DP-1656
Distribution Category: UC-10

PLUTONIUM-URANIUM SEPARATION IN THE PUREX PROCESS USING MIXTURES OF HYDROXYLAMINE NITRATE AND FERROUS SULFAMATE

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Publication Date: November 1983

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

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ABSTRACT

Laboratory studies, followed by plant operation, established that a mixture of hydroxylamine nitrate (HAN) and ferrous sulfamate (FS) is superior to FS used alone as a reductant for plutonium in the Purex first cycle. FS usage has been reduced by about 70% (from 0.12 to 0.04M) compared to the pre-1978 period. This reduced the volume of neutralized waste due to FS by 194 liters/metric ton of uranium (MTU) processed. The new flowsheet also gives lower plutonium losses to waste and at least comparable fission product decontamination. To achieve satisfactory performance at this low concentration of FS, the acidity in the 1B mixer-settler was reduced by using a "split-scrub" - a low acid scrub in stage one and a higher acid scrub in stage three - to remove acid from the solvent exiting the 1A centrifugal contactor.

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PLUTONIUM-URANIUM SEPARATION IN THE PUREX PROCESS USING MIXTURES OF HYDROXYLAMINE NITRATE AND FERROUS SULFAMATE

INTRODUCTION

In all Purex processes the plutonium is reduced to Pu(III) at the point in the process where plutonium is separated from uranium. The reductant used at the Savannah River Plant from 1954 to 1978 was ferrous sulfamate (FS). The principal advantage of FS is that it gives very rapid reduction of Pu(IV) to Pu(III) even in moderately strong nitric acid. However, FS has a major disadvantage; it is consumed in the large mixer-settler of the Purex first cycle greatly in excess of its stoichiometric requirement and adds considerably to the volume of waste.

In the Purex second plutonium cycle, laboratory and plant testing completed in 1970 led to the use of hydroxylamine nitrate (HAN) as a replacement for hydroxylamine sulfate for plutonium reduction. This work indicated that HAN might also have application in the first solvent extraction cycle where the plutonium-uranium separation takes place(1). HAN is a desirable reductant because when fed to the evaporator in normal waste processing, it oxidizes to gases and contributes no salts to waste. Since little information was available on its properties, laboratory and plant studies were made to determine if HAN could be used in the first cycle to reduce the required amount of ferrous sulfamate.

DISCUSSION

Flowsheet

The overall SRP Purex flowsheet is shown in a simplified schematic in Figure 1. A solution of dissolved irradiated targets of depleted uranium is clarified and then processed through solvent extraction. The first solvent extraction cycle cleanly separates uranium from plutonium and provides the initial decontamination from fission products. The partially purified aqueous streams of plutonium and uranium coming out of the first cycle are each processed through one additional solvent extraction cycle for further fission product decontamination.

Two types of solvent extraction equipment are used. The first "bank" (1A) consists of eighteen centrifugal contactors; all others are mixer-settlers that use gravity for the phase separation. The centrifugal contactors were designed at SRL(2) and were installed in the plant in 1966(3). The principal advantage of centrifugal contactors is that they give much less solvent radiation exposure than other types of solvent extraction equipment. Figure 2 shows in more detail the single-scrub flowsheet used in the Purex first cycle from 1954-1981.

First cycle feed (1AF) containing uranium, plutonium, and fission products enters stage 10 of the 1A centrifugal contactor (1ACC). Plutonium, uranium, and some HNO_3 are extracted into the 1AX solvent (30 vol % tributyl phosphate in n-paraffin diluent). The solvent is scrubbed with 3M HNO_3 (1AS stream) to remove fission products before leaving the 1ACC enroute to the 1B mixer-settler. Fission products exit the 1ACC in the aqueous waste stream (1AW).

The 1AP solvent stream containing uranium and plutonium is fed to stage 11 of the 1B mixer-settler. The reductant in the 1BX stream reduces Pu(IV) to the inextractable Pu(III). The aqueous phase can then strip plutonium from the solvent, thereby effecting a partitioning of plutonium from uranium. The aqueous plutonium stream is scrubbed with solvent (1BS) to remove traces of uranium. Typically the plutonium in the 1BP stream contains less than 50 ppm uranium and the uranium in the 1BU stream contains less than 10 ppb plutonium. FS alone at about 0.12M to 0.14M (depending on the Pu concentration) was used as the reductant from 1954-1977, but a mixed reductant of FS and HAN has been used since 1978.

Reductant Chemistry

As stated previously, ferrous ion rapidly reduces plutonium from plutonium (IV) to the inextractable plutonium (III).

$$Fe^{+2} + Pu^{+4}\text{ (solvent)} \longrightarrow Pu^{+3}\text{ (aqueous)} + Fe^{+3} \qquad 1)$$

Sulfamate acts as a "holding reductant" by rapidly destroying nitrite which is radiolytically generated from nitrate.

$$NH_2SO_3^{-1} + NO_2^- \longrightarrow N_2 + SO_4^{-2} + H_2O \qquad 2)$$

This minimizes (but does not eliminate) unwanted oxidation of iron (II) and plutonium (III).

$$Fe^{+2} + NO_2^- + 2H^+ \longrightarrow Fe^{+3} + NO + H_2O \qquad 3)$$

$$Pu^{+3} + NO_2^- + 2H^+ \longrightarrow Pu^{+4} + NO + H_2O \qquad 4)$$

This system works well except that the concentration of FS in the 1BX stream required to maintain plutonium (III) throughout SRP's large 1B mixer-settler was 0.12 to 0.14M depending on the plutonium concentration. This is far in excess of the stoichiometic amount. Excess consumption has been observed in all Purex operations, but is influenced by holdup time and volume. SRP's large mixer-settlers particularly aggravate the problem. Since all of the FS added ends up as ferric and sulfate salts in waste, the FS (when used alone) was responsible for about 290 to 340 liters of neutralized waste concentrate per metric ton of uranium processed.

HAN was adopted as the plutonium reductant in the Purex second cycle during the early 1970's(1). Based on this experience, an investigation was started to determine HAN's suitability for the uranium-plutonium partitioning in the higher acid first cycle. HAN had been shown to reduce not only plutonium (IV), but also iron (III).

$$2\ NH_3OH^+ + 4Pu^{+4} \longrightarrow 4Pu^{+3} + H_2O + N_2O + 6H^+ \qquad 5)$$

$$2\ NH_3OH^+ + 4Fe^{+3} \longrightarrow 4Fe^{+2} + H_2O + N_2O + 6H^+ \qquad 6)$$

These reactions are slower than 1) and 2), but they are much faster at lower acidity.(1,4) (It also destroys nitrite, but the reaction is slower at lower acidity.(5)) This suggested it might be possible to use a mixture of FS-HAN, with much lower FS concentration, instead of FS alone in the first cycle.

Laboratory Data

Laboratory experiments were conducted to:

- Determine the rate of plutonium reduction by HAN as a function of nitric acid concentration.
- Evaluate the effect of iron on plutonium reduction by HAN at high nitric acid concentrations.
- Verify HAN stability at the temperature and acidity to be used in the first cycle.
- Determine minimum concentrations of nitric acid (without nitrous acid present) needed to produce rapid and safe decomposition of HAN during waste evaporation.
- Establish the minimum concentration of nitrous acid (with varying nitric acid) needed to decompose HAN so that plutonium can be adjusted to Pu(IV) in the feed preparation step for the second plutonium solvent extraction cycle.

Earlier work(1) established that the rate of Pu(IV) reduction by HAN decreases sharply with increasing nitric acid concentrations, as shown in Figure 3. Barney(4) subsequently studied this reaction, and showed the rate to be an inverse function of the fourth power of the hydrogen ion concentration:

$$\frac{-d[Pu(IV)]}{dt} = \frac{K'\ [Pu(IV]^2\ [NH_3OH^+]^2}{[H^+]^4\ [Pu(III)]^2\ (K_d + [NO_3])^2}$$

where K' is the reaction constant, and K_d is the dissociation constant for $Pu(NO_3)^{+3}$. This rate dependance on acidity is of major significance because it indicated HAN's effectiveness could be sharply improved by reducing aqueous acidity in the 1B mixer-settler. At that time the aqueous acidity was 2.0 to 2.2M in about six stages (Figure 4).

