Purex Processing of Dissolved Sand, Slag, and Crucible Containing High Levels of Boric Acid and Calcium Fluoride

by

E. A. Kyser

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

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M.C. Thompson

M.C. Thompson

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Thomas G. Campbell

Thomas G. Campbell

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Date

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Acronyms and Definitions:

- ANN, Al - Aluminum nitrate nonahydrate, source of aluminum used to complex fluoride
- Bomb Reduction - Process by which FB-Line reduces $\text{PuF}_4/\text{PuO}_2$ with metallic calcium to Pu metal
- Ca, CaO, CaF_2 - Calcium metal or compounds potentially in SSC residue.
- $D_{o/a}$ - Distribution Coefficient, ratio of concentration in organic phase divided by concentration in aqueous phase
- DBP - DiButyl Phosphate, Degradation product from TriButyl Phosphate resulting from the loss of a butyl group and replacement by an acid group. Forms a sodium salt in sodium carbonate solution and is stripped from the solvent.
- F by ISE - SRTC analytical method for determination of total fluoride concentration utilizing an ion selective electrode with the sample pipetted into an acetic acid-sodium acetate buffer solution. The method appears to be unable fully compensate for the effects of the large amounts of boric acid and/or aluminum in high acid solutions used in this and related studies and tends to give results with a low bias.
- FS, HAN - Ferrous Sulfamate and Hydroxylamine Nitrate are the two primary reducing agents used to adjust Pu valence states in the Purex process.
- Free acid - SRTC analytical method with uses KF to complex metal ions such as Pu to give the acid concentration without the effects of the metal ions.
- Gamma Scan - Gamma counting method used in SRTC to determine the amount of Am241 in the samples after total alpha counting was performed by Radscreen. This allowed for the correction of the Radscreen results to calculate Pu concentrations.
- GTM - Generalized Truex Model, Argonne National Laboratory developed software and models used to develop solvent extraction flowsheets. SASSE was a calculational component developed to aid design of such processes.
- HLW - High Level Waste, liquid waste containing actinides that will be transferred to the tank farm
- ICPES - Inductively Coupled Plasma Emission Spectroscopy, Instrument used to analyze for certain cations such as Al and B
- ILC-1 - Intermediate Level Cell #1 laboratory where two banks of miniature mixer settler equipment is installed in a glovebox for Pu process development work.
- MgO - Magnesium oxide sand is used to fill void between crucible and pressure vessel
- Pickup Test - SRTC development laboratory test that involves the extraction of Pu into TBP solvent followed by the stripping of the Pu from the solvent by weak acid solution containing HAN or FS. Test may be used to test either the solvent quality for extraction, followed by stripping or alternately to test the suitability of a given feed solution for extraction or followed by stripping.
- Pu, PuO_2 , PuF_4 , PuF_3 - Pu metal or compounds potentially in SSC residue
- Radscreen - Liquid scintillation method used in SRTC for screening radioactive materials. In this work, the alpha counts were corrected from a general counting efficiency of 90% to a measured Pu efficiency of 97% to accurately determine total Pu and Am activity.
- SASSE - Excel spreadsheet based macros developed by Argonne National Laboratory for the solution of material balances of countercurrent solvent extraction processes.
- SEPHIS - Fortran computer code developed by Oak Ridge National Laboratory in 1975-9 for the solution of material balances of countercurrent solvent extraction processes. This code includes algorithms for the prediction of distribution coefficients for Pu and U based on TBP concentration, extractable and inextractable nitrate concentrations and Pu and U metal ion concentrations.
- Si - An impurity that is known to be present in the MgO crucibles. It contributes heavily to phase disengagement problems in solvent extraction and is normally removed by gelatin strike and centrifugation
- Slag - Solid hard mass of CaF_2 - CaO that remains after Pu button breakout.
- SOLVEX - Fortran computer code developed by SRS in 1975 for the solution of material balances of countercurrent solvent extraction process.
- SSC - Sand, Slag and Crucible, residue in FB-Line Bomb Reduction charge after button removal, consists of small Ca and Pu metal shot and PuO_2 trapped in CaF_2 , CaO slag, as well as MgO sand and crucible pieces
- Strip - The removal of an extracted component (i.e. Pu) via contact with weak acid, reducing agent or complexant
- TBP - TriButyl Phosphate is the extractant used in the Purex solvent extraction process. SRS uses a mixture of straight chain hydrocarbons called normal paraffin hydrocarbon (NPH) with an average carbon chain length of 12 to 14 as a diluent for its TBP processes.
- TRUEX - TRansUranium EXtraction, General description given to various processes proposed for the separation of many component waste streams containing actinides via countercurrent flow solvent extraction.
- Total acid - SRTC analytical method for determination of all species which are neutralized to pH 7.

Summary

The plutonium solution obtained from the dissolution of SSC in F-Canyon will be high in fluoride. Flowsheet adjustments must be made to increase the plutonium extraction in the solvent extraction cycle to keep Pu losses from being excessive. Either complexing the fluoride or increasing the total nitrate in the feed (2AF) stream will increase the plutonium extraction into TBP. The recommendation is to do minimal dilution of the dissolver solution to keep the nitrate high and to add sufficient ANN to give acceptable plutonium extraction. This minimizes additional waste generation from aluminum salts. The recommended target is to process the 2AF at 6M total nitrate with at least 0.5 molar ratio of aluminum to fluoride. This flowsheet has been experimentally verified in miniature mixer settler equipment in ILC-1 with total plutonium losses of 0.17 percent.

Background

In earlier work, modifications to the flowsheet for the dissolution of SSC in a nitric acid/boric acid solution in canyon dissolvers were developed^{1,2}. SSC principally consists of CaF_2 and MgO with lesser amounts of CaO , Ca metal, Pu metal, PuF_4 and PuO_2 . Boric acid had been added to the dissolution flowsheet as a neutron poison to increase the mass of PuO_2 solids that would be safe in the dissolver in analyzed criticality scenarios. The development of the current flowsheet came after the recognition that the high levels of boric acid had a significant complexation effect on the free fluoride in the solution. This caused a reduction in the rate of PuO_2 dissolution as well as a dramatic increase in the rate of CaF_2 dissolution. The latter allowed the elimination of the ANN that had been necessary for the dissolution of slag (primarily composed of CaF_2). Due to the high F:Pu ratio in the dissolver solution and the removal of ANN from the flowsheet, the potential for PuF_x complexes to interfere with either the Pu extraction or the F decontamination was recognized. Investigation of these issues was the thrust of the work described in this report.

Historical Purex Processing in F-Canyon

Typical Purex feed consisted of target or fuel slugs with a uranium core and aluminum cladding. The cladding was removed in the dissolver with a $\text{NaOH}/\text{NaNO}_3$ solution that was recycled for repeated decladdings or discarded. The irradiated uranium core (which contained Pu) was then dissolved in 50% HNO_3 . Typically the solution acidity was depleted during the dissolution operation to less than 2M HNO_3 (due to oxidation reactions with generation of NO_x and H_2O). The solution containing the dissolved U and Pu was then transferred through head end in batches. Gelatin strike was performed by adding gelatin, simmering the solution and then promptly centrifuging to remove solids. The gelatin removed silica by forming a gelatin-silica polymer, which was removed in the centrifuge along with any other solids. Silica was removed to prevent formation of solids that cause emulsions in solvent extraction equipment during later processing. The U-Pu solution was then adjusted to make it suitable for 1st Uranium Cycle processing.

1st Uranium Cycle feed was approximately 300 g U/l, 1 M HNO_3 , with small amounts of Al, Pu (IV) and fission products. The U and Pu were extracted into the 30% TBP solvent into the 1A bank. Pu was reductively stripped from the solvent in the 1B bank with FS or FS/HAN in ≈ 0.1 M HNO_3 . The solvent retained the U until it was stripped in the 1C bank. The Pu in the 1BP stream was Pu(III) in HNO_3 , FS, Ferric Sulfate, HAN solution. Prior to being fed to the 2nd Pu cycle, the Pu valence was adjusted from III to IV by oxidizing the Fe(II) with NaNO_2 . This was performed by the addition of sufficient nitrite to react with the remaining sulfamate. Excess nitrite then oxidized the Fe(II) and Pu(III). The Pu(IV) solution was adjusted to the desired 2AF feed condition of 4 M HNO_3 and approximately 0.5 g Pu/l.

The 2AF stream typically contained as much as 0.17M SO_4 as well as NaNO_3 and Fe(III). This level of sulfate in the 4 M HNO_3 reduced the Pu D_{O_a} from the range of 15 to 20 down to the range of 7 to 8. In the extraction stages of the 2A bank, the Pu and trace amounts of U were extracted into the 30% TBP solvent, while the Na, SO_4 , Fe and fission products were removed in the 2AW stream. The 2A bank used a scrub acid of 0.66 M HNO_3 at 30% of the flow rate of the 2AF. This reduced the level of extracted HNO_3 in the solvent to approximately 0.12 M in the 2AP stream. Extracted Pu in the solvent is transferred to stage 12 of the 2B bank via the 2AP stream. The 2BX stream consists of a low flowrate of 0.1 M HAN, 0.1 M HNO_3 that reductively stripped the Pu from the solvent stream. The solvent, after it was stripped of Pu, was then recycled via the solvent recovery system. The U rejection flowsheet involved the addition of a 2BS stream, which was 30% TBP, to stage 16. This flowsheet provided some uranium rejection capability to the 2nd Pu cycle process. With the 4 scrub stages in the 2B bank, U tended to remain with the solvent and was transferred to solvent recovery rather than being stripped into the 2BP-product stream.

