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PLUTONIUM PARTITIONING IN THE PUREX
PROCESS WITH HYDRAZINE-STABILIZED
HYDROXYLAMINE NITRATE

HANFORD ENGINEERING DEVELOPMENT LABORATORY
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by

G. L. Richardson

J. L. Swanson (Battelle-Northwest)

June, 1975

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ABSTRACT

The use of hydrazine-stabilized hydroxylamine nitrate (HAN) to partition plutonium from uranium in the Purex process was successfully demonstrated in a laboratory multistage contactor. Reduction rate constants for the HAN-Pu(IV) reaction were obtained and used in a generally satisfactory computer simulation of the partition behavior.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	3
LITERATURE REVIEW	4
EXPERIMENTAL	11
REAGENTS	11
ANALYTICAL PROCEDURES	12
EXPERIMENTAL PROCEDURES	13
Aqueous Phase Kinetic Studies	13
Two-Phase Equilibration Studies	14
Twelve-Stage Miniature Contactor Runs	15
RESULTS AND DISCUSSION	17
AQUEOUS PHASE REACTION MECHANISM STUDIES	19
Stoichiometry	19
Plutonium(IV) Disproportionation Studies	20
HAN Reduction of Pu(VI)	20
HAN-Pu(IV) Reduction Kinetics	21
Hydrazine-Pu(IV) Reduction Kinetics	27
COMPUTER SIMULATION STUDIES	30
SEPHIS Computer Code Revisions	30
Partition Modeling	31
SOLVENT EXTRACTION STUDIES	34
Batch Equilibration Studies	34
Single-Stage Continuous Flow Studies	36
Twelve-Stage 1B Contactor Runs	38
Reaction Stoichiometry in 12-Stage Contactor Runs	44
Extraction Performance of Plutonium Product	48
Six-Stage 1B Contactor Runs (Partition Only)	48
Computer Simulation of Multistage 1B Contactor Runs	49
Parametric Studies of 1B Contactor Partitioning with HAN	54
ACKNOWLEDGEMENTS	59
REFERENCES	60
APPENDIX	A-1

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Comparison of Hydrazine and Hydroxylamine Reaction Mechanisms	5
2	Effect of Temperature on Pu(IV)-HAN Rate Constants and PuNO ₃ ³⁺ Stability Constants	9
3	HAN-Pu(IV) and Hydrazine-Pu(IV) Reaction Stoichiometry	19
4	Summary of HAN Reduction Kinetics Studies	22
5	Batch Equilibration Data Summary	35
6	Twelve-Stage 1B Contactor Run Summary	39
7	Effect of HAN and Nitrate Concentration on Pu Partition Losses	43
8	Reaction Stoichiometry Obtained in 12-State 1B Contactor Runs. .	45
9	Six-Stage 1B Contactor Run Summary	50
10	Comparison of Actual Contactor Performance with SEPHIS-Calculated Performance	52

APPENDIX

A-1	Data Card Formats for SEPHIS Programming	A-3
A-2	Revised SEPHIS Computer Code Listing	A-6
A-3	Example Output from the SEPHIS Computer Code (12-Stage Runs 3 and 19)	A-23

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Single Stage Continuous Flow Apparatus	15
2	Assembled View of a Six-Stage Miniature Centrifugal Contactor	16
3	Exploded View of a Six-Stage Miniature Centrifugal Contactor. .	16
4	Typical 1B Contactor Flowsheet	18
5	Typical HAN-Pu(IV) Reduction Curve at Elevated Temperature. . .	24
6	Typical HAN-Pu(IV) Reduction Curve at Room Temperature.	25
7	Effect of Temperature on Overall HAN-Pu(IV) Rate Constants. . .	26
8	Effect of Fe(III) and Cu(II) Catalysts on HAN-Pu(IV) Reduction Kinetics	28
9	Effect of Temperature and Fe(III) Catalyst on Hydrazine-Pu(IV) Reduction Kinetics	29
10	Effect of Aqueous Phase Residence Time on Stripping Plutonium (IV) from Solvent with Aqueous HAN-HNO ₃ Solutions	37
11	Effect of 1B Scrub Section Solvent Phase Acidity on Formation of Hydrazoic Acid	47
12	Effect of HAN/Plutonium Mole Ratio on Six-Stage Contactor Plutonium Losses	51
13	Effect of HAN Concentration and Stage Volume on SEPHIS- Calculated Uranium and Plutonium Losses	55
14	Effect of Feed Composition and Flow Ratios on SEPHIS- Calculated Uranium and Plutonium Losses	56
15	Effect of 1BF Feed Point on SEPHIS-Calculated Uranium and Plutonium Losses.	58

PLUTONIUM PARTITIONING IN THE PUREX PROCESS WITH HYDRAZINE-STABILIZED HYDROXYLAMINE NITRATE

INTRODUCTION

Until recently, the most widely used reductant to partition plutonium from uranium in the Purex solvent extraction purification process has been ferrous sulfamate.⁽¹⁾ Use of this reagent, however, introduces a metal impurity into the plutonium stream and eventually contributes to an increase in the salt content and corrosivity of the solvent extraction waste streams.

A number of alternate plutonium reductants or valence adjustment techniques have been proposed to minimize or eliminate these objections. They include the use of hydrazine-stabilized ferrous nitrate⁽²⁾ and uranium(IV) nitrate,⁽³⁾ platinum-catalyzed hydrogen⁽⁴⁾ and hydrazine,⁽⁵⁾ in situ electrolytic reduction,⁽⁶⁾ and hydroxylamine salts.⁽⁷⁾ Of these, only uranium(IV) nitrate,^(8a) hydroxylamine sulfate,^(8b) and hydroxylamine nitrate^(8b, 8c, 9, 10) have been used extensively in production facilities. In addition, electrolytic reduction has been selected for use in the Barnwell Nuclear Fuel Plant on the basis of favorable pilot plant experience.⁽¹¹⁾

Hydroxylamine nitrate (HAN) has a number of advantages as a plutonium reductant. It is nonmetallic, it is readily decomposed to innocuous products by heating, and it is fully compatible with existing facilities and processes. Until recently, HAN use in fuel reprocessing has been limited to low-acid applications where the reduction kinetics were known to be favorable. However, recent work by Barney^(12, 13) on the aqueous phase kinetics of the HAN-Pu(IV) reaction has greatly clarified the reaction mechanism and should lead to more widespread use of HAN in other applications.

