Atlantic Richfield Hanford Company
Richland, Washington 99352

ARH-CD-510

PLUTONIUM - URANIUM PARTITIONING ALTERNATE FLOWSHEET
PLUTONIUM RECLAMATION FACILITY

L. A. Fort

NOTICE

December 1975

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L. A. Fort

Safety Analysis Engineering
Development Engineering
Research and Engineering Division

December, 1975

Operated for the U. S. Energy Research and Development Administration by
Atlantic Richfield Hanford Company under Contract E(45-1)-2130

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INTRODUCTION

The Plutonium Reclamation Facility (PRF) located in the 236-Z Building was satisfactorily modeled by the SEPHIS (Solvent Extraction Processes Having Interacting Solutes) computer program. The program was obtained from G. L. Richardson of Hanford Engineering Development Laboratory (HEDL) and modified for the Plutonium Reclamation Facility. With the aid of the computer program an alternate flowsheet for the Plutonium-Uranium Partitioning Flowsheet was constructed. The goal of the alternate flowsheet is to reduce plutonium losses from the initial stripping column (CC) and reduce the quantity of plutonium bearing wastes from the solvent extraction system.

SUMMARY

The SEPHIS computer program has been found to be a helpful tool in understanding the effects of interacting variables on the solvent extraction system and developing better process control methods. With the aid of the computer program an alternate flowsheet to the Plutonium-Uranium Partitioning Flowsheet was obtained and is shown in the attached drawing Sk-2-25160.

The alternate flowsheet has the following changes to the Plutonium-Uranium Partitioning Flowsheet:

- A. The CAS scrub stream is deleted.
- B. The CAX flowrate is decreased from 60 percent flowrate to 50 percent.
- C. The CCX nitric acid concentration is decreased to 0.15 M.

The improvements derived by the alternate flowsheet over the current Plutonium (IV) Flowsheet are:

- A. The amount of waste generated by the solvent extraction system is decreased 10 percent.
- B. The CCW plutonium concentration is decreased by a factor of 10.
- C. Steady-state conditions are reached sooner.

The alternate flowsheet improves the solvent extraction system's efficiency and decreases the amount of waste discharged by the system. The computer method of analyzing solvent extraction problems should facilitate decision-making about corrective action steps.

DISCUSSION

The SEPHIS computer program was used to predict the transient and steady-state concentrations in a stage-wise scheme for the PRF solvent extraction system. The program handles the simultaneous extraction of uranyl nitrate, plutonium (IV) nitrate (plutonium (III) nitrate) and nitric acid solutes between aqueous and tributylphosphate-carbon tetrachloride organic phases as a function of operating time (the Roman numerals indicate valances). A more detailed description of the computer program can be found in Appendix A.

Flowsheet

The standard Plutonium-Uranium Partitioning Flowsheet at 60 percent rates was modeled by the SEPHIS computer program and the results are shown in the attached drawing Sk-2-25142. The number of theoretical McCabe-Thiele type stages for the system is presented below:

<u>Column</u>	<u>Number of States</u>
CA	7
CC	
CP	3
CO	3
Cu	2
CX	1
OA	1

The theoretical steady-state is reached 12 hours after the start-up with a representative concentration profile for the CA and CC columns. Product removal occurs approximately 10 hours after start-up (based on removal of 32 gram/liter plutonium concentration).

A test matrix of different flow conditions and concentrations of the streams was performed for the Plutonium-Uranium Partitioning Flowsheet. An alternate flowsheet was generated from the output obtained with the goal to reduce the amount of waste generated by the system and improve efficiency. The alternate flowsheet is presented in the attached drawing Sk-2-25160.

Using the computer output of the standard Plutonium-Uranium Partitioning Flowsheet as a basis, the alternate flowsheet has the following changes:

- A. The acid scrub stream at the bottom of the CA column (CAS) is deleted, for the recycle stream from the CC column provides for adequate scrub of the organic discharged from the CA column.
- B. To maintain the optimum flow rates in the CA column the CAX flowrate is decreased to the 50 percent flowrate. This also improves the stripability in the CC column because of the increased flowratio in the CC column.
- C. The reduction of the quantity of nitrate ions in the aqueous (salting strength) of the CC column improves and promotes added stripping of plutonium from the organic and thus the nitric acid concentration in the CCX is reduced to 0.15 M.

The improvements that are derived by the alternate flowsheet over the basic flowsheet are:

- A. The amount of waste generated by the CA column is decreased by 10 percent because of the CAS stream deletion. The aqueous waste streams from the other columns are also decreased, for the organic flowrate through the solvent extraction system has been reduced. Thus the effective decrease in aqueous waste from the system is 10 percent.
- B. The improved flow ratio of the CC column and the decreased nitric acid concentration in the CCX improves stripping of the plutonium from the organic and thus decreases the amount of plutonium carried in the CCW by a factor of 10.
- C. The inventory of plutonium in the solvent extraction system is decreased causing steady-state conditions to be reached sooner.

