidestream in the extraction section of the A-bank is required to recover neptunium, because of the instability of Np(VI). Introducing the FeSA into Stage 13 allows plutonium to be extracted before FeSA reduces it to inextractable Pu(III), but allows sufficient stages for Np(IV) recovery. A TBP concentration of 7.5 vol % was chosen because current processing of enriched uranium at SRP uses 7.5 vol % TBP. Urea is used for nitrite scavenging in the 1AS stream; sulfamic acid, an alternative scavenger, is less desirable because it forms sulfate ion on reaction with nitrite. Sulfate ion complexes neptunium and plutonium and could increase losses to the waste. Heating B-bank and adding hydrazine give acceptable partitioning of neptunium and plutonium.

In the current anion exchange process, overall process losses are 0.1% neptunium and 0.1% plutonium with 0.05% neptunium or 0.05% plutonium contaminant in the product streams.[2] These values were chosen as arbitrary goals for the solvent extraction flowsheet.

COEXTRACTION OF NEPTUNIUM AND PLUTONIUM

Mixer-Settler Tests With Np(VI) and Pu(VI)

Iodine (including ^{131}I when short-cooled targets are processed) is removed in head end by *in situ* precipitation with MnO_2. MnO_2 oxidizes both neptunium and plutonium to M(VI). Effective iodine removal from plant dissolver solution requires at least 0.1M MnO_2.[3] Other common oxidizers such as dichromate, permanganate, or ceric ion were not used because of volatilization of fission product Ru as RuO_4 or because of equipment corrosion. Ceric ion would also be extracted, thereby decreasing decontamination of fission product cerium.

For the mixer-settler tests, solutions were adjusted to M(VI) by *in situ* precipitation of MnO_2. MnO_2 was then removed from the solution, and the solution was stored for 17 hours. Once MnO_2 has been removed, the valences begin to readjust to equilibrium values.[1] The first two tests (Table 1) demonstrated that urea added to the feed after removal of MnO_2 to scavenge HNO_2 decreases neptunium losses, but losses were still excessive. Even with a NO_2^- scavenger, the Np(VI)-Pu(VI) system was not stable for a practicable period of time for plant processing.

