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Mark L. Crowder

Major C. Thompson

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Westinghouse Savannah River Company
Aiken, SC 29808

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Mark L. Crowder and Major C. Thompson

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APPROVALS:

Mark L. Crowder — Nov. 22, 2002
Mark L. Crowder — Date
Actinide Laboratory Programs

Major C. Thompson — 11/25/02
Major C. Thompson — Date
Actinide Technology Section

11/22/02
John H. Gray, Technical Reviewer — Date
Actinide Laboratory Programs

Alice M. Murray — November 22, 2002
Alice M. Murray, Manager — Date
Actinide Laboratory Programs

Summary

A wide range of miniature mixer-settler tests were conducted to determine the source of iron and sulfur contamination in the uranium product stream (“1EU”) of H Canyon’s 2nd Uranium Cycle. The problem was reproduced on the laboratory scale mixer-settlers by changing the feed location of ferrous sulfamate from stage D4 to stage D1. Other process variables effected no change. It was later determined that ferrous sulfamate (FS) solids had plugged the FS line to stage D4, causing FS to backup a ventline and enter the Canyon process at stage D1. Pluggage was almost certainly due to precipitation of FS solids during extended process downtime. During the search for the root cause, tests showed that FS solids were quite small (1-10 μm), and a portion of them could bypass the current Canyon prefilter (3-μm). Also, additional tests were done to find an alternate means of reducing and thereby removing plutonium and neptunium from the uranium product. These tests showed that FS was a more effective reductant than either ascorbic acid or a hydroxylamine nitrate (HAN) / dilute FS combination.

Introduction

The Savannah River Site (SRS) is working to purify highly enriched uranium (HEU) to be blended with natural uranium for eventual use as fuel in Tennessee Valley Authority (TVA) reactors. The HEU materials in this campaign[1] are typically 60-70% enriched in uranium-235, and will be blended down to 4.95% enrichment. Since the blended product must meet strict purity specifications, the HEU will be purified by solvent extraction in the 1st and 2nd Uranium Cycles of H Canyon. These cycles are part of the “HM Process”, which has been in operation since the 1960’s.

In the 1st and 2nd Uranium Cycles, FS is added to provide plutonium and neptunium decontamination. Throughout 2001, H Canyon observed iron and sulfur contamination in the uranium product solution from 2nd Uranium Cycle. (The 1st U Cycle product, which becomes the 2nd U Cycle feed, had normal iron and sulfur levels). In addition, neptunium levels in 1EU were above the specification limit. This study was initiated to address these two concerns. Since neptunium could be removed by a second pass through 2nd U Cycle, more time was spent on the iron/sulfur contamination issue. In early 2002, the source of the iron and sulfur contamination was identified by Pickett[2] as a plugged FS line. Nevertheless, this report is useful for understanding FS, its effect in the 2nd Uranium Cycle, and the usefulness of miniature mixer-settlers in resolving processing problems.

Process Chemistry

Ferrous sulfamate [$Fe(NH_2SO_3)_2$] is a strong reducing agent. Its properties are explained more fully elsewhere.[3] In the HM Process, FS is used because it reduces all plutonium in

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[1] Frushour, R.A. to L.D. Olsen, et al, “HEU Blend Program,” NMM-ETS-2002-00148, Sept. 20, 2002.

[2] Frushour, R.A., “Engineering Path Forward PF-HCAN-02-0067: Iron & Sulfur Carryover in 2nd U Cycle”, Feb. 22, 2002.

[3] Hyder, M.L., et al, <u>Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant</u>, DP-1500, April 1979.

solution to Pu(III), which does not extract into the solvent, tributylphosphate (TBP) in n-paraffin. Since uranium extracts readily into TBP with sufficient nitric acid, FS effectively separates uranium and plutonium in the solvent extraction process.

The chemistry of neptunium, however, is different than that of plutonium. Neptunium has three valence states, Np(VI), Np(IV), and Np(V), in order of decreasing degree of extraction. Np(VI) is easily extracted. When Np enters D Bank, it is reduced by FS to Np(IV). Though Np(IV) is less extractabe than Np(VI), it is significantly more extractable than Pu(III). Thus, neptunium is more difficult to remove than plutonium. This behavior is evident in the test results that follow the experimental description.

