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SASSE MODELING OF FIRST CYCLE NEPTUNIUM (VI) RECOVERY FLOWSHEET

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1.0 EXECUTIVE SUMMARY

A flowsheet has been proposed 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 neptunium to neptunium(VI) (Np(VI)).[1] A SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) spreadsheet model indicates that the proposed flowsheet is a feasible method for separating neptunium and uranium from sulfates, thorium, and other metal impurities. The proposed flowsheet calls for stripping the sulfates, thorium, and other metal impurities into the 1AW stream and extracting and then stripping the neptunium and uranium into the 1BP stream. SASSE predicts that separation of thorium from the other actinides can be accomplished with actinide losses of 0.01% or less. It is assumed that other metal impurities such as iron, aluminum, and fission products will follow the thorium into 1AW. Due to an organic/aqueous distribution coefficient that is close to one, SASSE predicts that plutonium(VI) (Pu(VI)) is split between the A Bank and B Bank aqueous output streams, with 27% going to 1AW and 73% going to 1BP. An extrapolated distribution coefficient based on unvalidated Ce(IV) distribution measurements at a single nitrate concentration and a comparison with thorium(IV) (Th(IV)) distributions indicates that Ce(IV) could reflux in 1B Bank. If the Ce(IV) distribution coefficient is lower than would be predicted by this single point extrapolation, but still higher than the distribution coefficient for Th(IV), then Ce(IV) would follow Np(VI) and uranium(VI) (U(VI)) into 1BP. The SASSE model was validated using data from a 1964 oxidizing flowsheet for the recovery of Np(VI) in Second Cycle.[2]

For the proposed flowsheet to be effective in recovering neptunium, the addition of approximately 0.025 M ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) to both the 1AF and 1AS streams is required to stabilize the neptunium in the +6 oxidation state. The cerium added to 1AF and 1AS must remain in the +4 oxidation state to stabilize Np(VI).

2.0 INTRODUCTION

A flowsheet has been proposed to separate neptunium from solutions in H-Canyon Tanks 16.4, 12.5, and 11.7.[1] Those tank solutions contain concentrated first cycle aqueous product (1BP) recovered from solvent extraction of irradiated Savannah River fuel 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 0.75 M). The separation of the neptunium from the sulfate is necessary for either recovery or discard of the neptunium.

The proposed flowsheet calls for the separation of Np(VI) from the sulfate primarily in the A and B Banks of H-Canyon First Cycle solvent extraction system. The C Bank will continue to be operated so as not to disrupt the current extraction system configuration; any residual actinide or other metal ion constituent that may unexpectedly be carried over by 1BU would be stripped in C Bank. An addition of 0.025 M ceric (Ce(IV)) ammonium nitrate to the 1AF and 1AS aqueous feeds is planned to convert all of the neptunium to the +6 oxidation state so that the neptunium will extract. This report presents the results of a SASSE spreadsheet model of the proposed First Cycle Np(VI) flowsheet.

3.0 SASSE MODEL

SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) is a Microsoft Excel spreadsheet macro that models equilibrium countercurrent solvent extraction processes.[3] 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(VI). 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. The C Bank is depicted and modeled for completeness.

Before applying the model, the distribution coefficients were validated using historical data. Data are available from an oxidizing flowsheet for the separation of Np(VI) in the H Canyon Second Cycle Solvent Extraction Banks (2A and 2B) run in 1964.[2] The SASSE model of the 2A and 2B Banks for the validation case is shown by Figure 3-2. As in the SASSE model for the proposed First Cycle flowsheet, separate calculations were performed for the 2A and 2B Banks. The 2A and 2B models were connected by specifying the 2AU output from 2A Bank as input to 2B Bank.

Table 3-1 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.[4] 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 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. (See Section 4.0 for comparisons of distribution coefficients at different temperatures.)

Nitric acid concentrations are specified at 5.0 M in 1AF; 4.0 M in 1AS; 0.01 M in the feed, 1AX; 0.01 M in 1BX; 0.01 M in 1BS; and 0.01 M in 1CX. The model also includes Ce(IV), Th(IV), U(VI), Np(VI), and Pu(VI). All feed concentrations for these components 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 Th(IV) and Np(VI) concentrations for the validation case are normalized with respect to the 2AF feed concentration. Although the thorium concentration is of limited interest for the proposed flowsheet, a Th(IV) distribution is included in the SASSE model because it can be validated with Second Cycle data, and because it serves as a basis for the estimated Ce(IV) distribution.

Table 3-2 gives the flow rates, temperatures, and compositions for the SASSE validation calculation. Again, feed concentrations of components other than nitric acid are specified at a nominal value of 1 M. It should be noted that both the TBP concentration in the organic feed (30 vol. %) and the solution temperatures for the validation case differ from the proposed flowsheet, which specifies 7.5 vol. % TBP and a temperature of 45 °C.[1] These differences imply that the distribution coefficients used to model the proposed flowsheet must be adjusted for the validation calculations.

The mixer-settler stages in 1A, 2A, 1B, and 2B 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.[5,6]

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

Stream	**1AX**	**1AF**	**1AS**	**1BS**	**1BX**	**1CX**
Flow Rate (L/min)	10.5	5.78	1.25	18.16	6.1	6.15
Temperature (°C)	45	45	45	45	45	45
TBP (volume %)	7.5			7.5		
HNO_3 (M)	0.01	5.0	4.0	0.01	0.01	0.01
Ce (normalized basis)	0	1.0	1.0	0	0	0
Th (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 3-2. Flow Rates, Temperatures, and Compositions for Validation Case, Second Cycle Neptunium(VI) Solvent Extraction Flowsheet

Stream	**2AX**	**2AF**	**2AS**	**2BX**
Flow Rate (L/min, nominal)	4.0	1.0	1.5	2.84
Temperature (°C)	45	50	30	30
TBP (volume %)	30			
HNO_3 (M)	0.01	1.4	0.5	0.01
Th (normalized basis)	0	1.0	0	0
Np (normalized basis)	0	1.0	0	0