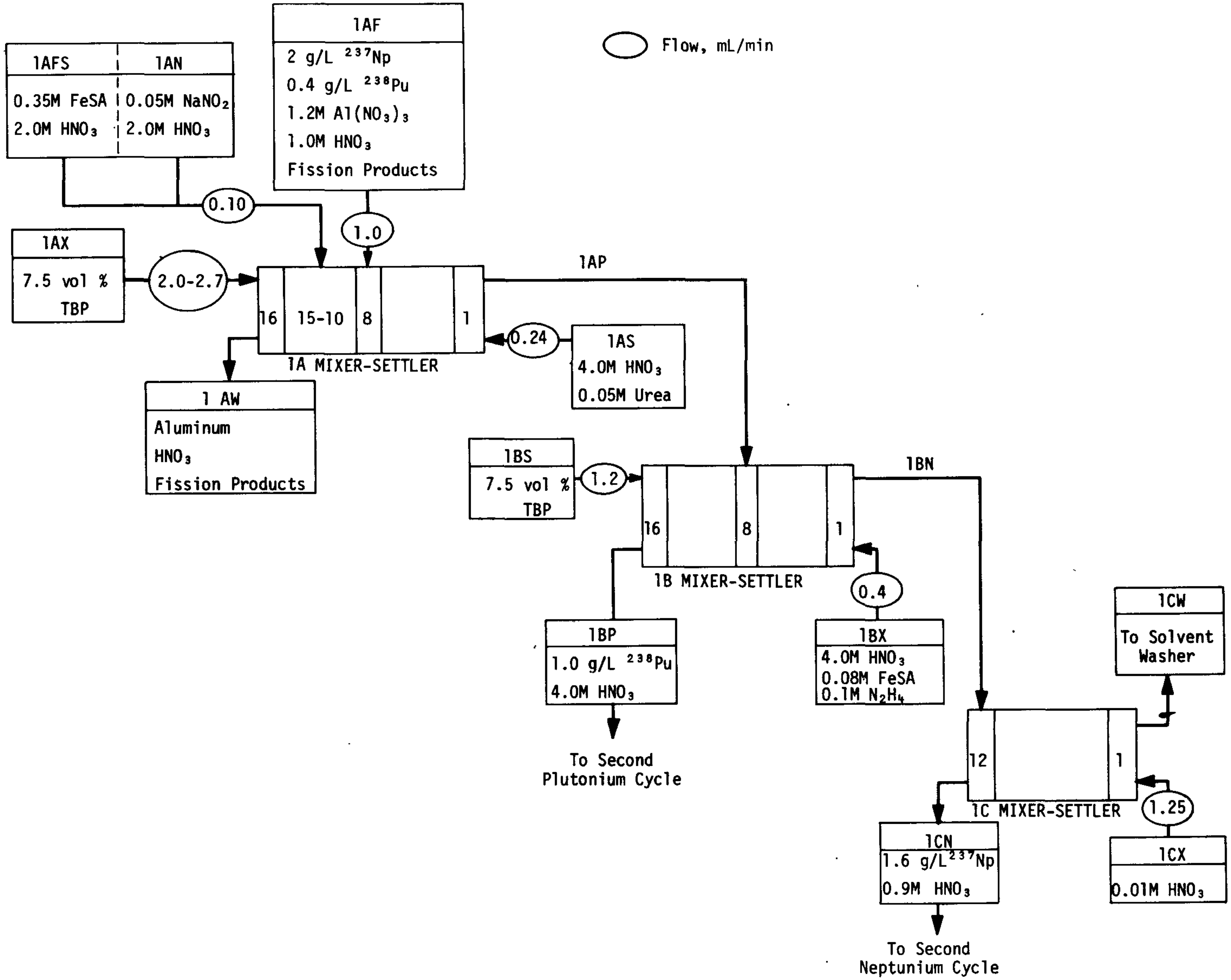

FIGURE 1. First-Cycle Neptunium-Plutonium Solvent Extraction Flowsheet

Additional tests investigated the effect of 0.35M FeSA added as a sidestream to the extraction section of the mixer-settler. After extraction of Pu(VI) and residual Np(VI), FeSA was added to reduce inextractable Np(V) to extractable Np(IV) *in situ*. Any unextracted Pu(VI) will be lost by reduction to inextractable Pu(III). Feed solutions were treated by MnO_2 either ∿16 or ∿40 hours before each 5- to 6-hour mixer-settler test; in some tests, urea was added after MnO_2 removal to stabilize Np(VI). The tests demonstrated that >99% of the neptunium can be recovered within 24 hours after valence adjustment, with or without urea as a stabilizer; however, plutonium losses were high. In tests delayed two days after MnO_2 removal, neptunium losses were decreased and plutonium losses were increased by the presence of urea. Urea removes radiolytically generated NO_2^-, which would otherwise reduce some Np(VI) to inextractable Np(V) (increasing neptunium loss) and reduce some Pu(VI) to more extractable Pu(IV) (decreasing plutonium loss).

TABLE 1

Solvent Extraction of Neptunium and Plutonium With MnO_2 Valence Adjustment

Time After MnO_2 Removal, days	*Concentration of Urea in Feed, M*	*FeSA Sidestream at Stage*[a]	*Losses to 1AW, %*	
			Np	*Pu*
1	0	None	20.0	0.05
1	0.05	None	14.0	0.05
1	0	11	0.36	4.82
2	0	11	2.22	2.86
1	0.05	11	0.57	4.57
2	0.05	11	1.59	4.17

---

a. 0.35M FeSA in sidestream.

The FeSA sidestream was effective in reducing neptunium losses; therefore, additional tests were made to determine the optimum sidestream position. Neptunium losses increased (except for the unexplained high losses in test with FeSA into Stage 11) and plutonium losses decreased as the FeSA sidestream was moved to higher stages (Table 2), providing more stages for Pu(VI) extraction before the remaining plutonium is reduced to inextractable Pu(III). However, with the optimum sidestream position, losses were still greater than the current overall process loss of 0.1% neptunium and 0.1% plutonium with anion exchange.