If excessive HNO_3 remained in the 2AP stream, it could interfere with the reductive stripping of Pu by HAN in the 2B bank and cause excessive refluxing of Pu in the 2B bank increasing the Pu inventory in the equipment. It appears that by design, the 2AS flowrate and HNO_3 concentration in the 2AS control the HNO_3 content of the 2AP stream³. With the modifications introduced to the B bank with the Uranium Rejection flowsheet, the critical variables that prevent excessive Pu refluxing were the 2BX flowrate and HAN concentration in the 2BX.

Small amounts of residual Pu activity, the rejected U and degradation products such as DBP were removed in the carbonate wash tank of the solvent recovery system using 2.5 weight percent Na_2CO_3 . The solvent was washed in 0.1M HNO_3 prior to being returned to the solvent storage tank. The entire 2nd Pu cycle process normally operated in the 35 to 50 °C range.

The 2BP product consisted of 2.5 to 3.5 g/l Pu(III) in approximately 0.3 to 0.4 M HNO_3 , 0.06 M HAN. This solution was later transferred to FB-Line for concentration by cation exchange, precipitation as PuF_3 and eventual reduction to Pu metal via Ca metal in Bomb Reduction. After button breakout, some of the MgO sand, much of the MgO crucible, excess Ca metal and the CaF_2 - CaO slag, became the SSC residue that is the subject of this report. Unreduced PuO_2 - PuF_4 and small pieces of Pu metal provided the incentive to retain this material for recovery.

Differences in the historical flowsheet for the current feedstock: SSC is significantly different in composition from the traditional uranium metal targets that were processed in F Canyon. Since there is no uranium or fission products in SSC, there was no incentive to process this material in 1st uranium cycle. Dissolving metal targets consumed much of the acid in the dissolver in historical processing. By comparison, SSC should consume very little acid. This is a difference that affects chemistry of gelatin strike for silica removal. The high levels of fluoride (from CaF_2 and KF) both complex Pu, thereby reducing its extractability into TBP, and further complicating gelatin strike with the chemical interactions between silica and fluoride. The high levels of boron do complex fluoride, but not as strongly as Al or Pu. Current plans are to avoid the use of sulfamate. The additional complexation caused by sulfate in addition to the fluoride would further complicate the extraction of the Pu.

Relevant Other Process Experience: There are some other separations processing experiences that have some relevance to the current chemistry. The traditional processing of SSC involved HNO_3 dissolution in FB-Line with large amounts of ANN to complex the F. Boric acid was not needed because processing was performed in geometrically favorable equipment. This process had problems with leftover solid residues left in the dissolver due to solubility limitations. This solution was processed through anion exchange to recover the Pu from the large amounts of Al, Ca and F present. At 8M HNO_3 and with a minimum of 1.5 moles Al per F, Pu was recovered on anion exchange as an anionic Pu nitrate complex. The combination of high HNO_3 and aluminum complexation of fluoride allowed the Pu to be separated from the fluoride. Scrub alloy processing and Pu metal dissolution in F-Canyon have some similar aspects to the current SSC recovery process. However the relative amounts of Pu, F, Al, and B in the dissolver solution were quite different from the SSC solutions.

Experimental

Stripping Problems in Past Pickup Tests: The inability to completely strip Pu from SRTC prepared solvent was a observation in earlier work. In pickup/stripping tests described in Ref 2, Pu was not stripped below 10^5 dpm/ml. Those stripping difficulties were traced to a batch of n-paraffin diluent used in the preparation of the 30% TBP solvent. Some unidentified impurity was present which retained a small amount of Pu in the absence of TBP. All solvent tests described in the current work, used either solvent from the F-Area Outside Facilities 906 solvent storage tank or solvent prepared from another source of diluent that was proven to not exhibit this extraction behavior.

Standard Plutonium Pickup Test: A relatively standard plutonium pickup test was performed in past work² with adjusted dissolver solutions to test the extractability/stripping of the plutonium. After feed adjustment, an equal volume of freshly prepared and triple washed solvent was used to extract the plutonium from the adjusted sample. Each step of the procedure included a one minute vortex mixing followed by a two minute centrifugation. After removal of the extracted aqueous phase, batch scrub and strip steps of 0.1M HNO_3 /0.1M HAN were performed to demonstrate the stripping of the plutonium from the solvent. Each phase was sampled and analyzed for alpha content by liquid scintillation counting. Due to the Am241 in the feed material, both

aqueous and organic solutions were analyzed for Am241 by gamma scan and the total alpha results were corrected for the Am241 ingrowth. The free acid-total acid was measured on both aqueous and organic samples to assure that proper feed adjustment had been performed and to determine the D_{α} for the acid species. All batch extraction tests were performed at 22-23 °C.

Simplified Plutonium/Impurity Pickup Test: The standard pickup test involved a large number of strips. The first four serve to scrub out the extracted acid to allow HAN to reduce the plutonium (IV) to plutonium (III) so that the plutonium easily strips out of the solvent. However, with the large number of strips, it is not possible to sample each phase at each stage due to the amount of sampling involved. A simplified test that used essentially equal volumes of strip acid to scrub the acid from the organic in one stage was developed. Three strip/scrub stages were used and both an aqueous and an organic sample were taken from the extraction and each strip stage. This procedure allowed a plutonium material balance to be performed and for Pu distribution coefficients to be calculated for each stage. All batch extraction tests were performed at 22-23 °C.

Due to the nitrate variation from the addition of nitrate salts such as aluminum, all tests used an adjustment based on calculated total nitrate rather than total or free acid. Extraction/Strip tests were performed in a 15 ml glass centrifuge tube for plutonium. Five ml of adjusted feed were extracted. The same centrifuge was retained throughout both the extraction and strip steps. Each strip used 5 milliliters of 0.1M HNO₃/0.1M HAN in contact with 4.5 ml down to 2 to 3 ml of the remaining organic phase in the centrifuge tube. A parallel test was performed with identical feed solutions to observe the behavior of the impurities of concern such as boron and fluoride. For impurity studies, the organic phase was contacted with 1 or 2M NaOH solution to strip the extracted acidic species (principally B or F) into an aqueous phase that was then analyzed by ICPEs and F by ISE. Vortex mixing and centrifugation were standard steps in all variants of the pickup test. All batch extraction tests were performed at 22-23 °C.

Extraction Only Pickup test for Distribution Coefficient Determination: An extraction only test was also used. In this test, a solution was prepared by dissolving boric acid, ferric nitrate, calcium fluoride, concentrated HNO₃, deionized water and/or 0.1M HNO₃ either by pipeting solution or by weighing on an analytical balance. After introducing this solution to the glovebox a well-characterized solution of plutonium (IV) nitrate in nitric acid was pipeted into the solution matrix to obtain the desired plutonium and nitrate concentrations to simulate the dissolver solution. Three ml. of the dissolver solution was then pipeted into a previously prepared vial containing weighed amounts of ANN dissolved in 0.1M HNO₃ to obtain the desired Pu, NO₃, and Al:F conditions. Two ml. of each vial was then pipeted into two ml of 30 percent TBP solvent in a 15 ml glass or plastic centrifuge tube. These solutions were then vortex mixed and centrifuged as was done in the standard pickup tests and each phase was sampled for analyses by the Radscreen, Gamma scan, and/or Total acid/Free acid methods. This allowed for calculation of distribution coefficients for Pu, Am, and/or Free acid between the phases. Gamma scan results for Am241 were used to correct the Radscreen alpha results and many times could be and were accurately estimated rather than measured.

Minibank Operation: Minibanks are miniature mixer settlers on the order of 1/10000th scale of canyon-sized equipment. Although the design is quite different from F-Canyon mixer settlers, this lab equipment has a long history of use for process development for counter-current-flow solvent extraction flowsheets for both F and H Canyons. The minibank equipment installed in the glovebox in ILC-1 was utilized to perform flowsheet demonstrations for this work. This equipment and its operation has been described in general terms in a number of past reports and will not be discussed in detail here. The equipment was operated without computer control. An HP8452A diode array spectrophotometer was utilized to perform online monitoring of the Pu concentrations in the 2BP and 2AW streams. Plant solvent from the 2nd Plutonium Cycle containing 30% TBP was obtained for these runs. Anion exchange purified Pu nitrate solution was used for a Pu source material. HAN solution obtained from FB-Line was used as a reductant. Reagent grade chemicals were used for the other necessary chemicals. Temperature was at laboratory ambient, approximately 25-27 °C for both experiments.

Results and Discussion:

Extraction of Impurities into TBP: A literature review suggested that fluoroboric acid (HBF₄) may extract into the solvent. Table 1 shows the distribution coefficients compiled by Shultz⁴ that appear applicable to this system along with results from the current study. Note that the distribution coefficients for both HF and boric

acid go up as the acid concentration goes down. This trend suggests that when fluoride and boron extract they will not easily strip back from the solvent. ANN added in the feed solution will suppress the initial extraction of these fluoride species due to competition for the fluoride, but should not affect the boric acid extraction.