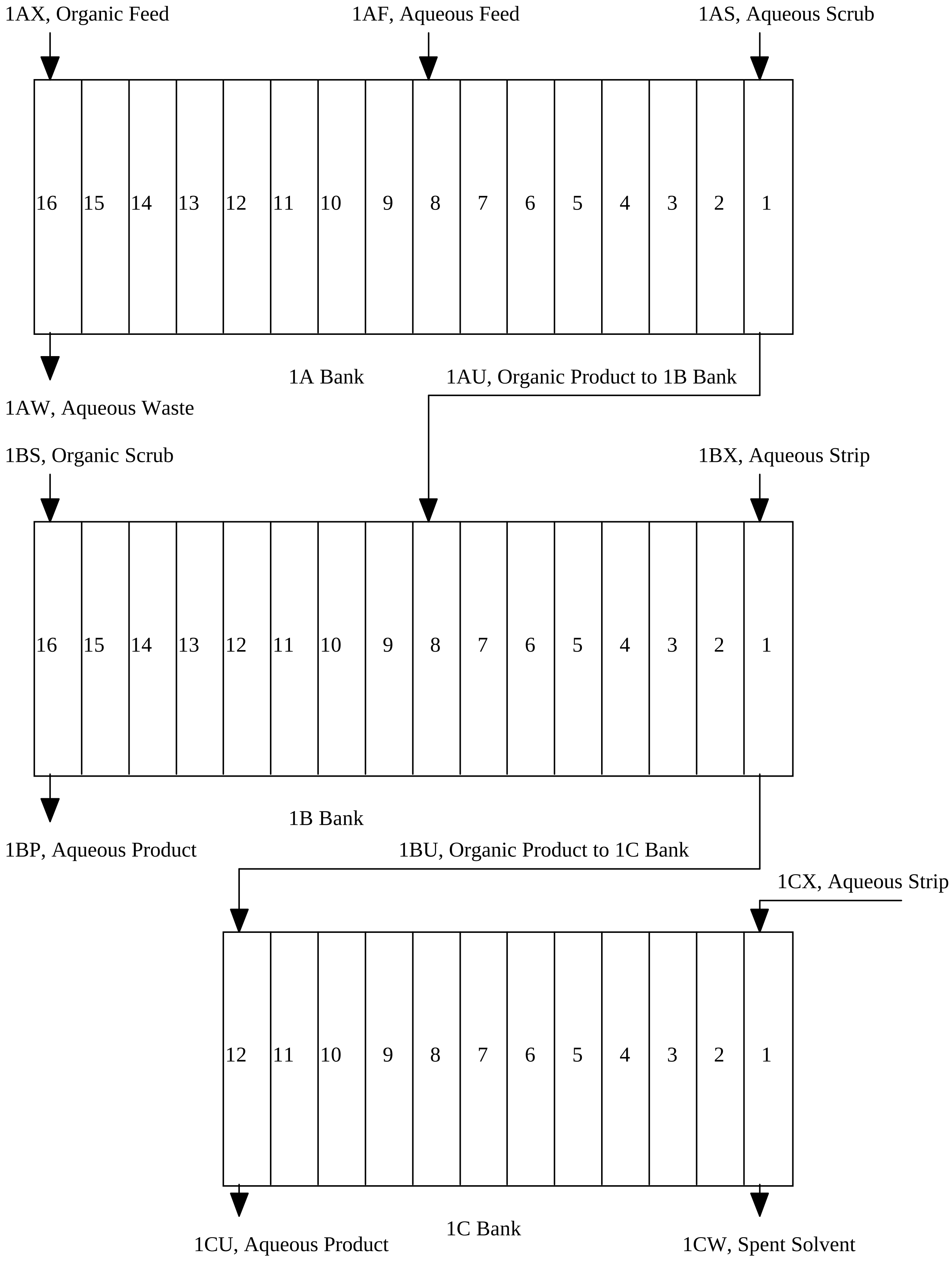

Figure 3-1. First Cycle Neptunium (VI) Recovery Flowsheet

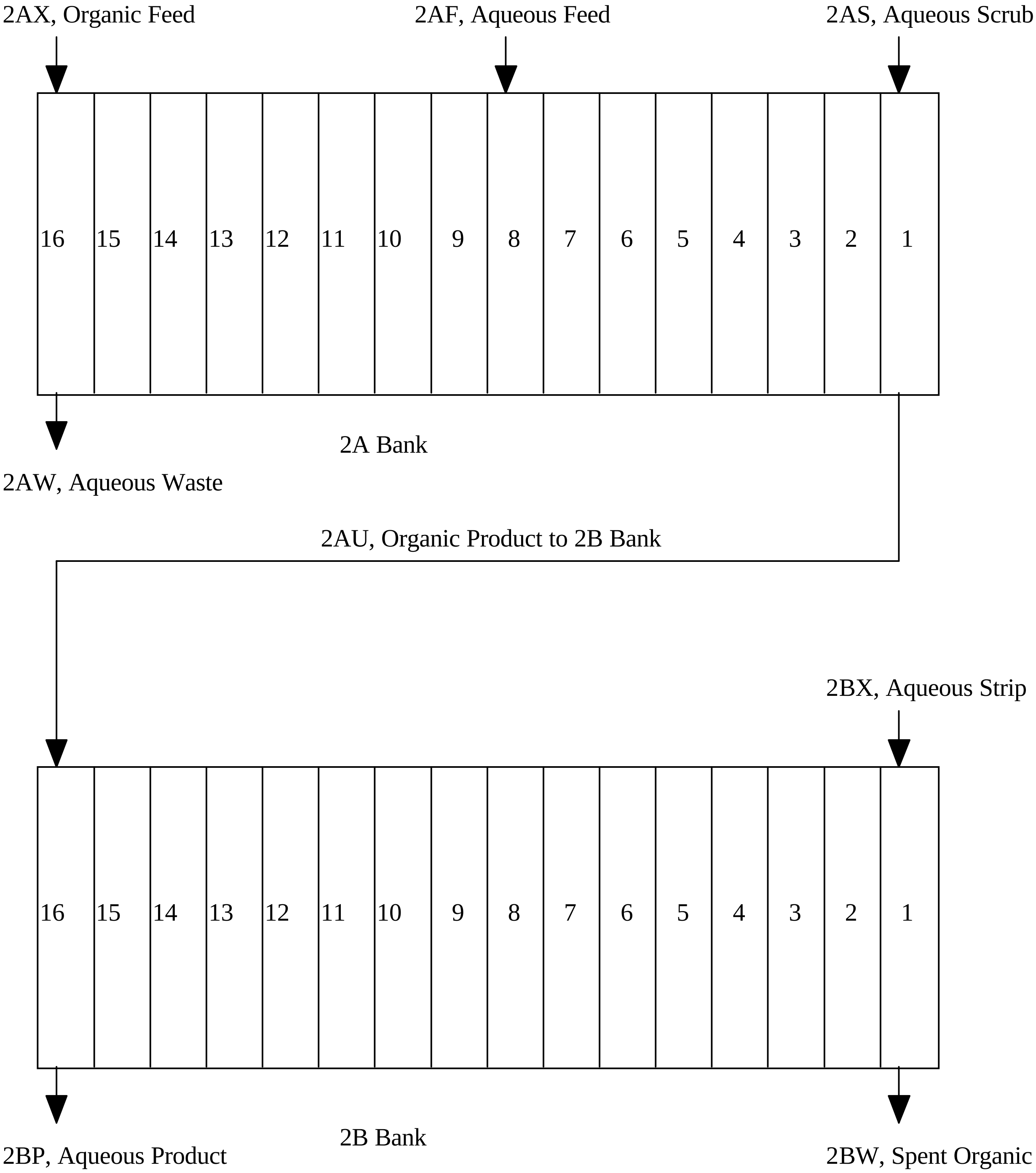

Figure 3-2. Second Cycle Neptunium (VI) Recovery Flowsheet (used for validating)

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.

Equilibrium stage efficiencies and entrainment ratios have been estimated in part by fitting the validation calculations to measured thorium and neptunium DF's and losses. Specifically, the equilibrium stage efficiencies for A and B Banks were estimated by matching measured and calculated thorium DF's for the 2A Bank, and the aqueous entrainment in the organic phase was estimated by matching measured and calculated neptunium losses for the 2B Bank. The aqueous entrainment in the organic phase has been determined for both A and B Banks. For the 1A Bank, two separate determinations give aqueous in organic entrainments of 0.65 and 0.68 %;[7,8] 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 in organic entrainments for B Bank range from 1.24 % to 2.33 % at normal flow rates,[9] and from 4.0 % to 9.3 % at high flow rates.[10] These studies did not report any measurable entrainment of organic in the aqueous phase. In view of the wide range of reported B Bank entrainments, the B Bank aqueous in organic entrainment was treated as an adjustable parameter in the validation calculations. 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.

4.0 DISTRIBUTION COEFFICIENT CORRELATIONS

The SASSE model for the proposed flowsheet included distribution coefficients for free acid, Ce(IV), Th(IV), U(VI), Np(VI),and Pu(VI). However, the SASSE validation model required only distribution coefficients for free acid, Th(IV), and Np(VI). The distributions coefficients for the modeled components are based on measured data, mostly from the Savannah River Site. The distribution coefficients are correlated as functions of the HNO_3 concentration. In general, the distribution coefficients increase rapidly with acid concentration up to about 4 to 5 M HNO_3, then plateau, and drop off at higher acid concentrations. Since the proposed flowsheet does not call for much high acid concentrations, correlations that account for the increases in the distribution coefficients at the lower acid concentrations, with an upper asymptote that comes into effect in the 3 to 5 M HNO_3 range, were deemed sufficient. Hence, all distribution coefficients take this asymptotic form.

Distribution coefficients for free acid and for U(VI) in 7.5 vol. % TBP have been measured.[11] The distribution coefficients for both HNO_3 and U(VI) are affected by the presence of significant uranium concentrations in the aqueous phase. At low uranium concentrations, the distribution coefficient for free acid at 45 °C is correlated by the asymptotic expression given by Equation 1(see Figure 10-1 in the Appendix):

$$D_{o/a,\mathrm{HNO_3}} = \min\left(0.047, 0.0281[\mathrm{HNO_3}]^{0.6439}\right) \tag{1}$$

A similar expression, based on the same data, gives the distribution coefficient for U(VI) (see Figure 10-2):

$$D_{o/a,\mathrm{U(VI)}} = \min\left(3.289, 0.6127[\mathrm{HNO_3}]^{1.4425}\right) \tag{2}$$

The HNO_3 distribution coefficient for the validation calculation is adjusted for 30 vol. % TBP by multiplying by a factor of four; the validation distribution coefficients were not adjusted for any change in temperature. Thus, for the validation case, the HNO_3 distribution coefficient is:

$$D_{o/a,\mathrm{HNO_3}} = \min\left(0.188, 0.1125[\mathrm{HNO_3}]^{0.6439}\right) \tag{3}$$

The distribution coefficients for Th(IV) are strongly affected by the presence of even low sulfate concentrations, as shown by Figure 10-3. Sulfate is not expected to extract into the aqueous phase. Therefore, in the proposed flowsheet, for the 1A Bank stages upstream from the feed stage on the aqueous side and the 1B and 1C Bank stages, the Th(IV) distribution coefficient should be correlated using data with no sulfate present. However, for the 1A Bank stages downstream from the feed stage, the Th(IV) distribution coefficient should be correlated based on the sulfate concentration in the mixed aqueous flow. The correlation in the lower acid range is based on the data for 30 vol. % TBP in contact with a solution containing no sulfate.[12] In the higher acid range, the same data are used but an extrapolation is added to account for the reduction in the maximum distribution coefficient as the sulfate concentration in the aqueous layers in the banks downstream from 1AF (Banks 8 through 16 in Figure 3-1) (see Figure 10-4) goes from 0.049 M to 0.60 M. This adjustment is deemed to be more important for the high acid range than for the low acid range because it limits the distribution coefficient below a value where it yields significant extraction of Th(IV). Both terms in the distribution coefficient correlation include a factor of four to account for the change to 7.5 vol. % TBP. The resulting distribution coefficient correlations for the proposed flowsheet are, for the lower acid concentration range:

$$D_{{}^{o}\!/_{a},\mathrm{Th(IV)}} = \min\left(0.72, 0.1219[\mathrm{HNO_3}]^{1.9526}\right) \tag{4}$$

and, for the higher acid concentration range with sulfate present:

$$D_{{}^{o}\!/_{a},\mathrm{Th(IV)}} = 0.0490 \tag{5}$$

No sulfate was present in the validation extraction, so the Th(IV) distribution coefficient correlation for the validation calculation is similar to that used for the proposed flowsheet in the low acid range. For the validation case, the temperature in the 2A Bank is estimated to equal the average of the temperatures of the 2AF and 2AS streams, (40 °C). Thus, in the low acid range, the correlation of the distribution coefficient is based on the average of the 30 °C and 50 °C data with no sulfate.[12] The upper asymptote is taken to be the maximum measured distribution coefficient at 50 °C. This gives, for the validation case:

$$D_{{}^{o}\!/_{a},\mathrm{Th(IV)}} = \min\left(2.88, 0.5118[\mathrm{HNO_3}]^{1.9924}\right) \tag{6}$$

The distribution coefficient correlation for Np(VI) is based on data for 7.5 vol. % TBP at 25 °C.[13] These data are corrected for an estimated temperature effect by multiplying by the ratio of distribution coefficients for U(VI) at 45 °C and 23 °C. The low acid range correlation is from a regression of the data, which is shown in Figure 10-5. The upper asymptote is taken to be equal to the measured distribution coefficient at 3.7 M HNO_3 adjusted for the change in temperature. The correlation for the Np(VI) distribution coefficient for the proposed flowsheet takes the form:

$$D_{{}^{o}\!/_{a},\mathrm{Np(VI)}} = \min\left(2.645, 0.4086[\mathrm{HNO_3}]^{1.5326}\right) \tag{7}$$

For the validation calculation, the correlation in the low acid range is multiplied by a factor of four to account for the change to 30 vol. % TBP, and adjusted for temperature by making a geometric interpolation based on the ratio of distribution coefficients for U(VI) at 23 °C and 45 °C. The distribution coefficient for 2A Bank is adjusted to a temperature of 40 °C, and the distribution coefficient for 2B Bank is adjusted to 35 °C. The upper asymptote is judged to be of less importance where it is applied in 2B Bank, so the asymptote is adjusted only by the concentration factor of four. The resulting correlations are, for 2A Bank:

$$D_{{}^{o}\!/_{a},\mathrm{Np(VI)}} = \min\left(10.58, 1.908[\mathrm{HNO_3}]^{1.5326}\right) \tag{8}$$

and, for 2B Bank:

$$D_{o/a,Np(VI)} = \min\left(10.58, 2.13[HNO_3]^{1.5326}\right) \quad (9)$$

The distribution coefficient for Pu(VI) is based on a correlation of data for 19 vol. % TBP at 25 °C,[14] shown in Figure 10-6. The correlation is adjusted to 7.5 vol. % TBP by multiplying by the appropriate volume factor and is adjusted for temperature by multiplying by the ratio of U(VI) distribution coefficients at 23 °C and 45 °C:

$$D_{o/a,Pu(VI)} = \min\left(0.767, 0.165[HNO_3]^{1.2684}\right) \quad (10)$$

Only limited, unvalidated data are available for the distribution of Ce(IV). Ce(IV) distribution coefficients are reported for pure TBP in contact with solutions containing HNO_3 and NH_4NO_3 with a total NO_3 concentration of 0.31 M, at 20 °C.[15] The distribution coefficients are nearly constant over the range of NH_4 concentrations (see Figure 10-7). Consequently, the estimated distribution coefficient is based on an average of the measured distribution coefficients (not including one outlier value). It is assumed that the ratio of the distribution coefficients for Ce(IV) and Th(IV) is independent of nitric acid concentration. Under this assumption, a multiplier for the distribution can be calculated by adjusting the measured Ce(IV) distribution coefficient for the volume percentage of TBP and for a temperature of 50 °C using a geometric extrapolation based on the ratio of distribution coefficients for U(VI) at 23 °C and 45 °C, and then comparing the result with the correlation for Th(IV) at 50 °C, no sulfate, and a total nitrate concentration of 0.31 M. The resulting multiplier is 107. When this multiplier is applied to the Th(IV) correlation for high acid concentration with sulfate present, the following equation results

$$D_{o/a,Ce(IV)} = 5.23 \quad (11)$$

When the multiplier of 107 is applied at low acid concentrations without sulfate, the distribution coefficient expression becomes

$$D_{o/a,Ce(IV)} = \min\left(76.8, 13.0[HNO_3]^{1.9526}\right) \quad (12)$$

The estimated Ce(IV) distribution coefficients appear to be somewhat high in the low acid range. For instance, according to the model predictions, Ce(IV) should be expected to extract with a distribution coefficient greater than one for any HNO_3 concentration exceeding 0.26 M. To determine the effect of changes in the Ce(IV) distribution coefficient on the cerium concentrations, a reduced distribution coefficient equal to 1/10 of the predicted coefficient for the low acid concentration range also was applied in the SASSE model:

$$D_{o/a,Ce(IV)} = \min\left(7.68, 1.3[HNO_3]^{1.9526}\right) \quad (13)$$

The value of the reduced distribution coefficient was arbitrarily selected to correspond to approximately half the calculated multiplier of 107 applied to the Th(IV) distribution coefficient, on a logarithmic basis.

