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SASSE MODELING OF FIRST CYCLE NEPTUNIUM (IV) FLOWSHEET

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2BX	Aqueous Strip to 2B Bank in Second Cycle Solvent Extraction

1.0 EXECUTIVE SUMMARY

Previous reports evaluated a flowsheet to separate neptunium from solutions in H-Canyon Tanks 16.4, 12.5, and 11.7 in the First Cycle solvent extraction banks, in which cerium(IV) (Ce(IV)) serves as an agent to oxidize all neptunium to neptunium(VI) (Np(VI)).[1,2] In this proposed oxidizing flowsheet, the Ce(IV) co-extracts with the Np(VI) in the 1BP aqueous product stream from 1B Bank. A SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) spreadsheet model indicates that a subsequent neptunium(IV) (Np(IV)) reducing flowsheet is a feasible method for separating the neptunium from the cerium and plutonium contained in the 1BP stream from the oxidizing flowsheet. The proposed reducing flowsheet calls for stripping cerium(III) (Ce(III)) and plutonium(III) (Pu(III)) from Np(IV) into the 1AW stream and extracting and then stripping Np(IV) and uranium(VI) (U(VI)) into the 1BP stream. Results from the SASSE model of the Np(VI) oxidizing flowsheet indicated that U(VI) could reflux in the 1B Bank over a certain range of acid concentrations.[2] If refluxing should occur during a Np(IV) solvent extraction, then the U(VI) could be flushed from the 1B Bank by flushing out the 1A Bank with acid and then stripping the 1B bank by adding a dilute acid to 1A Bank and process water to the 1BX stream fed to 1B Bank.

SASSE predicts that, with appropriate nitric acid (HNO_3) concentrations and/or the addition of aluminum nitrate ($Al(NO_3)_3$) as a salting agent, the separation of neptunium from cerium and plutonium can be accomplished with minimal neptunium losses from 1BP. The recommended flowsheet calls for adjustment of the 1AF stream to 1.5 M HNO_3 with addition of 1.5 M $Al(NO_3)_3$, for a total nitrate concentration of 6 M, a 1AS stream with 3.5 M HNO_3, and a 1AX:1AS volumetric flow ratio of 3:1. The recommended flowsheet also stipulates the use of process water (0.01 M HNO_3) in the 1BX stream. For these recommended conditions, the theoretical neptunium loss to 1AW is approximately 0.0036%. Predicted losses of Ce(III) and Pu(III) from 1AW and of U(VI) from 1BP are negligible. The SASSE model was validated using data from reducing flowsheets for the recovery of Np(IV) in First Cycle dating from May through December 1984.[3]

For the proposed flowsheet to be effective in recovering neptunium, the addition of a suitable valence adjustment agent such as sodium nitrite ($NaNO_2$) to the 1BP product from the oxidizing flowsheet is required to reduce Np(VI) to Np(V/IV), Ce(IV) to Ce(III), and Pu(VI) to Pu(IV/III). Ferrous sulfamate ($Fe(NH_2SO_3)_2$) also must be added to complete the reduction of neptunium to the +4 oxidation state and plutonium to the +3 oxidation state, and to stabilize Np(IV).

2.0 INTRODUCTION

Previously, a First Cycle solvent extraction of neptunium from solutions in H-Canyon Tanks 16.4, 12.5, and 11.7 was proposed, using a Np(VI) oxidizing flowsheet.[1,2] Those tank solutions contain concentrated first cycle aqueous product (1BP) recovered from solvent extraction of irradiated Savannah River fuel, dissolved unirradiated targets, and raffinate from HB-Line anion exchange processing. Because the 1BP stream and the anion exchange raffinate contain ferrous sulfamate, the tank solutions are high in sulfate (approximately 1.6 M). The separation of the neptunium from the sulfate is necessary for either recovery or discard of the neptunium.

Additionally, to recover the Np as an oxide, the preferred feed for HB-Line oxide production should be low in plutonium and cerium content.

The proposed Np(VI) flowsheet calls for the neptunium to be co-extracted with Ce(IV) and Pu(VI) into the 1BP stream. A significant amount of Ce(IV) is expected to be recovered with the Np in the 1BP stream and will consume $Fe(NH_2SO_3)_2$ needed for the valence adjustment of the neptunium. This Ce(IV) can be reduced to the inextractable Ce(III) by the addition of $NaNO_2$. Since there is significant uncertainty in the amount of Ce(IV) present in the 1BP stream from the oxidizing flowsheet, the amount of $NaNO_2$ to be added should be determined based on an analysis of the actual solution. An oxidizing normality test based on Fe(II) titration is currently being developed by SRNL/Analytical Development. The $NaNO_2$ treatment will reduce the Np(VI), Ce(IV) and Pu(VI) to Np(IV), Ce(III) and Pu(IV), respectively. The $NaNO_2$-treated 1BP may then be evaporated to increase the neptunium and HNO_3 concentrations. After evaporation, $Al(NO_3)_3$ and $Fe(NH_2SO_3)_2$ solutions will be added to the evaporated 1BP solution to prepare the neptunium solution for a reducing solvent extraction run. Evaporation of the 1BP solution may oxidize Np(V) to Np(VI). Ce(III) is not expected to oxidize to Ce(IV) during evaporation. The amount of $Fe(NH_2SO_3)_2$ added should be sufficient to provide a slight stoichiometric excess for the half-cell reaction:

$$Np^{6+} + 2Fe^{2+} \rightarrow Np^{4+} + 2Fe^{3+}$$

Recommended concentrations of HNO_3 and $Al(NO_3)_3$ salting agent for the proposed First Cycle Np(IV) flowsheet, as well as organic and aqueous stream flow rates, are calculated using a SASSE spreadsheet solvent extraction model. This report presents the results of the SASSE model of this proposed First Cycle Np(IV) flowsheet. In the proposed Np(IV) flowsheet, Np(IV) and U(VI) extract into the 1AU stream in A Bank, while Ce(III) and Pu(III) are rejected into the 1AW stream. Both Np(IV) and U(VI) then are stripped into the 1BP stream in B Bank.

3.0 SASSE MODEL

SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) is a Microsoft Excel spreadsheet macro that models equilibrium countercurrent solvent extraction processes.[4] The SASSE spreadsheet was developed by Argonne National Laboratory for use in modeling organic/aqueous solvent extraction of actinides. Input items for the SASSE spreadsheet include the number of stages, the feed and product stream locations, flow rates and compositions, organic and aqueous volumes, separation efficiencies, entrainments for each stage, and distribution coefficients for each stage. The distribution coefficients may be entered as functions of the aqueous concentrations in the stage. The SASSE models are limited to one bank and are normally set up for an organic feed to the first stage, an aqueous feed to an intermediate stage, and an aqueous scrub to the last stage.

Figure 3-1 depicts the SASSE models of the H Canyon 1A and 1B Banks for the proposed solvent extraction of Np(IV). Separate SASSE calculations are used to model 1A and 1B Banks. The models for the 1A and 1B Banks are connected by specifying the organic product from 1A

Bank (1AU) as the intermediate feed to 1B Bank and the organic product from 1B Bank as the feed to 1C Bank.

The SASSE model was validated using historical data before it was applied to the proposed Np(IV) flowsheet. Historical data are available from a reducing flowsheet for separations of Np(IV) in the H Canyon Second Cycle Solvent Extraction Banks (2A and 2B) between 1964 to 1967[5] and in the H Canyon First Cycle Solvent Extraction Banks (1A and 1B) between May and December 1984. The First Cycle solvent extraction runs were selected as the validation test case for the SASSE model. The SASSE model for the test case includes the same streams as the proposed flowsheet, which are depicted in Figure 3-1. Table 3-1 gives the flow rates, temperatures, and compositions for the SASSE validation calculation. Feed concentrations of components other than nitric acid are specified at a nominal value of 1 M.

Table 3-2 lists the flow rates, temperatures, and compositions used by SASSE to model the proposed flowsheet. The flow rates are based largely on recent First Cycle operating experience with unirradiated Mark 22 assemblies and Idaho National Laboratory (INL) blended materials.[6] The effect of an increase in the 1AX flow rate on reducing the neptunium loss to the 1AW stream is examined by analyzing an alternate flowsheet with a 1AX:1AF flow ratio of 3.0, which is the maximum ratio recommended by H-Canyon based on operating experience. The increase in the 1AX flow rate is offset by an equal decrease in the 1BS flow rate, so that the 1BU flow rate leaving the 1B Bank remains the same.

Temperatures are specified at an elevated temperature of 45 °C, which yields a lower bound for calculated distribution coefficients. Actual temperatures may differ slightly from the recommended flowsheet temperatures. The normal operating temperatures for 1B Bank and 1C Bank are 35 °C and 60 °C, respectively. At 35 °C, all modeled solution components would extract into the organic phase in 1B somewhat better than predicted by the SASSE model, which used 45 °C. By contrast, at 60 °C, the modeled solution components would strip into the aqueous phase better than predicted by SASSE.