The work described in this report was initiated to study the use of HAN to partition plutonium from uranium in a multistage solvent extraction contactor. The flowsheet used in these tests simulated the 1B (partition) contactor of a Purex process employing either 15 or 30 volume percent tri-n-butyl phosphate

(TBP) in a hydrocarbon diluent as the solvent. The plutonium and uranium content of the solvent feed simulated that which would be obtained in processing a fast breeder reactor (LMFBR) fuel (Pu/U ratio ≈ 0.12). Additional laboratory kinetic studies were made to extend the work of Barney to the conditions used in the tests, and the results were used to develop a computer program to perform the laborious stage-by-stage flowsheet calculations.

SUMMARY

The use of hydrazine-stabilized hydroxylamine nitrate to partition plutonium from uranium was successfully demonstrated in a 12-stage miniature contactor. Plutonium losses as low as $4 \times 10^{-4}\%$ were obtained with both 15 and 30% TBP flowsheets, with corresponding uranium losses to the plutonium product of 0.1% or less. This loss performance was obtained with 8 partition and 4 scrub (uranium reextraction) stages operated at 50°C. The aqueous phase residence time in the mixing zones of the partition stages was estimated to be about 0.5 minutes per stage.

Partitioning performance proved to be a complex function of many flow-sheet parameters. Factors favoring improved partitioning were high temperatures, low aqueous phase acid and nitrate concentrations, high uranium (plus plutonium) solvent loadings, and long aqueous phase residence times. The relative flow ratios in the partition and scrub sections were also of considerable importance because of their diluent effect on phase compositions, as well as their more direct role in determining the separation factors.

Additional HAN-Pu(IV) reduction rate data were obtained and used to obtain new reaction rate constants for use in Barney's rate law equation. The results were incorporated in a computer program for simulating the performance of the multistage contactor. The computer results were generally in fair to good agreement with the experimental results. The computer program, presented in the Appendix, is a useful tool for examining the interrelationships between the many flowsheet parameters. However, caution should be used in applying the computed results because of limitations inherent in the computer program: it does not include the effect of Pu(III) reoxidation in the solvent or the subsequent loss of the hydrazine holding reductant (nitrite suppressor); it is based on stage-wise calculations that are not truly applicable to differential (column) contactors; and it does not include a provision for backmixing (longitudinal mixing), a factor of considerable importance in differential column contactors.

The stoichiometries of the reduction of Pu(IV) by hydroxylamine and hydrazine were examined at 23 and 50°C; generally, 1.0 to 1.1 moles of plutonium were reduced per mole of reductant consumed for both reactants. The

approximate 1-to-1 stoichiometry was confirmed in the multistage contactor runs.

Approximately 0.1 mole of hydrazoic acid was formed per mole Pu(III) in the multistage contactor runs, the amount increasing with increasing solvent phase acidity. The formation of hydrazoic acid is considered to be confirmation of nitric acid oxidation of Pu(III) in the solvent phase. The reaction, directly or indirectly, yields nitrous acid which reacts with hydrazine to form hydrazoic acid. In the absence of hydrazine, the nitrous acid can react autocatalytically with Pu(III) and result eventually in partition failure. This effect was observed in a multistage contactor run made without hydrazine. Although HAN also reacts with nitrous acid, the rate is evidently too slow to provide adequate protection against the autocatalytic Pu(III)-nitrous acid reaction.

LITERATURE REVIEW

Extensive research has been conducted on the mechanisms of hydroxylamine and hydrazine reactions with various oxidants and reductants. A selected bibliography of some of the more recent work is included as references 12 through 41.

A review of this literature reveals several striking similarities in the reaction mechanisms for both hydrazine and hydroxylamine. These are illustrated in Table 1, which was compiled from several sources. For example, the reactive species with nitrous acid has been shown from kinetic experiments to be the protonated ion, the reaction rate in acidic solutions being first-order with respect to H^+ , HNO_2 , and $N_2H_5^+$ or NH_3OH^+ . (14-20) In contrast, the neutral hydrazine or hydroxylamine molecule is usually written as the reactive species in one-electron transfer reactions. (12, 22) This point has not been clearly established, although there is some evidence that metal ion complexes with N_2H_4 and NH_2OH are involved in the reactions. (12, 29, 31-35, 41)

TABLE 1
COMPARISON OF HYDRAZINE AND HYDROXYLAMINE REACTION MECHANISMS*

One-Electron Transfer Reactions:	
Hydrazine	Hydroxylamine
$\text{NH}_2\text{NH}_2 + \text{H}^+ \rightleftharpoons \text{NH}_3\text{NH}_2^+ \quad (1)$	$\text{NH}_2\text{OH} + \text{H}^+ \rightleftharpoons \text{NH}_3\text{OH}^+ \quad (1)$
$\begin{array}{c} \uparrow -e \\ \text{NHNH}_2 + \text{H}^+ \end{array} \quad (2)(-2)$	$\begin{array}{c} \uparrow -e \\ \text{NHOH} + \text{H}^+ \end{array} \quad (2)(-2)$
$\begin{array}{l} \text{Dimerization} \\ \rightarrow 1/2 (\text{NHNH}_2)_2 \rightarrow 1/2 \text{N}_2 + \text{NH}_3 \quad (3) \end{array}$	$\begin{array}{l} \text{Dimerization} \\ \rightarrow 1/2 (\text{NHOH})_2 \rightarrow 1/2 \text{N}_2 + \text{H}_2\text{O} \quad (3) \end{array}$
$\begin{array}{l} \text{Disproportionation} \\ \rightarrow 1/2 \text{N}_2\text{H}_4 + 1/2 \text{N}_2\text{H}_2 \quad (3a) \end{array}$	
$\begin{array}{c} \downarrow -e \\ \text{NNH}_2 + \text{H}^+ \end{array} \quad (4)$	$\begin{array}{c} \downarrow -e \\ \text{NOH} + \text{H}^+ \end{array} \quad (4)$
$\begin{array}{c} \downarrow -2e \\ \text{N}_2 + 2\text{H}^+ \end{array} \quad (5)$	$\begin{array}{c} \downarrow \text{Dimerization} \\ 1/2 (\text{NOH})_2 \rightarrow 1/2 \text{N}_2\text{O} + 1/2 \text{H}_2\text{O} \quad (5) \end{array}$
References (25-28)	References (12,13,21,30,31)
Reactions with Nitrous Acid:	
$\text{H}^+ + \text{HNO}_2 \rightleftharpoons \text{H}_2\text{NO}_2^+ \quad (6)$	$\text{H}^+ + \text{HNO}_2 \rightleftharpoons \text{H}_2\text{NO}_2^+ \quad (6)$
$\text{H}_2\text{NO}_2^+ + \text{NH}_3\text{NH}_2^+ \rightarrow \text{ONNHNH}_2 + \text{H}_2\text{O} + 2\text{H}^+ \quad (7)$	$\text{H}_2\text{NO}_2^+ + \text{NH}_3\text{OH}^+ \rightarrow \text{ONNHOH} + \text{H}_2\text{O} + 2\text{H}^+ \quad (7)$
$\downarrow$ $\text{HN}_3 + \text{H}_2\text{O} \quad (8)$	$\downarrow$ $\text{N}_2\text{O} + \text{H}_2\text{O}$
References (19,20)	References (14-18)

* Several of the reactions and reactive species are speculative and are not necessarily included in the cited references.