Experimental Description -- Miniature Mixer-Settler Tests

Two banks of miniature mixer-settlers were set up in a radiochemical hood. One of these mini-banks is shown in Figure 1.

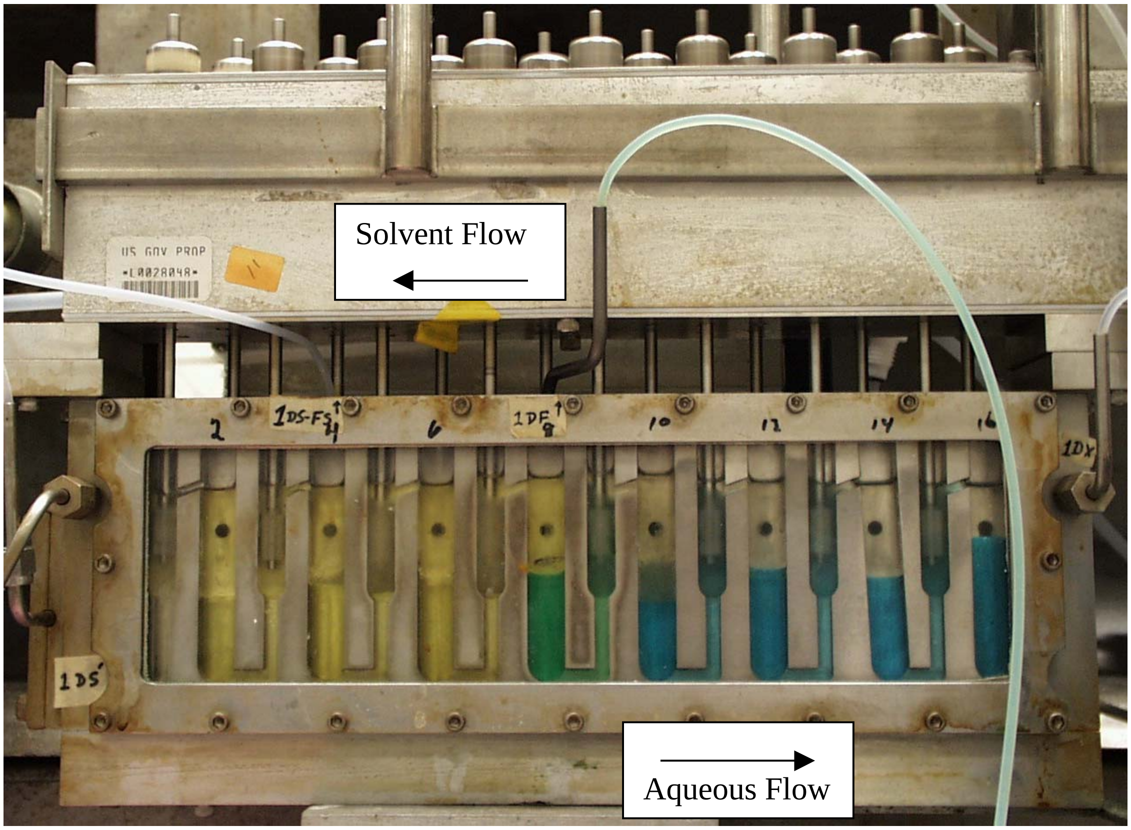

Figure 1. Miniature mixer-settler with uranium (yellow) and copper (blue) in the feed.

The flow streams to the mini-banks were specified to simulate H Canyon's 2nd Uranium Cycle. An experimental flowsheet is shown in Figure 2. Note that all mini-banks have 16 stages, while the H Canyon E Bank has only 12 stages. The additional mini-bank stages have no significant effect on the process.