Table I. Distribution Coefficients for HNO_3 , HF and $\text{B}(\text{OH})_3$ with TBP.

HNO_3 , M	HNO_3^1	HF ²	$\text{B}(\text{OH})_3^3$	HF ⁴	$\text{B}(\text{OH})_3^5$	H+ free ⁷
0.1	0.05					
0.5	0.1	0.4				
1	0.15	0.3	0.15			
2	0.2	0.2	0.08			
3	0.2	0.15	0.04			0.16
4	0.2	0.1	0.007	0.05-0.08	0.03-0.05	0.15-0.16
5	0.2	0.05				0.14-0.26
6	0.17	0.03				0.13-0.25
7						0.13-0.16
0.5M HF ⁷			0.44			

¹Solvent was 30% TBP 19-23°C Data smoothed, Reference 4.

²Solvent was 30% TBP in DEB 19-23°C, Data smoothed, Reference 4.

³Solvent was 100% TBP 19-23°C, Reference 4.

⁴Solvent was 30% TBP in NPH, Pu, F and $\text{B}(\text{OH})_3$ present, No Al, Pu109.

⁵Solvent was 30% TBP in NPH, Pu, F and $\text{B}(\text{OH})_3$ present, No Al, Pu109.

⁶Solvent was 30% TBP in NPH, Pu, Al, F and $\text{B}(\text{OH})_3$ present, Pu110-18.

⁷Solvent was 100% TBP, not clear if HNO_3 was present, 19-23°C, Reference 4.

The earlier work² where B and F extraction was studied without Pu, showed that 2 to 5% of the boron and fluoride remained in the solvent (when ANN was not present) and was stripped in the first contact with weak acid. However the literature $D_{\text{O/A}}$ values show a relationship that is inversely proportional to the acid concentration. Since the solvent was not analyzed for fluoride or boron, it is not certain that all the fluoride was removed from the solvent. For a single test run with an Al:F ratio of 1:1, the fluoride extraction was reduced to about 1 percent. With an Al:F ratio of 4:1, the extraction was further reduced to tenths of a percent. With $[\text{HNO}_3] = 9.9\text{M}$, both fluoride and boron extractions appeared to be suppressed due to mass action competition with HNO_3 .

Pu Extraction into TBP: Pickup Test Pu108 was the first Pu test run performed without any Al present. All earlier Pu extract tests used relatively high levels of Al to investigate the effects of those high levels of Al in the solvent extraction process. The high levels of Al enhanced the Pu extraction both by complexation of the F⁻ and by salting. Without Al in the feed, the Pu extraction was dramatically reduced. Test Pu108 corresponded to dissolver concentrations of 0 to 0.21 M boron and 0.05 to 0.52M fluoride at 9.5 M HNO_3 . A summary of the results is shown in Table II with more complete results included in the appendix as Table A1. The dramatic

Table II. Results from Pu108 Compared with Literature Values.

	B, M	F, M	NO_3^- , M	Pu D o/a
Pu108A	0.070	0.162	3.9	0.22
Pu108B	0.070	0.081	3.9	0.38
Pu108C	0.070	0.016	3.9	1.26
Pu108D	0	0.017	4.2	0.59
Literature ³	0	0	4	20+
0.17 M SO_4^{2-} ³	0	0	4	7 to 8

difference when fluoride is present with the literature values, either with or without sulfate is better shown in Figure 1. By comparing the $D_{\text{O/A}}$ for Pu108C and Pu108D it is noted that even at a B:F molar ratio of 4, boron has only a modest effect on the Pu extraction when compared with later results with Al. The

competition between Pu fluoride and Pu nitrate complexation appears to heavily favor fluoride in 4 M HNO_3 .

Impurity extraction test Pu109 was performed with the same feed solution as Pu108 and was done to quantify the extent that Pu might assist the extraction of boron and fluoride into the solvent. There was concern that PuF_4 or $\text{PuF}_x(\text{NO}_3)_{4-x}$ might significantly increase the carryover of F into the scrub stages. The makeup of Pu108/9 and the results are shown in Tables III and IV. These results are consistent with the values estimated in earlier work when Pu was not present². Due to a low bias in the fluoride analytical results when boron or aluminum was present, the $D_{\text{O/A}}$ for F is likely biased high by about 30%. Note that since this test did not involve any ANN, any addition of ANN should further reduce the amount of fluoride extracted.

Fluoride, Nitrate and Aluminum Effects on Plutonium Complexation and Extraction into TBP: Based on the low values for the Pu $D_{\text{O/A}}$ observed in Pu108, it is apparent that a chemical change to significantly increase the Pu extraction was needed. The options considered were diluting the F, complexing the F⁻ with Al or increasing the total nitrate concentration. Dilution is undesirable as the Pu concentration from the dissolution

Table III. Pu108/9 Extraction Solution Preparation. (22-23°C)

Description	Concentrations Based on Feed Makeup									Calculated			
	Pu g/l	Acid M	F M	B M	Al M	Pu M	NO3 M	Fe g/l	Ca M	F ppm	B ppm	Ca ppm	Fe ppm
Pu108/9A	2.08	10.0	0.52	0.21	0.00	0.009	9.49	2.2	0.26	9867	2269		
Pu108/9B	2.08	10.0	0.26	0.21	0.00	0.009	9.49	2.2	0.13	4933	2269		
Pu108/9C	2.08	10.0	0.05	0.21	0.00	0.009	9.49	2.2	0.03	987	2269		
Pu108/9D	2.08	9.4	0.05	0.00	0.00	0.009	9.49	2.2	0.03	987	0		
Pu108/9A Adj	0.65	4.1	0.16	0.07	0.00	0.003	3.92	0.70	0.08	3074	707	3242	699
Pu108/9B Adj	0.65	4.1	0.08	0.07	0.00	0.003	3.92	0.70	0.04	1537	707	1621	699
Pu108/9C Adj	0.65	4.1	0.02	0.07	0.00	0.003	3.92	0.70	0.008	307	707	324	699
Pu108/9D Adj	0.69	4.1	0.02	0.00	0.00	0.003	4.18	0.75	0.009	328	0	346	746

Table IV. Pu109 Impurity Extraction Results. (22-23°C)

	Analyzed				D o/a			
	F ppm	B ppm	Ca ppm	Fe ppm	F	B	Ca	Fe
Pu108/9A Adj	2086	780	3665	735	0.081	0.05	0.001	0.002
Pu108/9B Adj	1175	758	1878	771	0.071	0.03	0.001	0.002
Pu108/9C Adj	212	731	286	789	0.055	0.03	0.009	0.003
Pu108/9D Adj	201	20	251	718	0.066	n/a	0.009	0.002

Figure 1. Pu D_{o/a}: Effects of Sulfate Compared to Effects of F and Al. (22-25°C)

Table V. Pu Extraction Test Results with Varying F, NO₃⁻ and Al.