The reduction rate of ferric to ferrous ion by HAN at different HNO_3 concentrations was measured for conditions pertinent to our process as shown in Figure 5. Ferric nitrate, HAN, and HNO_3 were mixed to make solutions of 0.22M iron, 0.35M HAN (initial), and varying concentrations of HNO_3. HAN concentration decreased as expected as Fe^{+2} molarity increased; otherwise HAN was stable. The data confirmed the reduction rate was faster at lower acidity and lower ferrous to ferric ratios. This data indicated that there would be some beneficial continuous replenishment of ferrous ion by HAN reduction of ferric ion in the 1B mixer-settler. The rate of ferric ion reduction by HAN was subsequently studied by Bengtsson(6). The effect of this reaction on the rate of Pu(IV) reduction was found to be quite significant as shown in Figure 6.

HAN stability at the temperature and acidities expected in the 1B mixer-settler was verified. The mixer-settler operates with feed streams controlled at about 45°C, and the aqueous residence time per stage is about 15 to 20 minutes. Therefore, data were needed to show HAN stability for longer than 2 hours at 40°C in acidities up to at least 2.2N HNO_3. Experiments conducted at 2.4-2.6M HNO_3 and 0.2M HAN at 50°C produced autocatalytic decomposition of HAN after 62 hours; however at 40°C, no decomposition was noted after 64 hours.

Plant use of HAN offered a potential hazard that had to be avoided; HAN fed to an evaporator in a low acid stream will concentrate along with the acid until the acidity is high enough to initiate the autocatalytic decomposition. If the HAN concentration prior to the time of its decomposition were high enough, this could cause pressurization of the evaporator and expel solution from the evaporator.

Laboratory experiments were conducted to determine the minimum nitric acid concentration at which HAN would rapidly (and therefore safely) decompose as it was being fed at low concentration to evaporators. The decomposition of HAN in different boiling HNO_3 concentrations is shown in Figure 7. Solutions of nitric acid and HAN (0.02 and 0.05M) were mixed; solutions were brought quickly to boiling, immediately cooled and analyzed. In every case, either all the HAN was still present or none was found. 1.0 molar nitric acid was found to be the concentration at which HAN decomposition occurs; therefore plant operating limits were set at 2.0M acid as a conservatively safe concentration for nitric acid in the evaporator to ensure rapid and safe decomposition of HAN as fed to the evaporators.

The plutonium stream, 1BP, from mixer-settler 1B is subsequently treated with sodium nitrite to destroy residual ferrous sulfamate and oxidize plutonium to Pu(IV). Experiments were performed to determine conditions that would assure HAN destruction during this feed adjustment for the second plutonium cycle. Barney(5) indicated that nitrous acid reacts mole for mole, with HAN,

$$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O \qquad 7)$$

and that the initial kinetics follows the equation

$$\frac{-d[HNO_2]}{dt} = k[HNO_2]\,[NH_3OH^+]\,[H^+]$$

Laboratory experiments indicated that a ratio of nitrous acid (or nitrite ion) to HAN of at least 3/1 is needed to ensure HAN decomposition within 10 minutes. These results are consistent with earlier data by Swanson(7). Larger ratios, as shown in Figure 8, are needed to ensure faster decomposition.

Miniature mixer-settler tests were performed during 1974-75, testing flowsheets containing HAN-FS in the 1BX stream. Results were encouraging, even though it was recognized that the miniature tests did not simulate plant conditions in several respects. These included radiolytic effects, residence times, and stage efficiencies. Figure 9 shows the results of one test run. The test data demonstrated that the plutonium distribution in the 16 stage 1B mini-mixer-settler was normal at a 1BX concentration of 0.05M FS - 0.10M HAN. This supported the conclusion that the addition of HAN would make it possible to reduce FS from the standard 1BX concentration range then being used (0.12 to 0.14 M).

Plant Testing Without Split-Scrub

Several plant tests were made with mixtures of HAN and FS as the reductant for plutonium in the Purex first cycle 1BX stream (See Figure 2 Flowsheet) from 1978-1981. Actual operating time was about 15 months.

Good performance was demonstrated for a 1BX concentration of 0.08M FS - 0.056M HAN at a 1AS HNO_3 concentration of 3.0M. First cycle operating performance was satisfactory and 1BP product contained less than 100 parts uranium per million parts plutonium (ppm), which was the analytical limit of detection. The volume of neutralized low activity waste generated by FS was reduced by 33%, compared to comparable pre-1978 operation. This is equivalent to a net waste reduction of 97 liters/metric ton uranium (MTU). Details of results are given in Table 1.

Under these conditions some plutonium refluxing was experienced as indicated by a buildup of plutonium inventory in the 1B mixer-settler as measured by neutron monitors. This happened when the 1BX-FS concentration was lowered from 0.08M to 0.07M while using 3.0M HNO_3 in the 1AS stream. Samples of 1BP taken during reflux showed approximately 0.03M ferrous concentration compared to the 0.05 to 0.06M that would be expected under non-reflux conditions. The sulfamate concentration was only 0.02-0.03M. These data suggested that the sulfamate ion concentration, which acts as a "holding reductant" by reacting with nitrite ion, was too low at the lower FS concentration to provide adequate protection for the HAN-Fe^{++} reductant. Reflux occurred at 0.07M FS even when the 1BX-HAN concentration was increased from 0.056 to 0.098M. The mixer-settler plutonium inventory returned to normal within 4 hours after the 1BX-FS concentration was raised to 0.14M.

Nitric acid in the 1B mixer-settler comes primarily (90%) from the 1AS stream by extracting into the solvent which produces the 1AP stream. Since HAN reduced both Pu^{+4} and ferric ions faster in low HNO_3 concentrations, tests were conducted using a lower 1AS HNO_3 concentration of 2.2M to reduce the 1B mixer-settler acid profile and increase the effectiveness of the HAN. This change allowed satisfactory operation at a 1BX concentration of 0.07M FS - 0.061M HAN which gave an additional waste volume reduction of 25 liters/MTU (Table 1). However, the 2.2M 1AS acid also caused plutonium losses to the aqueous waste (1AW) to increase by approximately a factor of two, from 0.25% to 0.45%. Although this plutonium loss is subsequently recovered, it was decided to try an alternative method of lowering the 1B mixer-settler acid profile to avoid this undesirable effect.

Split-Scrub Flowsheet Development

By using two scrub streams, a higher acid stream in stage 3 and a lower acid stream in stage 1, two benefits were expected. It should be possible to maintain an acid profile high enough in the 1A centrifugal contactor to keep plutonium losses low, while also reducing the acid in the 1AP solvent stream to achieve the desired lower acid profile in the 1B mixer-settler.

The modified process was modeled using the SOLVEX(8) computer code to aid the determination of the optimum acid concentrations and flow ratios for the two scrub streams. The flowsheet selected and subsequently demonstrated in the plant is shown in Figure 10. It uses a 0.08M nitric acid stream (1AS') entering stage 1, and a 3.0M nitric acid stream (1AS) entering stage 3. This gives a calculated reduction of the 1AP solvent acidity from 0.15M to 0.10M and the maximum stage acidity in the 1B mixer-settler from about 2.0M to about 1.2M as shown in Figure 4.

The computer simulations indicated that decreasing the acidity in the 1AP, hence in the 1B mixer-settler, would tend to give higher uranium contamination in the plutonium product stream (1BP). However, as shown in Figure 11, the calculated increase in U content (U/Pu) was only a few parts per billion. It was recognized, however, that the quantitative reliability of the calculation was questionable even though the relative effects or trends were reliable.

The proposed split-scrub flowsheet was successfully demonstrated in 1981 in miniature mixer-settlers. Successful runs were made at 0.04M FS - 0.56M HAN in the 1BX stream. This suggested that it might be possible to attain an additional 50% reduction in FS usage in the plant compared to the then current mixed reductant flowsheet (0.08M FS - 0.056M HAN), without compromising product quality.

A comparison of concentration profiles from computer simulation to those obtained from sampling during the miniature mixer-settler runs showed only minor variations. This can be seen in figures 12, 13, and 14.

Plant Testing of Split-Scrub HAN-FS Flowsheet

Beginning in 1982, the split-scrub flowsheet was tested in the plant using mixtures of HAN-FS in the 1BX, as shown in Figure 10. Initially, the FS concentration was set conservatively at 0.08M, but was reduced stepwise. Good performance was demonstrated for a 1BX concentration of 0.04M FS - 0.056M HAN. First cycle operating performance was satisfactory and the plutonium in the 1BP product stream contained less than 100 ppm uranium.