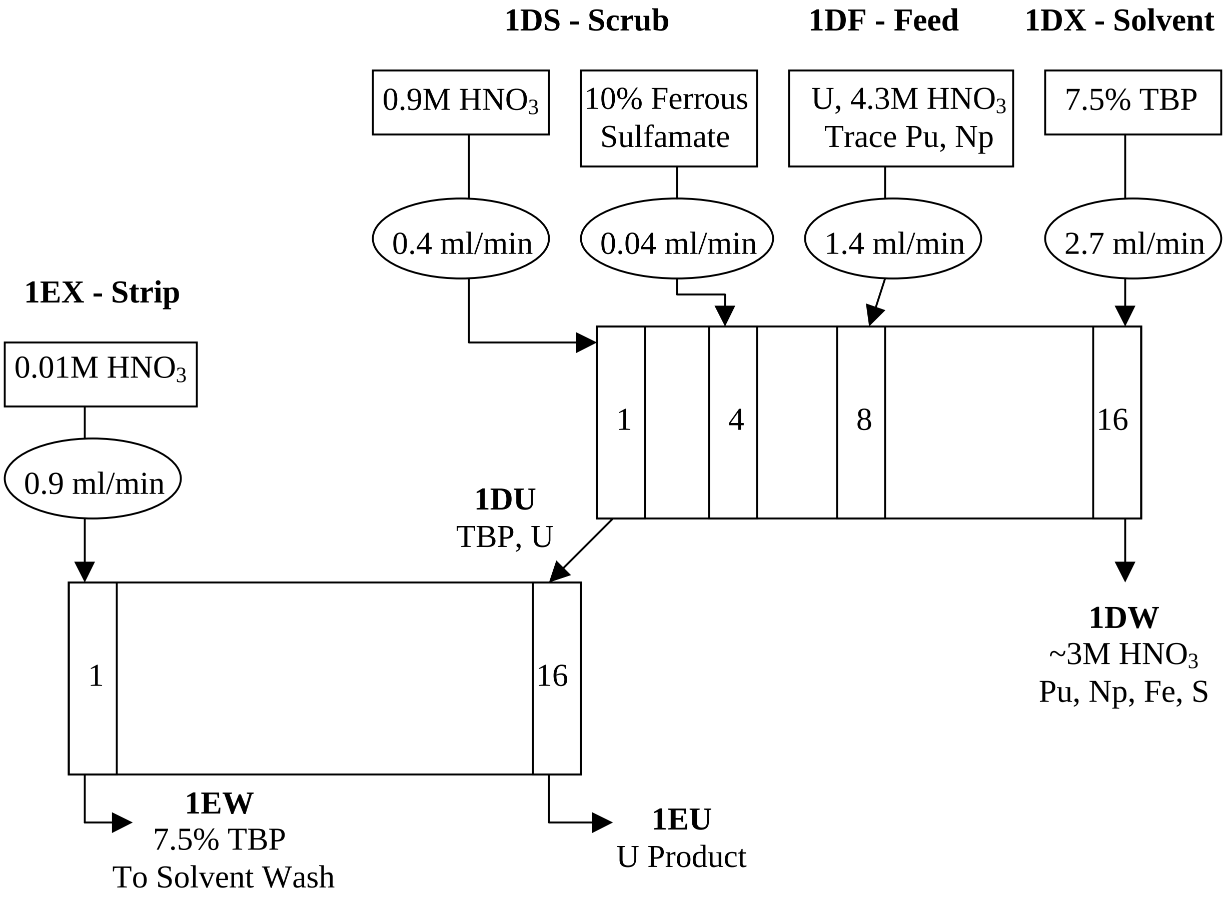

Figure 2. Schematic of 2nd Uranium Cycle: Standard Mini-bank Conditions

Piston pumps from FMI (Fluid Metering, Inc.) were used for all input streams, and special Tefzel fittings were used with the solvent pump to provide additional chemical resistance. Tubing was 1/8" Teflon, which allowed easy insert into bank openings. Graduated cylinders were modified to hold input streams. Volumes were recorded every 30 minutes to confirm flow rates. Solvent from H Canyon Tank 902 (7.5% TBP) was used. After each run, spent solvent was cleaned with 4 wt.% sodium carbonate (two 30-minute washes) followed by 0.1M nitric acid (two 30-minute washes). FS and hydroxylamine nitrate (HAN) were supplied by H Canyon. Nitric acid and ascorbic acid were reagent grade. All dilutions were by building-supplied distilled water. Experimental run sheets and results are recorded in a laboratory notebook.[4]

Optimization of Ferrous Sulfamate Concentration

The TVA specification for combined neptunium (Np) and plutonium (Pu) activity in the HEU product is 604 Bq per gram uranium (U). For perspective, a combination of 10 mg Np/kg U and 0.1 mg Pu/kg U yields roughly 600 Bq/g U with equal contributions from Np and Pu. To determine how much FS is needed, mini-bank runs were made at four different FS levels. The results are shown in Table 1, where the Baseline FS level is 0.05M FS in stage 4 of D Bank. "Decontamination factor" (DF) is the activity in the feed divided by that of the product. Table 1 assumes a 1EU product concentration of 5 g U/L, which is lower than typical values of 6-8 g U/L, and therefore yields conservative values for FS effectiveness.