Figures 1 and 2 show a comparison of alternate flowsheet to the Pu-U Partitioning Flowsheet concentration profiles for the CA and CC columns as a function of column height for uranium and plutonium. As can be observed in Figure 1 the profiles for the alternate flowsheet are not much different to those of the Pu-U Partitioning Flowsheet. This is due to the increased quantity of solutes present in the lower section of the column for the alternate flowsheet. Figure 2 profiles show the improvement in performance due to the increased flowratio (A/O) and the reduction of nitrate ions in the aqueous. The profile curves for the CC Column also show that the neutron monitors on the column do not show the actual bulge that exists. They do however provide the capability to detect a shift in the concentration profile in the downward direction and facilitate corrective action steps.

The operating data collected and the values calculated by the computer program were corrected to a normalized basis. Because of the variance that persists in the solvent extraction system, the values used and

calculated are mean values. Different feed conditions give different effects and to optimize the proper flowsheet would mean characterizing each type of feed processed by the solvent extraction system. The values calculated should, however, be extremely helpful in diagnostic and flowsheet changes.

CO Column Performance

Problems have been associated with the CO Column capability to prevent the plutonium tetrafluoride produced in the column from precipitating and causing pluggage of the column. The degradation product (di-n-butyl phosphoric acid, HDBP) of the tributylphosphate (TBP) forms an unstrippable bond with plutonium to require a nitric-hydrofluoric acid scrub of the organic to breakup the Pu-DBP complex. This is the function of the CO Column.

The major product plutonium tetrafluoride, because the solvent is exposed to plutonium (IV) the greatest amount of time, is slightly soluble in nitrate acid. The solubility of plutonium tetrafluoride in nitric acid decreases as the plutonium concentration in the organic increases at constant acid concentration. Significant precipitation of plutonium tetrafluoride exists at concentration above 0.2 grams/liter of plutonium in the organic feed stream (CCW) with COX. Plutonium trifluoride is not more soluble in the aqueous than plutonium tetrafluoride and thus does pose a problem with respect to precipitation. The reduction of plutonium (IV) to plutonium (III) by hydroxylamine nitrate in the CO column to produce plutonium trifluoride would not improve the problem of precipitation but increase it. However, the reaction of fluoride with plutonium (IV) is faster than the reaction of plutonium and hydroxylamine nitrate.

There is a slight effect due to the extraction of nitric acid into the organic in the CO column. The extraction of nitric acid decreasing the concentration of nitric acid present in the aqueous. This causes the localized precipitation of plutonium tetrafluoride in a poor mixing atmosphere and would promote the pluggage of the column by precipitation of PuF_4 .

The CO Column being a packed column is not conducive to the handling of solids. The one inch Kynor interlocking saddles are wetted by the organic and the low aqueous to organic flowratio (A/o) of 0.19, shown not to be the optimum (0.30), permits poor mixing of the phases. A new design would improve the problems inherent to the column. Methods that could be used to correct the solids problem are: 1) raise the interface to make the column organic continuous; or 2) change the packing to a more favorable type with aqueous wetting characteristics; and 3) improve the aqueous to organic flow ratio.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the work done by G. L. Richardson of HEDL for his contribution of the SEPHIS computer program and the project assistance of M. J. Klem. Gratitude is also due Dr. R. E. Felt for his farsightedness and support of this project.

FIGURE I

CA COLUMN CONCENTRATION PROFILE
FOR THE ALTERNATE FLOWSHEET

FIGURE 2

CC COLUMN CONCENTRATION PROFILE FOR
THE ALTERNATE FLOWSHEET

APPENDIX A

SEPHIS COMPUTER PROGRAM
SIMULATION OF THE RECLAMATION FACILITY

The SEPHIS computer program models the stage-wise operation of one or more solvent extraction columns operating in series. The program treats the columns as multistage units with a maximum allowable total number of 25 stages and will develop up to 1,500 simulated time intervals requiring a maximum of approximately 130 computer seconds to do so. The program works in terms of solute-free-solvent basis and deals with three solutes, uranyl nitrate, plutonium (IV) nitrate (plutonium III nitrate) and nitric acid between aqueous and, tributylphosphate-carbon-tetrachloride diluent, organic phases.

The input into the program includes the number of stages; the initial state concentration and temperature profile; the feed stream compositions, relative flows and temperature; the phase ratio within the stage; the volume of each stage; the defined outgoing streams other than end streams; the total amount of plutonium per hour entering the system in the feed; and the plutonium concentration of the solvent extraction product rate. The stages are numbered from the bottom up, thus stage 1 is the first stage where the aqueous feed stream enters and the organic end stream leaves. At the start, both phases must be present in each stage. The phases are mixed completely, separate with no entrainment for each time interval, and then sent to the correct adjacent stage. The aqueous/organic phase ratio can be specified for each stage, beginning with the first stage or it may be the same as the flow ratio.