This provided important confirmation that this lower acid profile in the 1B mixer-settler still allowed acceptable Pu/U partitioning. The 1BP acidity was 1.0-1.1M compared to the 0.9M SOLVEX estimate and the 0.6M value predicted from the miniature mixer-settler testing. Some plant data indicate that if the 1BP acidity drops to 0.8 to 1.0, the uranium contamination in the 1BP increases to about 200 ppm U/Pu.

Operation at 0.04M FS reduces waste volume from the FS by 194 liters/MTU compared to operation at 0.12M FS (Table 1). At the present costs of chemicals and interim waste processing, this is equivalent to a net cost saving of $288,000/1000 MTU processed. For permanent waste processing, it is about $\$10^6$/1000 MTU.

Plutonium losses to the 1AW stream leaving the 1ACC averaged about 0.10% while using the split-scrub flowsheet. Losses had typically been about 0.25% with the conventional flowsheet (these "losses" are subsequently recovered by anion exchange). The improvement is attributed to the higher HNO_3 concentration profile in the extraction section of the 1ACC which the split-scrub makes possible.

Fission product decontamination factors (DF) in the 1ACC were satisfactory. Limited data indicate zirconium-95 DF improved to about 1000 from 500-1200 (800 average) for the conventional flowsheet. The apparent improvement is attributed to the lower HNO_3 concentration in stages 1 and 2 of the 1ACC.

This program to reduce waste by the use of HAN is continuing, and it is hoped that the FS in the 1BX stream can be reduced below the 0.04M concentration by further manipulation of 1B bank acidity, HAN concentration, or temperature.

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TABLE 1

Summary of 1B Mixer-Settler Test Results
With Hydroxylamine Nitrate - Ferrous Sulfamate

	FS Only Pre-1978	Test of HAN-FS Without Split-Scrub			Test of HAN-FS With Split-Scrub	
		1978-1981	1979-1980		1982	
1AS' nitric acid, M	-	-	-	-	0.08	0.08
1AS nitric acid,[a] M	3.0	3.0	2.2	3.0	3.0	3.0
1BX or 1BP volume, L/MTU	1741	1741	1741	1741	1741	1741
1BX concentration,[b] M						
FS	0.12	0.08	0.07	0.07	0.08	0.04
$SO_3NH_2^{-1}$	0.25	0.17	0.15	0.15	0.17	0.09
HAN	---	0.056	0.049	0.098	0.056	0.056
1BP concentration, M						
Fe^{+2}	0.06	0.06	0.07	0.04[e]	0.07	0.03
$SO_3NH_2^{-1}$	0.14	0.08	0.07	0.03	0.10	0.04
HAN	---	0.04	0.025	0.075	0.027	0.04
Neutralized LAWC,[c] L/MTU	291	194	170	170	194	97
Processing cost[d], $/MTU						
Waste storage	435	290	254	254	290	145
Cold Chemicals	99	130	115	173	130	101
Total Cost	534	420	369	427	420	246
Net Cost Saving, $/MTU	---	114	165	107	114	288

[a] 3.0M HNO_3 gives a maximum acidity of 2.0M in the 1B mixer-settler; split-scrub flowsheet gives maximum acidity of approximately 1.2M (Fig 4).

[b] Ferrous sulfamate (FS); sulfamate ($SO_3NH_2^{-1}$) present as FS plus free sulfamic acid (0.01M); hydroxylamine nitrate (HAN). Concentrations are nominal flowsheet values.

[c] Low activity waste concentrate (28% solids) resulting from neutralizing HNO_3; solids are also formed by reaction of FS with $NaNO_2$.

[d] Interim storage cost based on $5.65/gal of waste shipped to Building 241-F. Cold chemical cost is $0.38/lb 50% FS and $0.51/lb 16% HAN. All costs quoted for 10/81.

[e] Test stopped due to plutonium reflux; 1BP analyses reflect samples taken during reflux.

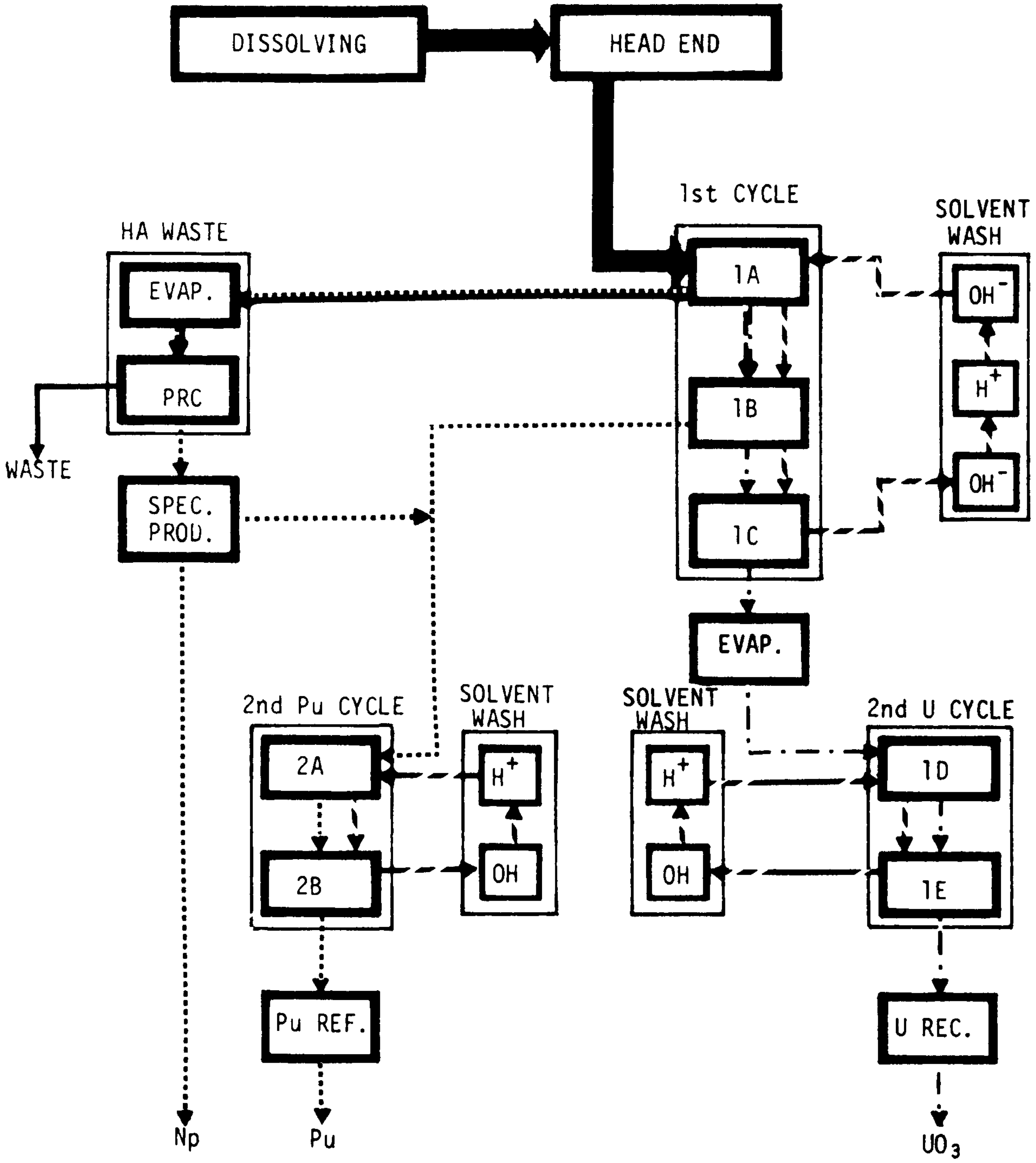
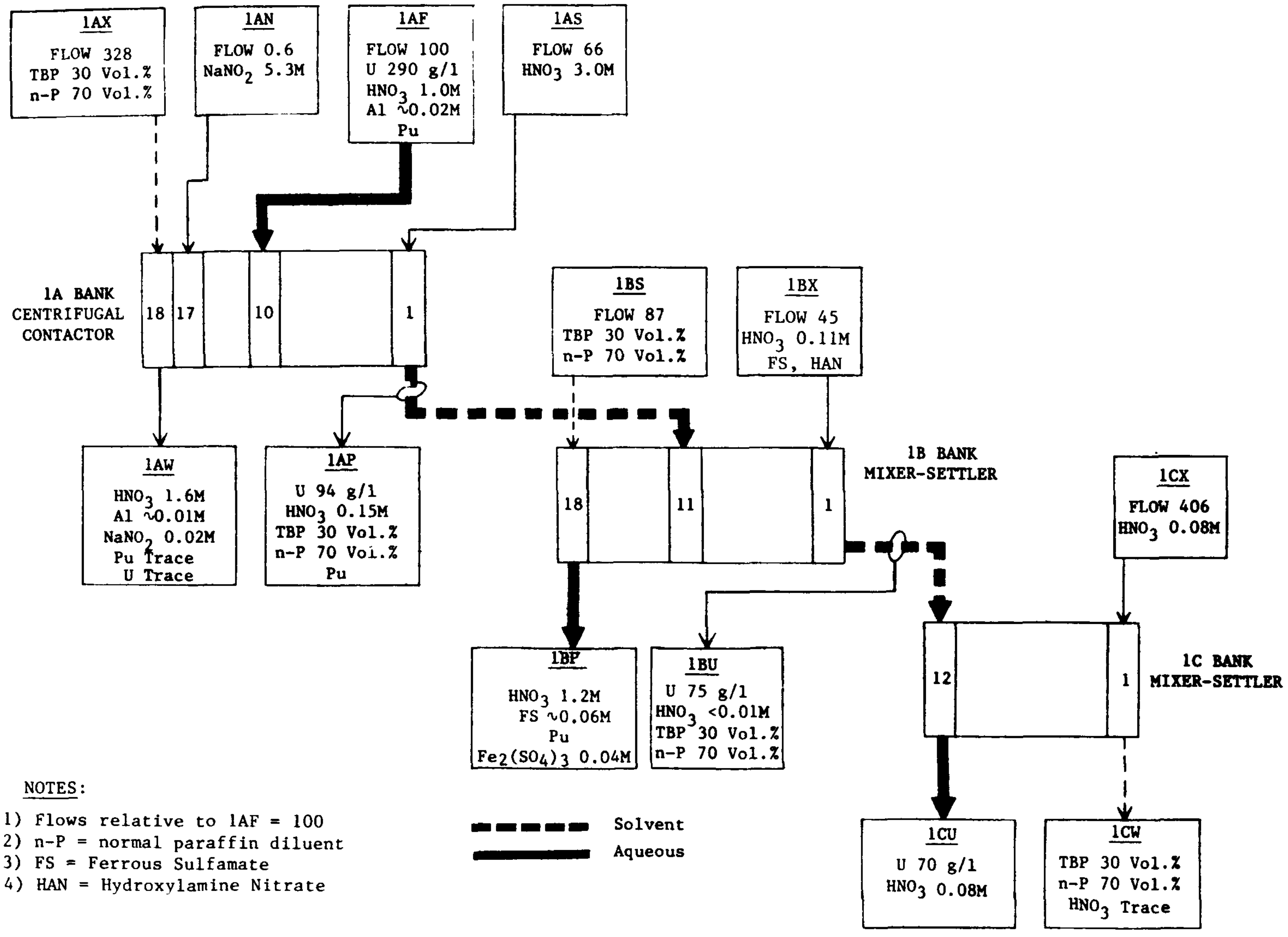