Nitric acid concentrations are specified at 0.01 M in 1AX, 1BX, 1BS, and 1CX. The model also includes aluminum(III) (Al(III)) (as $Al(NO_3)_3$), Ce(III), U(VI), Np(IV), and Pu(III). All feed concentrations for Ce(III), U(VI), Np(IV), and Pu(III) are set at a nominal concentration equal to a fraction of the concentration in the aqueous feed, 1AF, to allow a direct calculation of decontamination factors (DF's) for the product solutions. Likewise, the Np(IV) concentration for the validation case is normalized with respect to the 1AF feed concentration. The HNO_3 concentrations in the 1AF and 1AS streams and the Al(III) concentration in 1AF are expressed in molar units and are treated as variables which control the neptunium losses in A Bank.

The mixer-settler stages in 1A and 1B Banks have the same dimensions, so they should hold the same aqueous and organic volumes. The volumes in 1C Bank are larger. The aqueous and organic volumes contained in each stage depend to a small extent on the relative flow rates of the organic and aqueous phases. Table 3-3 lists the formulas used to compute the total organic and aqueous volumes contained in each stage.[7,8]

Equilibrium stage efficiencies and entrainment ratios were estimated in part by fitting the Second Cycle validation calculations for the proposed Np(VI) oxidizing flowsheet to measured thorium and neptunium DF's and losses.[2] Specifically, the equilibrium stage efficiencies for A and B Banks were calculated by matching measured and calculated thorium DF's for the 2A Bank, and the aqueous entrainment in the organic phase was calculated by matching measured and calculated neptunium losses for the 2B Bank. The aqueous entrainment in the organic phase was previously determined for both A and B Banks using historical operating data. For the 1A Bank, two separate calculations gave aqueous-in-organic entrainments of 0.65 and 0.68 %.[9,10] The SASSE models for both the validation case and the proposed flowsheet use the average of these two values, which is 0.665 %. Measured aqueous entrainments in the organic phase for B Bank range from 1.24 % to 2.33 % at normal flow rates,[11] and from 4.0 % to 9.3 % at high flow rates.[12] These studies did not report any measurable organic entrainment in the aqueous phase. In view of the wide range of reported B Bank entrainments, the B Bank aqueous in organic entrainment was fitted using the Np(VI) flowsheet validation calculations. An entrainment ratio of 1.75% was calculated.[2] Because there were no reports of organic in aqueous entrainment, the organic in aqueous entrainment for both A and B Banks was set at zero. The entrainments for C Bank were set at the same values used for B Bank.

Table 3-1. Flow Rates, Temperatures, and Compositions for Validation Case, First Cycle Neptunium(IV) Solvent Extraction Flowsheet

Stream	**1AX**	**1AF**	**1AS**	**1BX**	**1CX**
Flow Rate (L/min, nominal)	1.70	1.0	0.22	1.02	1.21
Temperature (°C)	40	40	40	35	60
TBP (volume %)	7.5				
HNO_3 (M)	0.01	1.50	2.94	1.55	0.01
Np (normalized basis)	0	1.0	0	0	0

Table 3-2. Flow Rates, Temperatures, and Compositions for Proposed First Cycle Neptunium(IV) Solvent Extraction Flowsheet

Stream	1AX	1AF	1AS	1BS	1BX	1CX
Flow Rate (L/min)	10.5 or 17.34	5.78	1.25	18.16 or 11.32	6.1	6.15
Temperature (°C)	45	45	45	45	45	45
TBP (volume %)	7.5			7.5		
HNO_3 (M)	0.01	variable	3.0	0.01	0.01	0.01
Al (M)	0	variable	0	0	0	0
Ce (normalized basis)	0	1.0	0	0	0	0
U (normalized basis)	0	1.0	0	0	0	0
Np (normalized basis)	0	1.0	0	0	0	0
Pu (normalized basis)	0	1.0	0	0	0	0

Table 3-3. Aqueous and Organic Volumes in A, B, and C Banks

	Aqueous	Organic
A and B Banks		
Mixer Volume (L/stage)	$2.36+9.439\frac{Q_{aq}}{Q_{aq}+Q_{or}}$	$9.439\frac{Q_{or}}{Q_{aq}+Q_{or}}$
Settler Volume (L/stage)	21.1	42.1
Total Volume (L/stage)	$23.46+9.439\frac{Q_{aq}}{Q_{aq}+Q_{or}}$	$42.1+9.439\frac{Q_{or}}{Q_{aq}+Q_{or}}$
C Bank		
Mixer Volume (L/stage)	$6.637+25.22\frac{Q_{aq}}{Q_{aq}+Q_{or}}$	$25.22\frac{Q_{or}}{Q_{aq}+Q_{or}}$
Settler Volume (L/stage)	84.93	169.83
Total Volume (L/stage)	$91.567+25.22\frac{Q_{aq}}{Q_{aq}+Q_{or}}$	$169.83+9.439\frac{Q_{or}}{Q_{aq}+Q_{or}}$

Note: Q_{aq} and Q_{or} represent the aqueous and organic phase flow rates in L/min.

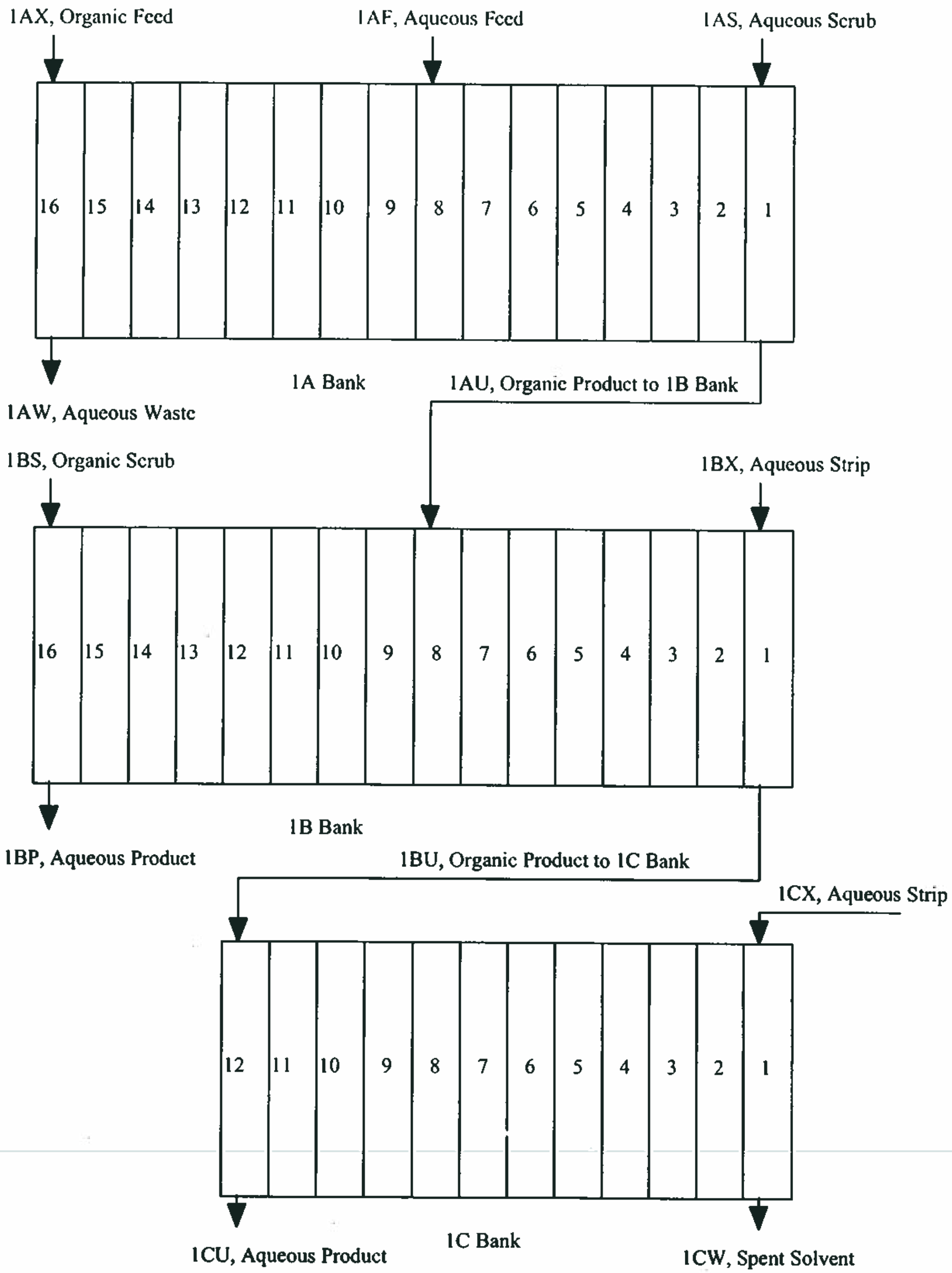

Figure 3-1. First Cycle Neptunium(IV) Recovery Flowsheet

4.0 DISTRIBUTION COEFFICIENT CORRELATIONS

The SASSE model for the proposed flowsheet includes distribution coefficients for free acid (HNO_3), Ce(III), U(VI), Np(IV),and Pu(III). However, the SASSE validation model requires only distribution coefficients for HNO3 and Np(IV). The distributions coefficients for the HNO_3, U(VI), and Pu(III) are based on measured data from the Savannah River Site, while the distribution coefficients for Ce(III) and Np(IV) were obtained from other sources. The distribution coefficients are correlated as functions of the HNO_3 concentration and the Al(III) concentration. In general, the distribution coefficients for HNO_3, U(VI), and Pu(III) increase rapidly with acid concentration up to about 4 to 5 M HNO_3, then plateau, and drop off at higher acid concentrations. The distribution coefficient for Np(IV) exhibits similar behavior, with a peak value at about 8 M HNO_3. Consequently, correlations that account for the increases in the distribution coefficients at the lower acid concentrations, with an upper asymptote that comes into effect at a higher acid concentration, were deemed sufficient and are used. The variation of the distribution coefficients with Al(III), or $Al(NO_3)_3$, concentration is covered later in this section.