The oxidation reaction, (2), in Table 1 is reversible; and the back reaction, (-2), was found to be an important limiting mechanism in several kinetic studies with both hydrazine and hydroxylamine. (12, 13, 21, 25-28) In such cases, the products of Reaction (2) must be removed by some other means [e.g., Reactions (3) or (4 + 5)] for the oxidation of hydrazine or hydroxylamine via Reaction (2) to approach completion. The ultimate rate limiting reaction,

then, is the one by which the product of Reaction (2) is removed. The overall stoichiometry also depends on which of these reactions predominates. To illustrate these conclusions, the proposed mechanisms for the Fe(III)-hydrazine and Pu(IV)-hydroxylamine reactions are described in the following discussion.

A generally accepted mechanism for the Fe(III)-hydrazine reaction⁽²⁵⁻²⁸⁾ is presented as follows:

The measured overall stoichiometry for the reaction ranged from 1.1 to 1.35 moles of Fe(III) reduced per mole of hydrazine,⁽²²⁾ indicating that Reaction (2) predominates over Reactions (3) and (4). The disproportionation reaction, (3), has been shown to be unimportant.⁽²⁵⁾ The overall stoichiometry and rate can be increased by adding a catalyst, such as Cu(II), which preferentially reacts with N₂H₃:^(24, 26-28)

For the Pu(IV)-hydroxylamine reaction, Barney⁽¹³⁾ has recently reported that the following rate law is obtained in nitric acid systems with excess HAN:

$$\frac{-d[\text{Pu(IV)}]}{dt} = \frac{k[\text{Pu(IV)}]^2}{[\text{Pu(III)}]^2}, \quad (7)$$

where

$$k = \frac{k'[\text{NH}_3\text{OH}^+]^2}{[\text{H}^+]^4[1 + \beta_1(\text{NO}_3^-)]^2} \quad (8)$$

and β_1 is the stability constant for the PuNO_3^{3+} complex. Barney has proposed the following mechanism, which is consistent with the above rate law:

The PuOH^{3+} species is postulated as the reactive plutonium species from the hydrogen ion dependency of the initial rate; thus,

followed by

The forward reaction of Equation (11) is initially rate controlling, so that

$$\frac{-d[\text{Pu(IV)}]}{dt} = k_1[\text{PuOH}^{3+}][\text{NH}_2\text{OH}] - k_{-1}[\text{Pu}^{3+}][\text{NH}_2\text{O}]. \quad (13)$$

This reaction rapidly approaches equilibrium so that, as an approximation,

$k_1/k_{-1} = K_1$ and

$$[\text{NH}_2\text{O}] = K_1 \frac{[\text{PuOH}^{3+}][\text{NH}_2\text{OH}]}{[\text{Pu}^{3+}]} \quad (14)$$

Reaction (12) then becomes rate controlling. Making the steady-state approximation,

$$\frac{d[\text{NH}_2\text{O}]}{dt} = 0 = -k_2[\text{NH}_2\text{O}]^2 + k_1[\text{PuOH}^{3+}][\text{NH}_2\text{OH}] - k_{-1}[\text{Pu}^{3+}][\text{NH}_2\text{O}] \quad (15)$$

and substituting Equation (14) into Equation (15) gives

$$\frac{-d[\text{Pu(IV)}]}{dt} = k_2[\text{NH}_2\text{O}]^2 \quad (16)$$

Substituting Equation (14) into Equation (16) gives

$$\frac{-d[\text{Pu(IV)}]}{dt} = k_2 K_1^2 \frac{[\text{PuOH}^{3+}]^2 [\text{NH}_2\text{OH}]^2}{[\text{Pu}^{3+}]^2} \quad (17)$$

From Reactions (9) and (10),

$$[\text{PuOH}^{3+}] = \frac{[\text{Pu(IV)}]}{1 + ([\text{H}^+]/K_h)(1 + \beta_1[\text{NO}_3^-])} \approx \frac{K_h[\text{Pu(IV)}]}{[\text{H}^+](1 + \beta_1[\text{NO}_3^-])} \quad (18)$$

and
$$[\text{NH}_2\text{OH}] = \frac{K_a[\text{NH}_3\text{OH}^+]}{[\text{H}^+]}, \quad (19)$$

where K_h and K_a are the equilibrium constants for the reactions forming the PuOH^{3+} and NH_2OH species, respectively (Reactions 9b and 10). Thus, in terms of measured quantities,

$$\frac{-d[\text{Pu(IV)}]}{dt} = \frac{k_2 K_1^2 K_h^2 K_a^2 [\text{Pu(IV)}]^2 [\text{NH}_3\text{OH}^+]^2}{[\text{Pu(III)}]^2 [\text{H}^+]^4 (1 + \beta_1 [\text{NO}_3^-])^2} \quad (20)$$

Rate constants, $k' = k_2 K_1^2 K_h^2 K_a^2$, were determined from a series of reduction experiments at an ionic strength of 2.3 to 2.7 in which the concentration of plutonium was low relative to the other reactants so that k (Equation 8) would be essentially constant for each run. The experimental constants (k) were obtained by plotting the integrated form of Equation (7):

$$kt = [(A + B)^2(A - x)/(Ax)] - 2(A + B)\ln(A/x) + A - x, \quad (21)$$

where A = initial Pu(IV) concentration,

B = initial Pu(III) concentration,

and x = Pu(IV) concentration at time t .

Rate constants (k') calculated from Barney's data and Equations (8) and (21) are presented in Table 2.

TABLE 2

EFFECT OF TEMPERATURE ON Pu(IV)-HAN RATE CONSTANTS AND
PuNO₃³⁺ STABILITY CONSTANTS

Temperature °C	Overall Rate Constant k' , (moles) ³ /(liter) ³ (min) (Data from Ref. 13)	PuNO ₃ ³⁺ Stability Constant, β_1 , liters/mole
30	42 ± 11*	5.5
35	156 ± 24	6.3
40	450 ± 0.5	7.3
45	1340 ± 61	8.3
*Standard deviation, applies to 30°C data only.		