TABLE 2

Solvent Extraction of Neptunium and Plutonium With MnO_2 Valence Adjustment

	FeSA Sidestream		*Losses to 1AW, %*	
Feed	*FeSA, M*	*Stage*	*Np*	*Pu*
Simulated	0.35	11	0.57	4.57
Simulated	0.35	13	0.25	0.72
Simulated	0.35	14	0.72	0.36
Simulated	0.35	15	2.11	0.09
Plant	0.50	13	0.16	0.94

Because total actinide losses were minimized by introducing FeSA into Stage 13, a test with plant dissolver solution was made with the same conditions. Solution from plant dissolution of neptunium targets was obtained and adjusted to 1.1M HNO_3 by denitration with 90% formic acid. After valence adjustment, the feed was filtered, adjusted to 0.05M urea, and allowed to stand overnight before being fed to the mixer-settler. Table 3 gives the composition of the adjusted feed. Extractant and scrub flows were increased to 2.7 and 0.32 mL/min, respectively. Neptunium and plutonium losses are shown in Table 2. Decontamination from fission products was good except for ^{95}Zr (Table 4) and is comparable to that achieved in reprocessing irradiated enriched uranium fuels.

TABLE 3

Composition of Adjusted Plant Feed Solution

Component	*Concentration*
$Al(NO_3)_3$, M	1.22
HNO_3, M	1.1
^{237}Np, g/L	1.82
Pu, g/L	0.47 (0.39 g/L ^{238}Pu)

Fission product, dis/(min)(mL)

^{95}Zr	1.30×10^{10}	^{134}Cs	1.63×10^{8}
^{95}Nb	1.60×10^{10}	^{137}Cs	5.37×10^{8}
^{103}Ru	1.09×10^{10}	^{141}Ce	6.51×10^{9}
^{106}Ru	6.10×10^{9}	^{144}Ce	7.80×10^{9}

TABLE 4

Fission Product Decontamination

Fission Product	*DF*[a]
^{103}Ru	9.2×10^5
^{134,137}Cs	1×10^5
^{144}Ce	$>7.2 \times 10^5$
^{95}Zr	$>4.7 \times 10^2$

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a. Activity in 1AF/Activity in 1AP.

Mixer-Settler Tests With Np(IV) and Pu(IV)

Another combination of extractable valences [the Np(IV)-Pu(IV) system] is used in the present anion exchange process. A miniature mixer-settler test of the Np(IV)-Pu(IV) system without added NO_2^- scavenger (Table 5) showed that neptunium losses to the 1AW stream increase with time after valence adjustment. The production of NO_2^- by radiolysis of HNO_3 causes oxidation of Np(IV) to inextractable Np(V). Pu(IV) is unaffected by NO_2^-, and plutonium losses were acceptably low. In the second test with the feed stabilized with sulfamic acid, neptunium losses were somewhat lower during the first few hours, but still excessive. The losses may be due to other radiolysis products, which can be present in the absence of nitrite.[1] Plutonium losses were essentially unchanged.

The third test used a FeSA sidestream into Stage 12 to decrease the neptunium lost as Np(V) by *in situ* reduction to extractable Np(IV). Neptunium and plutonium in the feed were adjusted to the M(IV) states, 0.05M sulfamic acid was added to the feed, and the feed was allowed to stand for 24 hours before the mixer-settler test was begun. Neptunium losses were much lower than in the previous tests (although higher than desired). Plutonium losses were higher apparently because there were fewer stages for extraction of Pu(IV) before its reduction to Pu(III) in Stage 12 by FeSA.* Therefore, the small amount of plutonium present at Stage 12 was lost to the waste. No further work was done on the Np(IV)-Pu(IV) system because Np(IV) could not be stabilized but rather reverts to the valences obtained without valence adjustment.