FIGURE 1. SRP Purex Process



NOTES:

1) Flows relative to 1AF = 100
2) n-P = normal paraffin diluent
3) FS = Ferrous Sulfamate
4) HAN = Hydroxylamine Nitrate

FIGURE 2. First Solvent Extraction Cycle, Standard Flowsheet (1954-1981)

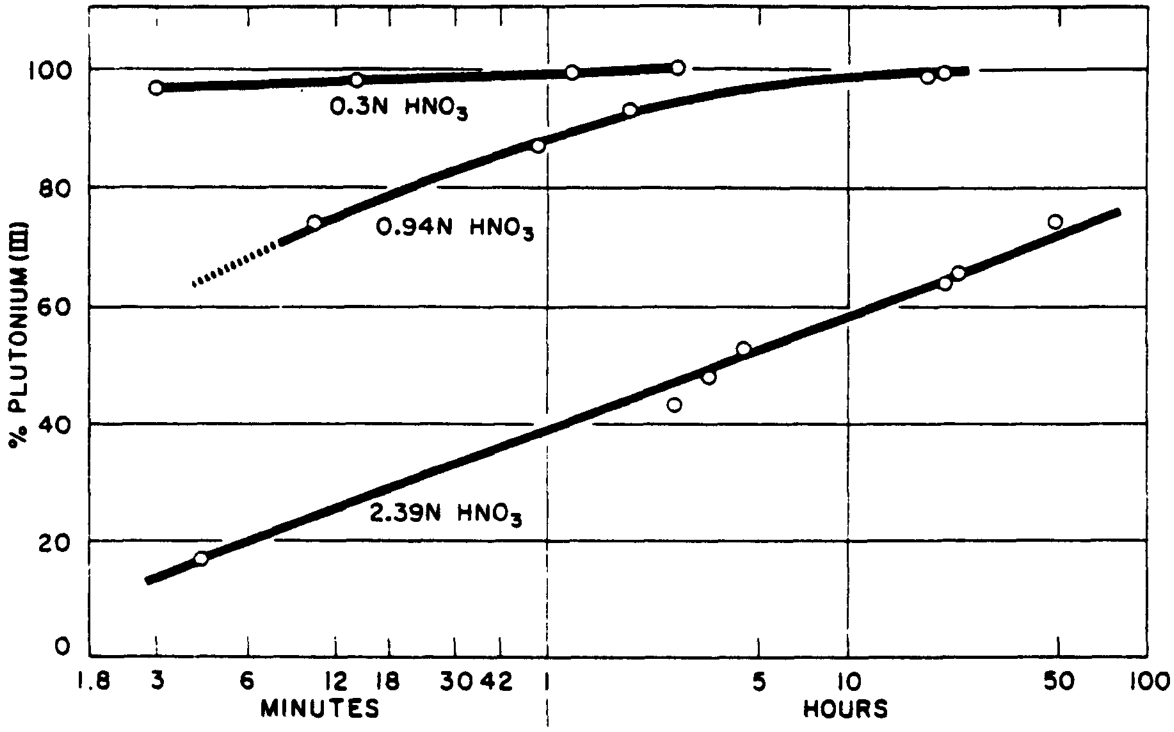


FIGURE 3. Effect of HNO_3 on Rate of Hydroxylamine Nitrate Reduction of Pu(IV)