Distribution coefficients for HNO_3 and for U(VI) in 7.5 vol % TBP have been measured.[13] At low uranium concentrations, a fit of these measured data give,[2] for the distribution of HNO_3 in 7.5% TBP (the proposed flowsheet conditions),

$$D_{\%_a,HNO_3} = \min\left(0.047, 0.0281[HNO_3]^{0.6439}\right) \tag{1}$$

and for the distribution of U(VI) in 7.5% TBP,

$$D_{\%_a,U(VI)} = \min\left(3.289, 0.6127[HNO_3]^{1.4425}\right) \tag{2}$$

The distribution coefficient correlations for Np(IV) are based on data for acid solutions in contact with 2.5 vol %, 7.5 vol %, and 30 vol % TBP in n-paraffin at 25 °C.[14,15,16] The low acid range correlation is from a regression of the data, which is shown in Figure 11-1. The upper asymptote is taken to be equal to the maximum measured distribution coefficient, which occurs for solutions in contact with 8 M HNO_3. The correlation for the Np(IV) distribution coefficient for nitric acid solutions for the proposed flowsheet is based on the 7.5 vol % TBP data and takes the form:

$$D_{\%_a,Np(IV)} = \min\left(1.5, 0.022[NO_3^-]^{2.0294}\right) \tag{3}$$

where $[NO_3^-]$ is the total nitrate ion concentration from both HNO_3 and metal nitrates. The nitrate concentration is expressed in this form to accommodate expressions for the salting effect of $Al(NO_3)_3$, described later in this section.

Limited data for the Np(IV) distribution coefficient for $HNO_3 - Al(NO_3)_3$ solutions at elevated temperatures indicate that Np(IV) becomes slightly more extractable as the temperature increases.[17] The conservative approach taken in this study (i.e., the approach that yields a conservatively low value for the Np(IV) distribution coefficient) is to neglect the variation with temperature.

The Pu(III) distribution coefficients are scaled linearly to measured distribution coefficients for acid solutions in contact with 19 vol % TBP and 36 vol % TBP in kerosene at 19 to 23 °C.[18,19,20] The 7.5% TBP correlation used to model the proposed flowsheet is scaled to the 19% TBP data, and the 30% TBP correlation used for the validation calculations is scaled to the 36% TBP data. Such scaling should yield conservatively high values for estimated distribution coefficients, since the measured 36% TBP coefficients are more that twice the measured 19% TBP coefficients. There was no attempt to correct the Pu(III) distribution coefficient for temperature effects.

The estimated Pu(III) distribution coefficients are based on power-law regressions of measured distribution data for acid solutions below about 2 M HNO_3, which are illustrated in Figure 11-2, and maximum measured distribution ratios at approximately 2 M HNO_3. The resulting asymptotic expressions for the Pu(III) distribution coefficients for acid solutions in contact with 7.5 vol % TBP for the proposed flowsheet is:

$$D_{\%_a,\mathrm{Pu(III)}} = \min\left(0.0163, 0.00209[NO_3^-]^{0.9865}\right) \tag{4}$$

Finally, distribution data for Ce(III) are correlated using data for acid solutions in contact with 48 vol % TBP in kerosene and 100% TBP.[21] Because it was not certain beforehand that the Ce(III) distribution would be sufficiently low to permit separation from Np(IV), an effort was made to base the scaling of the Ce(III) distribution coefficient on a power law relationship with the TBP concentration. A data comparison indicates that the distribution coefficients for 100 vol % TBP are approximately three times higher than the distribution coefficients for 48 vol % TBP, as Figure 11-3 shows. Based on this comparison, the Ce(III) distribution coefficient scales proportionally to the TBP concentration to the 1.5 power. When this factor is applied to scale the 48 vol % TBP data to 7.5 vol % TBP, the estimated distribution coefficient correlation in Figure 11-4 results:

$$\begin{aligned} D_{\%_a,\mathrm{Ce(III)}} &= 0.001(-0.6606 + 5.3739[NO_3^-] \\ &- 2.1451[NO_3^-]^2 + 0.3117[NO_3^-]^3 - 0.0157[NO_3^-]^4) \end{aligned} \tag{5}$$

4.1 CORRELATION OF DISTRIBUTION COEFFICIENTS WITH ALUMINUM NITRATE CONCENTRATION

The preceding distribution coefficient correlations do not account for the "salting" effect that would occur if inextractable metal nitrate salts were added to the aqueous solution. The addition of $Al(NO_3)_3$ to the 1AF feed has been proposed as an alternative that would reduce the need for high HNO_3 concentrations to make Np(IV) extract. Reducing the HNO_3 concentration would

To apply the "salting" effect of $Al(NO_3)_3$, the SASSE model must include a distribution coefficient for $Al(NO_3)_3$ or Al(III). It is assumed that the distribution coefficient for Al(III) is 1×10^{-4}. This low value ensures that nearly all the aluminum from the 1AF feed remains in the aqueous phase and, therefore, goes out with the 1AW waste stream.

The SASSE model does not explicitly include distribution coefficients for sulfates and metal impurities other than the actinides and cerium, such as iron, aluminum, sodium, and any fission products that may be present in the aqueous feed from the H-Canyon tanks. These constituents are expected to strip into the aqueous phase in A Bank during the processing of the Np(IV) flowsheet.

5.0 VALIDATION WITH FIRST NEPTUNIUM CYCLE FLOWSHEET

The validation test conditions were modeled using the flow rates, temperatures, and compositions listed in Table 3-2, the distribution coefficients listed in the previous section, a 1A Bank aqueous-in-organic entrainment of 0.665%, a 1B Bank aqueous in organic entrainment of 1.75%, and an equilibrium stage efficiency of 0.965. The stage separation efficiency for both 1A and 1B Banks (assumed to be equal) was estimated by matching calculated and measured values for the thorium DF and the neptunium loss in 2A Bank for the Second Product Cycle oxidizing Np(VI) flowsheet.[2] The aqueous in organic entrainment for B Bank was estimated by comparing calculated and measured neptunium losses in 2B Bank for the same flowsheet.[2]

Performance data for Np(IV) reducing flowsheets are available for Second Product Cycle extraction runs conducted between October 1964 and August 1967[5] and First Cycle extraction runs conducted between May and December 1984.[3] The validation calculations for the proposed Np(IV) reducing flowsheet model the First Cycle extraction runs from 1984, since conditions for the First Cycle runs more closely match the proposed flowsheet conditions. The validation calculations compare measured and calculated neptunium losses to the 1AW aqueous waste stream in terms of the percentage of neptunium fed in the 1AF stream. Measured 1AW losses, which are tabulated in Table 5-1, ranged from 0.17% to 3.61%; with 16 of the 19 measured losses lying below 1%. The losses above 1% probably resulted from process upsets, so the neptunium losses for normal process conditions varied from about 0.2% to slightly below 1%. Also listed in Table 5-1 are the measured losses to 1CU, both in terms of a decontamination factor (DF) and a percentage loss. Measured losses to 1CU ranged from 3.6% to 25%, far above what would be predicted by the SASSE model, even with the HNO_3 concentration of 1.55 M in the 1BX stream used during the 1984 runs. Due to the obvious discrepancy between predicted and measured 1CU losses, no attempt was made to validate these losses with the SASSE model.

The 1AW neptunium loss calculated from the SASSE model is 0.202%. This loss is approximately equal to the minimum measured 1AW loss, as Figure 5-1 shows. The approximate agreement between the calculated and the minimum measured neptunium losses indicates that the correlated Np(IV) distribution coefficient, which models ideal operation of the solvent extraction banks, is reasonably accurate for conditions in the 1A Bank. Figures 5-2 through 5-7 depict calculated stagewise distributions and organic/aqueous distributions of HNO_3

and Np(IV) in the 1A and 1B Banks. As these figures show, the SASSE model predicts that the Np(IV) almost completely extracts into the organic phase in the 1A Bank and is almost entirely stripped into the aqueous phase in the 1B Bank. Stagewise distributions in the 1C Bank are not shown, since calculated metal ion concentrations in the 1C Bank are negligible.