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* The sidestream was added at Stage 12 because Stage 13 was optimum for Np(VI)-Pu(VI) recovery, and Pu(IV) is more extractable than Pu(VI). Thus, moving the sidestream to Stage 12 gives an additional stage for Np(IV) extraction, but would not be expected to increase plutonium losses.

TABLE 5

Mixer-Settler Tests With Np(IV) and Pu(IV)

FeSA Sidestream	*Stabilizer*	*Time After Valence Adjustment, hr*	*Losses to 1AW, %*	
			Np	*Pu*
None	None	3	17.9	0.008
		4	33.4	0.012
		5	36.9	0.012
		6.5	40.1	0.013
None	Sulfamic acid[a]	3	18.7	0.006
		4	20.0	0.010
		5	25.1	0.008
		24	38.1	0.012
		25.5	43.9	0.014
Stage 12	Sulfamic acid[a]	27	1.9	0.20
		28	1.8	0.22
		29.5	1.5	0.20
		30.5	1.3	0.19

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[a] Feed was adjusted to 0.05M sulfamic acid after valence adjustment.

Mixer-Settler Tests With Neptunium and Plutonium Without Prior Valence Adjustment

Ferrous Sulfamate Sidestream

Because MnO_2 treatment of the dissolver solution increases waste and may not be necessary for reactor targets cooled >100 days, the flowsheet was tested without prior valence adjustment. A sidestream of FeSA was used to reduce Np(V) to Np(IV), and urea was added as a NO_2^- scavenger to the 1AS (scrub) stream. The 1AX (TBP) flow was 2.7 mL/min, and 1AS flow was 0.31 mL/min. Other stream compositions were shown in Table 1. Results with simulated and plant feeds are shown in Table 6.

Increasing the FeSA concentration (added at Stage 11) and adding urea to the 1AS stream decreased the neptunium losses substantially from the 6.73% loss in the initial test (Table 6) on simulated feed. As expected, neptunium losses were higher and plutonium losses were lower with the FeSA sidestream at Stage 11 compared to that of Stage 10 [fewer extraction stages for Np(IV)]. Tests were not made at higher stages because the earlier test at Stage 12 for the similar Np(IV)-Pu(IV) system (Table 5) resulted in higher neptunium losses with no change in plutonium losses. The higher neptunium losses and lower plutonium losses with plant dissolver solution may result from increased radiolysis by fission products and ^{238}Pu alpha radiation. Higher FeSA concentrations in the sidestream or higher urea concentrations in the 1AS and 1AF streams would tend to alleviate radiolytic effects resulting from higher NO_2^- and other radiolysis products.

TABLE 6

Solvent Extraction of Neptunium and Plutonium Without Prior Valence Adjustment

	FeSA Sidestream		*Losses to 1AW, %*	
Feed	*FeSA, M*	*Stage*	*Np*	*Pu*
Simulated	0.35	11	6.73	0.24
Simulated	0.50	11	0.15	0.25
Simulated	0.50	10	0.01	0.66
Plant	0.50	11	2.36	0.14

Nitrite Sidestream

A mixer-settler test was made with a NO_2^- sidestream into Stage 15. Stream flows and compositions of other streams were given in the basic flowsheet (Figure 1). Nitrite was tested because nitrate oxidation of neptunium with catalytic amounts of NO_2^- has been used to obtain Np(VI).[4] The concentration of HNO_2 must be carefully controlled because it forms during the oxidation reaction and excess HNO_2 causes reduction of Np(VI) to Np(V). Nitrite should be between 5×10^{-4} and 1×10^{-3}M; above 1×10^{-3}M, neptunium losses increase rapidly.[5] Preliminary mixer-settler tests with a NO_2^- sidestream entering Stage 15 of the 1A bank established that NO_2^- was between 5×10^{-4} and 1×10^{-3}M throughout the bank with a 0.1 mL/min sidestream of 0.05M $NaNO_2$. HNO_2 was extracted into 7.5 vol % TBP with a distribution coefficient of $\sim$1.