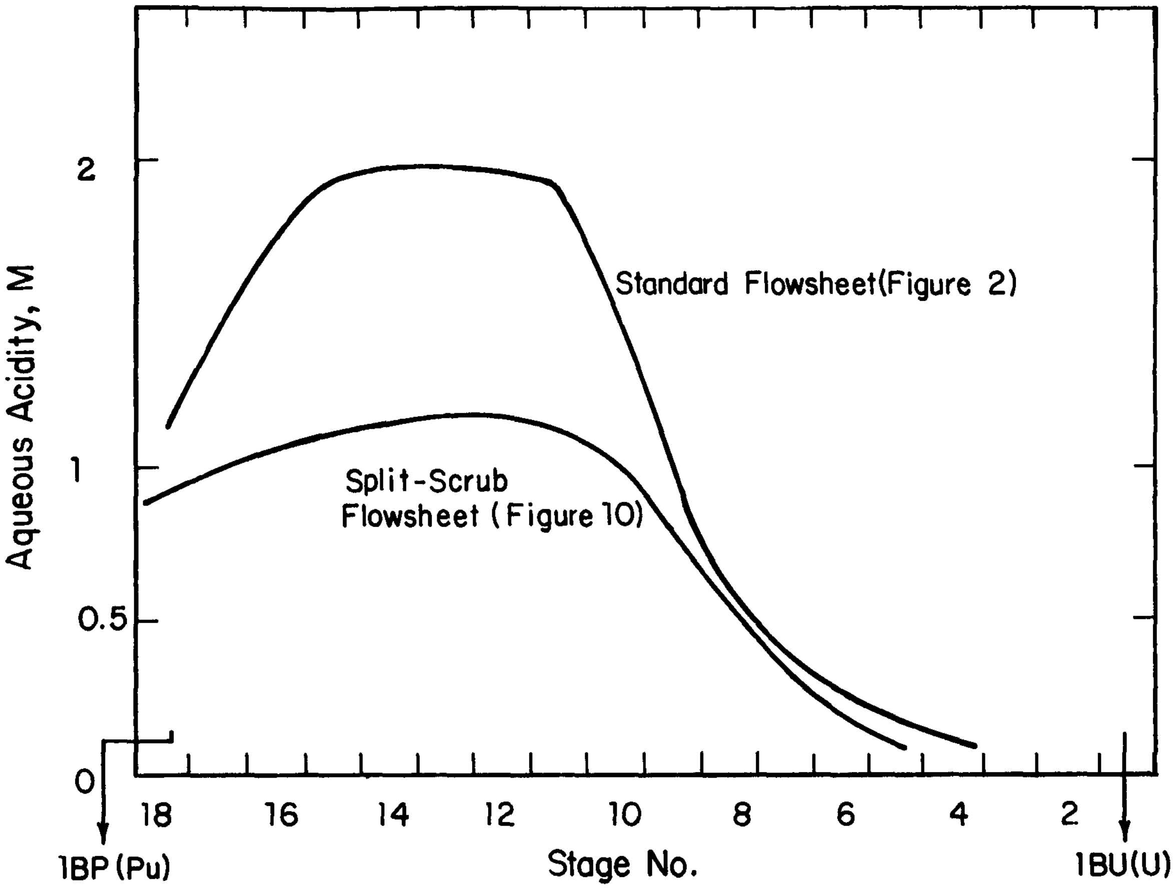


FIGURE 4. Acid Profiles of 1B Mixer-Settler

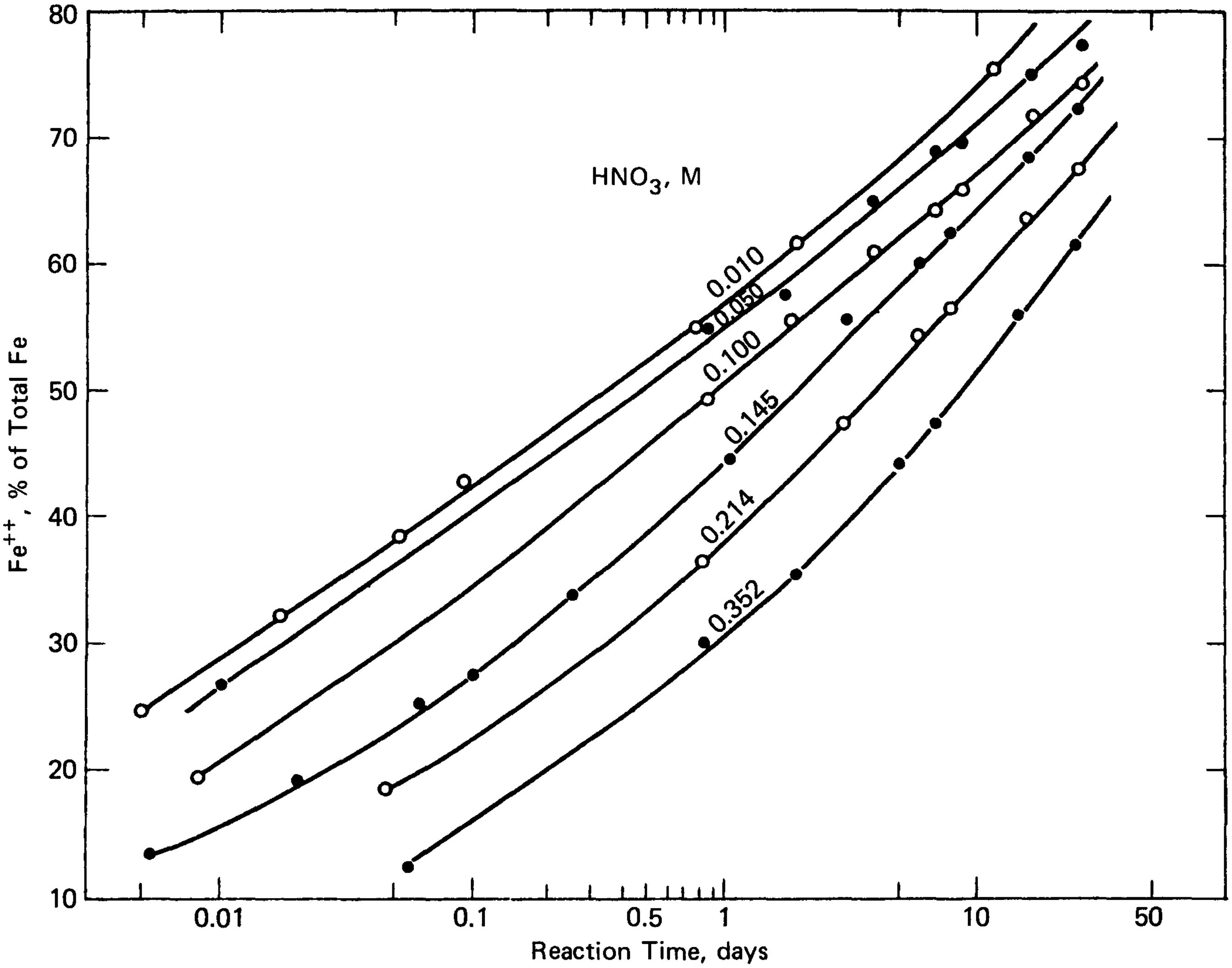


FIGURE 5. Rate of Ferric Reduction to Ferrous in 0.24-0.35M HAN at Various HNO_3 Concentrations. Note: Total Fe = 0.22M.

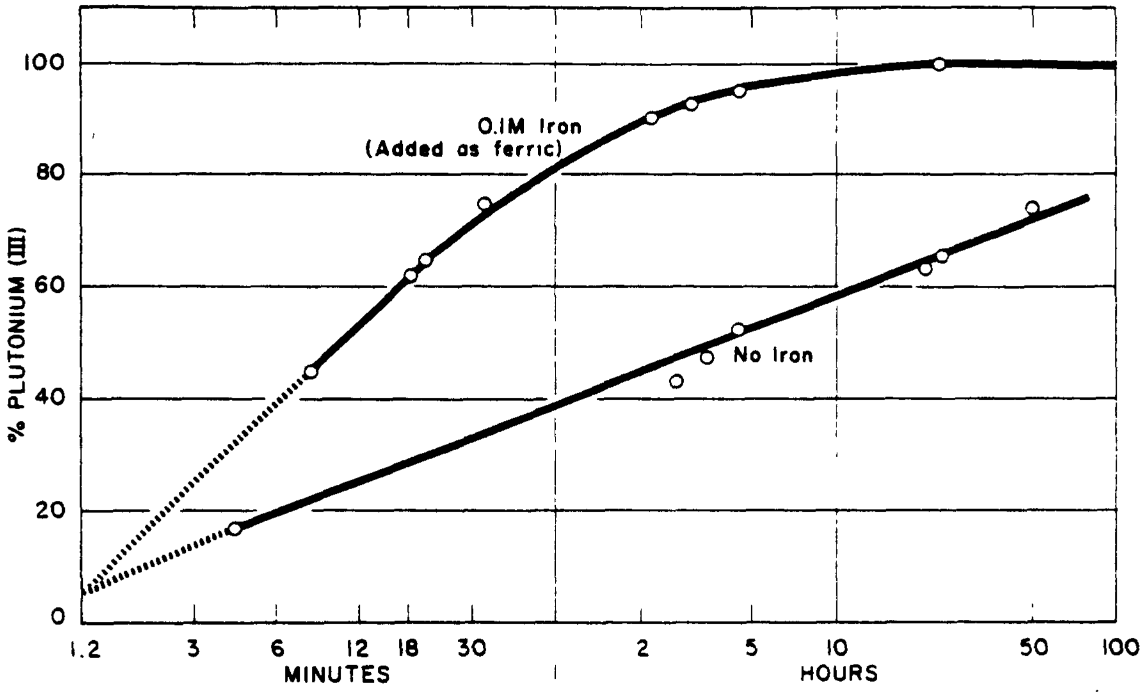


FIGURE 6. Effect of Iron on Rate of Pu(IV) Reduction by 0.1N Hydroxylamine Nitrate at 2.4N HNO_3