The SASSE model does not include a distribution coefficient for sulfate. It is anticipated, based on previous experience, that sulfate does not extract into the organic phase to any appreciable extent. In the proposed flowsheet model, it is implicitly assumed that the sulfate remains in the aqueous phase in the 1A Bank stages downstream from the feed stage and exits in the 1AW aqueous waste. The small amount of sulfate that is carried over by entrainment into the organic phase in 1A Bank is ignored.

The SASSE model also excludes metal impurities other than the actinides and cerium, such as iron, aluminum, and any fission products that may be present in the 1AF feed. These other metals are expected to remain in the aqueous phase and follow the 1AW aqueous waste.

5.0 VALIDATION WITH SECOND 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, and a 2A Bank aqueous in organic entrainment of 0.665%. The stage separation efficiency for both 2A and 2B Banks (assumed to be equal) and the aqueous in organic entrainment for 2B Bank were treated as adjustable parameters used to match calculated with measured values for the DF for the thorium DF and the neptunium loss in 2A Bank and the neptunium loss from 2B Bank, respectively.

A stage efficiency of 96.5%, somewhat fortuitously, matched both the measured thorium DF of 166 and the measured neptunium loss to 2AW of 0.02%. The calculated values were a thorium DF of 164 and neptunium loss of 0.0197%. This value for the stage efficiency seems reasonable.

An aqueous in organic entrainment of 1.75% gave a 2.26% neptunium loss from 2BW, compared to the measured value of 2.25%. The SASSE value for the B Bank entrainment falls in the middle of reported entrainments for normal, low flow operation of 2B, which range from 1.24% to 2.33%.[9] The ability of the SASSE model to predict measured neptunium and thorium separations for Np(VI) extraction in Second Cycle verifies generally that SASSE is capable of modeling the proposed flowsheet and confirms, more specifically, that the distribution coefficient correlations for Th(IV) and Np(VI) are reasonably accurate.

For the SASSE model of the validation test, Figures 5-1, 5-2, and 5-3 show the aqueous and organic phase concentration distributions and the distribution coefficients for HNO_3, Th(IV), and Np(VI) in the individual stages of 2A Bank. Figures 5-4, 5-5, and 6-6 depict the same parameters for HNO_3 and Np(VI) in the stages of 2B Bank. These stagewise plots show that Th(IV) mostly goes into the 2AW aqueous waste off Stage 16 of 2A Bank, while the Np(VI) extracts into the organic phase in 2A Bank and strongly strips into the aqueous phase in 2B Bank. The very strong stripping of Np(VI) in 2B Bank implies that the Np(VI) losses in 2B are almost entirely due to entrainment of the aqueous phase in the organic phase. One additional item to note is the peaking of the Th(IV) concentration above the feed concentration in 2A Bank, shown in Figure 5-1. The Th(IV) concentration peaking indicates refluxing of Th(IV) in 2A Bank, which indeed had been observed during Second Cycle product operation.

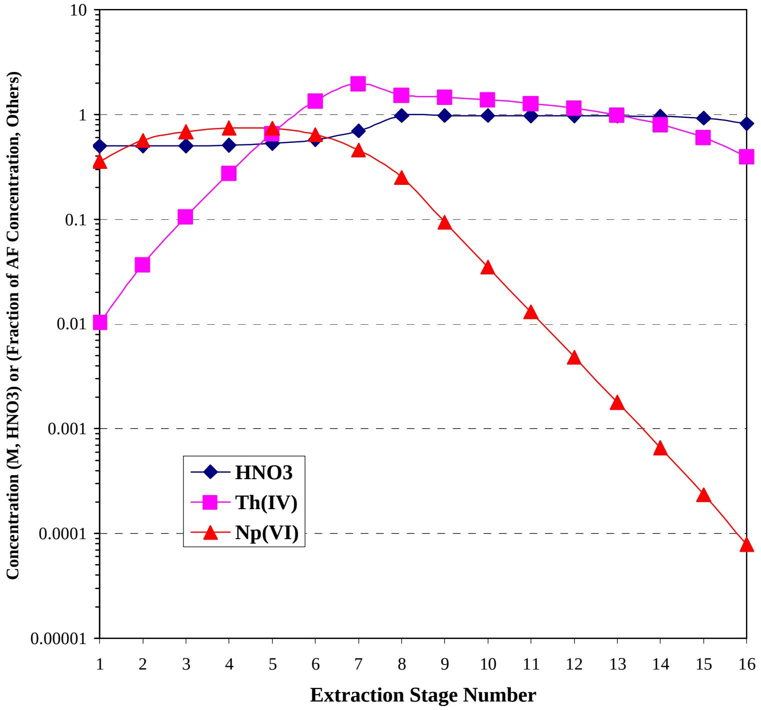

Figure 5-1. SASSE Predictions of Aqueous Phase Concentrations in 2A Bank for 1964 Test

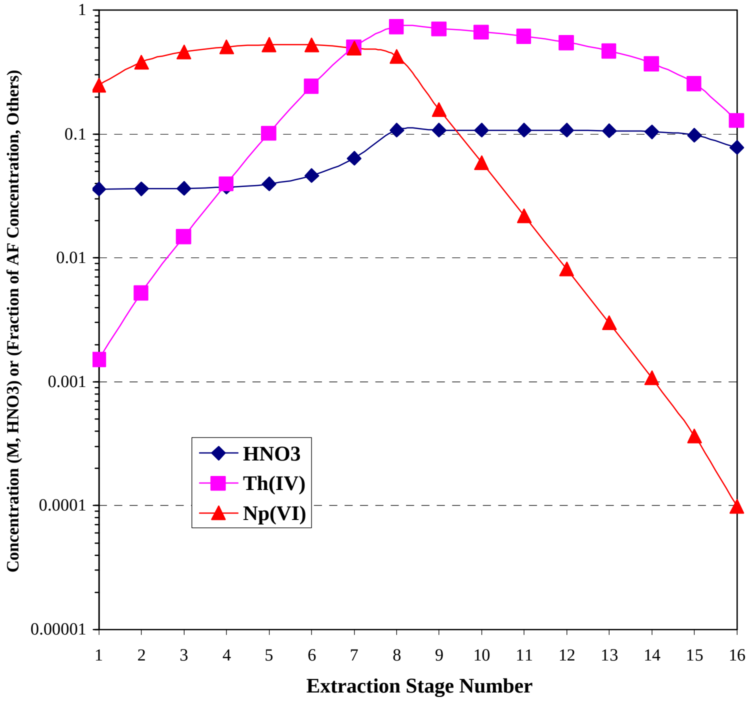

Figure 5-2. SASSE Predictions of Organic Phase Concentrations in 2A Bank for 1964 Test

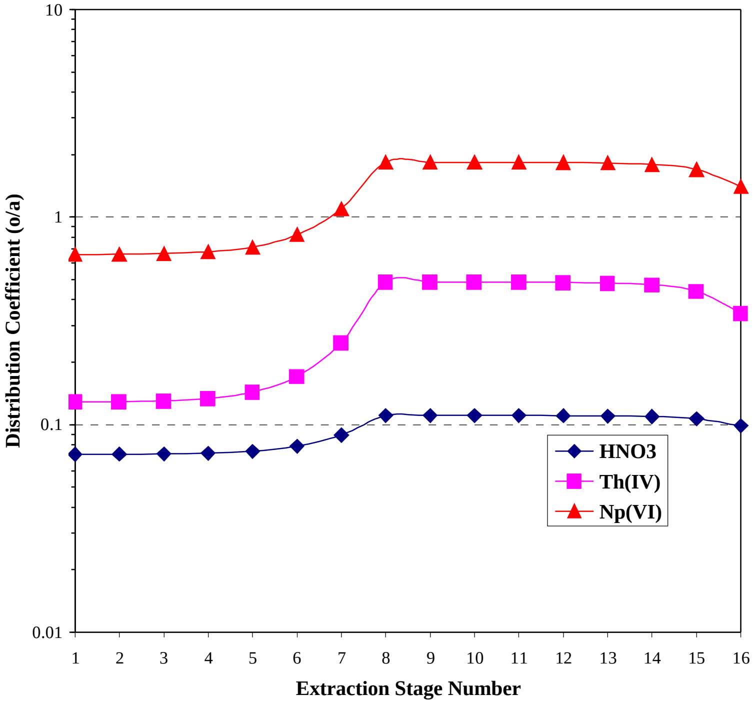

Figure 5-3. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 2A Bank for 1964 Test

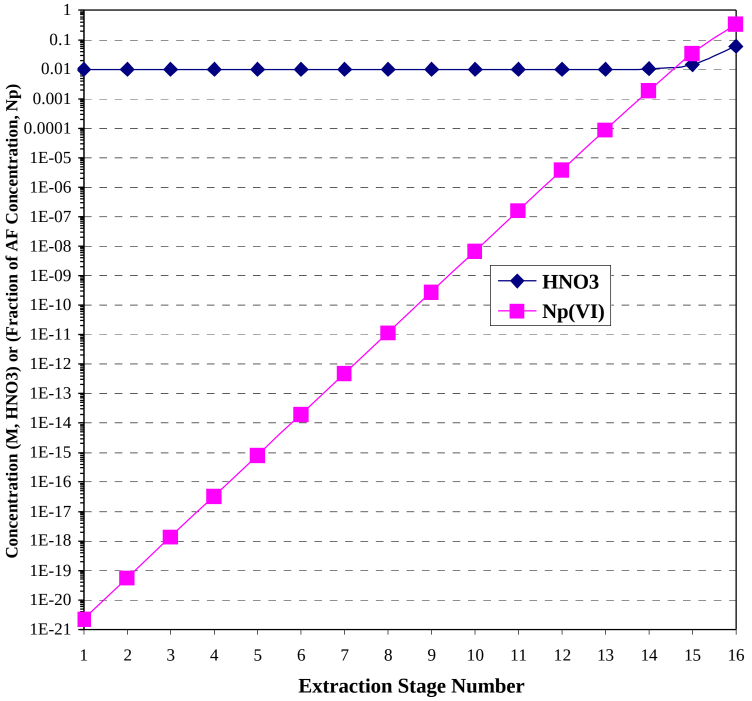

Figure 5-4. SASSE Predictions of Aqueous Phase Concentrations in 2B Bank for 1964 Test

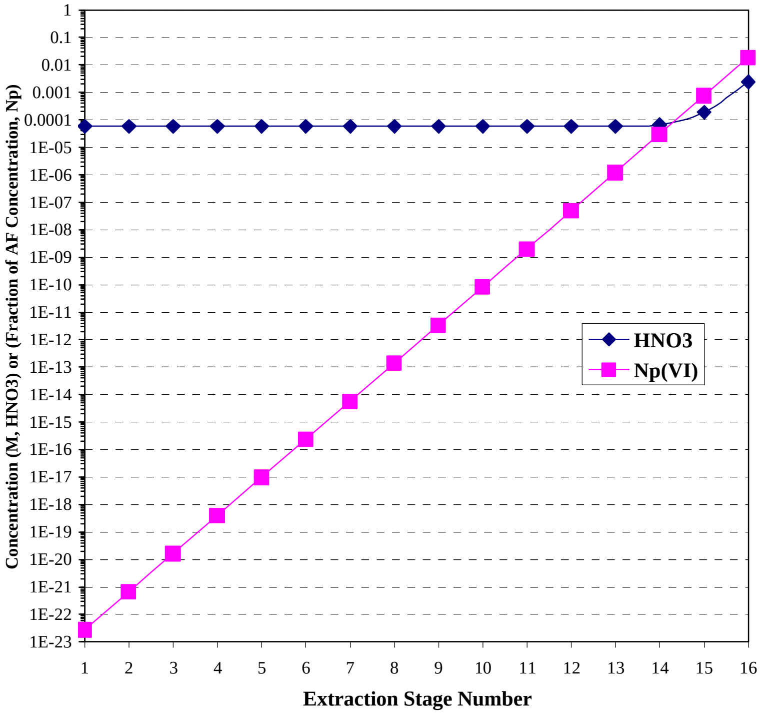

Figure 5-5. SASSE Predictions of Organic Phase Concentrations in 2B Bank for 1964 Test