Table 1. Effect of Ferrous Sulfamate Concentration in 2nd Uranium Cycle

	Pu DF	Np DF	Pu + Np (Bq/gU)	Pu + Np (dpm/mL)
Baseline	1700	780	54	16
½ FS	12,000	580	32	10
¼ FS	220	40	600	180
No FS	4	160	12,000	3600

As seen in the table, reducing the FS level by one-half had no negative impact on decontamination. In the ½ FS case, the especially high Pu DF was likely due to reduced detection limits, not better separation. However, reducing the FS level to one-fourth of the baseline significantly reduced DF and increased the total Pu + Np activity unacceptably close to the specification limit. Interestingly, the case with no FS still showed appreciable Np decontamination. This result indicates that much of the neptunium entering the process was in the +5 valence, which does not extract into the solvent phase. In the plant, Np leaves 1st Cycle as Np(IV). It is then oxidized during the evaporation step between 1st and 2nd U Cycles. Thus, the Np entering D Bank in the 1DF stream is expected to be a mixture of Np(V) and Np(VI).

Apparently, the amount of FS used in 2nd U Cycle was increased in the 1970's during low enriched uranium (LEU) processing. The initial LEU product was not shippable due to high Pu and especially high Np. After FS was increased, the necessary purity was attained. The FS was kept at the higher level when HEU processing was resumed shortly thereafter.[5] Since high purity is needed for the HEU Blenddown campaign, it seems prudent to keep FS at its current level.

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[4] WSRC-NB-99-00096, M.L. Crowder.

[5] Pickett, C., personal communication, Dec. 2001.

Stage Number

Tests were conducted to compare FS addition to stage 4 versus stage 8. The results, shown in Figure 3, demonstrate that stage 4 addition is much more effective. This result was expected, because the stage 4 addition ensures that plutonium and neptunium that are extracted in stage 8 are reduced in stages 4-7.

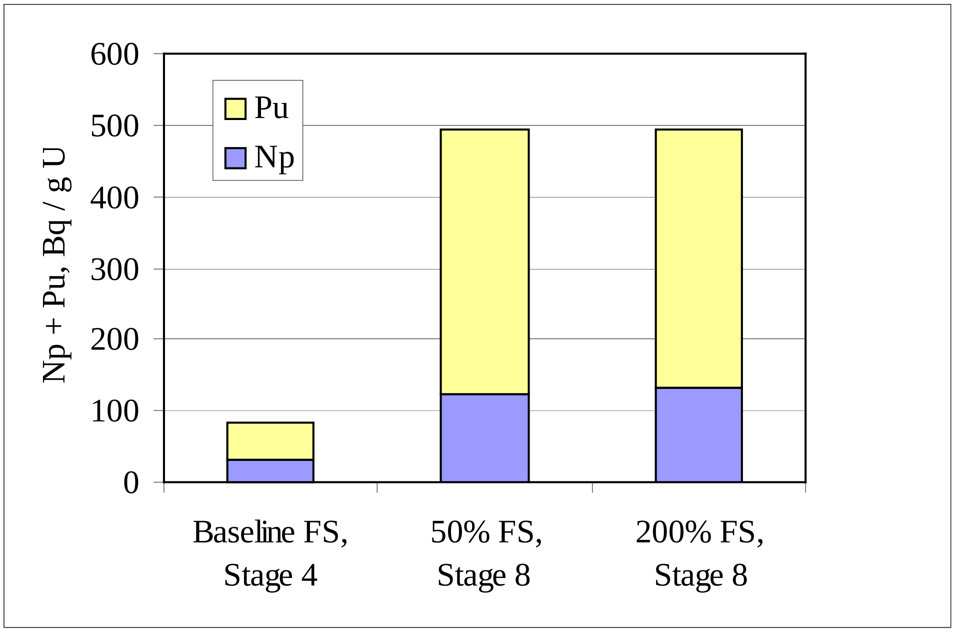

Figure 3. Comparison of Ferrous Sulfamate Addition to Different Stages

Alternate Reductants

The effectiveness of FS was compared to ascorbic acid and to mixtures of HAN and dilute FS. As seen in Figure 4, the current baseline amount of FS was more effective at neptunium and plutonium removal than any of the other combinations. Note that in Figures 3 and 4, the “Baseline FS” case is an average of five runs and 5 g U/L was used.