Sample	ID	F M	NO ₃ ⁻ M	Al:F	F:Pu	NO ₃ :Pu	B:F	Pu mg/l	D O/A
Pu110A	AlF=0 NO ₃ =4	0.11	4.01	0.00	29	1067	0.8	923	0.80
Pu110B	AlF=0.25 NO ₃ =4	0.11	4.04	0.25	29	1089	0.8	907	1.02
Pu110C	AlF=0.5 NO ₃ =4	0.10	4.01	0.49	29	1110	0.8	879	1.19
Pu110D	AlF=1 NO ₃ =4	0.10	4.01	1.01	29	1156	0.8	838	1.69
Pu110E	AlF=2 NO ₃ =4	0.09	4.01	2.03	29	1245	0.8	767	3.66
Pu110F	AlF=3 NO ₃ =4	0.09	3.99	3.00	29	1331	0.8	707	5.54
Pu110G	AlF=4 NO ₃ =4	0.08	3.99	4.02	29	1420	0.8	656	7.00
Pu111A	AlF=0 NO ₃ =4	0.15	4.01	0.00	39	1067	0.5	971	0.58
Pu111B	AlF=0.25 NO ₃ =4	0.14	4.02	0.25	39	1098	0.5	954	0.75
Pu111C	AlF=0.5 NO ₃ =4	0.14	4.02	0.51	39	1129	0.5	924	0.92
Pu111D	AlF=1 NO ₃ =4	0.13	4.01	0.99	39	1187	0.5	881	1.54
Pu111E	AlF=2 NO ₃ =4	0.12	4.03	2.03	39	1313	0.5	807	5.52
Pu111F	AlF=3 NO ₃ =4	0.11	4.03	3.02	39	1433	0.5	744	7.43
Pu111G	AlF=4 NO ₃ =4	0.10	4.02	3.99	39	1549	0.5	690	10.16
Pu112A	AlF=0 NO ₃ =4	0.11	4.01	0.00	29	1067	0.0	965	0.40
Pu112B	AlF=0.25 NO ₃ =4	0.11	4.02	0.25	29	1089	0.0	947	0.58
Pu112C	AlF=0.5 NO ₃ =4	0.10	3.98	0.51	29	1112	0.0	918	0.87
Pu112D	AlF=1 NO ₃ =4	0.10	3.95	1.01	29	1156	0.0	875	2.03
Pu112E	AlF=2 NO ₃ =4	0.09	3.89	2.04	29	1246	0.0	801	4.45
Pu112F	AlF=3 NO ₃ =4	0.08	3.84	3.01	29	1332	0.0	739	10.22
Pu112G	AlF=4 NO ₃ =4	0.08	3.81	4.08	29	1426	0.0	685	9.79
Pu113A	AlF=0 NO ₃ =2.5	0.07	2.50	0.00	29	1084	0.8	590	0.22
Pu113B	AlF=0 NO ₃ =3	0.08	2.99	0.00	29	1076	0.8	713	0.34
Pu113C	AlF=0 NO ₃ =4	0.11	4.01	0.00	29	1067	0.8	965	0.86
Pu113D	AlF=0 NO ₃ =4.5	0.12	4.51	0.00	29	1064	0.8	1087	1.48
Pu113E	AlF=0 NO ₃ =5	0.13	4.97	0.00	29	1062	0.8	1201	2.07
Pu113F	AlF=0 NO ₃ =5.6	0.15	5.55	0.00	29	1060	0.8	1343	3.19
Pu113G	AlF=0 NO ₃ =6	0.16	6.01	0.00	29	1058	0.8	1457	4.75
Pu114A	AlF=0 NO ₃ =5	0.13	4.97	0.00	29	1062	0.8	1201	2.05
Pu114B	AlF=0.25 NO ₃ =5	0.13	4.97	0.27	29	1086	0.8	1174	2.45
Pu114C	AlF=0.5 NO ₃ =5	0.13	4.95	0.49	29	1105	0.8	1149	3.15
Pu114D	AlF=1 NO ₃ =5	0.13	5.01	1.01	29	1150	0.8	1118	4.17
Pu114E	AlF=2 NO ₃ =5	0.12	5.04	1.99	29	1236	0.8	1046	8.91
Pu114F	AlF=3 NO ₃ =5	0.11	5.00	2.99	29	1323	0.8	968	12.17
Pu114G	AlF=4 NO ₃ =5	0.10	5.03	4.00	29	1412	0.8	913	15.03
Pu115A	AlF=0 NO ₃ =6	0.16	6.01	0.00	29	1058	0.8	1457	5.46
Pu115B	AlF=0.25 NO ₃ =6	0.16	5.97	0.26	29	1081	0.8	1418	6.35
Pu115C	AlF=0.5 NO ₃ =6	0.15	5.93	0.52	29	1103	0.8	1380	7.01
Pu115D	AlF=1 NO ₃ =6	0.15	5.98	1.05	29	1149	0.8	1336	7.66
Pu115E	AlF=2 NO ₃ =6	0.14	6.03	1.98	29	1231	0.8	1258	14.78
Pu115F	AlF=3 NO ₃ =6	0.13	6.01	3.02	29	1321	0.8	1166	20.28
Pu115G	AlF=4 NO ₃ =6	0.12	5.97	4.01	29	1408	0.8	1088	18.48
Pu116A	AlF=0 NO ₃ =7	0.27	7.05	0.00	40	1055	0.6	1285	0.98
Pu116B	AlF=0.25 NO ₃ =7	0.26	7.01	0.27	40	1088	0.6	1250	9.07
Pu116C	AlF=0.5 NO ₃ =7	0.25	6.96	0.51	40	1118	0.6	1217	10.07
Pu116D	AlF=1 NO ₃ =7	0.25	6.98	0.73	40	1145	0.6	1178	10.52
Pu116E	AlF=2 NO ₃ =7	0.24	7.03	0.99	40	1177	0.6	1109	12.51
Pu118A	AlF=0 NO ₃ =4	0.16	4.00	0.00	486	11985	0.4	82	0.68
Pu118B	AlF=0.25 NO ₃ =4	0.16	3.98	0.27	486	12382	0.4	79	0.87
Pu118C	AlF=0.5 NO ₃ =4	0.15	3.95	0.50	486	12735	0.4	76	1.11
Pu118D	AlF=1 NO ₃ =4	0.14	3.91	1.00	486	13482	0.4	71	1.86
Pu118E	AlF=2 NO ₃ =4	0.12	3.84	1.99	486	14965	0.4	63	5.01
Pu118F	AlF=3 NO ₃ =4	0.11	3.79	3.02	486	16497	0.4	56	7.99
Pu118G	AlF=4 NO ₃ =4	0.10	3.74	4.00	486	17975	0.4	51	8.77

effectively limits it to only one. Pu nitrate complexes are not as strong as any of the F⁻ complexes mentioned (log K₁=0.97), however with 4 to 6 M total nitrate present, mass action contributes to significant Pu nitrate complex formation. Calculations have been performed to attempt to quantify these effects and are summarized in the Table VI. Increasing the total nitrate or raising the Al:F ratio both serve to shift Pu complexation in favor of nitrate complexes. This favors the extraction of Pu into TBP. The neutral species, Pu(NO₃)₄, is believed to

process is expected to be low. Addition of ANN as a solution of 60% ANN to an Al:F ratio of 3 to 4 would both dilute the solution and contribute significant additional HLW. Since the dissolver solution was already at greater than 9 M HNO₃, operating the solvent extraction cycle at a higher than normal total nitrate held the potential to both keep the Pu concentration up and significantly improve the Pu extraction. A series of batch extraction tests (Pu110 through Pu118) were performed to investigate the effects of Al:F ratio and total nitrate on the Pu extraction. Results from those tests are briefly summarized in the Table V and illustrated in Figures 2 and 3. A more complete listing of the conditions and results are included in Table A1 in the Appendix. The data shows the effect of Al:F ratio and [NO₃]_{total} on the Pu D_{0.05} in nitric acid solutions with B, Ca and Fe present in solution. As expected, Pu extraction is enhanced both by the increase in Al:F ratio as well as increase [NO₃]_{total}. This is most likely due to shifts in the complexation of Pu-F and Pu-NO₃. Complexation of F⁻ by Al and B reduces the F available to complex Pu, however B is much less effective at complexing F⁻ than Al. Based on complexation constants obtained in the literature⁴, Pu is by far the best F⁻ complexant present (log K₁= 6.77). Al is not as strong a complexant (log K₁= 3.2), but with Al/Pu > 100 and having the capacity to complex three F⁻ ions in significant amounts, Al effectively makes the F⁻ unavailable for Pu complexation. B is only a fair F⁻ complexation agent (log K₁=1.4). Although B can complex up to four F⁻ ions, the presence of Al

Figure 2. Observed Pu D_{0/a} Showing Effect of Al:F Ratio as a Function of Total Nitrate. (22-25°C)

Figure 3. Observed Pu D_{0/a} Showing Effect of Total Nitrate as a Function of Al:F Ratio. (22-23°C)

Table VI. Pu-F and Pu-NO₃⁻ Complexation Competition.

	Species, M							
Pu, total	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
F, total	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Al, total	0	0	0	0.12	0.12	0.23	0.23	0.46
B, total	0	0.23	0.23	0.23	0.23	0.23	0.23	0.23
HNO ₃ , total	4	4	6	4	6	4	6	4
PuF ₄ /Pu(NO ₃) _x ^{+4-x}	3.61	1.13	0.47	0.27	0.11	0.10	0.04	0.03

be the only extractable species. This is why the formation of Pu-nitrate complexes favors extraction. The mechanism is the conversion of other complexes to the neutral species as the neutral species is consumed from the aqueous phase by extraction with TBP.

The effect of temperature on the complexation equilibria was briefly investigated using the constants available for F, B, and Al complexation⁴. No information was located for the effect of temperature on Pu

Table VII. Complexation Equations and Equilibrium Constants.

	Log K _n	Ref	Eq #
H ⁺ + F ⁻ = HF	log K ₁ =3.08	8	(1)
HF + F ⁻ = HF ₂ ⁻	log K ₂ =0.65	8	(2)
B(OH) ₃ + nHF = H ⁺ + H _{3+n} BO ₃ F _n ; n=0,4	log K ₁ =1.38	8	(3)
	log K ₂ =2.41		
	log K ₃ =5.96		
	log K ₄ =8.11		
Al ⁺³ + nHF ⁻ = AlF _n ⁺³⁻ⁿ + nH ⁺ ; n=0,6	log K ₁ =3.21	8	(4)
	log K ₂ =5.37		
	log K ₃ =6.38		
	log K ₄ =6.09		
	log K ₅ =4.59		
	log K ₆ =1.81		
Pu ⁺⁴ + nF ⁻ = Pu(F) _n ⁴⁻ⁿ ; n=0,2	log K ₁ =6.77	9	(5)
	log K ₂ =7		
Pu ⁺⁴ + nNO ₃ ⁻ = Pu(NO ₃) _n ⁴⁻ⁿ ; n=0,6	log K ₁ =0.97		(6)
	log K ₂ =0.46		
	log K ₃ =-1.82		

complexation with F⁻ or NO₃⁻. Calculations with F, B, and Al complexation showed a 10 percent increase in the free F⁻ as the temperature was increased from 25 to 55°C. The increase in free F⁻ is estimated to cause a corresponding increase in PuF_x^{4-x} complex formation and a resultant reduction in the Pu D_{o/a}. This may be offset by the general trend of D_{o/a} for Pu to increase with temperature.