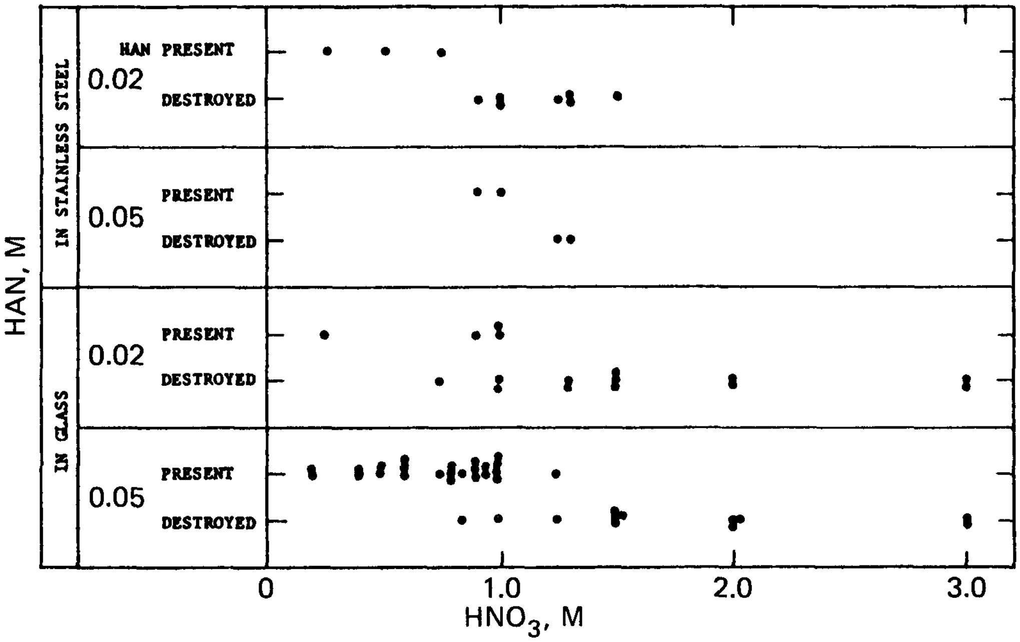


FIGURE 7. Nitric Acid Destruction of HAN.
Procedure: Solution mixed, brought to boil, removed from heat as soon as boiling began, cooled, analysed for HAN.