Table 5-1. Neptunium Losses during Processing of the First Cycle Reducing Flowsheet from May 1984, to December 1984

Date	Np Loss to 1AW (%)	Np DF (1AF/1CU)	Np Loss to 1CU (%)
5/21/1984	0.98	9	11.1
5/28/1984	0.59	12	8.3
6/4/1984	0.23	9	11.1
6/11/1984	0.67	13	7.7
6/18/1984	0.32	12	8.3
8/20/1984	0.49	19	5.3
8/27/1984	0.26	11	9.1
9/3/1984	0.53	11	9.1
9/17/1984	0.37	10	10.0
9/24/1984	0.26	10	10.0
10/1/1984	1.45	4	25.0
10/8/1984	0.26	11	9.1
10/15/1984	0.29	12	8.3
10/22/1984	0.16	28	3.6
10/29/1984	3.16	---	---
11/5/1984	0.17	15	6.7
11/12/1984	1.61	---	---
11/26/1984	0.38	---	---
12/3/1984	0.23	22	4.5

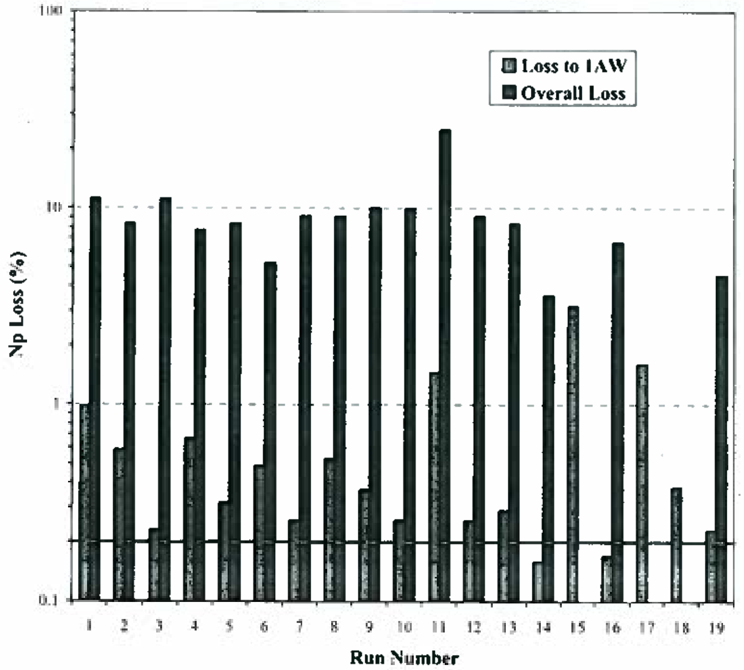

Figure 5-1. Comparison of Np(IV) Loss Calculated by SASSE with Measured Np(IV) Losses in the 2A Bank

Note: The horizontal blue line represents the 1AW loss predicted by the SASSE model.

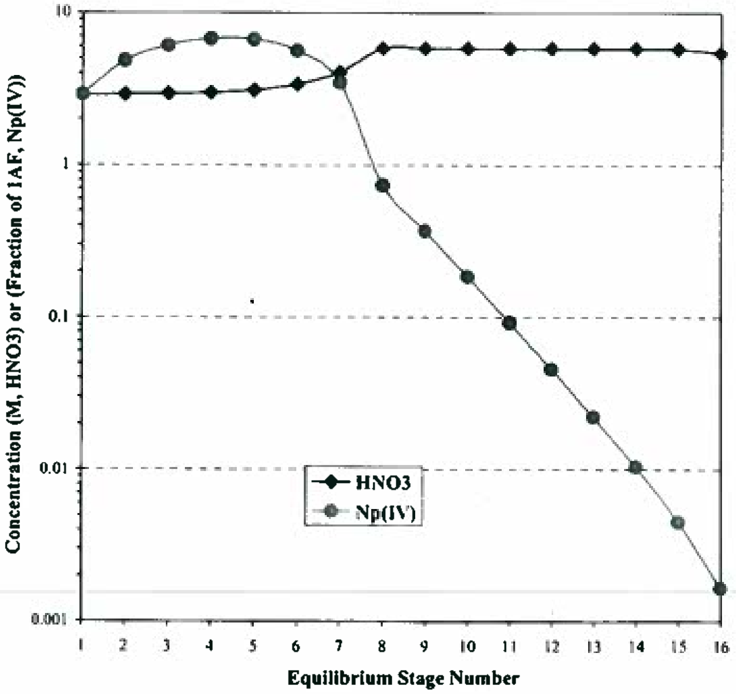

Figure 5-2. SASSE Predictions of Aqueous Phase Concentrations in 1A Bank for Validation Calculation

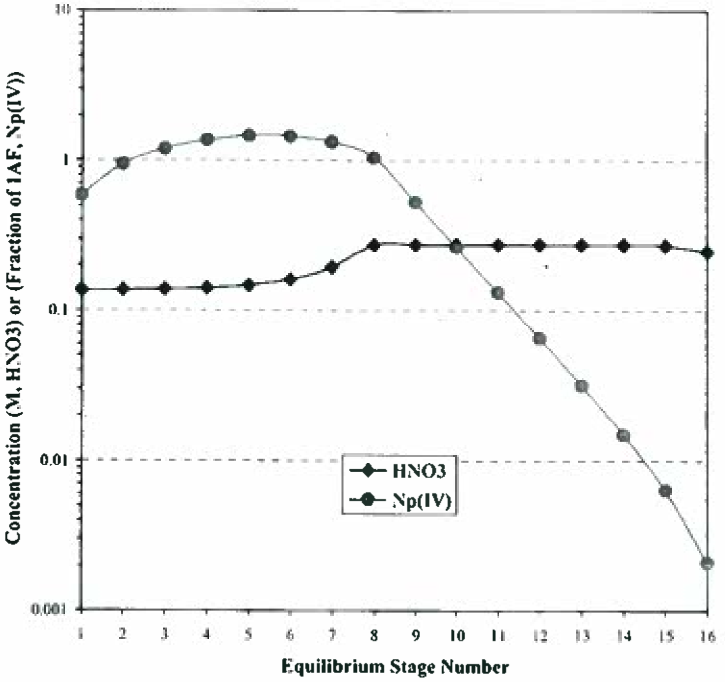

Figure 5-3. SASSE Predictions of Organic Phase Concentrations in 1A Bank for Validation Calculation

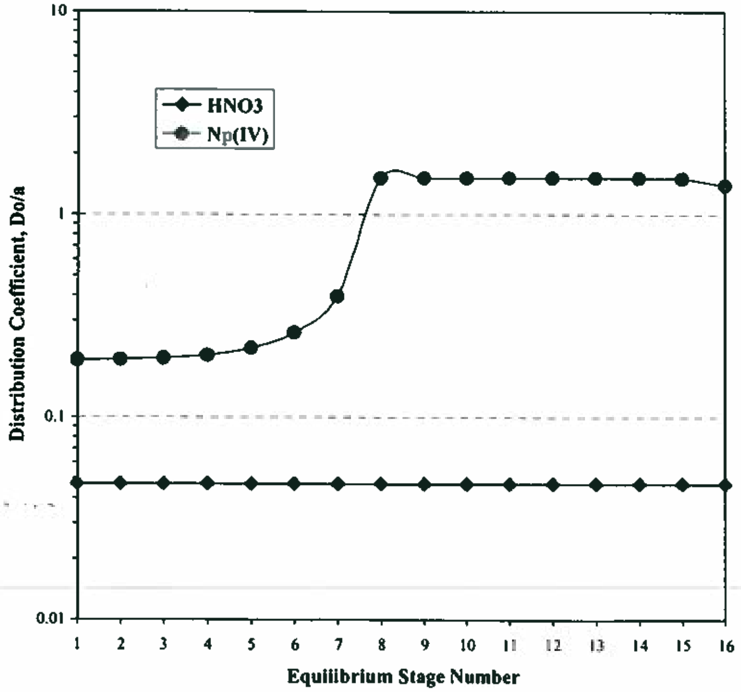

Figure 5-4. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1A Bank for Validation Calculation

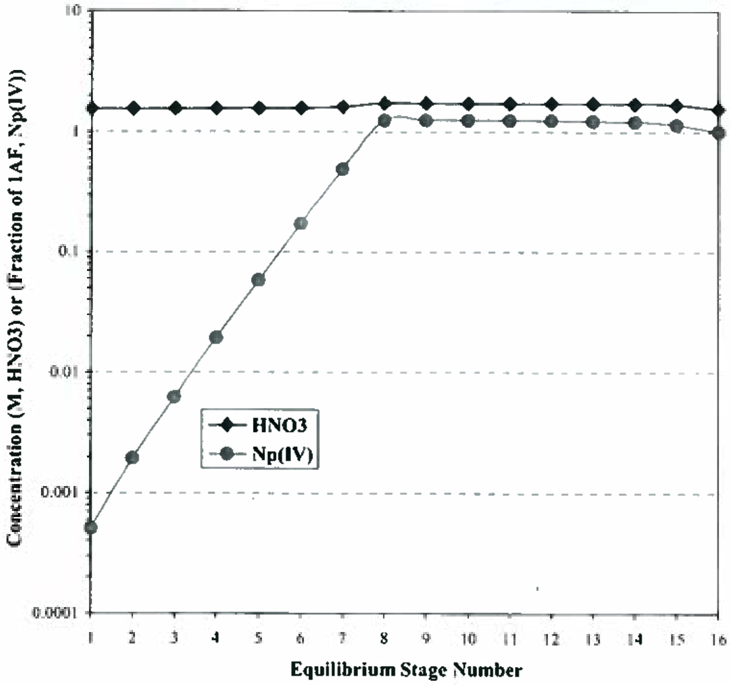

Figure 5-5. SASSE Predictions of Aqueous Phase Concentrations in 1B Bank for Validation Calculation