Computer Simulation: Predicting how solvent extraction is affected requires process modeling. SEPHIS is not useful in this situation, as the program does not allow for modification of the D_{o/a}. McKibben et al³ used the SOLVEX program to perform similar modeling for the effects of sulfate in the feed stream, but a working copy of the code was not located. (H-Canyon has since been found to be still using SOLVEX.) As part of the development of the GTM, Argonne National Laboratory has developed a program that runs in an Excel environment as a macro. This program is called SASSE and allows the calculation of steady-state material balances for counter-current flow solvent-extraction processes with user input of appropriate values of D_{o/a}⁶.

McKibben et al³ performed a process sensitivity analysis on the PUREX process. That work showed that increases in the 2AF acidity both reduced Pu losses and reduced the Pu inventory in the process equipment. Modeling with SASSE was limited to effects on losses, impurity decontamination and acid scrubbing studies. Figure 4 shows A Bank results for a SASSE model. This model used values for the HNO₃ D_{o/a} in the scrub section of 0.14 to 0.22 for acid extraction and found the acid differed 0.11 percent between the normal 4M HNO₃ and the proposed 6M total nitrate feed if all the nitrate was in the form of HNO₃. Using a D_{o/a} of 0.2 for HF and 0.08 for boric acid, DF's of 30 to 50 were calculated for the A Bank in a similar simulation. Some separation might be obtained in the B Bank, but this was not studied. Calculation of Pu losses was limited by the ability to predict both a realistic D_{o/a} and stage efficiency that would be achieved in actual equipment.

Three conclusions were reached from the SASSE modeling that was performed:

- 1) Seven scrub stages will remove virtually all the acid, even with 6M HNO₃ in the feed.
- 2) At observed values of D_{o/a} for B or F, the DF for B and F should be moderate.
- 3) With adjustment of the feed such that a D_{o/a} of 7 or greater is obtained in batch tests, the process losses should be on the order of 0.01 to 0.1 percent.

Figure 4. Calculated Effect of Acid Scrubbing with 2AF Containing 6M HNO₃.

Minibank Experimental Conditions and Results: Two minibank experiments were performed for a comparative test of a proposed altered flowsheet with a historical flowsheet. The first run was made with a 4 M HNO₃ Pu feed solution that contained 0.17 M sulfate to simulate the base case for historical operation of the process. A second run with a 6M HNO₃ Pu feed solution that contained high levels of F complexed 0.5:1 with

Table VIII. Feed Concentrations for the Minibank Runs.

Description	Vol	Pu	HNO ₃	F	B	Al	Pu	NO ₃	Fe	Ca	SO ₄
	gms	ml	g/l	M	M	M	M	M	g/l	M	M
CR175PC1	15	79.5	2.24				0.333	3.57			0.000
Na ₂ SO ₄ *10H ₂ O	110										
Conc HNO ₃	717	505	15.8					15.80			
DI H ₂ O	1425	1425									
Minibank Run #1	2268	2007	0.594	3.99				4.00			0.170
CR175PC1	15	79.5	2.24				0.333	3.57			
Ferric Nitrate*9H ₂ O	22	9									
H ₃ BO ₃	17										
CaF ₂	18										
DI H ₂ O	1234	1234									
Conc HNO ₃	994	700	15.8					15.80			
ANN Powder	86	37									
MiniBank Run #2	2387	1995	0.598	5.97	0.231	0.138	0.116	0.003	6.00	1.52	0.116

Al was run as a proposed feedstock for an altered flowsheet. The details of the feed concentrations are shown in Table VIII. Flowrates and concentrations of other streams are shown in Figure 5. Details of sampling points and flowrate

measurements are contained in appendix Table A3

Figures 6 and 7 show measured Pu concentration profiles for the 2A and 2B bank of each experiment. Figures 8 and 9 show a comparison of the $D_{o/a}$ for Pu in each bank. The main difference observed was in the 2A bank on stage 6. The concentrations appeared to be flat between stages 8 and 6. This may have a sulfate complexation effect or a flow hydraulics problem, but neither has been confirmed. The B bank showed no significant difference between the experiments. The 2BP-product solution was analyzed for F contamination. This stream should have been absent the B or Al that was found to interfere an accurate analysis of the F. Total F was determined to be less than the detection limit of 10 ppm in the 2BP-product solution.

Figure 5. Solvent Extraction Flowsheet for Minibank Operation

Table IX lists actual flowrates and shows material balances for each bank and the overall flowsheet. The 2AF Pu concentration was intended to be the same in both experiments, but the analytical results are different. The material balances for both banks and each bank individually are within experimental uncertainties. The total losses for both experiments differed in how much was lost to the 2AW versus the 2BW. The reason for the apparent increased losses to the 2BW in MB2 are not clear, however this result was observed with repeated samples and cross-contamination did not appear to be a mechanism. The Pu $D_{o/a}$ in stage 4 was a factor of 5 higher in MB2 than MB1, but was not significantly different on stages 4, 6, 8 or 10 (see Figure 9). This is similar to effects observed when DBP levels in the solvent prevent complete stripping. The solvent was carbonate washed between the two experiments. Possibly this was not complete. Contamination of the solvent with an epoxy used on the 2AX feed container used in the first experiment did occur, however that problem should have affected both experiments similarly. There is no direct evidence that supports that any component in the 2AF was responsible for this result. However it is

prudent to be especially observant for any unusual losses to either the 2AW or 2BW whenever a major flowsheet change is implemented.

Table IX. Flowrates, Pu Material Balance and Losses for Minibank Runs. (25-27°C)

Run		2AF	2AX	2AS	2AW*	2AP*	2BX	2BS	2BW*	2BP*			
		ml/min											
	Target Rate	2.22	1.11	0.67	2.89	1.11	0.45	0.89	2.00	0.45			
MB1	Measured Rate	2.17	1.16	0.67	2.84	1.16	0.47	0.92	2.08	0.47			
MB2	Measured Rate	2.09	1.19	0.65	2.73	1.19	0.47	0.94	2.13	0.47			
		Pu											
		g/l											
MB1		0.66			0.0008	1.18	0.0001			3.13			
MB2		0.76			0.0005	1.28	0.0006			2.99			
		Pu, mg/min											
MB1	Both Banks	1.43							0.0002	1.47	-0.03	-2.4%	
MB2	Both Banks	1.59							0.0014	1.41	0.17	10.9%	
MB1	A Bank	1.43			0.0022	1.37					0.06	4.4%	
MB2	A Bank	1.59			0.0013	1.53					0.06	3.7%	
MB1	B Bank					1.37	0.0002			1.47	0.06	4.2%	
MB2	B Bank					1.53	0.0014			1.41	0.11	7.5%	
	Total	Losses, %											
MB1	0.17%				0.15%				0.02%				
MB2	0.17%				0.08%				0.09%				
* Flowrates for the 2AW, 2AP, 2BW and 2BP streams are not measured values													

* Flowrates for the 2AW, 2AP, 2BW and 2BP streams are not measured values

Uncertainties: There are both experimental and calculational uncertainties throughout this work that can affect the conclusions of this work. These were constantly evaluated during the course of this work to minimize the effect on the most important results.

Sample dilution error of less than 5 percent would be expected due to the accuracy of the pipets. Technician error on an individual dilution sometimes results in much larger errors. Such errors probably occur more often with radioactive samples due to awkward working conditions. Obviously inconsistent data points in the Radscreen analyses were routinely reanalyzed and when necessary the test repeated, until a Pu alpha value was obtained that appeared to be consistent with the other data points. Organic samples were found to be

somewhat more difficult to accurately pipet based on the number of samples where inconsistencies were observed. Counting errors are generally minor contributors to the total analytical uncertainty.

The wet chemistry methods of Free Acid and F by ISE were used only to a limited degree. The complex solution matrix had earlier been shown to cause a low bias in the F by ISE method². The ability of the Free Acid method to handle the complex solution matrix was not validated and thus was not relied on heavily in this work. Most solutions were made up gravimetrically based on estimated densities of the final solution. The solution density for these solutions was primarily determined by the nitric acid and $\text{Al}(\text{NO}_3)_3$ concentrations and the uncertainties in the estimated density are probably only about 1 percent.

All experimental work was performed at laboratory ambient conditions that ranged from 22 to 27°C whereas the plant process will run at 40 to 50°C. The literature indicates that the free F⁻ should increase slightly⁸ (which should reduce the Pu $D_{\alpha/a}$) while the general trend would be for a small increase in the Pu $D_{\alpha/a}$ ⁷. Overall the temperature is expected to have only a small influence on the Pu $D_{\alpha/a}$ based on the limited available data, however the complex solution matrix involved makes this expectation relatively weak and there are no experimental data to verify the magnitude of the effect.