Values of β_1 used in these calculations are included in Table 2; they were interpolated from values obtained by Zebroski and Neumann⁽⁴²⁾ at an ionic strength of 6.

The overall stoichiometry obtained by Barney for Pu(IV)-HAN reactions in 1 M HNO₃ (23°C) ranged from 0.91 with excess HAN to 1.53 with excess Pu(IV),⁽¹³⁾ indicating that both Reactions (22) and (23), below, can take place:

Both the overall stoichiometry and the stoichiometry of Barney's rate limiting reaction (Equation 12) indicate that the overall reaction (22) predominates with excess HAN.

Iron(III) has been used as a catalyst to accelerate the Pu(IV) reduction rate.^(43, 44) The overall mechanism proposed by McKibben and Bercaw⁽⁴³⁾ involves the following reactions:

The observed rate improvement was relatively unimportant at reaction times less than five minutes or Fe/HAN mole ratios below 0.2.

Although the above discussion has emphasized the similarities in the hydroxylamine and hydrazine reactions, there are also some pronounced differences, most notably in the comparative reaction rates. For example, hydrazine reduces Pu(IV) much more slowly than does hydroxylamine, and there is little evidence that a back reaction takes place.⁽⁴¹⁾ On the other hand, hydrazine reacts much faster with nitrous acid than does hydroxylamine, the relative rate constants at 50°C being 36 and 2860 $\text{M}^{-2}\text{sec}^{-1}$, respectively.^(18, 20) These properties are complementary in fuel reprocessing operations, and it is common to add hydrazine to the HAN reductant to prevent nitrous acid from reacting with HAN and the Pu(III) product.

Hydrazoic acid (HN_3) is an undesirable byproduct of the hydrazine-nitrous acid reaction.⁽¹⁹⁾ It is extractable in TBP, and most of that formed in TBP extraction contactors will leave in the solvent phase.⁽³⁾ Hydrazoic acid will react further with an excess of nitrous acid according to the following reaction:

EXPERIMENTAL

REAGENTS

The hydroxylamine nitrate used in these studies was obtained from the Atlantic Richfield Hanford Company (ARHCO). It was prepared by them from technical grade hydroxylamine sulfate by a cation exchange technique developed by Wheelwright.⁽⁴⁵⁾ The HAN was received as a solution containing about 1.5M HAN and 0.3M free HNO_3 .

Ferrous nitrate was prepared by dissolving reagent grade iron powder in hydrazine-stabilized ferric nitrate-nitric acid.

Reagent grade hydrazine was used as a holding reductant in many of the tests to protect the reactants against attack by nitrous acid. The as-received material (ca. 20M) was neutralized to the mono-nitrate, $\text{N}_2\text{H}_5\text{NO}_3$, before dilution and use.

Tri-n-butyl phosphate (TBP) and normal paraffin hydrocarbon diluent (NPH—a mixture of C-10 to C-14 normal paraffins) were obtained from ARHCO and were representative of materials used in the fuel reprocessing facilities at Hanford. The TBP was obtained originally from the Commercial Solvent Corp. and the NPH from the South Hampton Co. *n*-dodecane, obtained from the Phillips Petroleum Company, was used as the TBP diluent in some tests. The TBP was diluted to 15 or 30 volume percent and used without further treatment other than a dilute sodium carbonate wash to remove dibutyl phosphate.

The plutonium used in these studies was purified by an anion exchange technique and concentrated by boiling to about 1M Pu(IV), 5M HNO_3 . In several instances, the Pu(III) product solution from the multistage contactor studies was reused without further purification after acidifying and boiling to destroy the reductant, to oxidize the Pu(III) to Pu(IV), and to concentrate the product to the desired stock composition. Results with both types of stock solution were comparable.

Prolonged boiling at the relatively high nitrate concentrations used to prepare the stock solutions oxidized some of the plutonium to Pu(VI). In most cases, the stock solution was aged for several days before use to allow

radiolytic reactions to reduce the Pu(VI) to Pu(IV). In one test with a 0.9M Pu-5M HNO₃ solution (~0.6W/1), the Pu(VI) self-reduction rate was about 0.012 moles/liter per day, with 22% Pu(VI) found 7 days after boildown, 12% after 14 days, and 0% after 24 days.

Organic feed (1BF) preparation was accomplished typically by blending two organic solutions. One solution contained the uranium and was prepared by dissolving uranyl nitrate hexahydrate crystals in 30% TBP-NPH and removing the resulting water phase. The other solution contained the plutonium(IV) and HNO₃ and was prepared by essentially quantitative extraction of Pu(IV) and nitric acid from an aluminum nitrate-salted aqueous solution. The acidity of the plutonium stock solution was adjusted to the desired HNO₃/Pu(IV) ratio by neutralization with dibasic aluminum nitrate before extraction.

ANALYTICAL PROCEDURES

Low levels of HAN were determined by measuring the amount of Fe(II) formed rapidly when an aliquot was added to an acetate solution containing Fe(III) and orthophenanthroline. The Fe(II)-orthophenanthroline complex was analyzed spectrophotometrically, using a Cary Model 14 H recording spectrophotometer. A prior separation of plutonium was accomplished by precipitation of the hydroxide. HAN was found to be fairly unstable in basic solution, so the analyses were performed immediately after precipitation of the plutonium hydroxide. Hydrazine, if present, also reduces Fe(III), but much more slowly than does HAN under these conditions.

Higher levels of HAN were sometimes determined by measuring the "nitrite demand" of the solution (after separation of plutonium by precipitation of the oxalate). In this method, excess nitrite was added to react with HAN and hydrazine. The residual nitrite concentrations were measured spectrophotometrically, using the peak at 370 nm. The nitrite demand due to the hydrazine (two moles/mole hydrazine) was subtracted from the total nitrite demand to give the HAN content, assuming one mole of nitrite destroyed/mole HAN.

Hydrazine was determined spectrophotometrically by the p-dimethylamino-benzaldehyde method.⁽⁴⁶⁾ Occasionally the nitrite demand method was also employed, when appropriate.

Nitric acid concentrations were determined by titration with sodium hydroxide, using oxalate complexing to minimize interference from plutonium and uranium.