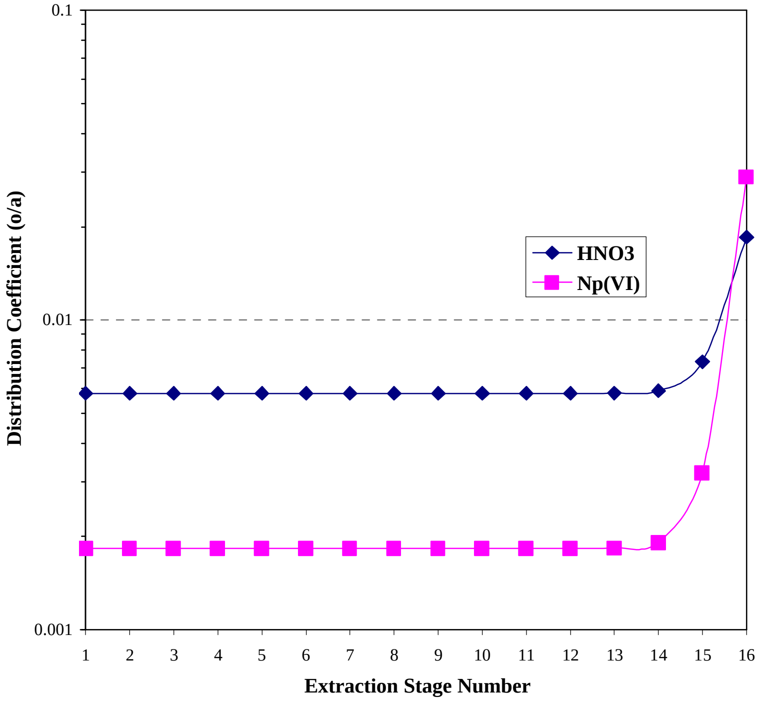

Figure 5-6. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 2B Bank for 1964 Test

6.0 PREDICTIONS FOR PROPOSED FIRST CYCLE FLOWSHEET

The stage efficiency of 0.965 and the B Bank aqueous-in-organic entrainment of 1.75% 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. Figures 6-1, 6-2, and 6-3 portray the stagewise aqueous and organic phase concentration and distribution coefficients for 1A Bank. Figures 6-4, 6-5, and 6-6 depict the same parameters for 1B Bank. Figures 6-7, 6-8, and 6-9 show these parameters for 1C Bank. Figures 6-1 and 6-2 indicate that in 1A Bank, the SASSE model predicts that Ce(IV), U(VI), and Np(VI) strongly extract into the 1AU organic product, while Th(IV) strips into the 1AW aqueous waste. The model further indicates that Pu(VI) weakly extracts into 1AU, since it has a distribution coefficient relatively close to one (see Figure 6-3). If the Ce(IV) distribution coefficient, indeed, is as high as predicted by the comparison of the limited, unvalidated data available,[15] the model predicts that in 1B Bank any residual Th(IV), as well as U(VI), Np(VI),and Pu(VI), all strip into 1BP. Meanwhile, Ce(IV) refluxes at the 1AU feed stage, as shown in Figures 6-4 and 6-5. This postulated refluxing would occur because the Ce(IV) extracts into the 1BS organic scrub upstream from the feed and strips into the 1BX aqueous strip upstream from the feed, so that the Ce(IV) is carried toward the feed stage (Stage 8) in both phases. The ultimate cause of the refluxing would be the relatively high Ce(IV) distribution coefficient in Stages 8 through 16 due to the moderate amount of acid carried over from 1A Bank in 1AU. (The calculated distribution coefficient in Stages 8 through 16 ranges between 2 and 3; see Figure 6-6.) In 1C Bank, as Figures 6-7 and 6-8 illustrate, all residuals left in the 1BU organic stream strip into the aqueous phase and exit via 1CU.

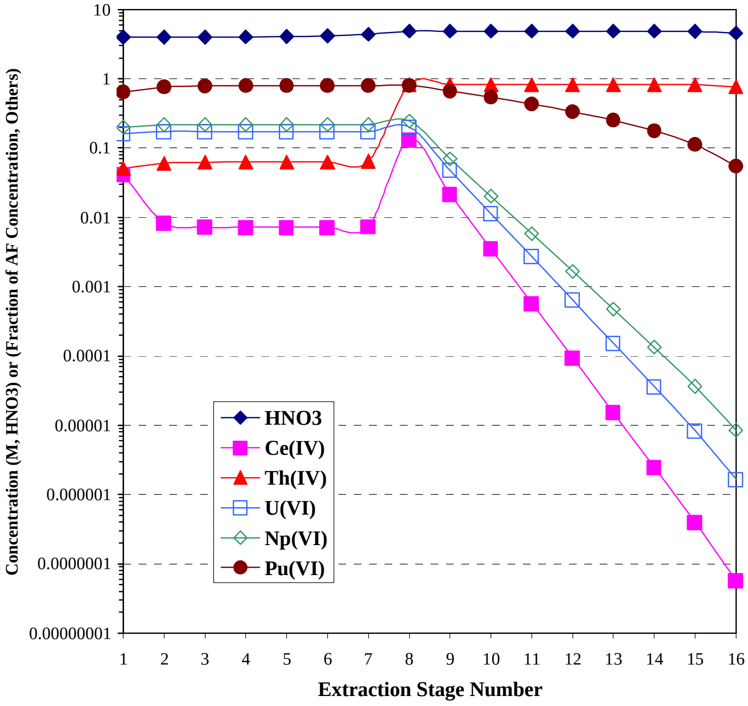

Figure 6-1. SASSE Predictions of Aqueous Phase Concentrations in 1A Bank for Proposed Flowsheet

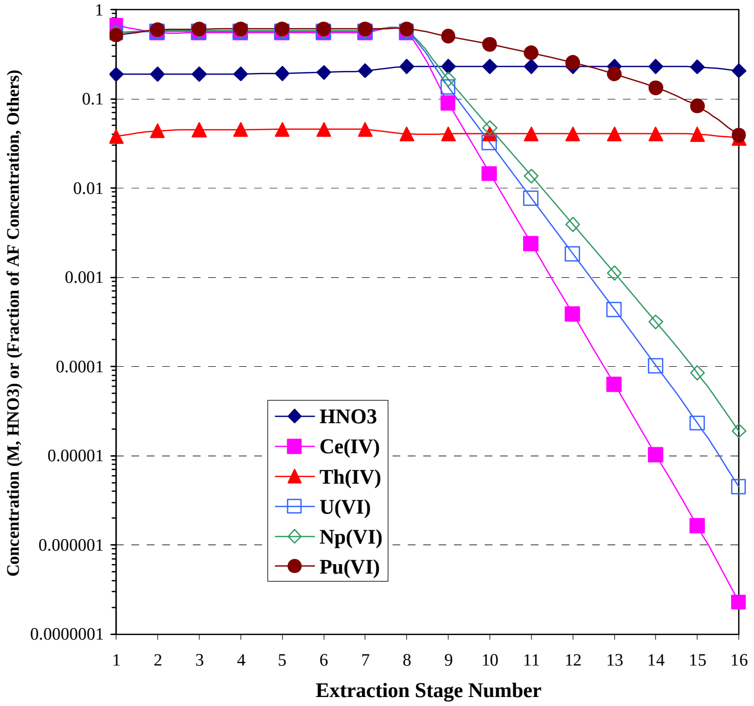

Figure 6-2. SASSE Predictions of Organic Phase Concentrations in 1A Bank for Proposed Flowsheet

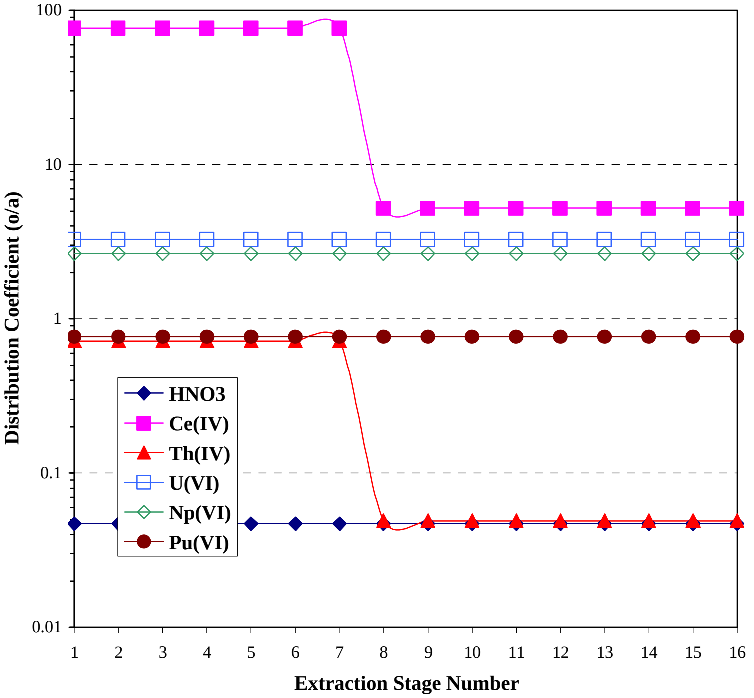

Figure 6-3. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1A Bank for Proposed Flowsheet

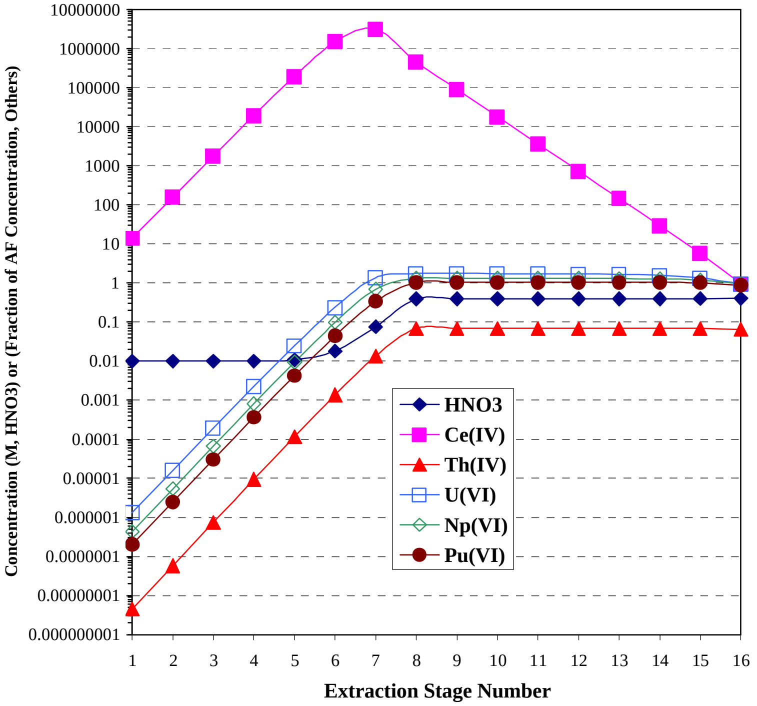

Figure 6-4. SASSE Predictions of Aqueous Phase Concentrations in 1B Bank for Proposed Flowsheet