Cross contamination of the samples was generally not believed to be a significant problem. Where this type of problem was most likely to affect results would have been when there was a large difference between the alpha activity of samples that were physically nearby and the lower sample was contaminated. This would have had the greatest impact on the batch extraction tests and would have lowered the measured Pu $D_{\alpha/a}$. Modest inconsistencies (20 to 30 percent) were observed between some data values that could have been due to this or small sample dilution errors. The number of data points taken reduces the impact of 20 to 30 percent errors that may have occurred on an isolated data point.

A limited effort was put into modeling and computer simulation of the minibank experiment. The results from those simulations have a limited value due to several effects that were not modeled. As discussed earlier, temperature effects on the $D_{\alpha/a}$ and complexation were not included due to the limited data available. This combined with the uncertainty in the relative values of $D_{\alpha/a}$ for F compared with Al and B in stages 5, 6 and 7 of the scrub section of the 2A Bank, leaves a lot of uncertainty in the Pu concentration profile in the scrub section. The large effect of F on the extraction of Pu could be significant under conditions where Al is scrubbed better than F. The minibank experiment showed this did not occur with the operating conditions tested at room temperature, but some complexation and extraction changes have to be expected for a 20°C operating temperature change.

Figure 6. 2A Bank Concentration Profiles from Minibank Experiments.

Figure 7. 2B Bank Concentration Profiles from Minibank Experiments.

Figure 8. Observed 2A Bank Pu $D_{o/a}$ from Minibank Experiments. Figure 9. Observed 2B Bank Pu $D_{o/a}$ from Minibank Experiments.

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Table A1. Experimental Conditions and Results from Batch Extraction Tests.

Sample ID		H+ M	F M	B M	Al M	Pu mM	NO3- M	Fe g/l	Ca M	Al:F	F:Pu	NO3:Pu	B:F	Am241 uCi/ml	Pu uCi/ml	Pu mg/l	D O/A	Mat'l Bal
Pu108A	AEA	4.1	0.162	0.07	0.00	2.7	3.92	0.7	0.08	0.00	60	1442	0.4	0.506	43.0	596	0.22	100%
Pu108B	BEA	4.1	0.081	0.07	0.00	2.7	3.92	0.7	0.04	0.00	30	1442	0.8	0.429	37.9	526	0.38	100%
Pu108C	CEA	4.1	0.016	0.07	0.00	2.7	3.92	0.7	0.01	0.00	6	1442	4.0	0.353	24.8	344	1.26	107%
Pu108D	DEA	4.1	0.017	0.00	0.00	2.9	4.18	0.7	0.01	0.00	6	1440	0.0	0.500	33.3	462	0.59	101%
Pu110A	AlF=0 NO3=4	4.2	0.11	0.08	0.00	3.8	4.01	1.0	0.05	0.00	29	1067	0.8	0.564	66.5	923	0.80	100%
Pu110B	AlF=0.25 NO3=4	4.2	0.11	0.08	0.03	3.7	4.04	1.0	0.05	0.25	29	1089	0.8	0.554	65.3	907	1.02	99%
Pu110C	AlF=0.5 NO3=4	4.0	0.1	0.08	0.05	3.6	4.01	0.9	0.05	0.49	29	1110	0.8	0.537	63.3	879	1.19	101%
Pu110D	AlF=1 NO3=4	3.9	0.1	0.08	0.10	3.5	4.01	0.9	0.05	1.01	29	1156	0.8	0.512	60.4	838	1.69	97%
Pu110E	AlF=2 NO3=4	3.6	0.09	0.07	0.19	3.2	4.01	0.8	0.05	2.03	29	1245	0.8	0.469	55.3	767	3.66	95%
Pu110F	AlF=3 NO3=4	3.4	0.09	0.07	0.26	3.0	3.99	0.8	0.04	3.00	29	1331	0.8	0.432	51.0	707	5.54	96%
Pu110G	AlF=4 NO3=4	3.2	0.08	0.06	0.32	2.8	3.99	0.7	0.04	4.02	29	1420	0.8	0.401	47.3	656	7.00	96%
Pu111A	AlF=0 NO3=4	4.2	0.15	0.07	0.00	3.8	4.01	1.0	0.07	0.00	39	1067	0.5	0.643	70.0	971	0.58	99%
Pu111B	AlF=0.25 NO3=4	4.1	0.14	0.07	0.04	3.7	4.02	1.0	0.07	0.25	39	1098	0.5	0.632	68.7	954	0.75	96%
Pu111C	AlF=0.5 NO3=4	3.9	0.14	0.06	0.07	3.6	4.02	0.9	0.07	0.51	39	1129	0.5	0.612	66.6	924	0.92	96%
Pu111D	AlF=1 NO3=4	3.8	0.13	0.06	0.13	3.4	4.01	0.9	0.07	0.99	39	1187	0.5	0.584	63.5	881	1.54	93%
Pu111E	AlF=2 NO3=4	3.4	0.12	0.06	0.25	3.1	4.03	0.8	0.06	2.03	39	1313	0.5	0.534	58.2	807	5.52	101%
Pu111F	AlF=3 NO3=4	3.1	0.11	0.05	0.33	2.8	4.03	0.7	0.06	3.02	39	1433	0.5	0.493	53.6	744	7.43	83%
Pu111G	AlF=4 NO3=4	2.9	0.1	0.05	0.41	2.6	4.02	0.7	0.05	3.99	39	1549	0.5	0.457	49.7	690	10.16	87%
Pu112A	AlF=0 NO3=4	4.0	0.11	0.00	0.00	3.8	4.01	1.0	0.05	0.00	29	1067	0.0	0.590	69.5	965	0.40	103%
Pu112B	AlF=0.25 NO3=4	3.9	0.11	0.00	0.03	3.7	4.02	0.9	0.05	0.25	29	1089	0.0	0.579	68.3	947	0.58	101%
Pu112C	AlF=0.5 NO3=4	3.8	0.1	0.00	0.05	3.6	3.98	0.9	0.05	0.51	29	1112	0.0	0.561	66.2	918	0.87	100%
Pu112D	AlF=1 NO3=4	3.6	0.1	0.00	0.10	3.4	3.95	0.9	0.05	1.01	29	1156	0.0	0.535	63.1	875	2.03	96%
Pu112E	AlF=2 NO3=4	3.3	0.09	0.00	0.18	3.1	3.89	0.8	0.04	2.04	29	1246	0.0	0.490	57.8	801	4.45	96%
Pu112F	AlF=3 NO3=4	3.1	0.08	0.00	0.25	2.9	3.84	0.7	0.04	3.01	29	1332	0.0	0.451	53.2	739	10.22	104%
Pu112G	AlF=4 NO3=4	2.8	0.08	0.00	0.31	2.7	3.81	0.7	0.04	4.08	29	1426	0.0	0.419	49.4	685	9.79	95%
Pu113A	AlF=0 NO3=2.5	2.6	0.07	0.05	0.00	2.3	2.50	0.6	0.03	0.00	29	1084	0.8	0.361	42.6	590	0.22	101%
Pu113B	AlF=0 NO3=3	3.1	0.08	0.06	0.00	2.8	2.99	0.7	0.04	0.00	29	1076	0.8	0.436	51.4	713	0.34	102%
Pu113C	AlF=0 NO3=4	4.2	0.11	0.09	0.00	3.8	4.01	1.0	0.05	0.00	29	1067	0.8	0.590	69.5	965	0.86	95%
Pu113D	AlF=0 NO3=4.5	4.7	0.12	0.10	0.00	4.2	4.51	1.1	0.06	0.00	29	1064	0.8	0.664	78.3	1087	1.48	100%
Pu113E	AlF=0 NO3=5	5.2	0.13	0.11	0.00	4.7	4.97	1.2	0.07	0.00	29	1062	0.8	0.734	86.6	1201	2.07	95%
Pu113F	AlF=0 NO3=5.6	5.8	0.15	0.12	0.00	5.2	5.55	1.4	0.08	0.00	29	1060	0.8	0.821	96.8	1343	3.19	97%
Pu113G	AlF=0 NO3=6	6.3	0.16	0.13	0.00	5.7	6.01	1.5	0.08	0.00	29	1058	0.8	0.891	105.0	1457	4.75	98%
Pu114A	AlF=0 NO3=5	5.2	0.13	0.11	0.00	4.7	4.97	1.2	0.07	0.00	29	1062	0.8	0.734	86.6	1201	2.05	97%
Pu114B	AlF=0.25 NO3=5	5.1	0.13	0.10	0.04	4.6	4.97	1.2	0.07	0.27	29	1086	0.8	0.718	84.6	1174	2.45	99%
Pu114C	AlF=0.5 NO3=5	5.0	0.13	0.10	0.06	4.5	4.95	1.2	0.06	0.49	29	1105	0.8	0.702	82.8	1149	3.15	133%
Pu114D	AlF=1 NO3=5	4.9	0.13	0.10	0.13	4.4	5.01	1.1	0.06	1.01	29	1150	0.8	0.683	80.6	1118	4.17	103%
Pu114E	AlF=2 NO3=5	4.6	0.12	0.09	0.23	4.1	5.04	1.1	0.06	1.99	29	1236	0.8	0.639	75.4	1046	8.91	96%
Pu114F	AlF=3 NO3=5	4.2	0.11	0.09	0.32	3.8	5.00	1.0	0.05	2.99	29	1323	0.8	0.592	69.8	968	12.17	94%
Pu114G	AlF=4 NO3=5	4.0	0.1	0.08	0.41	3.6	5.03	0.9	0.05	4.00	29	1412	0.8	0.558	65.8	913	15.03	82%
Pu115A	AlF=0 NO3=6	6.3	0.16	0.13	0.00	5.7	6.01	1.5	0.08	0.00	29	1058	0.8	0.891	105.0	1457	5.46	91%
Pu115B	AlF=0.25 NO3=6	6.1	0.16	0.13	0.04	5.5	5.97	1.4	0.08	0.26	29	1081	0.8	0.866	102.2	1418	6.35	98%
Pu115C	AlF=0.5 NO3=6	6.0	0.15	0.12	0.08	5.4	5.93	1.4	0.08	0.52	29	1103	0.8	0.844	99.5	1380	7.01	99%
Pu115D	AlF=1 NO3=6	5.8	0.15	0.12	0.16	5.2	5.98	1.3	0.07	1.05	29	1149	0.8	0.817	96.3	1336	7.66	93%
Pu115E	AlF=2 NO3=6	5.5	0.14	0.11	0.28	4.9	6.03	1.3	0.07	1.98	29	1231	0.8	0.769	90.6	1258	14.78	97%
Pu115F	AlF=3 NO3=6	5.1	0.13	0.10	0.39	4.5	6.01	1.2	0.07	3.02	29	1321	0.8	0.713	84.1	1166	20.28	92%
Pu115G	AlF=4 NO3=6	4.7	0.12	0.10	0.49	4.2	5.97	1.1	0.06	4.01	29	1408	0.8	0.665	78.4	1088	18.48	88%
Pu116A	AlF=0 NO3=7	7.4	0.27	0.15	0.00	6.7	7.05	1.7	0.14	0.00	40	1055	0.6	0.785	92.6	1285	0.98	71%
Pu116B	AlF=0.25 NO3=7	7.1	0.26	0.15	0.07	6.4	7.01	1.7	0.13	0.27	40	1088	0.6	0.764	90.1	1250	9.07	116%
Pu116C	AlF=0.5 NO3=7	6.9	0.25	0.14	0.13	6.2	6.96	1.6	0.13	0.51	40	1118	0.6	0.744	87.7	1217	10.07	112%
Pu116D	AlF=1 NO3=7	6.8	0.25	0.14	0.18	6.1	6.98	1.6	0.12	0.73	40	1145	0.6	0.720	84.9	1178	10.52	108%
Pu116E	AlF=2 NO3=7	6.6	0.24	0.13	0.24	6.0	7.03	1.5	0.12	0.99	40	1177	0.6	0.678	79.9	1109	12.51	115%
Pu117A	AlF=0 SO4=0	4.7	0	0.00	0.00	2.2	4.74	0.0	0.00		0	2117		0.327	38.5	535	21.31	106%
Pu117B	AlF=0 SO4=0.07	4.7	0	0.00	0.07	2.2	4.87	0.0	0.00		0	2207		0.322	38.0	527	10.52	99%
Pu117C	AlF=0 SO4=0.14	4.6	0	0.00	0.12	2.2	4.97	0.0	0.00		0	2278		0.319	37.6	522	9.72	100%
Pu117D	AlF=0 SO4=0.17	4.6	0	0.00	0.14	2.2	5.03	0.0	0.00		0	2314		0.317	37.4	519	7.90	101%
Pu117E	AlF=0 SO4=0.21	4.6	0	0.00	0.17	2.2	5.08	0.0	0.00		0	2350		0.315	37.2	516	5.69	99%
Pu118A	AlF=0 NO3=4	4.1	0.16	0.07	0.00	0.3	4.00	1.0	0.08	0.00	486	11985	0.4	0.050	5.9	82	0.68	99%
Pu118B	AlF=0.25 NO3=4	4.0	0.16	0.06	0.04	0.3	3.98	0.9	0.08	0.27	486	12382	0.4	0.048	5.7	79	0.87	96%
Pu118C	AlF=0.5 NO3=4	3.9	0.15	0.06	0.08	0.3	3.95	0.9	0.08	0.50	486	12735	0.4	0.047	5.5	76	1.11	96%
Pu118D	AlF=1 NO3=4	3.6	0.14	0.06	0.14	0.3	3.91	0.9	0.07	1.00	486	13482	0.4	0.044	5.1	71	1.86	92%
Pu118E	AlF=2 NO3=4	3.2	0.12	0.05	0.25	0.3	3.84	0.8	0.06	1.99	486	14965	0.4	0.038	4.5	63	5.01	91%
Pu118F	AlF=3 NO3=4	2.9	0.11	0.04	0.34	0.2	3.79	0.7	0.06	3.02	486	16497	0.4	0.034	4.1	56	7.99	80%
Pu118G	AlF=4 NO3=4	2.6	0.1	0.04	0.40	0.2	3.74	0.6	0.05	4.00	486	17975	0.4	0.031	3.7	51	8.77	67%