Prior to the test, the feed was sparged with air to remove NO_2^-. The test was run 5 hours, stopped, and then resumed the following day to determine the effect of radiolysis. Samples taken at 4 and 5 hours (Table 7) show that the 1A bank is in equilibrium. Plutonium loss is acceptable, but neptunium loss is very high. Allowing the feed to stand overnight doubled the neptunium loss. Benedict, et al. showed that the organic phase NO_2^- concentration had to exceed 0.01M to give neptunium losses of 30%.[5] Apparently, additional NO_2^- generated by alpha radiolysis of HNO_3 prevented the close control of NO_2^- concentration necessary for oxidation of Np(V) to Np(VI). Thus, extraction of neptunium and plutonium with a NO_2^- sidestream is not a viable process.

TABLE 7

Mixer-Settler Recovery of Neptunium and Plutonium With Sodium Nitrite Sidestream

Time After	*Losses to 1AW, %*	
NO_2^- Removal, hr	*Np*	*Pu*
4	17	0.12
5	17	0.12
25	33	0.09

PARTITIONING OF NEPTUNIUM AND PLUTONIUM

Neptunium and plutonium are partitioned by reducing Pu(IV) or (VI) to inextractable Pu(III); neptunium is simultaneously reduced to Np(IV). Neptunium is kept in the organic phase by adjusting the acid in the aqueous strip solution (1BX) and the organic-to-aqueous flow ratio to maintain the extraction factor of neptunium greater than one.

Table 8 gives the results of partitioning tests with both the M(IV) and M(VI) combinations. For the M(VI) case, 0.06M and 0.08M FeSA are ∿80% and 105%, respectively, of the stoichiometric amount of reductant necessary to completely reduce neptunium and plutonium. Increasing the FeSA concentration lowered neptunium loss but appeared to increase plutonium loss. The higher plutonium loss might be caused by too low a Fe^{2+}/Fe^{3+} ratio in the scrub section of the mixer-settler. When enriched uranium solutions were processed, Fe^{2+}/Fe^{3+} ratios less than 0.18 led to oxidation of Pu(III) and Np(IV).[6] The Fe^{2+}/Fe^{3+} ratio of 0.054 in the scrub section would allow oxidation and re-extraction of plutonium. Neptunium loss is not changed because most of the neptunium does not reach the scrub section. Rather than increase waste volumes by adding additional FeSA, hydrazine was added to act as both a reducing agent and a nitrite scavenger. The temperature was increased to increase the rate of hydrazine reduction reactions. This resulted in lower plutonium losses although not as low as desired. Plutonium remaining in the first cycle neptunium product would be rejected to waste in the second neptunium cycle.

For the M(IV) case, 0.06M FeSA represents a tenfold stoichiometric excess so 0.08M FeSA does not lower plutonium losses. Adding hydrazine and increasing the temperature gave excellent partitioning.

TABLE 8

Partitioning of Neptunium and Plutonium

Temp, °C	*N_2H_4, M*	*FeSA, M*	*Pu Product, % Np*	*Np Product, % Pu*
Np(VI)-Pu(VI)				
30-35	0	0.06	0.59	0.96
30-35	0	0.08	0.01	1.9
45	0.10	0.08	0.01	0.32
Np(IV)-Pu(IV)				
30-35	0	0.06	0.04	0.25
30-35	0	0.08	0.05	0.29
45	0.15	0.08	0.07	0.06

SECOND PLUTONIUM CYCLE

The plutonium product from the first cycle (1BP) must be further purified and concentrated before precipitation as Pu(III) oxalate.[7] Concentrations of 3 to 8 g/L plutonium and 0.5 to 1.5M HNO_3 are desired for precipitation in plant operation. Radiolysis of the solvent by ^{238}Pu to form nonstrippable plutonium dibutyl phosphate (DBP) complexes was expected to be the main problem with second plutonium cycle operation. Thus, the second plutonium cycle was tested (Figure 2) to demonstrate that solutions in the desired concentration range could be readily extracted and stripped.