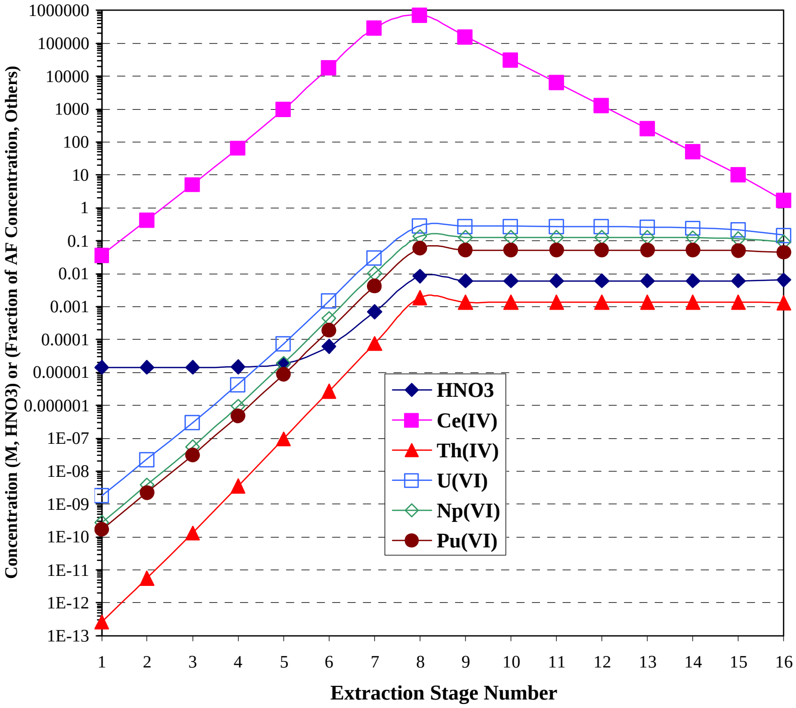

Figure 6-5. SASSE Predictions of Organic Phase Concentrations in 1B Bank for Proposed Flowsheet

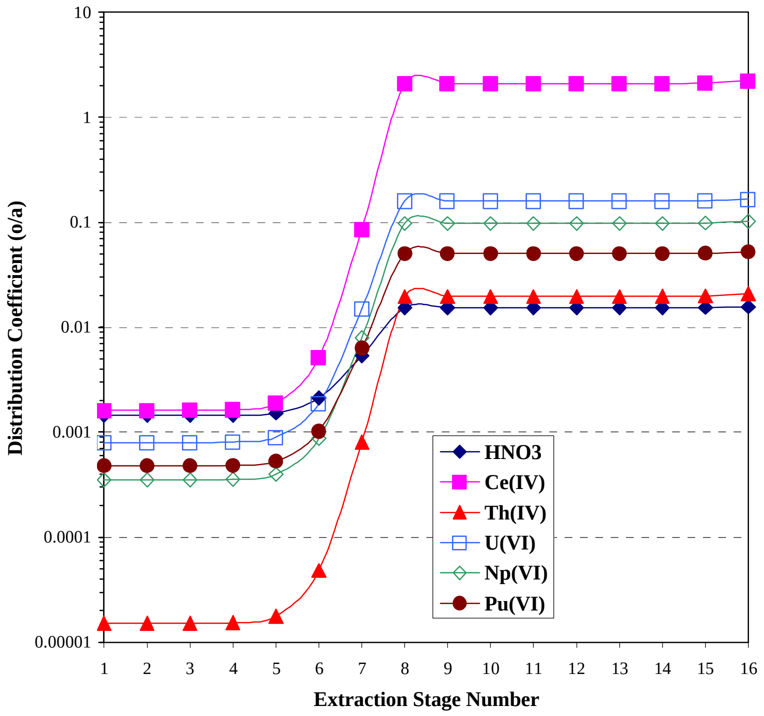

Figure 6-6. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1B Bank for Proposed Flowsheet

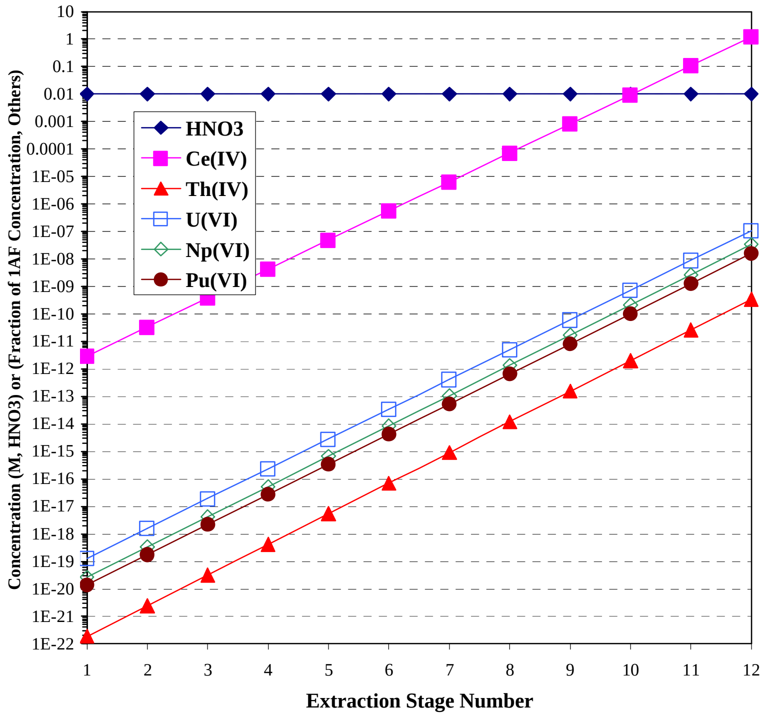

Figure 6-7. SASSE Predictions of Aqueous Phase Concentrations in 1C Bank for Proposed Flowsheet

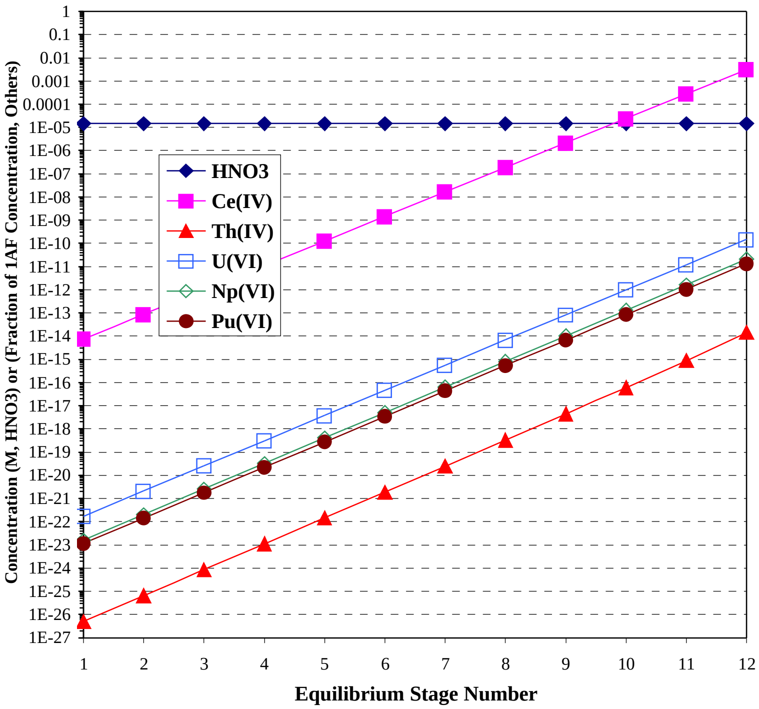

Figure 6-8. SASSE Predictions of Organic Phase Concentrations in 1C Bank for Proposed Flowsheet

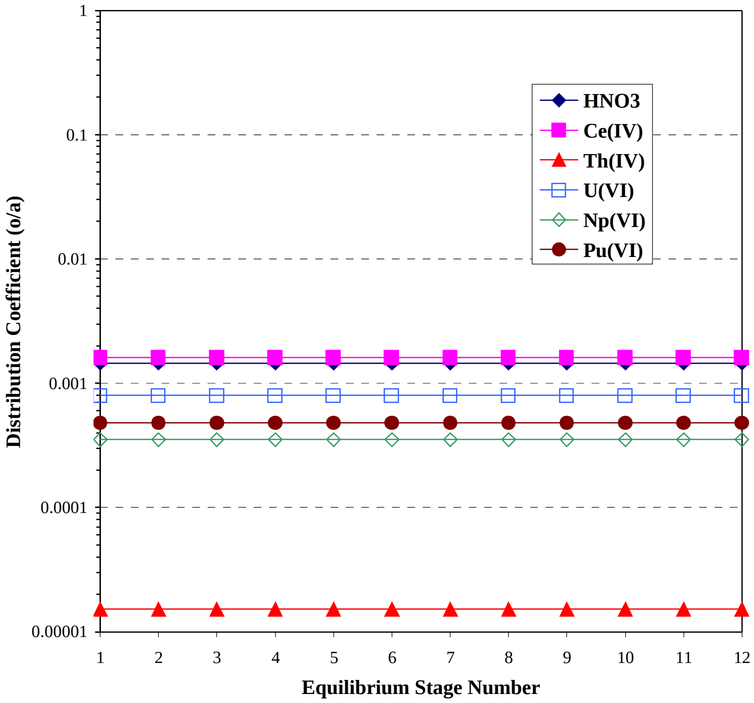

Figure 6-9. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1C Bank for Proposed Flowsheet

To demonstrate the effect of the Ce(IV) distribution coefficient on organic and aqueous phase concentrations, the SASSE model was rerun with a Ce(IV) distribution coefficient that was 1/10 of the predicted value for the low acid range with no sulfate. As stated in Section 4.0, the reduced Ce(IV) distribution coefficient corresponds to a Th(IV) distribution coefficient multiplied by approximately half the predicted ratio between the distribution coefficients for Th(IV) and Ce(IV), on a logarithmic basis. Figure 6-10 through Figure 6-18 depict the aqueous and organic concentrations and the distribution coefficients for this reduced Ce(IV) distribution coefficient formula. The results for HNO_3, Th(IV), U(VI), Np(VI), and Pu(VI) are identical with those for the previous case. The Ce(IV) distribution coefficient in the 1B Bank stages upstream from the feed stage on the organic side (Stages 8 through 16) is now reduced from the previous range of 2 to 3 to a range of 0.2 to 0.3, as shown by Figure 6-15. As a result, the Ce(IV) extracts into the aqueous phase in 1B and goes out with 1BP, as Figures 6-13 and 6-14 illustrate.