Process Variables

While trying to determine the source of iron and sulfur contamination in the H canyon 1EU product, mini-bank runs were made at a wide range of conditions: (1) high mixer speed (i.e., 2200-2400 rpm versus the typical value of 1500), (2) pre-evaporated feed (which ensured that all iron in the feed was in the ferric state), (3) old and new solvent, and (4) low acid (~30% below normal) in all aqueous streams. In none of these cases were significant amounts of iron and sulfur found in the 1EU product. However, a run was conducted in which FS was added to stage D1. In this case, the iron and sulfur concentrations in 1EU were 9.5 and 12.5 mg/L, respectively (or, 1900 and 2500 µg/g U at

5 g U/L). Later, Pickett[2] determined that a plugged FS feed line was causing FS addition into stage D1 of the H Canyon mixer-settlers. Once this was corrected, the iron and sulfur contamination problem was corrected.

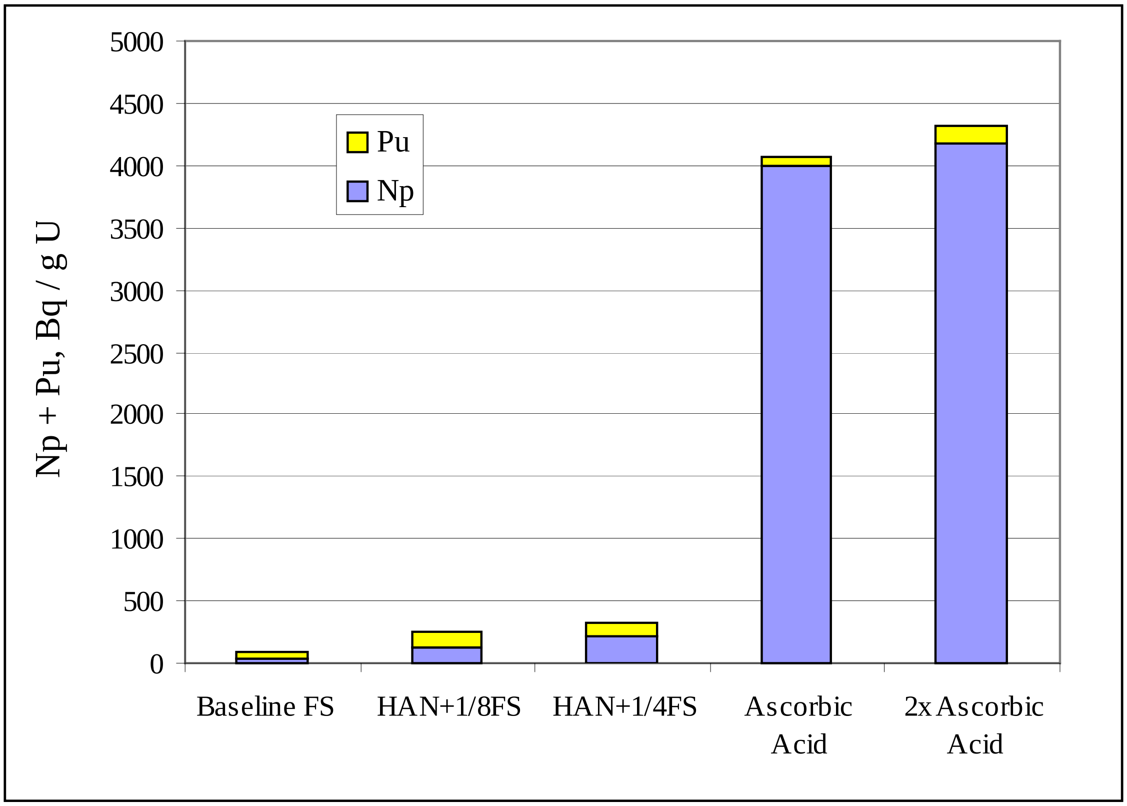

Figure 4. Comparison of Ferrous Sulfamate (FS) to Other Reductants.