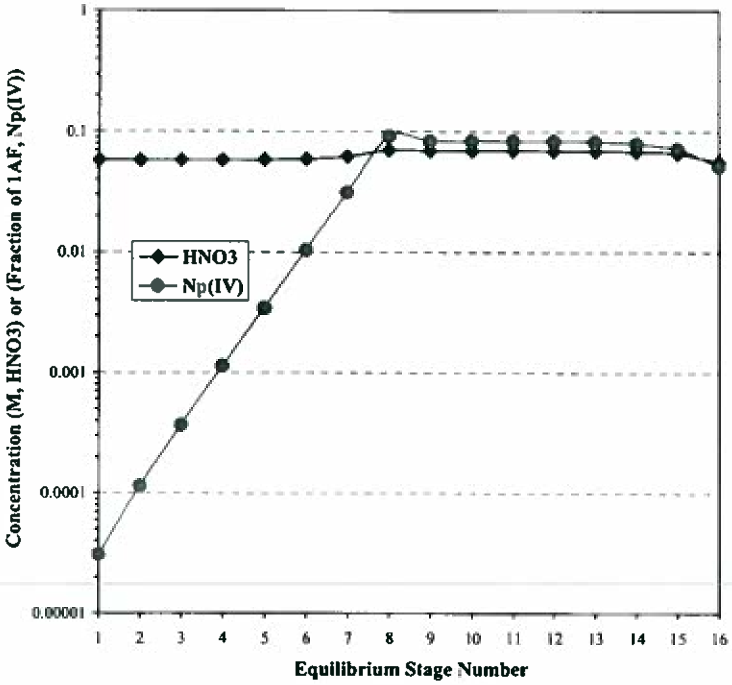

Figure 5-6. SASSE Predictions of Organic Phase Concentrations in 1B Bank for Validation Calculation

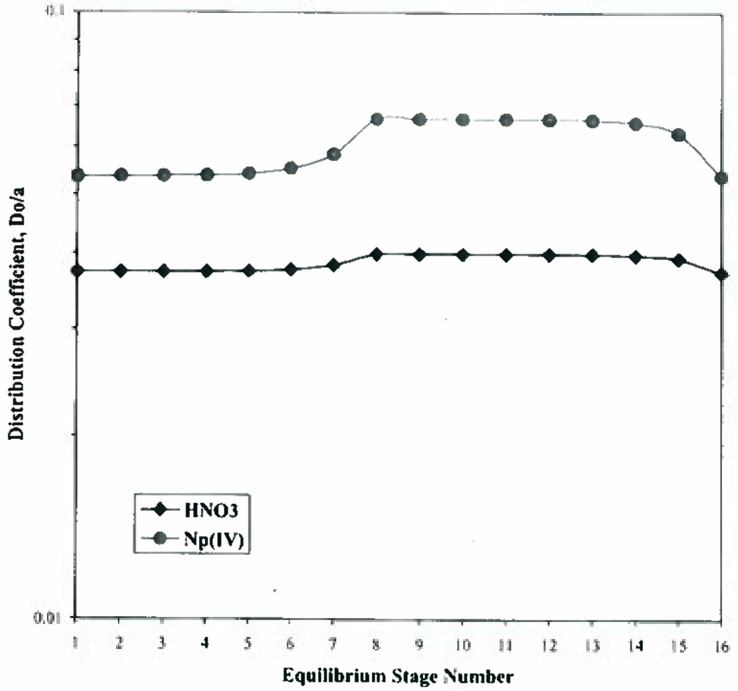

Figure 5-7. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1B Bank for Validation Calculation

6.0 PREDICTIONS FOR PROPOSED FIRST CYCLE FLOWSHEET

The same stage efficiency and aqueous-in-organic entrainment ratios that were used to fit the results of the validation test were applied to model the proposed First Cycle flowsheet, along with the flow rates, temperatures, and compositions listed in Table 3-1 and the distribution coefficient formulas listed in Section 4.0. The SASSE model does not account for changes in the stage efficiency and the entrainment due to variations in the organic and aqueous flow rates. An increase in the organic flow rate may be expected to increase the aqueous-in-organic entrainment and decrease the stage efficiency.

Np(IV) losses to 1AW were estimated for total NO_3^- concentrations (including both HNO_3 and $Al(NO_3)_3$) ranging from 3.5 M to 6.0 M and for $Al(NO_3)_3$ concentrations in 1AF ranging from 0.0 M to 1.5 M. The maximum total NO_3^- concentration of was limited to 6 M to prevent the formation of the inextractable anionic species $Np(NO_3)_6^{2-}$, which forms at total NO_3^- concentrations above 7.0 M[24,25] and reaches a maximum concentration at 7.5 to 8 M total NO_3^-.[26] The maximum $Al(NO_3)_3$ concentration of 1.5 M leaves free HNO_3 over the entire specified range of total NO_3^- concentrations and lies somewhat below the $Al(NO_3)_3$ solubility limit of approximately 2 M. The HNO_3 concentration in 1AS was set at a constant 3 M to approximately match the nominal 1AS concentration of 2.94 M from the validation case.

Tables 6-1 and 6-2 list calculated Np(IV) losses to 1AW for ranges of HNO_3 and $Al(NO_3)_3$ concentrations at 1AX:1AF volumetric flow ratios of 1.81 and 3.0, respectively. At the flow ratio of 1.81, losses vary from 76.2% for 3.5 M HNO_3 with no $Al(NO_3)_3$ to less than 1% for acid concentrations with 1.5 M $Al(NO_3)_3$. At the flow ratio of 3.0, losses range from 41.8% for 3.5 M HNO_3 with no $Al(NO_3)_3$ to less than 1% for total NO3- concentrations of 5.0 M or greater and $Al(NO_3)_3$ concentrations of 0.5 M or greater. The recommended flowsheet has a 1AX:1AF flow ratio of 3.0 with a 1AF feed composition of 6.0 M total NO_3^- with 1.5 M $Al(NO_3)_3$, which gives a Np(IV) loss of 0.0022%. This loss is deemed satisfactory even with the uncertainties built into the correlation of distribution coefficients and the SASSE model. Figures 6-1 through 6-6 depict the stagewise aqueous and organic phase concentrations and distribution coefficients in 1A and 1B Banks for the recommended feed conditions. As these figures show, Ce(III) and Pu(III) strip into the 1AW aqueous stream in 1A Bank, and Np(IV) and U(VI) extract into the 1AU stream and then strip into the 1BP aqueous stream in 1B Bank. Stagewise phase concentrations in the 1C Bank are not shown, because the calculated metal ion concentrations in 1C Bank are negligible.

Table 6-1. Np(IV) Losses to 1AW as a Function of Nitric Acid and Aluminum Nitrate Concentrations in 1AF at a 1AS Nitric Acid Concentration of 3.0 M and a 1AX:1AF Volumetric Flow Ratio of 1.81

Total [NO_3^-] (M)	[$Al(NO_3)_3$[(M)			
	0.0	**0.5**	**1.0**	**1.5**
3.5	76.2%	62.0%	33.6%	
4.0	65.5%	47.5%	20.2%	
4.5	51.9%	31.6%	10.4%	
5.0	36.4%	17.7%	4.7%	0.67%
5.5	21.6%	8.4%	2.0%	0.31%
6.0	10.8%	3.6%	0.84%	0.15%

Table 6-2. Np(IV) Losses to 1AW as a Function of Nitric Acid and Aluminum Nitrate Concentrations in 1AF at a 1AS Nitric Acid Concentration of 3.0 M and a 1AX:1AF Volumetric Flow Ratio of 3.0

Total [NO_3^-] (M)	[$Al(NO_3)_3$] (M)			
	0.0	**0.5**	**1.0**	**1.5**
3.5	41.8%	17.8%	2.5%	
4.0	23.0%	6.8%	0.86%	
4.5	9.5%	2.2%	0.29%	
5.0	3.2%	0.67%	0.10%	0.011%
5.5	0.98%	0.21%	0.036%	0.0049%
6.0	0.30%	0.069%	0.014%	0.0022%

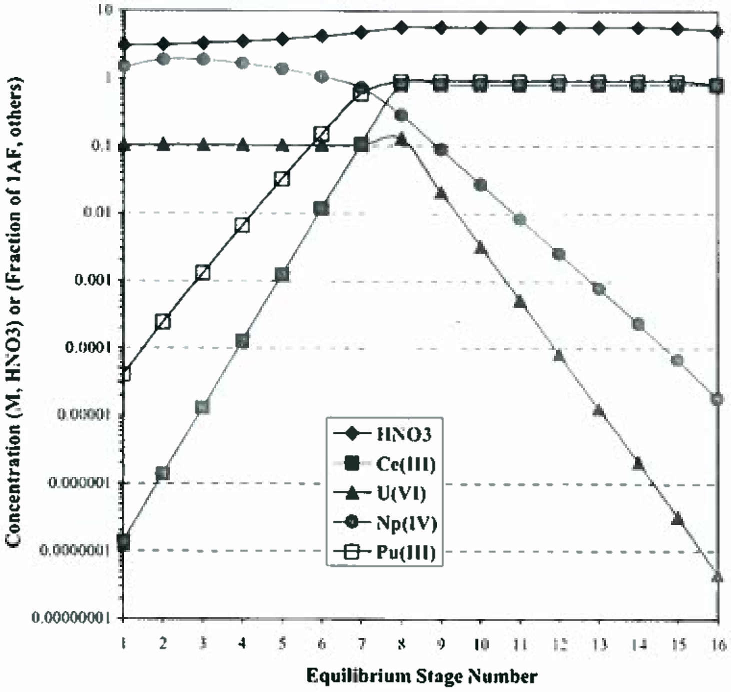

Figure 6-1. SASSE Predictions of Aqueous Phase Concentrations in 1A Bank for Proposed Flowsheet, with 1.5 M HNO_3 and 1.5 M $Al(NO_3)_3$ in 1AF and 3.0 M HNO_3 in 1AS