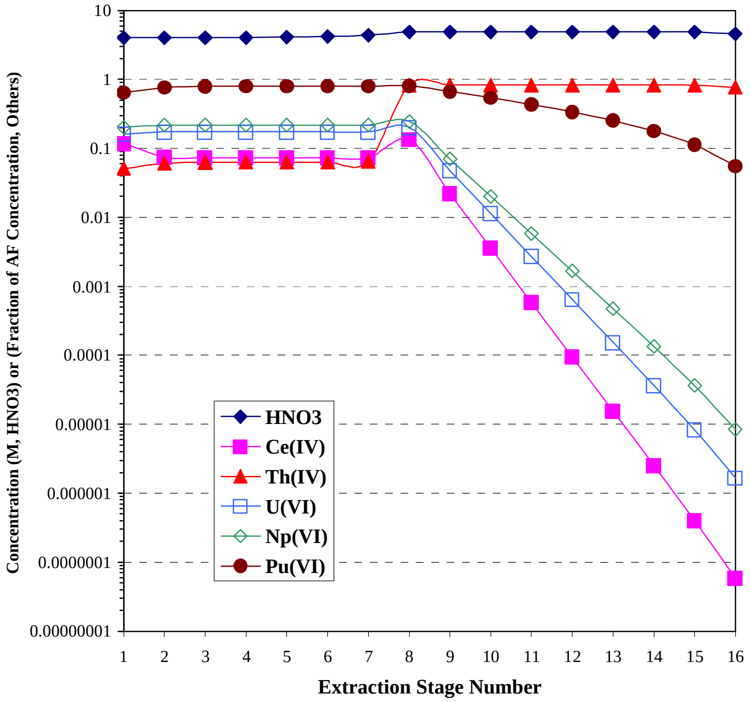

Figure 6-10. SASSE Predictions of Aqueous Phase Concentrations in 1A Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

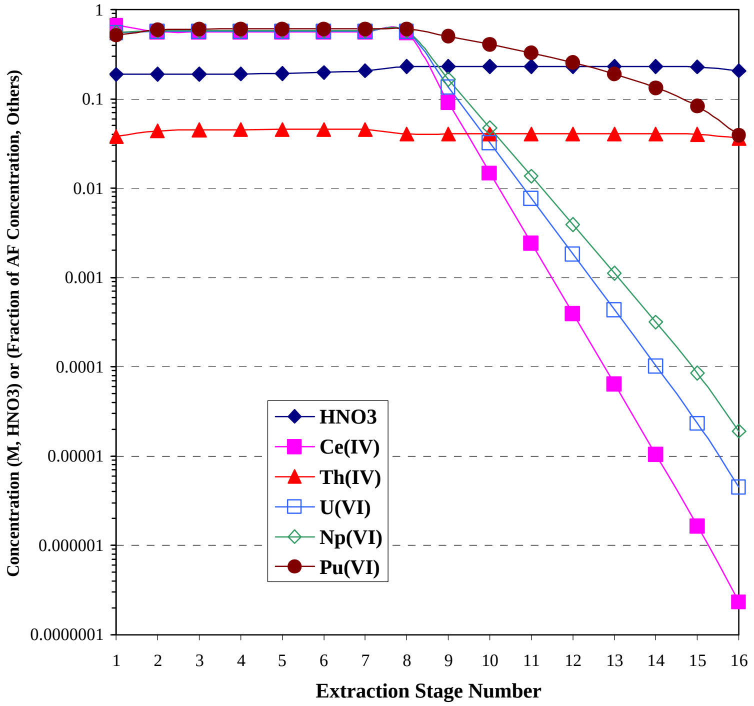

Figure 6-11. SASSE Predictions of Organic Phase Concentrations in 1A Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

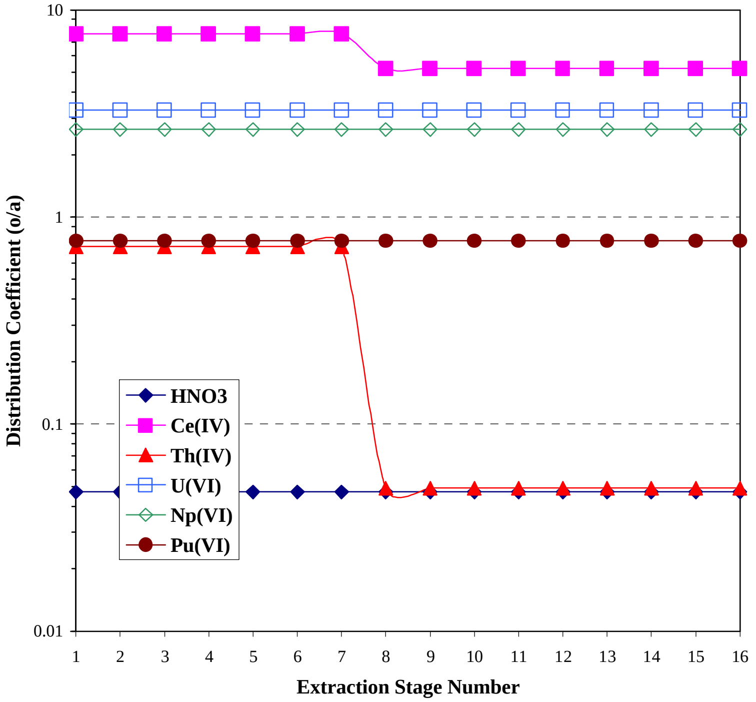

Figure 6-12. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1A Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

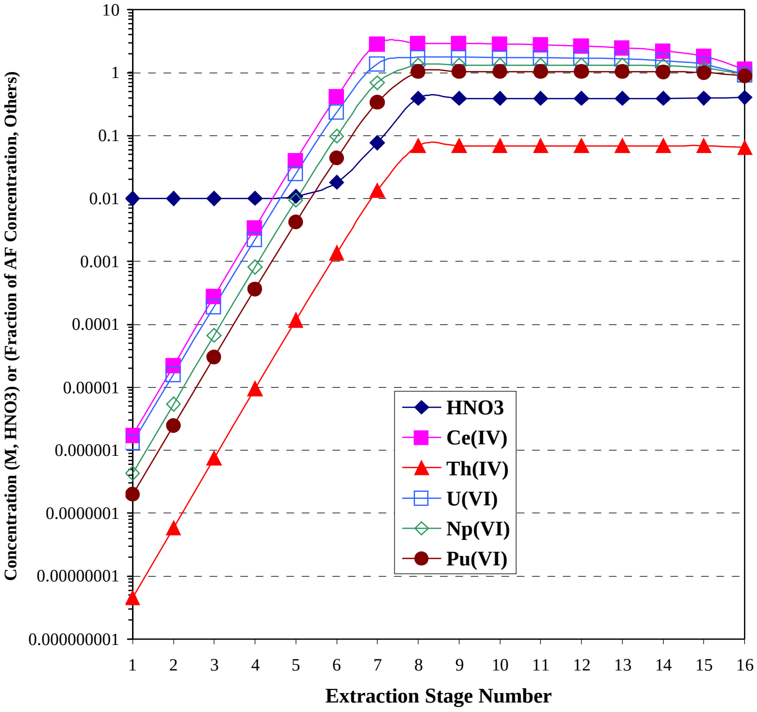

Figure 6-13. SASSE Predictions of Aqueous Phase Concentrations in 1B Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

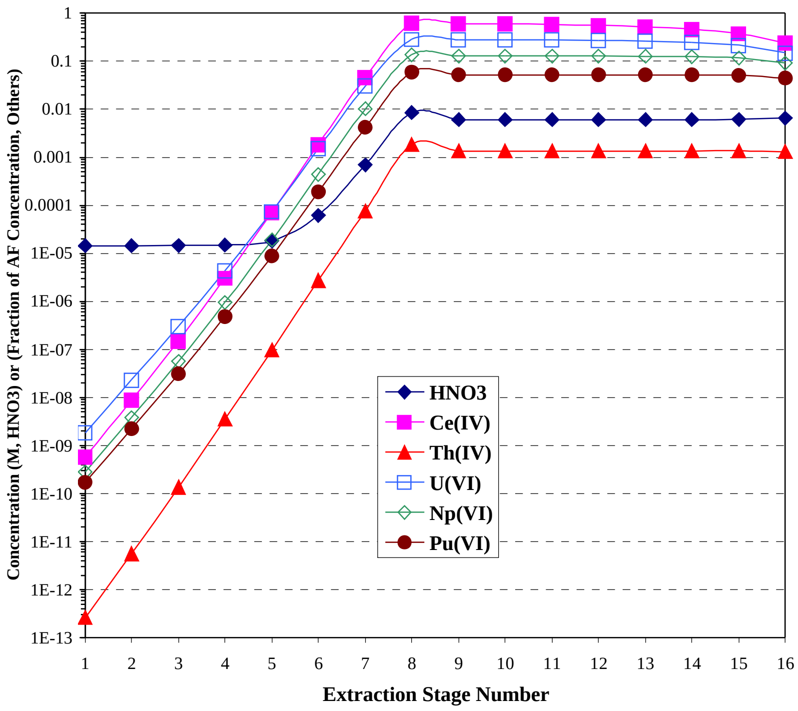

Figure 6-14. SASSE Predictions of Organic Phase Concentrations in 1B Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

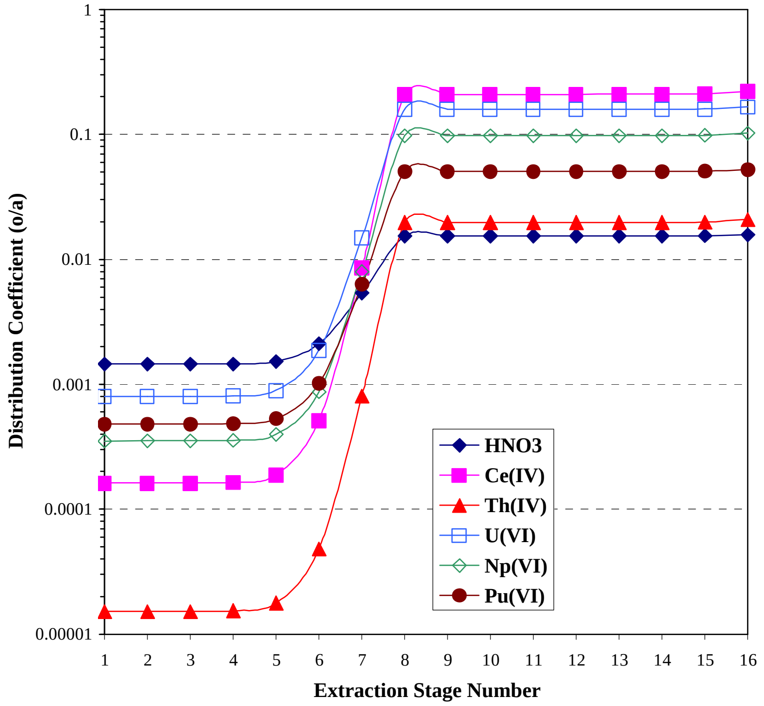

Figure 6-15. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1B Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

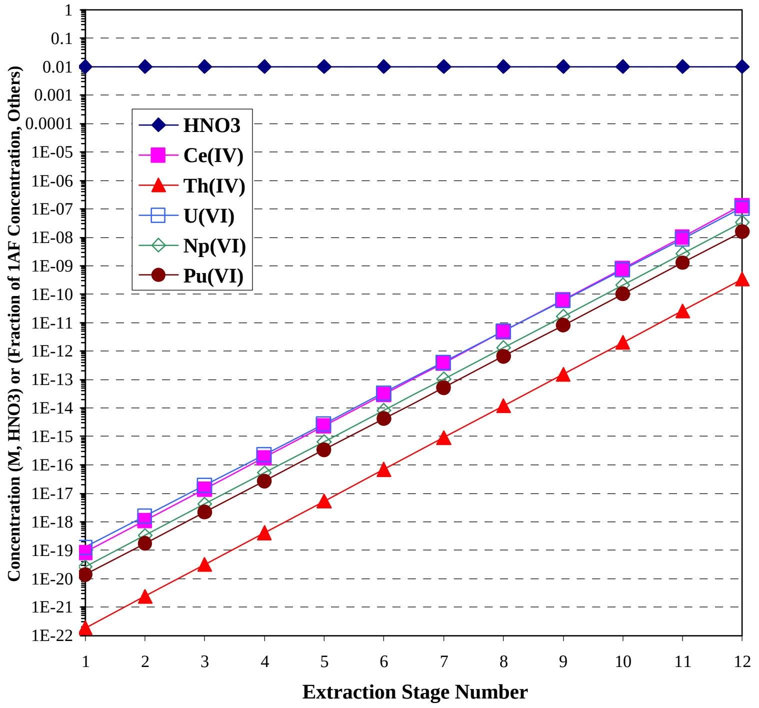

Figure 6-16. SASSE Predictions of Aqueous Phase Concentrations in 1C Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