Hydrazoic acid concentrations were determined employing spectrophotometric measurements of the ferric-azide complex.⁽⁴⁷⁾ In some cases the measurements were made on Fe(III)-HNO₃ scrubs of the organic phase, and in other cases the HN₃ was stripped into carbonate solution which was then added to a Fe(III)-HNO₃ solution. After reading the color intensity produced by the sample, a known amount of sodium azide was added and the intensity read again, thereby providing a standard in each case.

Dilute uranium in IBP was determined fluorimetrically. Spectrophotometric measurements were sometimes employed in more highly concentrated solutions after removal of the plutonium by oxalate precipitation.

Plutonium concentrations were determined employing both alpha counting and spectrophotometric techniques, using a calculation procedure similar to that described by Hagan and Miner⁽⁴⁸⁾. Molar extinction coefficient values determined in this work were found to be in good agreement with those determined by Hagan and Miner.

EXPERIMENTAL PROCEDURES

Three types of experiments were performed in this program:

1. Aqueous phase kinetic studies in which the rate of plutonium(IV) reduction was determined spectrophotometrically as a function of temperature and aqueous phase composition.
2. Two-phase equilibration studies in which plutonium distribution ratios were measured as a function of contact times, starting with plutonium(IV) in the organic phase (30% TBP in *n*-dodecane).
3. Twelve-stage, miniature contactor runs simulating LMFBR 1B contactor flowsheet conditions.

The basic experimental procedures used in each study are described below.

Aqueous Phase Kinetic Studies

In most of the tests, all reagents except the stock Pu(IV) solution were mixed and heated to the desired temperatures. A small aliquot of a concentrated

plutonium(IV) stock solution was then added and an aliquot of the resulting solution was placed in a thermostat controlled spectrophotometric cell. The absorbence of the plutonium(IV) peak was followed as a function of time by repeatedly scanning the region from 500 to 450 nm and measuring the difference between the Pu(IV) peak at 475 nm and the valley at 495 nm. Toward the end of the test period, the Pu(III) concentration was also followed by measuring the distance between the Pu(III) peak at 600nm and the valley at 640nm. One millimeter spectrophotometer cells were used for improved accuracy at plutonium concentrations above 0.01M.

Tests made at ca 35°C used a variation of the above procedure. The plutonium and reactants were mixed as before. Aliquots were then taken at various time intervals, diluted about 10-fold with 1 or 2M HNO_3 to effectively "freeze" the reaction, and the diluted aliquots were then scanned by the spectrophotometer at room temperature. In most cases, repeated scans of each sample were used to confirm that the reaction was essentially stopped by the dilution procedure. A minor correction was required for some of the results to extrapolate the Pu(IV)-Pu(III) concentrations back to the original aliquot sample time.

Two-Phase Equilibration Studies

Two types of experiments were made to determine the effect of contact time on removal of plutonium from typical 1B contactor organic feed solutions (0.2 to 0.3M U, 0.02 to 0.04M Pu, and 0.1 to 0.2M HNO_3 in 30% TBP-n-dodecane). In the simpler test, the organic feeds were contacted batchwise with various aqueous reductant solutions at temperatures and volume ratios comparable to those used in the twelve-stage contactor runs. Samples of each phase were withdrawn periodically during agitation and analyzed for total plutonium.

A more complicated experiment was devised to simulate the effect of aqueous phase residence time in a stage with continuous flow of feed and effluent streams. A schematic diagram of the test stand is shown in Figure 1. Organic and aqueous feed streams, designated as 1BF and 1BX in Figure 1, were continuously introduced to the contactor, which was a jacketed 30 ml glass vessel maintained at 47-48°C. The two phases were intimately mixed by a high-speed stirrer and separated by continuous overflow into a small decanter. The aqueous phase holdup volume in the decanter and recycle system was about 5-6 ml.

FIGURE 1. Single Stage Continuous Flow Apparatus

The IBX/IBF flow ratio was set at about 0.25 and the flows adjusted, in conjunction with the aqueous recycle flow, to maintain an average organic phase residence time of about three minutes within the contactor. The aqueous phase residence time was varied from about 3 to 30 minutes by adjusting the IBX flow rate and the overall input aqueous/organic flow ratio, which in turn determined the aqueous/organic phase ratio within the contactor.

Run lengths ranged from 30 to 120 minutes, depending on the estimated time required to reach steady state concentrations at the test conditions. Overall material balances and plutonium analyses of organic samples taken at intervals during the last half of the longer runs generally confirmed a close approach to steady state; effluent samples taken at the end of each run were assumed to be representative of steady state compositions. The measured phase ratio in the contactor at the end of the run, together with the input IBX and IBF flow rates, were used to calculate the average phase residence times.

Twelve-Stage Miniature Contactor Runs

Two six-stage miniature centrifugal contactors, similar to those used in a previous study, ⁽⁴⁹⁾ were connected in series to test various IB contactor flowsheet parameters. Assembled and exploded views of a six-stage contactor are shown in Figures 2 and 3.

Each stage consisted of individual mixer and centrifugal settling sections of a design essentially the same as that developed by the Savannah River

(704597-1)

FIGURE 2. Assembled View of a Six-Stage Miniature Centrifugal Contactor

(PNL0690989-3)

FIGURE 3. Exploded View of A Six-Stage Miniature Centrifugal Contactor

Laboratory.⁽⁵⁰⁾ The calculated holdup volumes were about three ml and seven ml for the mixer and centrifuge sections, respectively. Electrical strip heaters were mounted on the side of the contactor blocks to maintain the operating temperature at about $50 \pm 2^\circ\text{C}$; temperatures were monitored by inserting Weston thermometers into wells drilled into the solid blocks. The agitators and centrifuges were belt-driven to a speed of about 5000 rpm to assure intimate phase contact and clean separation. The entire apparatus was installed in an enclosure containing a nitrogen atmosphere to minimize the possible effect of air oxidation.

Feed streams were introduced through side ports leading into the mixing section of the stage. The reductant stream (1BX) was introduced into the first stage; the organic feed (1BF) was introduced into either the sixth or the eighth stage, and the organic scrub (1BS) was introduced into the twelfth stage. The standard 1BF flow rate was 4 ml/min; 1BX and 1BS flows varied according to the run objectives. The flowsheet for a typical run (Run 3) is shown in Figure 4.

Runs lasted typically six hours. End stream effluent samples (1BP and 1BU) were taken periodically throughout the run to confirm the degree of approach to steady state. Runs in which steady-state was not attained are noted in the table of run results. Individual stage samples could be taken from lines interconnecting the two contactors and through sample risers connecting with centrifuge discharge channels. These risers were normally plugged to minimize evaporation losses, and only a limited number of such samples were taken (usually at the end of the run to preclude interference with attainment of steady state).