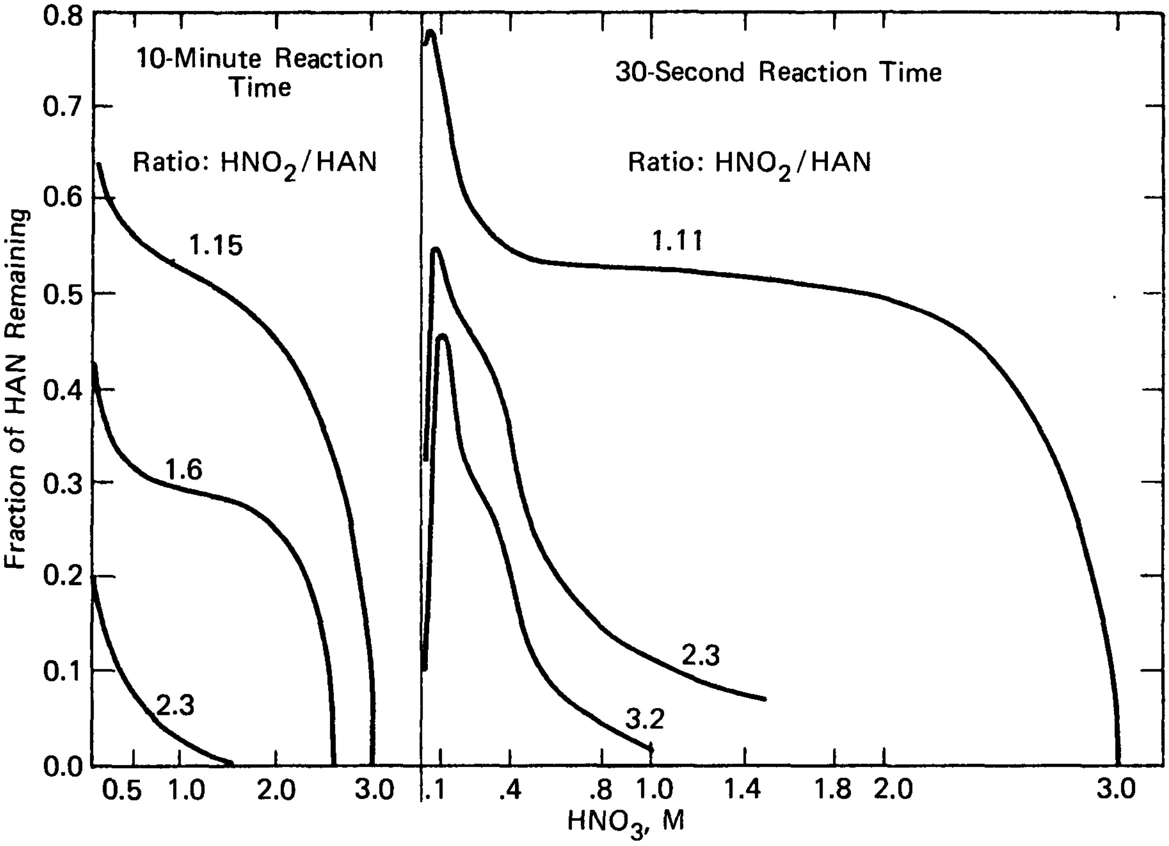


FIGURE 8. Nitrite Reaction With HAN

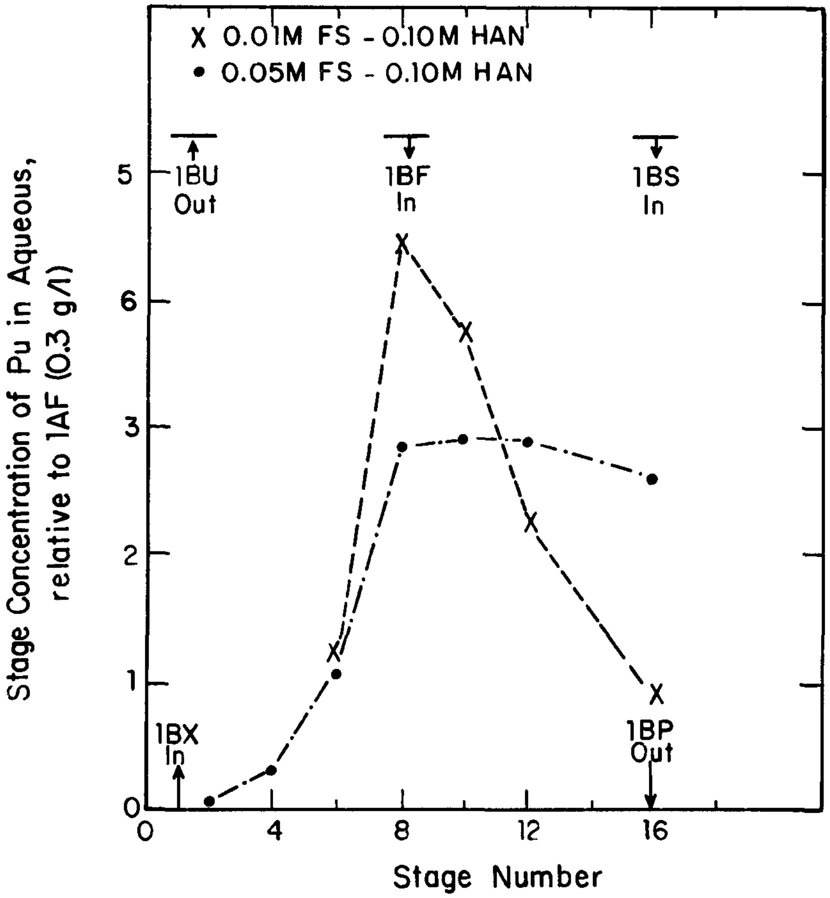
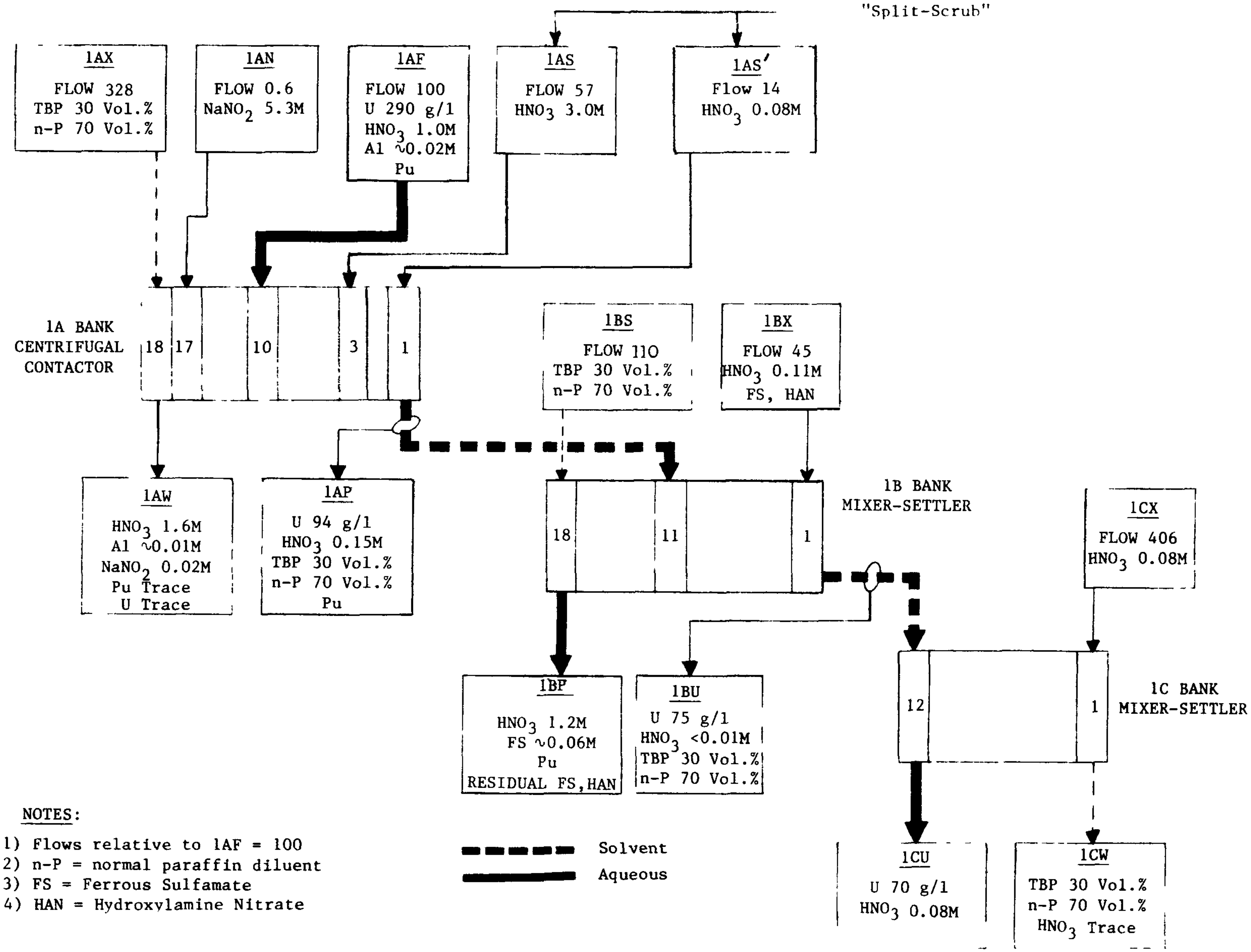


FIGURE 9. Aqueous Plutonium in Laboratory 1B Mixer-Settler



NOTES:

1) Flows relative to 1AF = 100
2) n-P = normal paraffin diluent
3) FS = Ferrous Sulfamate
4) HAN = Hydroxylamine Nitrate

FIGURE 10. First Solvent Extraction Cycle, Split Scrub Flowsheet (1982)

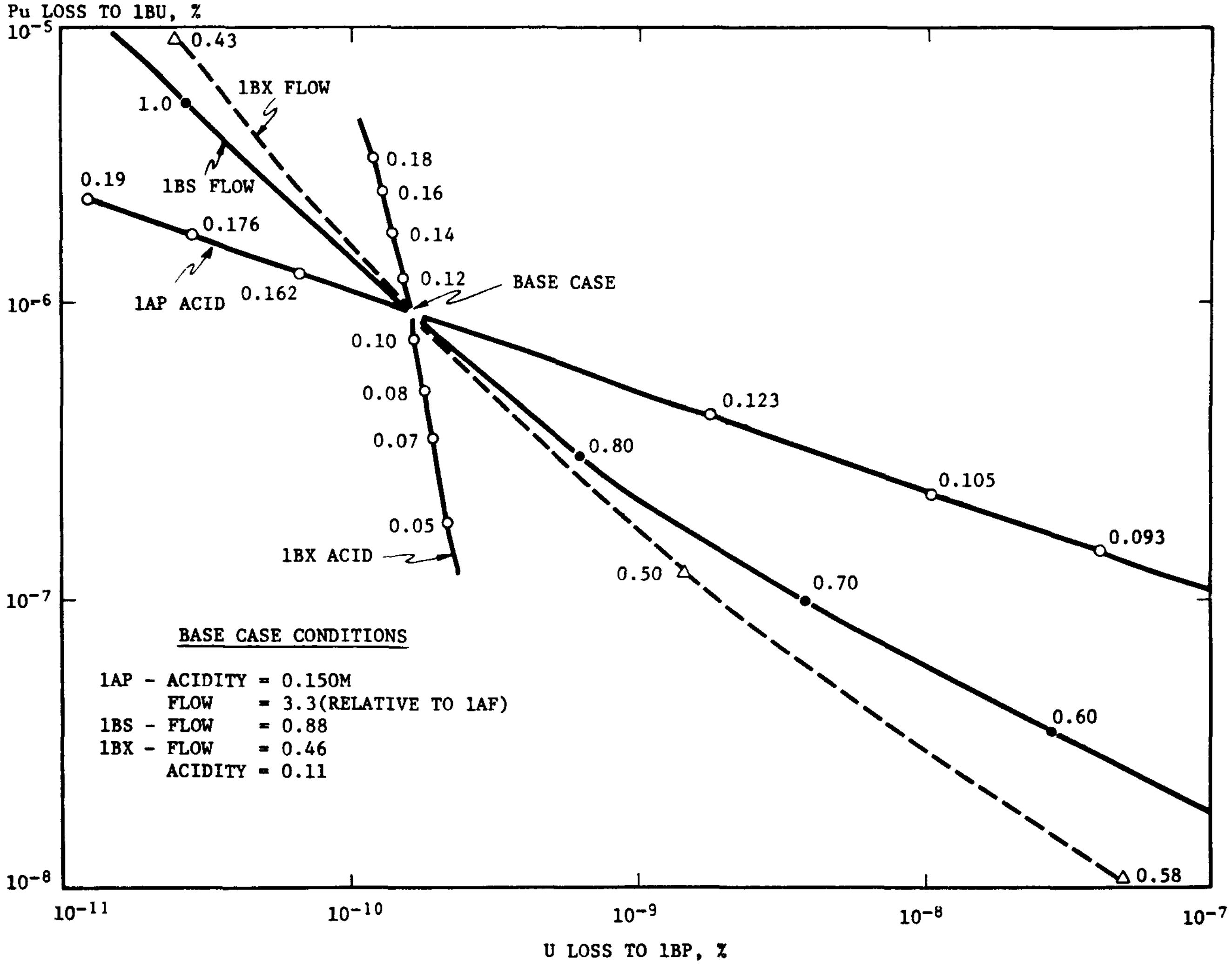


FIGURE 11. 1B Bank - Effect of Process Variables on Plutonium Loss to 1BU and Uranium Loss to 1BP