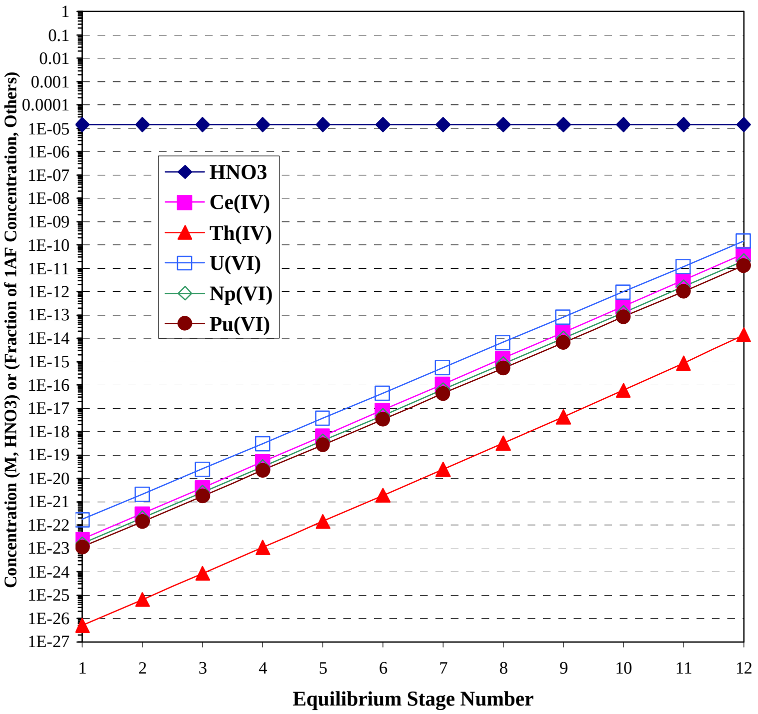

Figure 6-17. SASSE Predictions of Organic Phase Concentrations in 1C Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

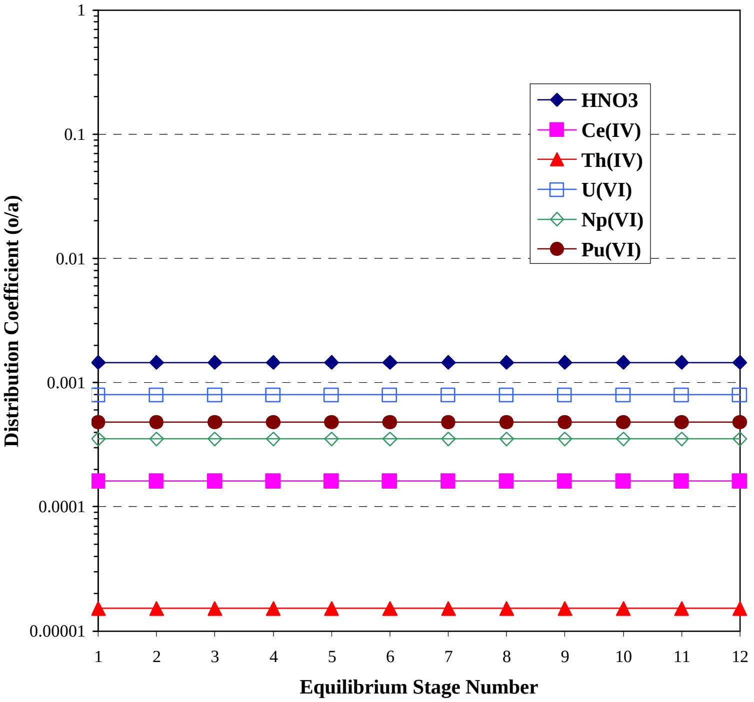

Figure 6-18. SASSE Predictions of Organic/Aqueous Distribution Coefficients in 1C Bank for Proposed Flowsheet, with Reduced Ce(IV) Distribution Coefficient

Calculated distributions of Ce(IV), Th(IV), U(VI), Np(VI), and Pu(VI) in the proposed flowsheet output streams 1AW, 1BP, 1CU and 1CW are listed in Table 6-1. As these distributions show, the SASSE model predicts that U(VI) and Np(VI) quantitatively extract into the 1AU and then strip into 1BP, with very low losses. The model predicts that Th(IV) almost completely strips into the aqueous phase in 1A Bank. This behavior is due to the strong effect of sulfate in reducing the Th(IV) distribution coefficient. According to the model, the Pu(VI) distribution coefficient in 1A Bank is close to one. Therefore, significant fractions of Pu(VI) leave the 1A Bank in both 1AU and 1AW. Based on a comparison with a single datum point for Ce(IV), the model predicts that Ce(IV) refluxes in 1B Bank if the Ce(IV) distribution coefficient is set at a multiple of 107 times the Th(IV) distribution coefficient. If the ratio of the Ce(IV) distribution coefficient to the Th(IV) distribution coefficient is reduced to 10.7 (approximately halved on a logarithmic basis), then the model predicts that Ce(IV) follows U(VI) and Np(VI), with extraction in 1A Bank and stripping into 1BP in 1B Bank. Table 6-1 does not list the distributions of fission products and other nonactinide metal impurities. These metals not listed should quantitatively strip into the aqueous phase and exit with the 1AW aqueous waste.

Table 6-1. Distribution of Cerium and Actinide Species among Proposed Flowsheet Output Streams

	% in 1AW	**% in 1BP**	**% in 1CU**	**% in 1CW**
Ce(IV), 107 x Th(IV) Do/a	----------------------Refluxes in 1B Bank----------------------------			
Ce(IV), 10.7 x Th(IV) Do/a	0.0025	99.9974	<0.0001	0.0001
Th(IV)	99.2250	0.7750	<0.0001	<0.0001
U(VI)	0.0011	99.9988	<0.0001	0.0001
Np(VI)	0.0054	99.9946	<0.0001	<0.0001
Pu(VI)	27.3	72.7	<0.0001	<0.0001

A concern associated with the proposed flowsheet is possible refluxing of U(VI) in 1B Bank. The distribution shown in Figure 6-4 indicates that the U(VI) concentration remains below the feed concentration; thus the SASSE model predicts that refluxing of U(VI) does not occur. By varying the acid concentration in the 1BX aqueous strip, it can be demonstrated that the reason that U(VI) does not reflux is that it is effectively stripped into 1BP. Figure 6-19 shows that increasing the 1BX acid concentration to approximately 0.3 M results in an increasing uranium holdup in 1B Bank, which is perhaps indicative of refluxing. However, this calculation demonstrates that uranium should not reflux in 1B Bank, so long as the 1BX HNO_3 concentration remains substantially below 0.3 M.

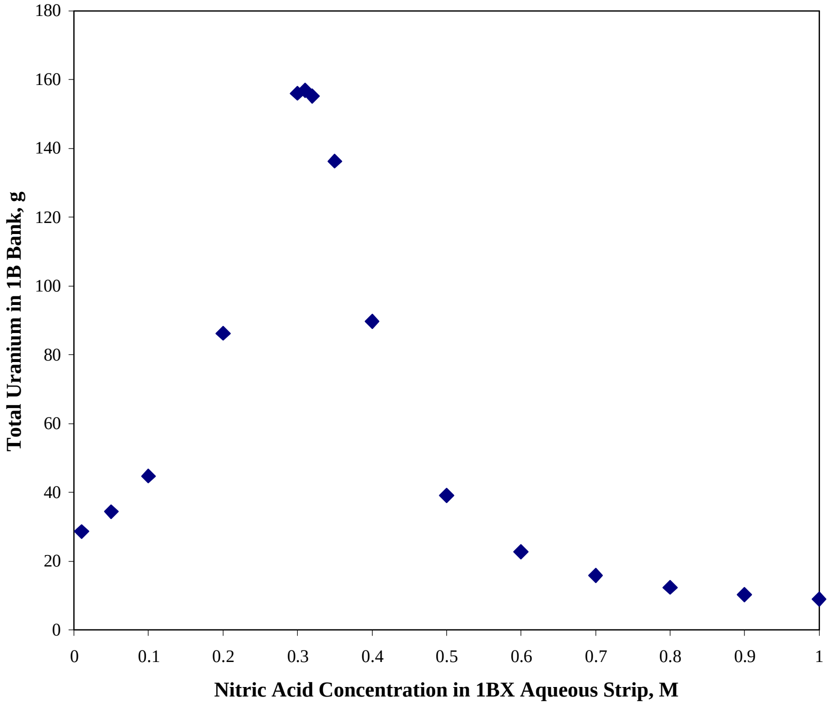

Figure 6-19. Variation of Uranium Content in 1B Bank with Nitric Acid Concentration in 1BX

7.0 CONCLUSIONS

A SASSE spreadsheet model indicates that a proposed Np(VI) oxidizing flowsheet[1] is a feasible method for separating neptunium and uranium from sulfates, thorium, and other metal impurities. The proposed flowsheet calls for stripping the sulfates, thorium, and other metal impurities into 1AW, and extracting and then stripping the neptunium and uranium into 1BP. SASSE predicts that separation of thorium from the other actinides can be accomplished with losses of 0.01% or less. It is assumed that other metal impurities such as iron, aluminum, and fission products will follow the thorium into 1AW. Due to an organic/aqueous distribution coefficient that is close to one, SASSE predicts that plutonium is split between the A Bank and B Bank aqueous output streams, with 27% to 1AW and73% going to 1BP. An extrapolated distribution coefficient based on unvalidated Ce(IV) distribution measurements at a single nitrate concentration and a comparison with Th(IV) distributions indicates that Ce(IV) could reflux in 1B Bank. This refluxing behavior runs contrary to experience with the addition of Ce(IV) to Second Cycle. If the Ce(IV) distribution coefficient is lower than would be predicted by this single point extrapolation, but still higher than the distribution coefficient for Th(IV), then Ce(IV) would follow Np(VI) and U(VI) into 1BP. The SASSE model was validated using data from a 1964 oxidizing flowsheet for the recovery of Np(VI) in Second Cycle.[2]

8.0 RECOMMENDATIONS

Phase distribution data for sulfate and for Ce(IV) at nitrate concentrations above 0.31 M are lacking and should be provided as part of the flowsheet development if scope and schedule permit.

9.0 REFERENCES

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[15] N. A. Skorik, O. G. Sakovich, and I. V. Kotlyarova, “Extraction of Cerium (IV) from Nitric Acid Solutions by Tributyl Phosphate,” Russ. J. Inorg. Chem., 25(10), 1530-1532, 1980.