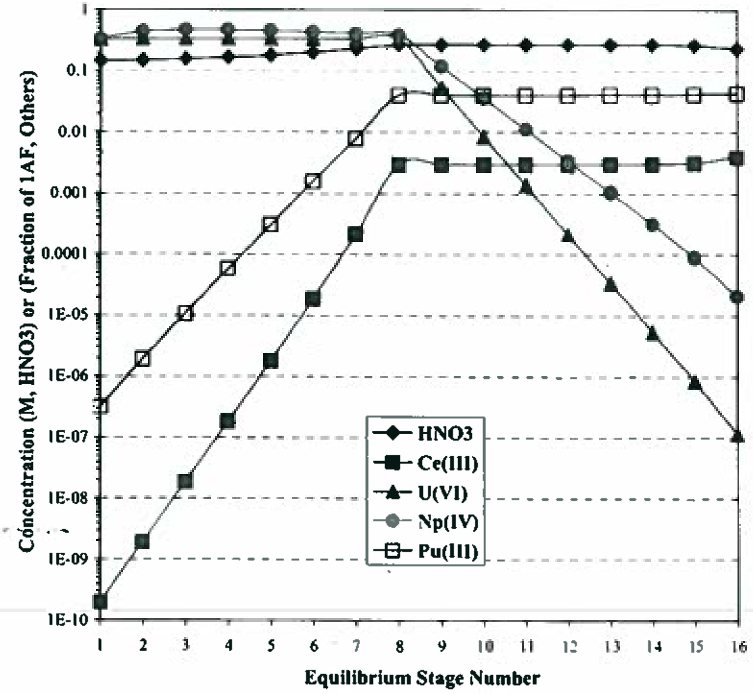

Figure 6-2. SASSE Predictions of Organic Phase Concentrations in 1A Bank for Proposed Flowsheet, with 1.5 M HNO_3 and 1.5 M $Al(NO_3)_3$ in 1AF and 3.0 M HNO_3 in 1AS

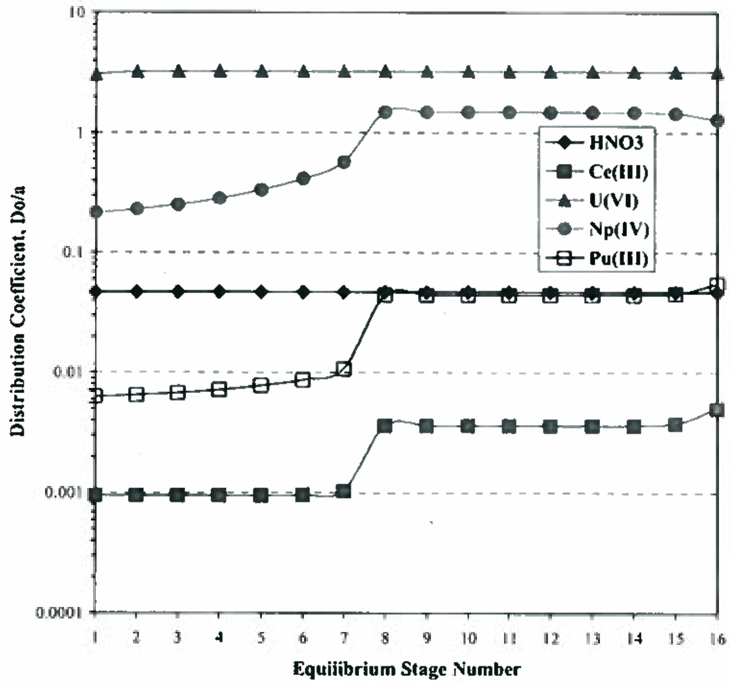

Figure 6-3. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1A Bank for Proposed Flowsheet, with 1.5 M HNO_3 and 1.5 M $Al(NO_3)_3$ in 1AF and 3.0 M HNO_3 in 1AS

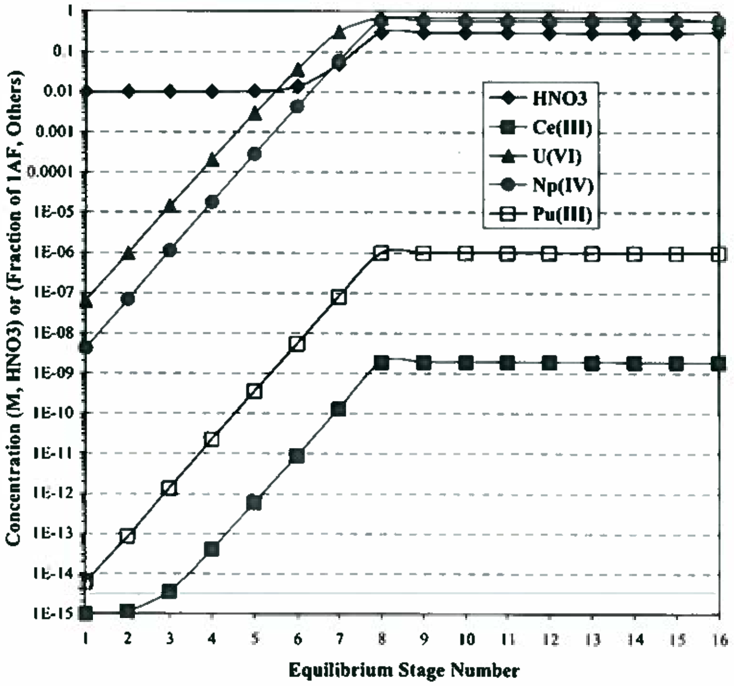

Figure 6-4. SASSE Predictions of Aqueous Phase Concentrations in 1B Bank for Proposed Flowsheet, with 1.5 M HNO_3 and 1.5 M $Al(NO_3)_3$ in 1AF and 3.0 M HNO_3 in 1AS

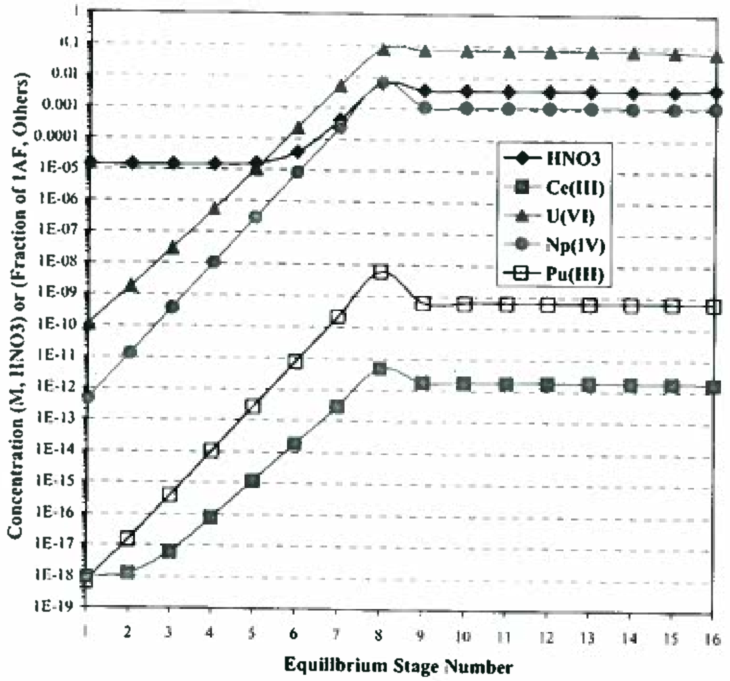

Figure 6-5. SASSE Predictions of Organic Phase Concentrations in 1B Bank for Proposed Flowsheet, with 1.5 M HNO_3 and 1.5 M $Al(NO_3)_3$ in 1AF and 3.0 M HNO_3 in 1AS