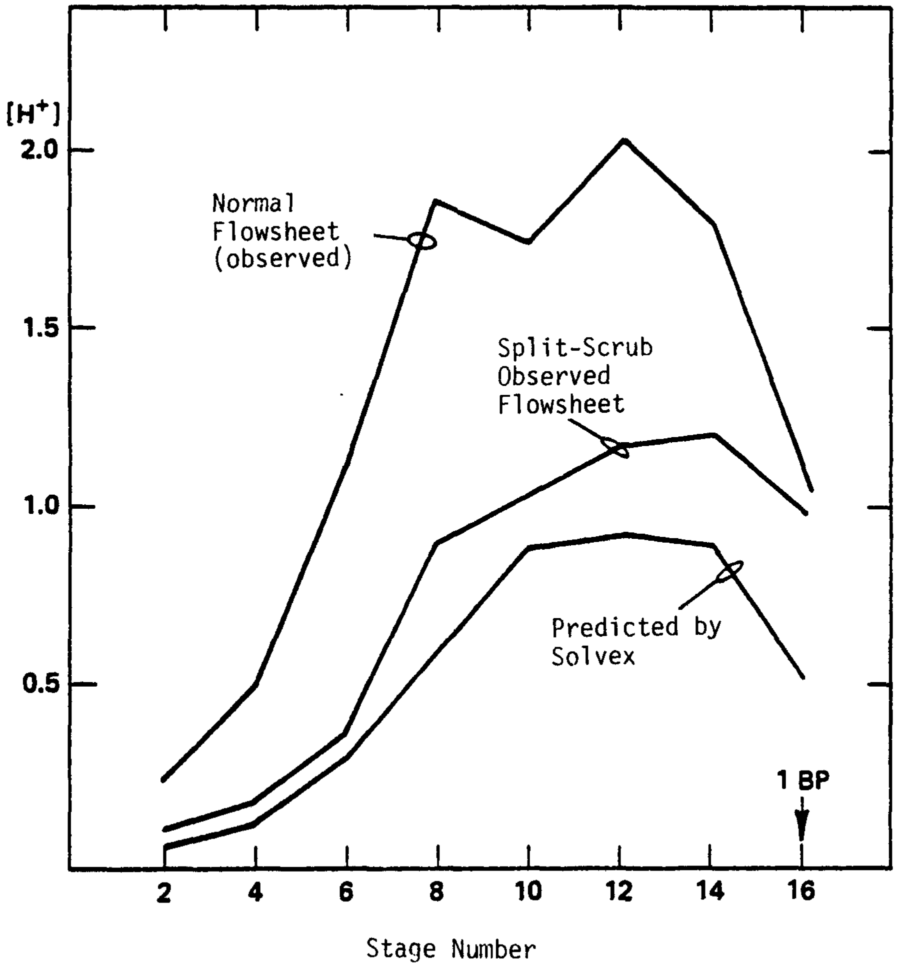


FIGURE 12. Aqueous Acidity Profiles, B-Bank From Miniature Mixer-Settler Runs

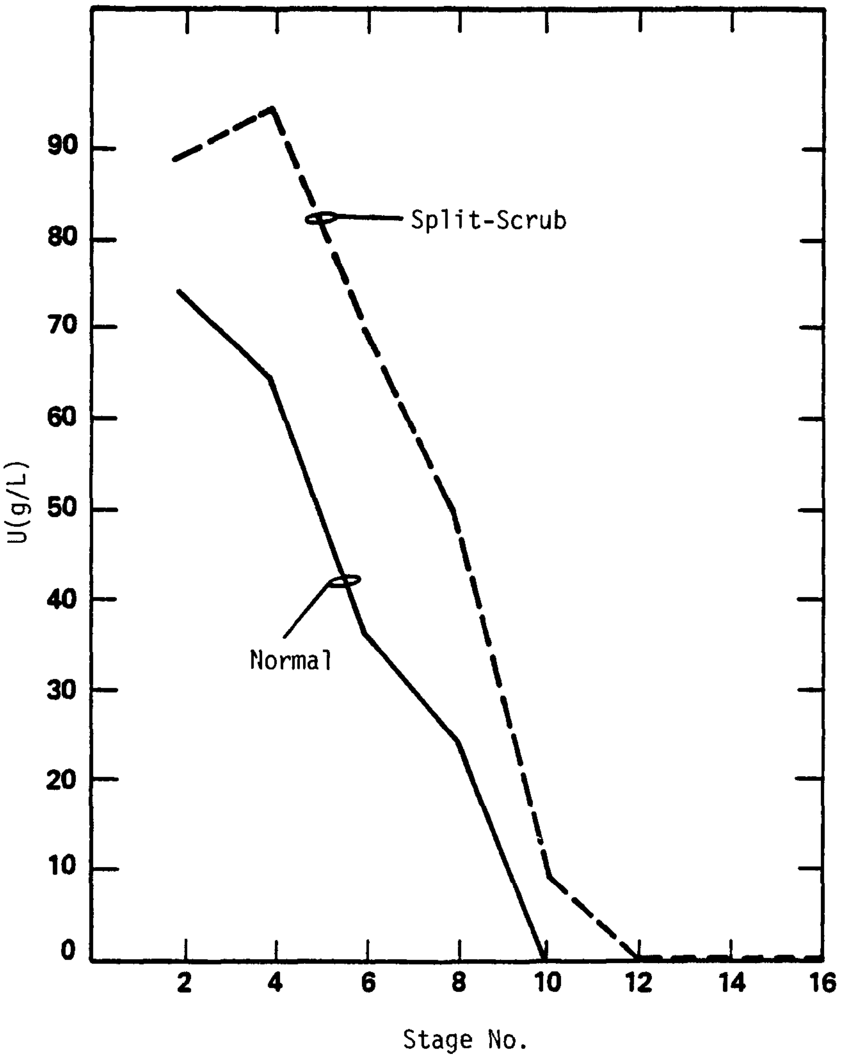


FIGURE 13. **Aqueous Phase U Profiles Observed in Miniature Mixer-Settler Runs**

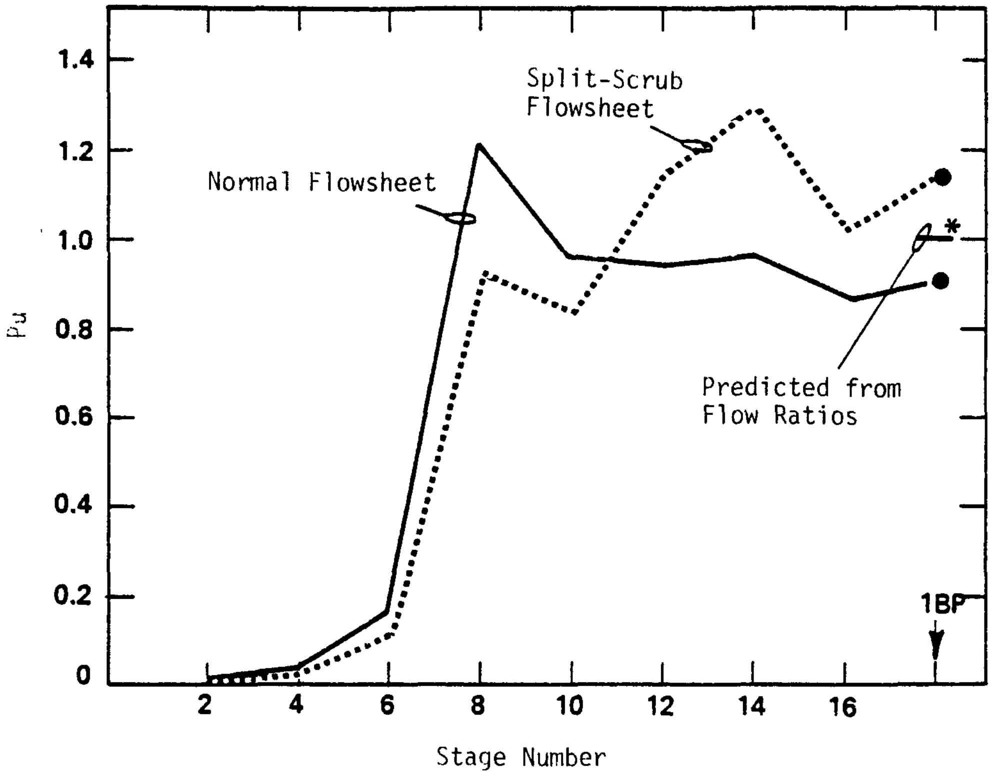


FIGURE 14. Aqueous Pu Profiles, B-Bank, From Miniature Mixer-Settler Runs