To minimize computer time, the phase ratios, stage volumes and interstage recycle, and total stage flows are calculated on the solute-free volume basis. This basis avoids correcting for volume change caused by extraction of solutes. Input feed streams are corrected to the solute-free volume basis at the start of the program by subtracting the approximate solute volumes from the feed stream volumes. At the end of the program, new solute volumes are calculated and added to the solute-free volumes leaving each stage to give the actual output solution volumes. Solute concentrations during the stage calculations are on a solute-free volume basis, but those in the print-outs are converted back to molarities. The volumes correction factor for converting from solution volumes to solute-free-solvent volumes are:

Aqueous

Phase

Solvent: 1 - 0.724 (M Uranium) - 0.0309 (M HNO₃)_a
 - 0.13 (M Plutonium^{IV})_a - 0.1 (M Plutonium III)_a
 - 0.049 (M Reductant)_a - 0.03 (M Nitrate salts)_a

Organic

Phase

$$\text{Solvent: } 1 - 0.097 (\underline{M} \text{ Uranium})_0 - 0.043 (\underline{M} \text{ HNO}_3)_0 - 0.139 (\underline{M} \text{ Plutonium IV})_0 - 0.0174 (\underline{M} \text{ H}_2\text{O})_0$$

The volume correction factors for converting from solute-free solvent volumes to solution volumes are:

Aqueous

Phase

$$\begin{aligned} \text{Solvent: } 1 + 0.0724 (\text{Uranium})_a + 0.0309 (\text{HNO}_3)_a + 0.13 (\text{Plutonium IV})_a \\ + 0.1 (\text{Plutonium III})_a + 0.049 (\text{Reductant})_a + 0.03 (\text{Salts})_a \end{aligned}$$

Organic

Phase

$$\text{Solvent: } 1 + 0.092 (\text{Uranium})_0 + 0.043 (\text{HNO}_3)_0 + 0.139 (\text{Plutonium IV})_0 + 0.0174 (\text{H}_2\text{O})_0$$

Where concentrations (in parenthesis) are given in moles per liter in solute-free solvent.

Water concentration in the organic solvent phase are approximated by the following equation which assumes a linear displacement of water from the organic solvent by other extracting solutes:

Solution concentration basis,

$$\underline{M} \text{ H}_2\text{O in water - saturated TBP} + [3.95 - 0.0144 (t, ^\circ\text{C})] \left(\frac{\% \text{TBP}}{100} \right)^{1.65}$$

Correction factor with other solutes present,

$$\frac{\underline{M} \text{ H}_2\text{O with other solutes}}{\underline{M} \text{ H}_2\text{O no other solutes}} = \frac{(\underline{M} \text{ U})_0}{(\underline{M} \text{ U})_0 \text{ SAT}} - \frac{(\underline{M} \text{ Pu})_0}{(\underline{M} \text{ Pu})_0, \text{ SAT}} - \frac{0.65 (\underline{M} \text{ HNO}_3)_0}{(\underline{M} \text{ HNO}_3)_0, \text{ SAT}}$$

Solute-free concentration basis,

$$\frac{\text{Moles H}_2\text{O}}{\text{Liter Solvent}} = [4.2 - 0.015 (t, ^\circ\text{C})] \left[1 - \frac{2\text{U}_0}{\text{TBP}} - \frac{2 \text{Pu}_0}{\text{TBP}} - \frac{0.6 (\text{HNO}_3)_0}{\text{TBP}} \right] \left(\frac{\% \text{TBP}}{100} \right)^{1.69}$$

Solute concentrations are converted to the desired solvent volume basis by the appropriate volume correction factor.

The mass action equilibrium constants at 25°C, for 20 volume percent TBP in carbon-tetrachloride diluent as a function of salting strength (SS).

Concentrations in moles per liter solvent-free solvent are:

$$K_U = \text{EXP} [1.8586 + 1.4209 \ln (SS)] = \frac{(U)}{(U)_a (SS)_a^n (TBP)_f^2}$$

$$K_{Pu} = \text{EXP} [0.1135 + 0.8516 \ln (SS) - 0.1719 \ln (SS)^2 + 0.171 \ln (SS)^3] \\ = \frac{(Pu)_0}{(Pu)_a (SS)_a^m (TBP)_f^2}$$

$$K_{H_1} = \text{EXP} [-2.135 - 0.1808 \ln (SS) + 0.2358 \ln (SS)^2 - 0.0379 \ln (SS)^3]$$

$$K_{H_2} = \text{EXP} [-2.394 - 0.2622 \ln (SS) + 0.2817 \ln (SS)^2 + 0.0276 \ln (SS)^3]$$

$$K_H = \frac{[HNO_3 \cdot TBP]}{(H^+)_a (SS)_a (TBP)_f} \text{ where } (TBP) = \text{moles of free TBP/liter solvent} \\ = \text{moles TBP/l solvent} - 2[(U)_0 + (Pu)_0 + 1/2 (HNO_3)_0]$$

m = extent of complexing of $Pu(NO_3)_m^{4-m}$ as a function of total nitrate concentration in the aqueous.