Table A2. Measured Flowrates from Minibank Runs.

Run	2AF	2AX	2AS	2AP	2BX	2BS	2AF	2AX	2AS	2BX	2BS	2AF	2AX	2AS	2BX	2BS
	ml/min						ml						Flowrates calculated from total volume			
	Target Rate	2.22	1.11	0.67	1.11	0.45	0.89									
MB1	8:58 AM Hot Feed							1015	990	1370	1240	410				
	9:15 AM Pulled #0 Samples															
	9:56 AM	1.81	1.14	0.60		0.44	0.76	910	925	1335	1215	366	1.81	1.12	0.60	0.43
	10:30 AM	2.34	1.14	0.67		0.46	0.88									
	11:00 AM Pulled #1 Samples															
	11:03 AM		0.97	0.52		0.52	0.96		860	1300	1180	300		1.04	0.56	0.48
	11:30 AM	2.14	1.11	0.63		0.48	0.93									
	12:06 PM	2.38	1.25	0.93		0.30	0.94	635	780	1240	1160	240	2.02	1.12	0.69	0.43
	12:58 PM							500					2.15			0.90
	1:00 PM Pulled #2 Samples															
	1:02 PM		1.34	0.54		0.46	0.89		705	1210	1125	190		1.17	0.66	0.47
	1:31 PM		1.19	0.79			0.83	420	668	1188	1120	165	2.18	1.18	0.67	0.44
	2:02 PM	2.07	1.12	0.69		0.50	0.86	360	640	1170	1105	140	2.15	1.15	0.66	0.44
	3:00 PM Pulled #3 Samples															
	3:06 PM	2.26	1.21	0.75			0.98	215	560	1120	1033	75	2.17	1.17	0.68	0.56
	3:11 PM						0.68									0.91
	3:35 PM		1.14	0.65												
	3:50 PM						0.46									
	4:00 PM Pulled #4 Samples															
	4:04 PM Shut Down							92	495	1085	1040	20	2.17	1.16	0.67	0.47
MB2	7:20 AM	2.14		0.68		0.43	0.76		1240	765	720	792				
	8:00 AM					1.25	0.93				270	752				
	8:13 AM					0.41	0.98				500	742				0.94
	8:27 AM						0.91				447					
	8:30 AM Hot Feed							1167	1175		445			0.93		3.93
	8:45 AM		0.93	0.46												
	8:30 AM Pulled #0 Samples															
	9:12 AM	2.02	0.47	0.45		0.46	0.90	1082		690	423	690	2.02		0.63	0.52
	10:15 AM Visually Detected Pu(III) in B Bank															0.88
	10:30 AM	2.00	1.11	0.67		0.45	0.94	917		635	387	620	2.08		0.75	0.48
	11:10 AM							838					2.06			0.89
	11:10 AM	1.98						838					2.06			
	11:30 AM Pulled #1 Samples															
	11:37 AM	2.22	1.18	0.65		0.47	0.92	783	940	590	355	557	2.05	1.26	0.70	0.48
	1:12 PM	2.13	1.21	0.68		0.45	0.97	581	825	525	313	465	2.08	1.24	0.68	0.47
	1:35 PM Pulled #2 Samples															
	1:50 PM	2.05	1.13	0.68		0.45	0.92	503				432	2.08			0.92
	1:58 PM							147				73				
	1:58 PM	2.11						485				425	2.08			0.92
	2:05 PM	2.05														
	2:25 PM Pulled #3 Samples															
	2:46 PM	2.15	1.06	0.70		0.47	0.93	382	725	460	268	375	2.09	1.20	0.74	0.47
	3:17 PM	2.03	1.17			0.47	0.97	317	690	445	255	345	2.09	1.19	0.65	0.47
	3:29 PM Pulled #4 Samples															
	3:30 PM	2.09	1.14	0.67		0.47	0.98									
	3:30 PM Shut Down							290	675	430	247	333	2.09	1.19	0.65	0.47

Table A3. Detailed Sample Results from Minibank Run 1.