RESULTS AND DISCUSSION

The experimental program concentrated initially on the 12-stage 1B miniature contactor runs. However, attempts to explain the performance obtained in these runs led to additional laboratory studies on the kinetics and mechanism of the hydroxylamine-Pu(IV) reaction and eventually to a computer simulation of the 1B contactor system. The results of the reaction mechanism studies and the computer model will be discussed first, followed by a discussion of the

FIGURE 4. Typical 1B Contactor Flowsheet

solvent extraction studies

AQUEOUS PHASE REACTION MECHANISM STUDIES

Stoichiometry

The results of experiments to determine the stoichiometry of the reaction of HAN and hydrazine with Pu(IV) are presented in Table 3.

TABLE 3

HAN-Pu(IV) AND HYDRAZINE-Pu(IV) REACTION STOICHIOMETRY

Initial Aqueous Phase Composition, M				Temp., °C	% Pu(IV) Reduced	$\frac{\Delta[\text{Pu(IV)}]}{\Delta[\text{Reductant}]}$
Pu(IV)	HNO ₃	HAN	N ₂ H ₄ ⁺			
0.087	0.93	0.098	0	47	99	1.06
0.092	1.0	0.098	0	47	97	1.00
0.088	1.0	0.063	0	43	83	1.17*
0.088	1.0	0.050	0	48	66	1.15*
0.075	0.93	0.098	0	23	78	0.92
					94	1.02
0.082	1.0	0	0.10	50	64	1.03
					92	1.10
					96	1.06
0.082	1.0	0	0.10	50	90	1.10
* ΔPu(IV)/mole HAN added; residual HAN concentration not measured.						

The results show that about 1 to 1.1 moles of Pu(IV) were reduced per mole of HAN or hydrazine consumed with an excess of reductant present. The stoichiometries found here for HAN are comparable to the more recent values reported by Barney and support the overall reaction mechanism (Reaction 22) on which Barney's revised rate law is based.⁽¹³⁾

The stoichiometry of the Pu(IV)-hydrazine reaction indicated that the following overall reaction predominated:

Plutonium(IV) Disproportionation Studies

Since Pu(VI) and Pu(III) both extract less strongly than does Pu(IV), disproportionation of Pu(IV) to Pu(III) and Pu(VI) can be an important mechanism favoring low-acid stripping of Pu(IV) from the solvent. In one test, addition of 0.008M Pu(IV) to 0.3M HNO₃ at 48°C resulted in the disproportionation of about 40% of the Pu(IV) after two minutes, about 50% after five minutes, and about 80% after several hours.

HAN Reduction of Pu(VI)

Addition of 0.07M HAN to the equilibrium mixture of the preceding disproportionation experiment (48°C) resulted in rapid (<2 min.) disappearance of the Pu(IV) and Pu(VI) peaks; however, only about 75% of the plutonium had been converted to Pu(III) after 5 minutes, the remainder presumably being Pu(V). About one hour was required for complete reduction of the plutonium to Pu(III). The absence of a Pu(IV) peak during the final stage of Pu(V) reduction indicates that the rate of Pu(V) reduction by HAN [or Pu(III)] is less than the rate of Pu(IV) reduction by HAN, under these conditions (0.3M HNO₃).

These results indicate that use of HAN to partition plutonium from solvent containing Pu(VI) will result in the rapid reduction of the Pu(VI) to inextractable Pu(V). The effectiveness of partitioning will then depend on the relative rates of reduction of the Pu(V) to Pu(IV) and of Pu(IV) to Pu(III), which in the latter case depends strongly on the acidity of the solution. However, even if increased acidity favors accumulation of Pu(IV), the partitioning should be no worse than would be obtained with Pu(IV) alone in the solvent feed, provided that sufficient

HAN is present to meet the added reductant requirement.

HAN-Pu(IV) Reduction Kinetics

The results of a series of HAN-Pu(IV) reduction kinetic studies are summarized in Table 4. The rate constants shown in Table 4 (k and k') are defined by Equations (7) and (8), respectively. The values of k were determined by the use of Equation (21). In many cases, the reactant compositions varied significantly over the run period as a result of the reaction. To improve accuracy, the kinetic runs were divided into several sections for calculation, using the average reactant concentration for each time period to calculate k . The stoichiometry of Equation (22) was used to estimate the changes in HNO_3 and HAN concentrations during the run. A similar procedure was used in the runs at elevated temperature to establish the effect on k and k' of slow drifts in temperatures that occurred during the tests.

Plutonium reduction rate data for two typical experiments are presented in Figures 5 and 6. Included in these figures are plots of the rate of change of the Pu(IV) concentration versus the square of the average Pu(IV)/Pu(III) ratio (calculated on a point to point basis). The straight lines obtained provide a confirmation that Barney's rate law, Equation (7), was applicable to the conditions of the experiments.

The effect of temperature on the overall reaction rate constant, k' , is shown in Figure 7 in the form of an Arrhenius plot. Although the data scatter more than would be desired, the data can be fit reasonably well by the equation

$$k' = 6 \times 10^{42} \exp(-28,500/^\circ\text{K}), \quad (28)$$

from which an apparent activation energy of 57 kcal/mole can be derived.

Barney's k' data are also plotted in Figure 7. Again a straight line is obtained, with the equation

$$K' = 2 \times 10^{33} \exp(-22,100/^\circ\text{K}). \quad (29)$$

The reason for the considerable discrepancy between the two sets of data has not been resolved; however, data obtained in the solvent extraction runs, described later, tend to confirm the validity of our higher rate constants under our experimental conditions.