Two miniature mixer-settler tests were made with feed composition similar to that expected from the 1BP. The results (Table 9) demonstrate that ^{238}Pu can be extracted and stripped with small losses to waste and solvent. The losses of plutonium to the 2AW are dependent on the flow ratio of 2AX/2AF. The loss to the waste solvent (2BW) is dependent on flow of the solvent (2AX). Lowering the 2AX flow increases the loss to 2BW because of radiolysis. The lower flow increases the ^{238}Pu concentration and the ^{238}Pu residence time in the solvent giving a higher total radiation dose. Thus, the increase in loss to 2BW was less than expected even though the total dose increased a factor of $\sim$3 (increase in time and concentration is equal to the ratio of 2AX flow rates, 1.78 to 1 and therefore the increase is 1.78^2). The poor mass balance obtained in the first test indicates that steady state operation may not have been attained or that plutonium reflux occurred in the 2B mixer-settler. The product from the second plutonium cycle (2BP) contained 5.0 g/L ^{238}Pu and $\sim$0.6M HNO_3, which is within the desired concentration range for oxalate precipitation.

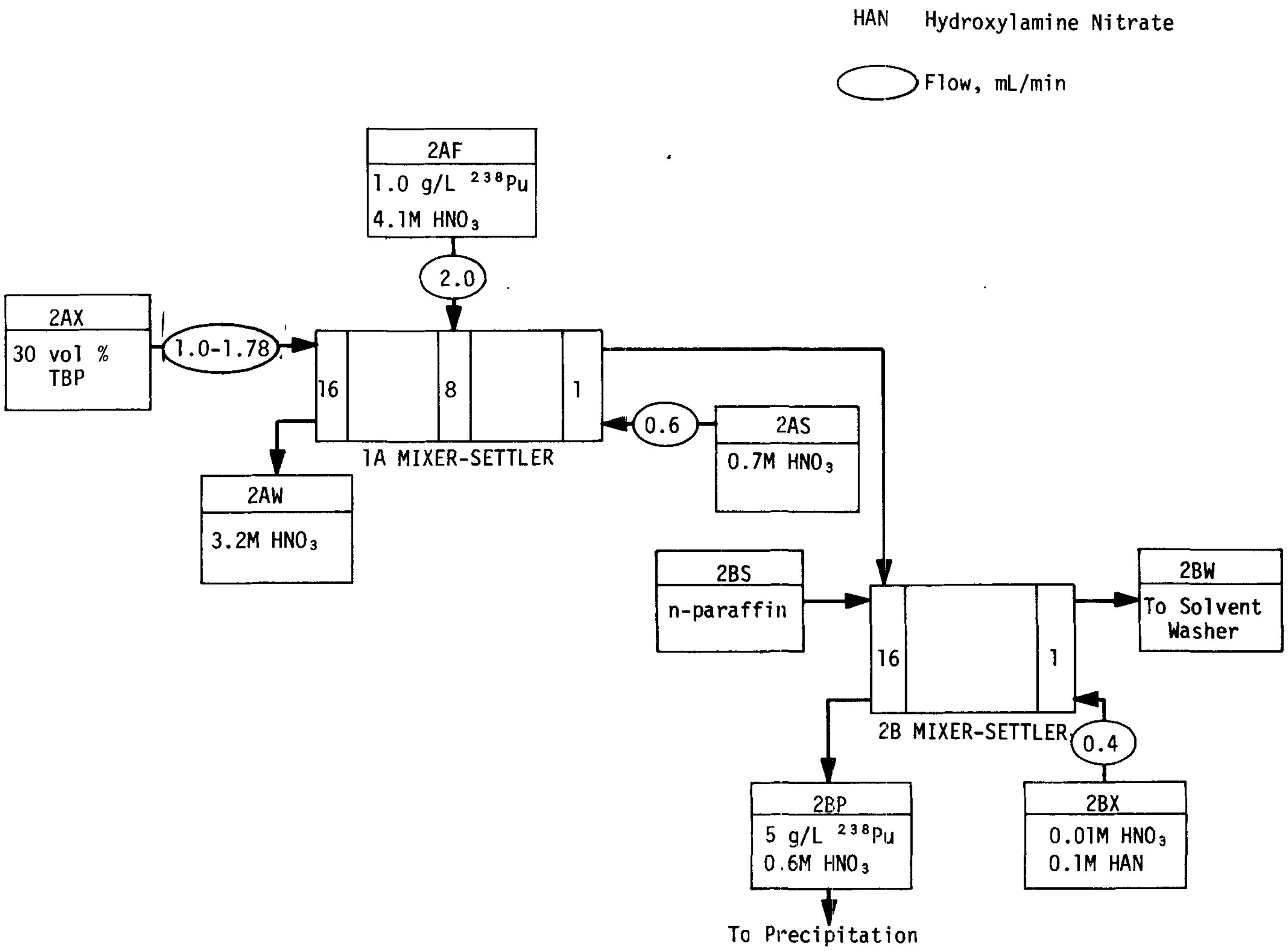

FIGURE 2. Second Plutonium Cycle

TABLE 9

Second Plutonium Cycle

Stream	*Flow, mL/min*	*Composition*
2AF	2.0	$\sim$1.0 g/L ^{238}Pu, $\geq$4.1M HNO_3
2AX	[a]	30% vol % TBP
2AS	0.60	0.70M HNO_3
2BX	0.40	0.01M HNO_3, 0.056M HAN[b]

---

[a]

2AX Flow, mL/min	*Plutonium, %*		
	2AW	*2BP*	*2BW*
1.78	0.002	68.5	0.05
1.00	0.06	98.8	0.08

[b] HAN - hydroxylamine nitrate.

To test the stability of the 2BP product, it was divided into two equal portions. One portion was washed with 1 vol % n-paraffin, and the other was left untreated. Within 24 hours, solids formed in the unwashed portion of solution. No solids formed in the n-paraffin washed portion for more than a month. The solids were not analyzed, but are believed to be plutonium DBP compounds formed by radiolytic decomposition of dissolved and entrained TBP.