Sample ID	ADD No.	Total alpha uCi/ml	Am241 uCi/ml	Pu uCi/ml	Pu mg/l	Alpha Am241 %	Acid Free M	D o/a Pu
MB1 A01A	3-104183	43.47	0.00349	43.46	603.0	0.008%	0.635	
MB1 A01O	3-104173	84.84	0.00539	84.84	1177.1	0.006%		1.952
MB1 A02A	3-104184	58.93	0.00473	58.93	817.6	0.008%	0.629	
MB1 A02O	3-104174	106.99	0.00574	106.99	1484.5	0.005%	0.101	1.816
MB1 A04A	3-104185	45.97	0.0069	45.97	637.8	0.015%	0.771	
MB1 A04O	3-104175	116.19	0.00739	116.18	1612.0	0.006%	0.215	2.527
MB1 A06A	3-104186	22.23	0.01182	22.22	308.3	0.053%	1.305	
MB1 A06O	3-104176	104.07	0.00593	104.06	1443.9	0.006%	0.290	4.683
MB1 A08A	3-104187	22.19	0.29835	21.89	303.8	1.34%	3.154	
MB1 A08O	3-104177	91.95	0.01416	91.93	1275.6	0.015%	0.730	4.199
MB1 A10A	3-104188	5.39	0.30425	5.09	70.6	5.64%	3.253	
MB1 A10O	3-104178	24.78	0.01221	24.77	343.7	0.049%	0.667	4.869
MB1 A12A	3-104189	1.24	0.31179	0.93	12.9	25.12%		
MB1 A12O	3-104179	4.97	0.01379	4.96	68.8	0.50%		5.336
MB1 A14A	3-104190	0.50	0.30277	0.20	2.8	60.37%	3.340	
MB1 A14O	3-104180	0.89	0.00931	0.88	12.2	1.05%	0.739	4.411
MB1 A16A	3-104191	0.37	0.29803	0.07	1.0	81.31%	2.965	
MB1 A16O	3-104181	0.14	0.01711	0.12	1.7	12.26%	0.703	1.788
MB1 B02A	3-104192	0.22		0.22	3.0			
MB1 B02O	3-104182	0.01		0.01	0.1			0.034
MB1 B04A	3-104193	3.13		3.13	43.4			
MB1 B04O	3-104212	0.08		0.08	1.0			0.024
MB1 B06A	3-104194	25.16		25.16	349.1		0.402	
MB1 B06O	3-104213	1.23		1.23	17.1		0.054	0.049
MB1 B08A	3-104195	104.07		104.07	1443.9			
MB1 B08O	3-104214	9.86		9.86	136.9			0.095
MB1 B10A	3-104196	201.03		201.03	2789.3		0.582	
MB1 B10O	3-104215	28.34		28.34	393.2		0.077	0.141
MB1 B11A	3-104197	232.79		232.79	3230.0		0.601	
MB1 B11O	3-104216	35.98		35.98	499.3		0.063	0.155
MB1 B12A	3-104198	252.86		252.86	3508.4		0.575	
MB1 B12O	3-104217	47.65		47.65	661.1		0.068	0.188
MB1 B13A	3-104199	242.83		242.83	3369.2		0.565	
MB1 B13O	3-104218	29.51		29.51	409.4		0.065	0.122
MB1 B14A	3-104200	229.87		229.87	3189.4		0.535	
MB1 B14O	3-104219	8.99		8.99	124.7		0.071	0.039
MB1 B16A	3-104201	225.27		225.27	3125.6		0.333	
MB1 B16O	3-104220	2.35		2.35	32.6		0.050	0.010
MB1 2AF	3-104010	48.06	0.39184	47.67	661.4	0.82%	3.836	
MB1 2AW0	3-104202	0.01	0.00061	0.008	0.11	6.93%	2.925	
MB1 2AW1	3-104203	0.38	0.31686	0.063	0.88	83.31%	3.136	
MB1 2AW2	3-104204	0.38	0.32148	0.058	0.81	84.62%	3.078	
MB1 2AW3	3-104205	0.38	0.30581	0.070	0.98	81.30%	3.027	
MB1 2AW4	3-104206	0.37	0.31666	0.055	0.77	85.13%	2.999	
MB1 2BP0	3-104207	0.05		0.05	0.7		0.320	
MB1 2BP1	3-104208	60.18		60.18	835.1		0.375	
MB1 2BP2	3-104209	185.57		185.57	2574.7		0.300	
MB1 2BP3	3-104210	241.99		241.99	3357.6		0.323	
MB1 2BP4	3-104211	251.60		251.60	3491.0		0.447	
MB1 2BW0	3-104221	0.000		0.000	0.00		0.027	
MB1 2BW1	3-104222	0.003		0.003	0.04		0.000	
MB1 2BW2	3-104223	0.007		0.007	0.10		0.000	
MB1 2BW3	3-104224	0.006		0.006	0.09		0.000	
MB1 2BW4	3-104225	0.008		0.008	0.11		0.022	

Table A4. Detailed Sample Results from Minibank Run 2.

Sample ID	ADD No.	Total alpha uCi/ml	Am241 uCi/ml	Pu uCi/ml	Pu mg/l	Alpha Am241 %	Acid Free M	D o/a Pu
MB2 A01A	3-104397	48.90	0	48.90	678.48	0.01%	0.618	
MB2 A01O	3-104424	85.68	0	85.68	1188.79	0.00%	0.115	1.752
MB2 A02A	3-104398	65.62	0	65.62	910.44	0.00%	0.652	
MB2 A02O	3-104425	122.04	0	122.04	1693.30	0.00%	0.117	1.860
MB2 A04A	3-104399	71.47	0	71.47	991.62	0.02%	0.816	
MB2 A04O	3-104426	128.73	0	128.73	1786.08	0.00%	0.159	1.801
MB2 A06A	3-104400	66.45	0	66.45	922.04	0.00%	1.541	
MB2 A06O	3-104427	115.77	0	115.77	1606.31	0.00%	0.305	1.742
MB2 A08A	3-104401	34.19	0.31412	33.87	470.00	0.92%	4.388	
MB2 A08O	3-104428	78.99	0.00628	78.99	1095.92	0.01%	0.831	2.332
MB2 A10A	3-104402	13.00	0.28663	12.71	176.37	2.21%	3.900	
MB2 A10O	3-104429	40.16	0.01453	40.15	557.08	0.04%		3.159
MB2 A12A	3-104403	1.70	0.3621	1.33	18.52	21.34%		
MB2 A12O	3-104430	7.61	0.01217	7.59	105.37	0.16%		5.690
MB2 A14A	3-104404	0.56	0.34719	0.21	2.90	62.46%	4.553	
MB2 A14O	3-104431	1.27	0.01083	1.26	17.54	0.85%	0.925	6.057
MB2 A16A	3-104405	0.40	0.3709	0.03	0.38	93.12%	4.484	
MB2 A16O	3-104432	0.23	0.01214	0.21	2.96	5.38%	0.878	7.794
MB2 B02A	3-104406	0.27		0.27	3.81			
MB2 B02O	3-104433	0.04		0.04	0.60			0.158
MB2 B04A	3-104407	2.69		2.69	37.35			
MB2 B04O	3-104434	0.13		0.13	1.80			0.048
MB2 B06A	3-104408	18.68		18.68	259.21		0.352	
MB2 B06O	3-104435	0.94		0.94	13.05		0.031	0.050
MB2 B08A	3-104409	84.42		84.42	1171.39		0.430	
MB2 B08O	3-104436	6.35		6.35	88.14		0.053	0.075
MB2 B10A	3-104410	201.03		201.03	2789.30		0.612	
MB2 B10O	3-104437	21.19		21.19	294.01		0.364	0.105
MB2 B12A	3-104411	256.62		256.62	3560.57		0.534	
MB2 B12O	3-104438	19.23		19.23	266.75		0.076	0.075
MB2 B14A	3-104412	232.79		232.79	3230.03		0.493	
MB2 B14O	3-104439	5.31		5.31	73.65		0.071	0.023
MB2 B16A	3-104413	215.66		215.66	2992.27		0.382	
MB2 B16O	3-104440	2.55		2.55	35.32		0.033	0.012
MB2 2AF	3-104012	55.17	0.44302	54.73	759.32	0.80%	5.345	
MB2 2AW0	3-104414	0.01	0.00042	0.008	0.11	5.07%	3.122	
MB2 2AW1	3-104415	0.40	0.33765	0.066	0.92	83.63%	4.209	
MB2 2AW2	3-104416	0.38	0.33296	0.045	0.62	88.13%	3.982	
MB2 2AW3	3-104417	0.38	0.34432	0.038	0.52	90.14%	4.267	
MB2 2AW4	3-104418	0.38	0.34949	0.035	0.49	90.89%	4.223	
MB2 2BP0	3-104419	0.91		0.91	12.58		0.214	
MB2 2BP1	3-104420	48.48		48.48	672.68		0.345	
MB2 2BP2	3-104421	186.40		186.40	2586.34		0.326	
MB2 2BP3	3-104422	229.03		229.03	3177.84		0.365	
MB2 2BP4	3-104423	228.20		228.20	3166.24		0.371	
MB2 2BW0	3-104441	0.028		0.028	0.39		0.007	
MB2 2BW1	3-104442	0.029		0.029	0.40			
MB2 2BW2	3-104443	0.041		0.041	0.56			
MB2 2BW3	3-104444	0.038		0.038	0.53			
MB2 2BW4	3-104445	0.046		0.046	0.64		0.009	