TABLE 4
SUMMARY OF HAN REDUCTION KINETICS STUDIES

45-49°C

Run No.	Initial Composition, M					INPUT HAN Pu(IV)	°C	k_p $\frac{\text{moles}}{\text{L-min}}$	k'_p $\frac{(\text{moles/L})^3}{\text{min}}$	Notes
	HNO ₃	HAN	Pu(IV)	Pu(III)	NO ₃ ⁻					
2a	0.59	0.027	0.0086	0	0.65	3.1	45	0.87	8,500	
2b	0.65	0.018	0.0086	0.0086	0.73	2.1	45.5	0.34	33,000	
							47.8	0.26	28,000	
6	0.59	0.0096	0.0099	0	0.64	0.97	45	0.038	(~200,000)	(a)
							46.8	0.043	(~200,000)	(a)
13	1.06	0.37	0.0050	0.15	2.03	74	47	11.5	39,000	(b)
4	1.07	0.14	0.0088	0	1.24	16	45	0.49	5,100	
							46.3	1.34	15,000	
5	1.05	0.14	0.042	0	1.35	3.3	45.5	0.22	5,600	
							46	0.36	9,100	
							47	0.36	9,700	
3	1.03	0.027	0.0086	0	1.06	3.2	45.5	0.027	8,500	
							47.5	0.047	17,000	
							48	0.054	20,000	
							49	0.055	22,000	
7	0.93	0.098	0.0867	0	1.38	1.1	~47	0.21	(~180,000)	(a)
33-35°C										
24	1.83	0.205	0.111	0	2.70	3.6	33.0	0.0025	240	
							33.5	0.0026	210	
							34.0	0.0029	350	
20	1.83	0.28	0.108	0	2.54	2.6	34.5	0.0036	410	(f)
22-23°C										
8	0.93	0.098	0.075	0	1.33	1.3	~23	0.00073- 0.0017	3.4-18	
10	1.01	0.33	0.0079	0	1.37	42	~23	0.0082	4.3	
12	1.02	0.32	0.0078	0	1.44	41	~23	0.0084- 0.010	3.4- 6.3	(c)
9	1.02	0.32	0.095	0	1.72	3.4	~23	0.0045- 0.0067	10-11	
11	1.00	0.32	0.092	0	1.75	3.4	~23	0.0048- 0.0073	11-15	(c)
15	1.05	0.31	0.096	0	1.74	3.2	~23	0.0047- 0.0062	15-16	
16	1.00	0.31	0.098	0	1.70	3.2	~23	0.0047- 0.0058	9.8-14	
17	1.00	0.31	0.094	0	1.73	3.3	~23	0.0089- 0.0104	20-25	(d)
23c	1.06	0.019	0.0024	0.0041	1.10	8.1	~22.5	3.7×10^{-5}	4.2	(e)
22d	1.06	0.020	0.0030	0.0036	1.10	6.7	~22.5	8.1×10^{-5}	3.5	(e)
22b	1.06	0.021	0.0037	0.0028	1.10	5.5	~22.5	5.8×10^{-5}	6.1	(e)
20a	1.11	0.022	0.0029	0.0091	1.18	7.5	~22.5	9.8×10^{-5}	11.5	(e)

TABLE 4 (Cont'd)
SUMMARY OF HAN REDUCTION KINETICS STUDIES

Run No.	Initial Composition, M					INPUT HAN Pu(IV)	°C	k, moles/l-min	k', (moles/l) ³ /min	Notes
	HNO ₃	HAN	Pu(IV)	Pu(III)	NO ₃ ⁻					
23a	1.11	0.037	0.0059	0.0063	1.19	6.4	~22.5	9.6x10 ⁻⁵	3.9	(e)
22c	1.10	0.037	0.0065	0.0054	1.18	5.7	~22.5	2.3x10 ⁻⁴	9.2	(e)
22a	1.10	0.038	0.0072	0.0045	1.18	5.2	~22.5	1.2x10 ⁻⁴	5.0	(e)
18	1.76	0.33	0.098	0	2.48	3.4	~23	~4.0x10 ⁻⁴	7.2-9.4	
19	1.74	0.34	0.100	0	2.48	3.4	~23	~3.5x10 ⁻⁴	5.2-9.1	
14	1.81	0.31	0.096	0	2.50	3.2	~23	~3.6x10 ⁻⁴	7.8-11.6	
21	1.85	0.40	0.111	0	2.70	3.6	22.5	2.6x10 ⁻⁴	6.0	
22	1.85	0.40	0.111	0	2.70	3.6	22.5	4.0x10 ⁻⁴	9.3	(f)
23	1.85	0.40	0.111	0	2.70	3.6	22.5	3.1x10 ⁻⁴	7.3	
23b	1.99	0.040	0.0063	0.0066	2.07	6.3	22.5	9.7x10 ⁻⁶	9.6	(e)

Notes

- (a) Overall rate constant, k', may be considerably in error in these runs because of the large decrease in HAN concentration during the test and uncertainty in the representative HAN concentration to use in Equation (8).
- (b) The starting material was day-old IBP from Run 15 of the miniature contactor test series with 0.005M fresh Pu(IV) added. It also contained ~0.08M N₂H₅⁺ and ~0.026M UO₂⁺⁺.
- (c) The solution also contained 0.024M Fe³⁺.
- (d) The solution also contained 0.02M Cu⁺⁺.
- (e) The starting solutions for these tests were 10 to 20 fold dilutions of aliquots taken during the kinetic runs having the same cardinal number.
- (f) Stirred during the test. All other tests were made without stirring after the starting reagents were mixed.

FIGURE 5. Typical HAN-Pu(IV) Reduction Curve At Elevated Temperature.

FIGURE 6. Typical HAN-Pu(IV) Reduction Curve at Room Temperature.

FIGURE 7. Effect of Temperature on Overall HAN-Pu(IV) Rate Constants.

The results of tests 6 and 7 were not included in Figure 7. These runs had 1/1 HAN/Pu(IV) input mole ratios, and the calculated overall rate constants were nearly an order of magnitude greater than obtained at higher reactant ratios. The high rate constants are in doubt because of uncertainties in the HAN concentrations used to calculate them. It is possible, however, that the second reaction mechanism, defined by Equation 23, occurred to a significant extent at the low HAN/Pu ratios in these tests.

Three kinetic runs were made to determine the possible catalytic effect of Fe(III) and Cu(II) addition on HAN reduction of Pu(IV). The data are plotted in Figure 8; rate constants for the runs are included in Table 4. The data show that a small, but apparently consistent, improvement was obtained by addition of the catalysts at Pu/catalyst ratios of $\sim 4/1$, with copper being about twice as effective as iron at essentially the same concentrations. Iron catalysis was surprisingly ineffective at a 10-fold lower plutonium concentration (Pu/Fe=0.3). The results with iron generally confirm the work of other researchers.^(43,44) The beneficial effect of copper (II) is similar to that observed in copper-catalyzed hydroxylamine reduction of Fe(III).⁽³⁵⁾

Hydrazine-Pu(IV) Reduction Kinetics

The proposed application of HAN as reductant will also include hydrazine as a holding reductant to prevent Pu(III) reoxidation by nitrous acid. Accordingly, several kinetic runs were made to determine the extent of hydrazine reaction with Pu(IV). The results are presented in Figure 9.