EXPERIMENTAL PROCEDURE

The neptunium and plutonium valences in the dissolver solution were adjusted to M(VI) by *in situ* precipitation of 0.1M MnO_2 by adding 0.2M $KMnO_4$ to solutions containing a 5 to 10% stoichiometric excess of $Mn(NO_3)_2$. Valences were adjusted to M(IV) by reduction with FeSA, followed by oxidation of Pu(III) to Pu(IV) with NO_2^-. The solution was adjusted to 0.02M FeSA and then titrated with 2.8M $NaNO_2$ solution; the titration was monitored potentiometrically to prevent addition of excess NO_2^-. Potentials were measured as described in Reference 6.

Ferrous sulfamate was obtained from SRP as a 40 wt % solution. Ferrous ion concentration was determined by titration with standard ceric ion to a ferrous o-phenanthroline end point. Hydroxylamine nitrate was obtained as a 16 wt % solution from Baker and Adamson. Diluent was obtained from SRP and consisted of a mixture C_{12} to C_{15}, n-paraffin hydrocarbons with an average molecular weight of $\sim$190. Diluent was mixed with reagent-grade 100 vol % TBP to make 7.5 ±0.1 vol % TBP solution. The 7.5 vol % TBP was washed with

0.5M Na_2CO_3 solution to remove phosphoric acid degradation products, and then washed 3 to 5 times with distilled water to remove entrained Na_2CO_3. All other chemicals were reagent grade and were used without further purification. The 16-stage miniature mixer-settlers are described in Reference 8.

Plutonium and neptunium were first separated by thenoyltrifluoroacetone extraction with valence adjusted by FeSA. Then, they were determined by gross alpha and alpha pulse height analyses Solvent radiolysis did not cause significant problems during mixer-settler tests; however, organic samples had to be diluted within 3 to 4 hours to obtain reproducible analyses. Erratic results without dilution indicated precipitation of ^{238}Pu although no solids were visible.

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