n = extent of complexing of $UO_2(NO_3)_n^{2-n}$ as a function of total nitrate concentration in the aqueous.

To account for the fact that uranium will complex more strongly than plutonium with the TBP, the correction is:

$$K_{Pu} = K_{Pu} [\text{EXP}(-1.08 \ln(TNM) - 0.722 \ln(U)_a - 2.867)]$$

TNM = total aqueous nitrate concentration

IS = ionic strength, i.e. for Pu IS is $= 1/2[(4-m)^2 + (4-m)]$

SS = salting strength $= \sqrt{TNM * IS}$

Temperature correction factors are made by multiplying the K values by:

EXP (2,200 Δ (1/T) for Uranium,

EXP (200 Δ (1/T) for Plutonium,

EXP (340 Δ (1/T) for HNO_2 ,

where Δ (1/T) = (1/0 Kelvin) - (1/298)

The desired distribution ratios are obtained by the following steps:

1. Convert concentration from molarity to moles/liter solute-free solvent.
2. Determine the total aqueous phase nitrate concentration.
3. Calculate the extent of complexing for $\text{UO}_2(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, $\text{Pu}(\text{NO}_3)_4 \cdot m\text{H}_2\text{O}$
4. Calculate the ionic strength for U, Pu
5. Determine the salting strength.
6. Determine the K values from the empirical correlation based on salting strength.
7. Solve for free TBP concentration by substituting the equivalent values of $(\text{U})_0$, $(\text{Pu})_0$, and $(\text{HNO}_3)_0$ from the mass action equation into the equation defining the free TBP concentration as follows:

$$(\text{TBP})_f = \frac{-B + \sqrt{B^2 + 4AC}}{2A}$$

$$A = 2 K_U (\text{U})_a + K_{\text{Pu}} (\text{Pu})_a + (\text{PuIII}) K_{\text{Ph}}$$

$$B = K_H (\text{HNO}_3)_a + 1$$

$$C = \text{moles TBP/l solvent} - 0.7302$$

8. Calculate approximate distribution ratio from equilibrium constant equation. The distribution coefficient is on a solute-free solvent basis.

The temperature profile in the column is calculated by a simple, stage-wise heat balance based on the temperature and volumes of the solute-free flows entering each stage. Specific heats are assumed to be 1.0 for the aqueous phase and about 0.5 for the organic phase.

The time scale of a time interval is calculated when the actual stage volumes and the flow rate of one of the interstage streams are known:

$$\text{Time Interval} = \frac{\text{Minutes} \quad (\text{Relative interstage flow rate}) \quad (\text{Actual stage volumes})}{(\text{Calc. relative total stage flow}) \quad (\text{Actual interstage flow/min.})}$$

The program has two options for determining when the desired steady-state operation has been achieved. For shutdown calculations where the time to strip uranium and plutonium from the system is desired, the program tests each stage after each time interval to see if the uranium and plutonium concentrations in each phase decreased to less than 10^{-6} M. For the startup case, the approach to steady-state is defined by the percent

of the overall material balance of that component which is furthest from the steady-state value:

Percent Steady-State - $100 [1 - (1 - \text{moles solute out} / \text{moles solute in})]$.

The percent material balance that terminate the program depends on the rate at which steady-state is approached. The program will terminate at 99.9 percent material balance if 99.5 percent material balance is achieved within 100 time intervals. If considerable reflux of one of the transferring solutes occurs, the program will be terminated at 99 percent of steady state. The overall percent steady-state is printed out at the end of the program and at the end of each 100 time intervals along with the number of the time interval at which it reached 90, 95, 99, 99.5 percent of steady state.

APPO		CASE	U. S. ATOMIC ENERGY COMMISSION RICHLAND OPERATIONS OFFICE
APPO			Astlanic Richfield Hanford Company Richland Washington 99352
APPO			PLUTONIUM-URANIUM PARTITIONING ALTERNATE FLOWSHEET
ENGR	W. A. FOR		
DRAWN AND			
CHECKED			
DESIGN	M. J. F.		
SCALE	NONE		
DATE FILED	10-6-67	PROJECT	250-B
FILE NO.	10-6-67	SHEET	70-2
			REVISIONS