Plant Tests

An order-of-magnitude difference exists between the decontamination factors (DFs) observed using miniature mixer-settlers and those observed in recent plant operations. Whereas mini-banks give DFs on the order of 1400 for plutonium and 480 for neptunium, plant runs over the past year have produced DFs on the order of 100 for plutonium and 20 for neptunium. Clearly, there are differences between the mini-banks and plant-scale mixer-settlers that affect performance. One difference is that the mini-banks give excellent phase separation, and therefore little entrainment or carryover of aqueous with organic or vice-versa. Traditionally, plant mixer-settlers are expected to have stage efficiencies of 70% along with 1 to 2 % carryover of aqueous with the organic stream. It is worth noting that the mixer-settlers of the 2nd Uranium Cycle are original H Canyon equipment, in use for nearly 50 years. Deposits of crud or scale are possible.

Plant tests to date include three runs at non-typical conditions. In the first, the impeller speeds (in D Bank) were reduced by 15%. However, this reduction did not cause an appreciable reduction in iron and sulfur contamination in the 1EU product. A second plant test was done with the Stage D1 impeller turned off. This change effectively doubled the time available for separation of solvent and aqueous phases that enter the stage D1 mixer. The result of this test was that the iron and sulfur in 1EU were cut by 50% and 40%, respectively. We know now that FS was being added to stage D1 along with the scrub acid. But iron and sulfur do not dissolve or extract into TBP. Therefore, significant entrainment or carryover of aqueous solution into E Bank (and eventually the 1EU product) must have occurred, even with the stage D1 impeller off. A third plant test has been completed in which 20% FS was used instead of the standard 40% FS solution. As expected, iron and sulfur levels in the 1EU product were significantly reduced.

Ferrous Sulfamate Solids

FS is received as a 40 wt% solution. Over time, ferrous ions oxidize to ferric ions, and precipitation follows. During 2nd U Cycle operation, an in-line filter removes the solids from the 1DS-FS stream. The solids that precipitate have been identified by x-ray diffraction as $Fe(NH_2SO_3)_2{*}4H_2O$ and $(NH_4)Fe_3(SO_4)_2(OH)_6$. A scanning electron microscope (SEM) micrograph of the solids is shown in Figure 5.

Figure 5. Solids from ferrous sulfamate solution at 10,200X. Line shown is 0.98 microns.

Particle size analyses determined that the particles are in the 1 to 10-micron range. Particle size was measured on FS solids from a dry filter cake re-suspended in water and from a slurry of solids in FS solution, and the results were essentially the same. Certainly some solids agglomerate under process conditions, and begin to form a filter cake that catches smaller particles. However, these results indicate that approximately 45% of solids are smaller than the 3-micron filter currently used for the 2nd U Cycle. These fine solids would tend to have low settling velocities, and could therefore be suspended and carried over in the solvent. When added to stage D1, FS solids may have been entrained and carried into E Bank, where uranium is stripped back into the aqueous phase. Since E Bank has large settling sections, FS solids in E Bank would have ended up in the aqueous uranium product, gradually dissolving over time.

The presence of FS solids in the 2nd U Cycle process has not been confirmed. However, if FS solids enter the process, they would slow disengagement, resulting in increased entrainment, which leads to lower decontamination factors for the overall process.

It should be noted that particle size analyses of sludge from a degraded FS drum were taken about a year ago. The particle sizes were much higher than those observed in this study. However, the 1-10 micron particles are more representative of the solids which reach the FS feed tank. Hence, filters with smaller particle size ratings need to be considered. Perhaps the current filters could be left in place and a finer filter could be used downstream.

Conclusions

The results of this study lead to the following conclusions:

1. The current level of FS addition into 2nd U Cycle is effective for removing neptunium and provides an excess for the removal of plutonium.
2. Using mini mixer-settlers, the only way to produce elevated iron and sulfur levels in the 1EU product stream was by switching the FS feed from stage 4 of D Bank to stage 1.
3. Ferrous sulfamate is a more effective reductant in the 2nd U Cycle than either ascorbic acid or a mixture of HAN and dilute FS.
4. Ferrous sulfamate addition to stage 4 of D Bank is much more effective than addition to stage 8.
5. Approximately 45% of typical FS solids are smaller than the current H Canyon prefilter.

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