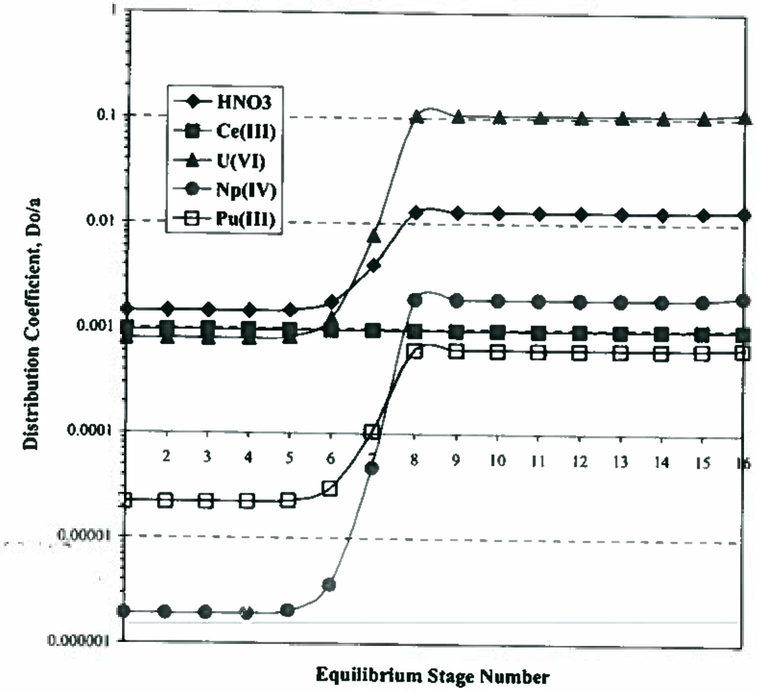

Figure 6-6. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1B Bank for Proposed Flowsheet, with 1.5 M HNO_3 and 1.5 M $Al(NO_3)_3$ in 1AF and 3.0 M HNO_3 in 1AS

Calculated distributions of Ce(III), U(VI), Np(IV), and Pu(III) in the proposed flowsheet (6.0 M total NO_3^- and 1.5 M $Al(NO_3)_3$ in 1AF, 3.0 M HNO_3 in 1AS, and a 1AX:1AF flow ratio of 3.0) are listed in Table 6-3. As these distributions show, the SASSE model predicts that Ce(III) and Pu(III) are stripped into 1AW in A Bank, and Np(IV) and U(VI) are stripped into 1BP in B Bank, all with low losses. Table 6-3 does not list the distributions of aluminum and other nonactinide metal impurities. These metals not listed should quantitatively strip into the aqueous phase and exit with the 1AW aqueous waste.

Table 6-3. Distribution of Cerium and Actinide Species among Proposed Flowsheet Output Streams

	% in 1AW	**% in 1BP**	**% in 1CU**	**% in 1CW**
Ce(III)	>99.9999	<0.0001	<0.0001	<0.0001
U(VI)	<0.0001	>99.9999	<0.0001	<0.0001
Np(IV)	0.0036	99.9964	<0.0001	<0.0001
Pu(III)	99.9999	0.0001	<0.0001	<0.0001

7.0 RECOMMENDED FIRST CYCLE NP(IV) FLOWSHEET CONDITIONS

At the request of H-Canyon Engineering, results of the SASSE modeling were combined with historical operating temperatures,[3] the valence adjustment stoichiometry outlined in Section 2.0, and estimates of the 1AF stream composition to generate a recommended First Cycle Np(IV) flowsheet. The 1AF stream composition in this recommended flowsheet is defined by the composition of the 1BP aqueous product from the proposed Np(VI) oxidizing flowsheet and post solvent extraction solution additions associated with evaporation. These conditions utilize a somewhat higher 1AX flow rate than is currently used to provide additional confidence of high neptunium recovery. Even higher 1AX :1AF flow ratios were modeled, but somewhat lower plutonium rejection to 1AW was observed.

Table 7-1 lists the recommended operating conditions for the proposed First Cycle Np(IV) flowsheet. Ranges of feed concentrations and flow rates are set to comply with H-Canyon control capabilities, and temperature ranges are specified in 5 °C intervals.

Table 7-1. Recommended Operating Conditions for the First Cycle Np(IV) Flowsheet

Stream	Parameter	Units	Minimum	Nominal	Maximum
1AF	HNO_3	M	1.3	1.5	a
1AF	$Al(NO_3)_3$	M	1.3	1.5	a
1AF	Np	g/L	3	4.5	5
1AF	$Fe(NH_2SO_3)_2$	M		0.02 b	
1AS	HNO_3	M	3.2	3.5	3.8
1AS'	$Fe(NH_2SO_3)_2$	M	2.0	2.4	c
1BX	HNO_3	M	0.005	0.01	0.04
1CX	HNO_3	M	0.005	0.01	0.04
1AX/1AF	flow ratio	(L/min)/(L/min)	2.2	2.7	3.2
1AS/1AF	flow ratio	(L/min)/(L/min)	0.20	0.23	0.29
1AS'/1AF	flow ratio	(L/min)/(L/min)	0.009	0.014	0.017
1BX/1AF	flow ratio	(L/min)/(L/min)	1.03	1.21	1.39
1BS/1AF	flow ratio	(L/min)/(L/min)	2.2 d	2.7 d	3.2 d
1CX/1AF	flow ratio	(L/min)/(L/min)	1.15	1.37	1.59
1AF	temperature	°C	35	40	45
1AS	temperature	°C	35	40	45
1AS'	temperature	°C	35	40	45
1AX	temperature	°C	35	40	45
1BS	temperature	°C	30	35	40
1BX	temperature	°C	30	35	40
1CX	temperature	°C	55	60	60

Note a) $Al(NO_3)_3$ and HNO_3 should be limited to < 7.0 M total nitrate to avoid formation of inextractable $Np(NO_3)_6^{2-}$ complexes.[24,25,26] This is within the operating range of $Al(NO_3)_3$ solubility.

Note b) Excess $Fe(NH_2SO_3)_2$ of 0.02M over that required to reduce the Np(VI) to Np(IV).

Note c) Fresh $Fe(NH_2SO_3)_2$ is to be used and no maximum concentration is given.

Note d) The 1BS flow rate should be adjusted to compensate for changes in the 1AX flow rate, so that the total 1BU organic flow rate remains approximately equal to that used in the current plant flowsheet.

8.0 CONCLUSIONS

A SASSE spreadsheet model indicates that a Np(IV) reducing flowsheet is a feasible method for separating the neptunium from the cerium and plutonium contained in the 1BP stream from the Np(VI) oxidizing flowsheet.[2] The proposed reducing flowsheet calls for stripping Ce(III) and Pu(III) from Np(IV) into the 1AW stream and extracting and then stripping Np(IV) and U(VI) into the 1BP stream. Results from the SASSE model of the Np(VI) oxidizing flowsheet indicated that U(VI) could reflux in the 1B Bank over a certain range of acid concentrations.[2] If refluxing should occur during a Np(IV) solvent extraction, then the U(VI) could be flushed from the 1B Bank by flushing out the 1A Bank with acid and then stripping the 1B bank by adding a dilute acid to the 1AF and 1AS streams fed to 1A Bank and process water to the 1BX stream fed to 1B Bank.

SASSE predicts that, with appropriate nitric acid (HNO_3) concentrations and/or the addition of aluminum nitrate ($Al(NO_3)_3$) as a salting agent, the separation of neptunium from cerium and plutonium can be accomplished with minimal neptunium losses from 1BP. The recommended flowsheet calls for adjustment of the 1AF stream to 1.5 M HNO_3 with addition of 1.5 M $Al(NO_3)_3$, for a total nitrate concentration of 6 M, a 1AS stream with 3 M HNO_3, and a 1AX:1AS volumetric flow ratio of 3:1. The recommended flowsheet also stipulates the use of process water (0.01 M HNO_3) in the 1BX stream. For these recommended conditions, the theoretical neptunium loss to 1AW is approximately 0.0036%. Predicted losses of Ce(III) and Pu(III) from 1AW and of U(VI) from 1BP are negligible. The SASSE model was validated using data from reducing flowsheets for the recovery of Np(IV) in First Cycle dating from May through December 1984.[3]

9.0 RECOMMENDATIONS

The accuracy of the SASSE model of the proposed Np(IV) reducing flowsheet depends primarily on the accuracy of the Np(IV) distribution correlations for TBP/diluent in contact with HNO_3 and $Al(NO_3)_3$ solutions. Therefore, it is recommended that Np(IV) distributions be measured at anticipated flowsheet design conditions.

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11.0 APPENDIX: CORRELATION OF DISTRIBUTION COEFFICIENTS

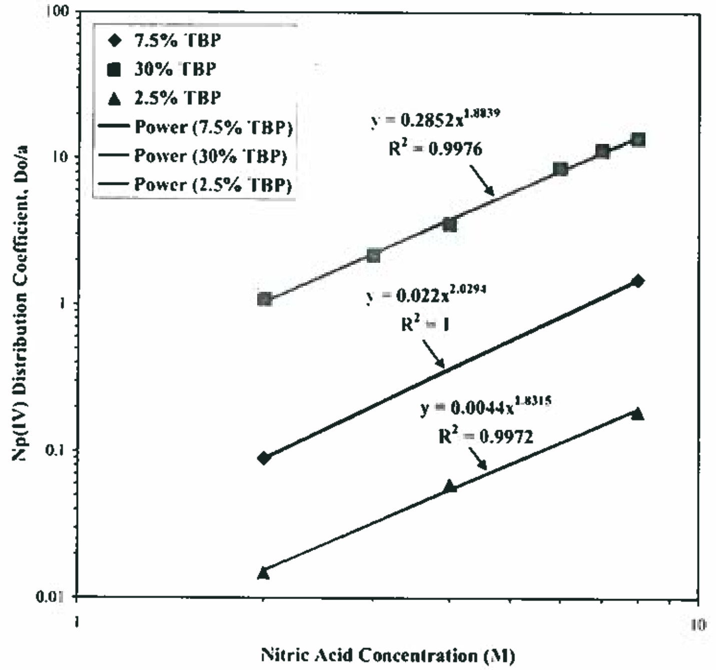

Figure 11-1. Correlation of Distribution Coefficient for Neptunium(IV) in Nitric Acid without any Nitrate Salts