10.0 APPENDIX: CORRELATION OF DISTRIBUTION COEFFICIENTS

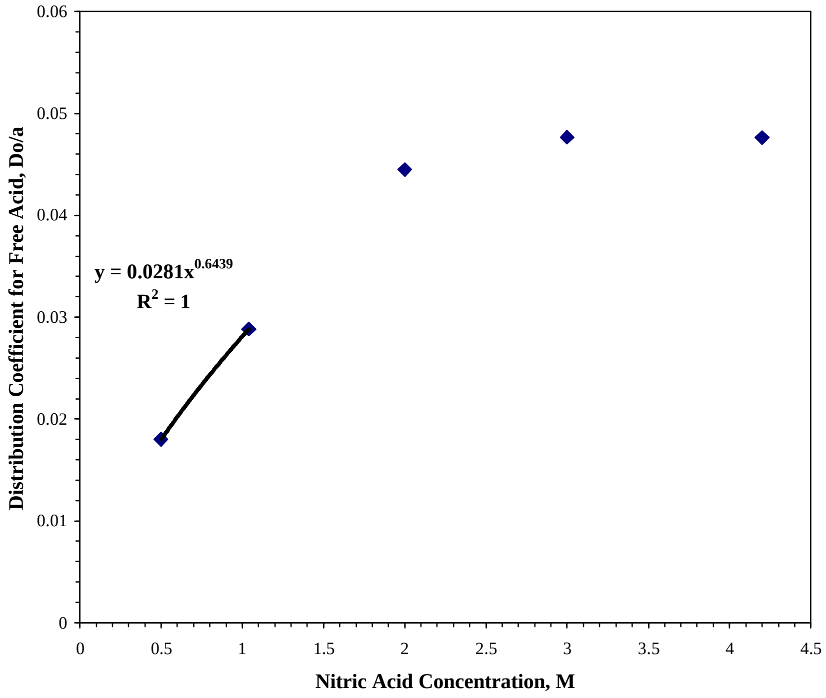

Figure 10-1. Correlation of Organic/Aqueous Distribution Coefficient for HNO_3

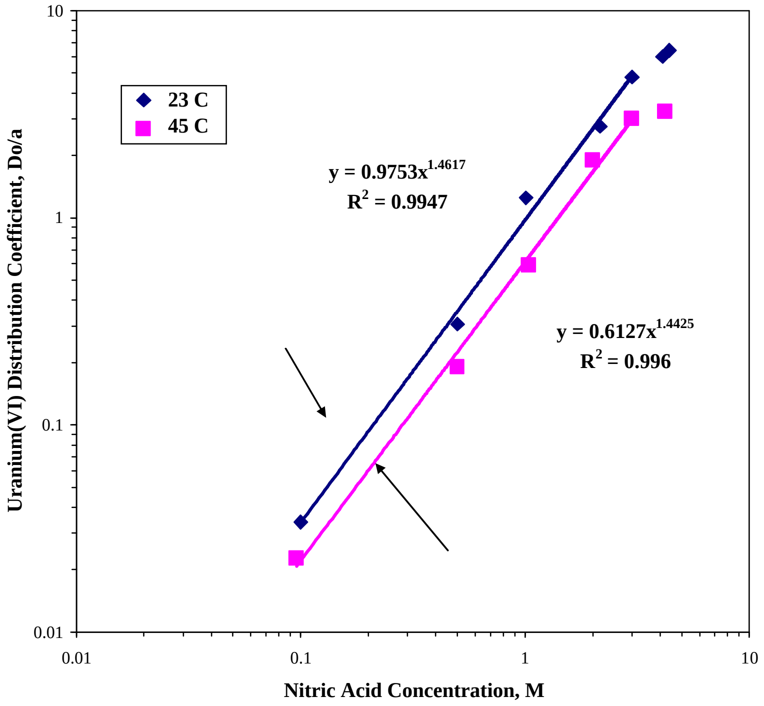

Figure 10-2. Correlation of Organic/Aqueous Distribution Coefficient for Uranium(VI)

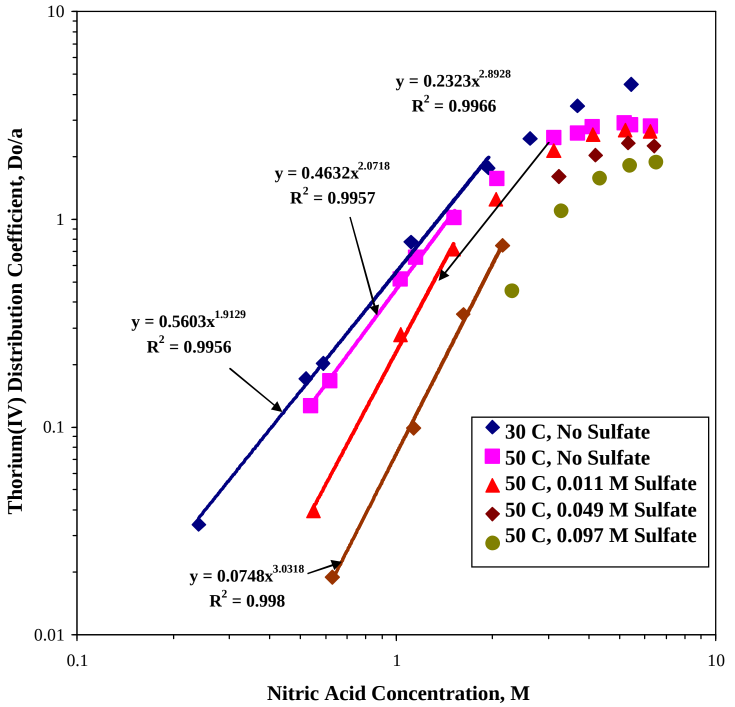

Figure 10-3. Correlation of Organic/Aqueous Distribution Coefficient for Thorium(IV)

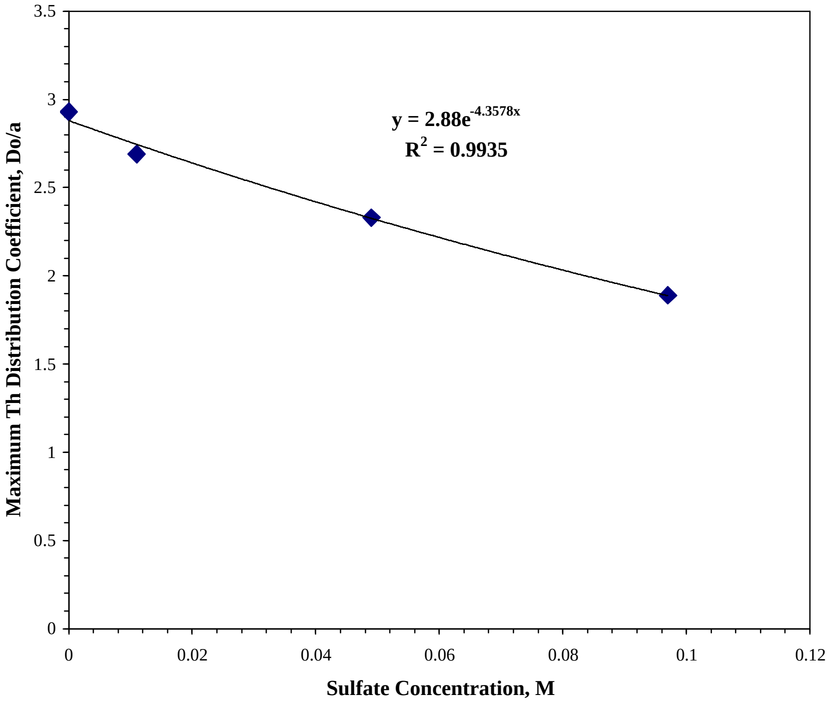

Figure 10-4. Correlation of Effect of Sulfate Concentration on Maximum Thorium(IV) Distribution Coefficient (for Approximately 5 M Nitric Acid)

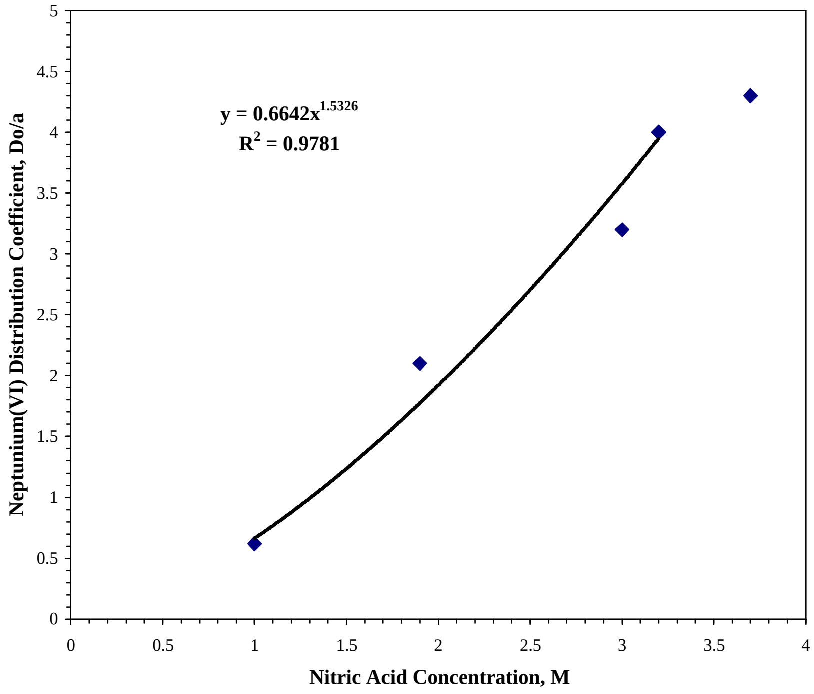

Figure 10-5. Correlation of Distribution Coefficient for Neptunium(VI)

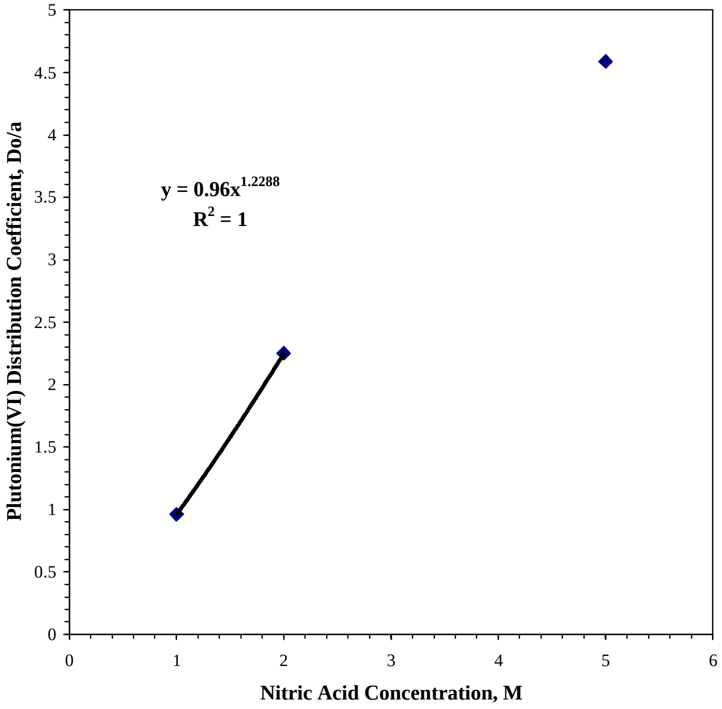

Figure 10-6. Correlation of Distribution Coefficient for Plutonium(VI)

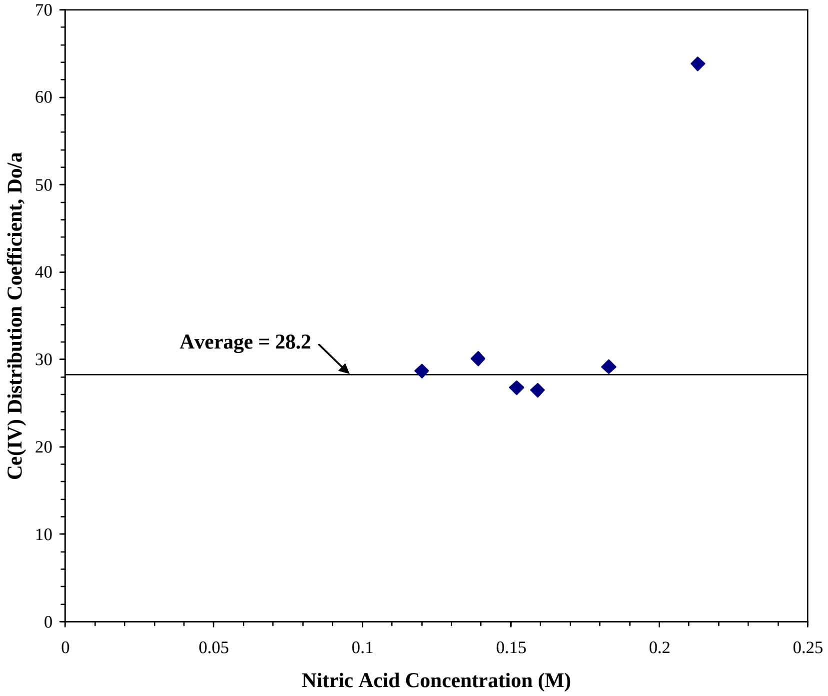

Figure 10-7. Correlation of Distribution Coefficient for Cerium(IV)