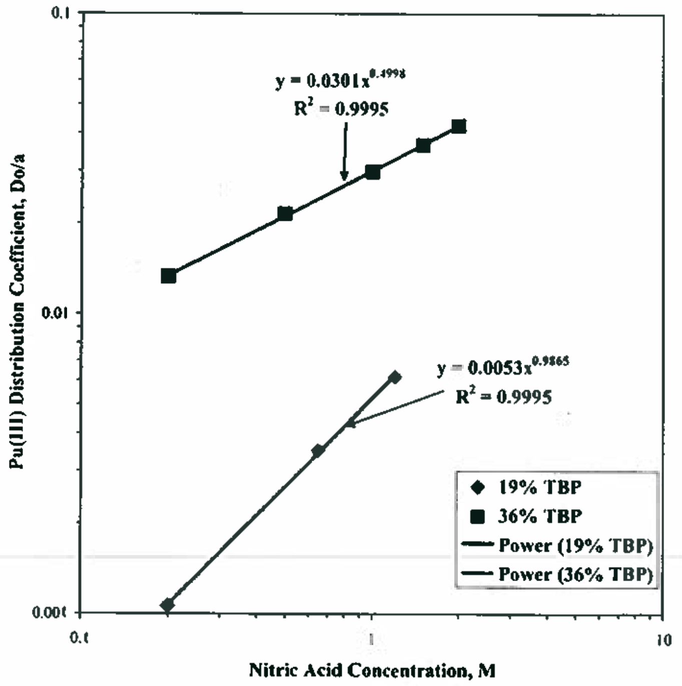

Figure 11-2. Correlation of Distributions Coefficient for Plutonium(III)

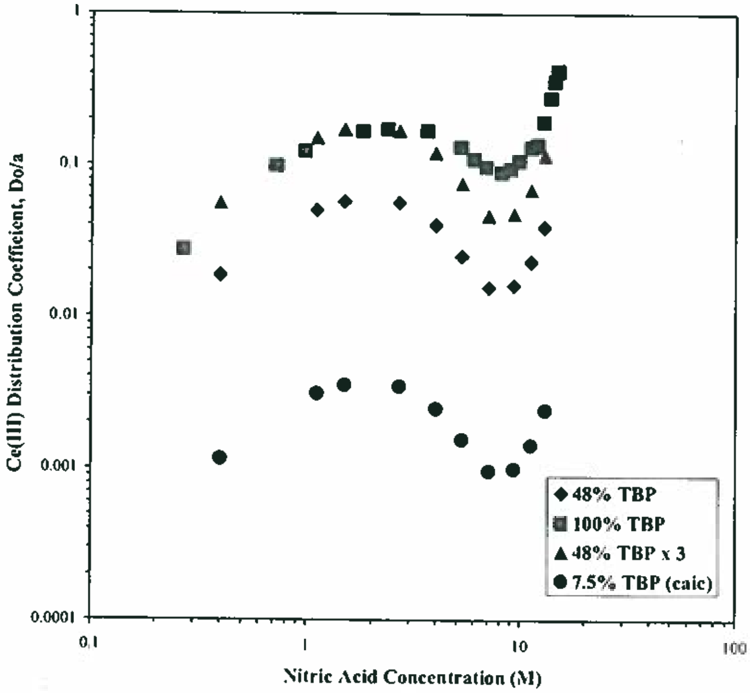

Figure 11-3. Variation of Distribution Coefficient for Cerium(III) in Nitric Acid without any Nitrate Salts

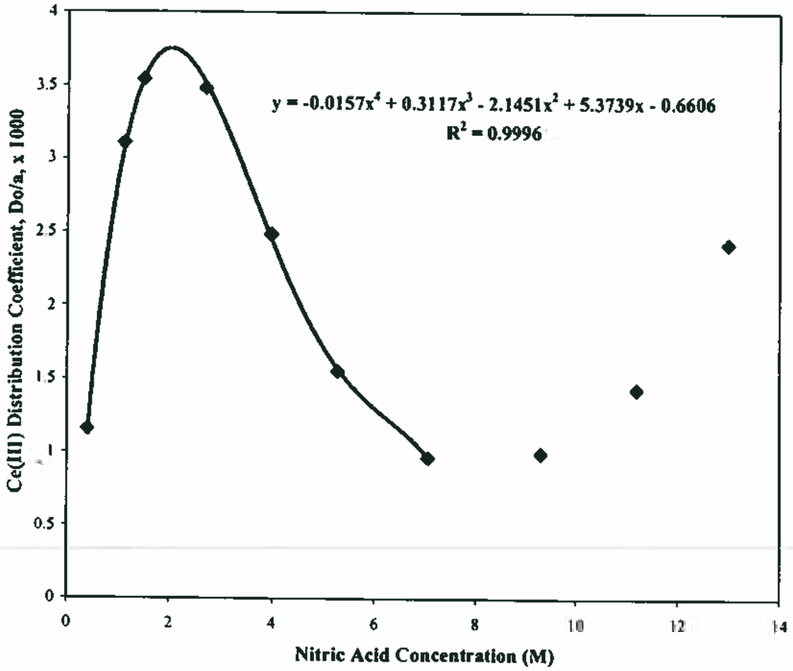

Figure 11-4. Correlation of Distribution Coefficient for Cerium(III) for 7.5 vol % TBP and Nitric Acid without any Nitrate Salts

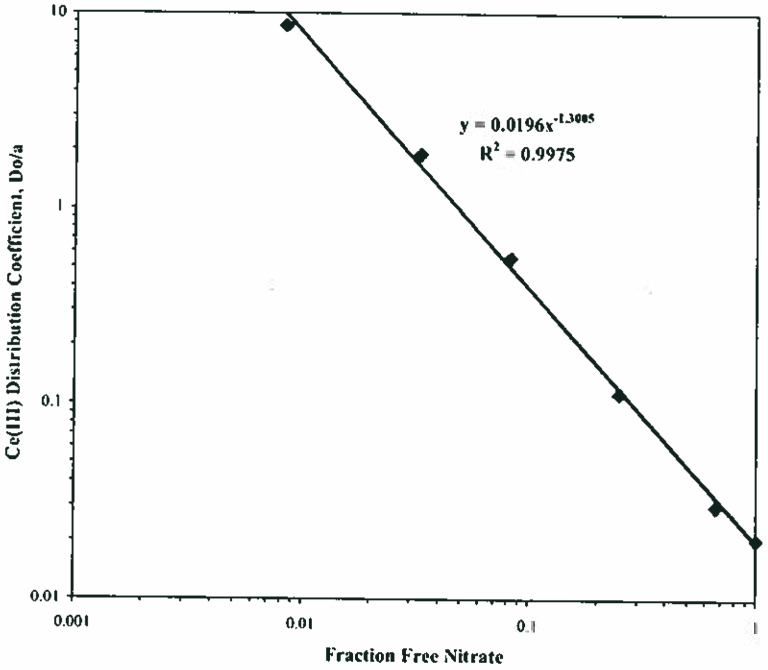

Figure 11-5. Correlation of Distribution Coefficient for Cerium(III) for 7.5 vol % TBP and Nitric Acid with Sodium Nitrate Salts

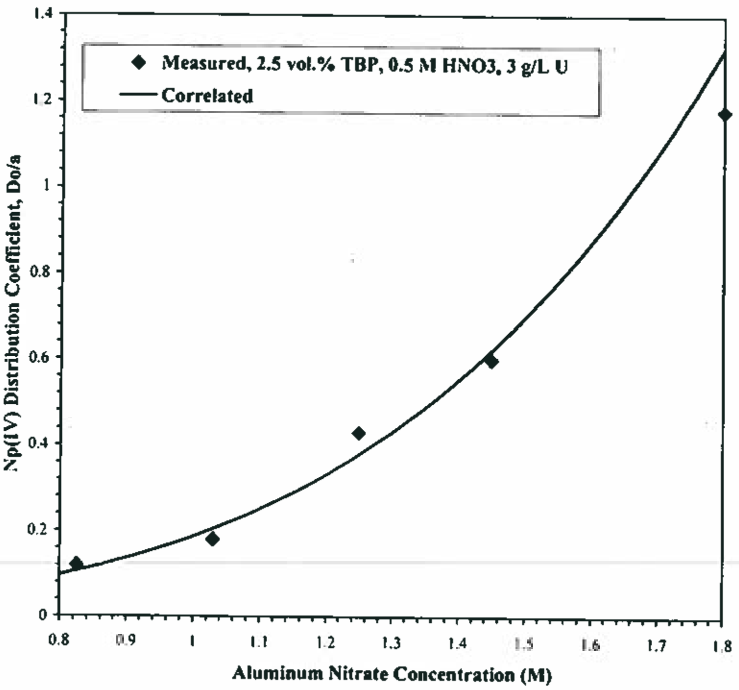

Figure 11-6. Correlation of Distribution Coefficient for Neptunium(IV) in Nitric Acid with Aluminum Nitrate Salts