The data show that the reaction follows a first order reaction with respect to Pu(IV). In $1M$ HNO_3 , the half life of Pu(IV) varied from 180 min at room temperature ($0.33M$ $N_2H_5^+$) to 9 min at $50^\circ C$ ($0.18M$ $N_2H_5^+$). The half life at $50^\circ C$ compares favorably with the 12 minute half life calculated from the correlation of Koltunov and Zhuravleva:⁽⁴¹⁾

$$\frac{-d[Pu(IV)]}{dt} = \frac{0.361 [Pu(IV)] [N_2H_4]}{0.14 + [H^+]}; \quad 50^\circ C, \mu=2, \quad (30)$$

where $[N_2H_4]$ is assumed to be equivalent to $[N_2H_5^+]$.

Addition of $0.023M$ Fe(III) catalyst was ineffective at high plutonium concentrations (Pu/Fe=4); however, unlike HAN, Fe(III) catalysis greatly increased the reaction rate at low plutonium concentrations (Pu/Fe=0.3).

FIGURE 8. Effect of Fe(III) and Cu(II) Catalysts on HAN-Pu(IV) Reduction Kinetics.

FIGURE 9. Effect of Temperature and Fe(III) Catalyst on Hydrazine-Pu(IV) Reduction Kinetics.

COMPUTER SIMULATION STUDIES

SEPHIS Computer Code Revisions

Purex solvent extraction flowsheet development has been greatly facilitated in recent years by the development of computer codes to do the tedious stage-by-stage equilibrium calculations. One such code, a HEDL revision of the SEPHIS code developed by Groenier⁽⁵¹⁾, was described in a previous report.⁽⁴⁹⁾ The HEDL version of SEPHIS was extensively revised during this program to incorporate a core reduction modification proposed by J. Cooper of ARHCO in 1974 and to calculate partition performance with HAN and ferrous nitrate reductants. A listing of the revised code, along with a description of the input cards and a sample of the output is presented in the Appendix.

The revised SEPHIS code provides transient stage-wise calculations for the simultaneous mass transfer of uranium, plutonium(IV), plutonium(III), and nitric acid between aqueous and TBP-hydrocarbon phases. Equilibrium correlations used in the code (subroutine UCOR) were derived from an extensive body of published and unpublished equilibrium data, with the majority of the plutonium data coming from Reference (52). The source data used in the correlations covered a range of TBP concentrations from 2.5 to 100% [2 to 40% TBP for Pu(IV), 10 to 100% for Pu(III)]; equilibrium temperatures from 0 to 70°C; and aqueous phase concentrations to 2M U, 0.2 M Pu(IV), tracer levels of Pu(III), and 6M HNO₃. Calculations made with the revised code have been compared with the published results of several multistage batch countercurrent contacts with reasonably good agreement. However, several compromises had to be made in fitting the data from so many diverse sources; and caution should be applied in using the computer results, particularly the predicted plutonium(IV) behavior at low acidities where disproportionation and hydrolysis can have significant effects.

The computation is divided into discrete time intervals, defined as the time required to fill the stages with the interstage flows from the preceding time interval calculation. The two phases countercurrently leave the stages in equilibrium at the end of the time interval. Provision is provided for internal recycle within each stage to maintain desired phase ratios. The length of a time interval is determined by the total input feed stream flow

rates (including internal recycle, which is determined by the specified phase ratios within each stage) and the individual stage volumes. The relationship is given by Equation (31):

$$\theta = \frac{\text{Stage volume, liters}}{\text{Total input flow rate, l/min.}} = \frac{\text{minutes}}{\text{time interval}} \quad (31)$$

Partition Modeling

The partitioning calculations are made in subroutine STAGES. The calculations with ferrous nitrate reductant are based on a stoichiometric reaction between the Fe(II) and Pu(IV) entering a stage, according to Reaction (25). That is, an excess of Fe(II) over the Pu(IV) entering the stage during the time interval will convert all of the Pu(IV) to Pu(III). With excess Pu(IV), all of the Fe(II) will be converted to Fe(III); and an equivalent amount of Pu(III), together with the remaining Pu(IV), will leave the stage at the end of the time interval.

Calculations with HAN reductant are considerably more complex. Consider the simple stage model below:

x_3, x_4 = input aqueous phase Pu(III) and Pu(IV) concentrations.

x_3, x_4 = output aqueous phase Pu(III) and Pu(IV) concentrations.

y_3, y_4 = input solvent phase Pu(III) and Pu(IV) concentrations.

y_3, y_4 = output solvent phase Pu(III) and Pu(IV) concentrations.

A, S = aqueous and solvent holdup volumes in the stage, which are equal to the total inflow and outflow of aqueous and solvent phases over a time interval.

In a continuous flow stage at steady state, the compositions of the two phases leaving the stage are the same as the average compositions within the stage during the residence time interval. Thus, the rate of Pu(IV) reduction by HAN within a stage will be constant as defined by Equation (7). The amount of Pu(III) formed in a stage over a time interval will be given by:

$$\Delta \text{ moles Pu(III)} = - \Delta \text{ moles Pu(IV)} = kA\theta(X_4/X_3)^2 \quad (32)$$

where k and θ have previously been defined in Equations (8) and (31), respectively. By material balance over a time interval,

$$\Delta \text{ moles Pu(III)} = AX_3 + SY_3 - Ax_3 - Sy_3 = kA\theta(X_4/X_3)^2. \quad (33)$$

After defining the Pu(III) distribution ratio as $D_3 = Y_3/X_3$ and the phase volume ratio in the stage as $R = A/S$, Equation (33) can be rewritten as:

$$(X_4)^2 = \frac{(X_3)^3(R + D_3) - (X_3)^2(Rx_3 + y_3)}{kR\theta}. \quad (34)$$

By overall plutonium material balance, we have

$$A(X_3 + X_4) + S(Y_3 + Y_4) = A(x_3 + x_4) + S(y_3 + y_4). \quad (35)$$

By rearranging and substituting D_4X_4 for Y_4 , D_3X_3 for Y_3 and R for A/S , we obtain

$$X_3 = \frac{R(x_3 + x_4) + y_3 + y_4 - X_4(R + D_4)}{R + D_3}. \quad (36)$$

Equations (34) and (36) can be solved simultaneously to obtain the two unknowns, X_3 and X_4 . Tentative values for the distribution ratios D_3 and D_4 are provided by subroutine UCOR; all other values are known. The method used in STAGES employs the Newton-Raphson method, which says that if r_1 is an approximation to a root of the equation $f(x) = 0$, a better approximation, r_2 , is given by

$$r_2 = r_1 - \frac{f(r_1)}{f'(r_1)}, \quad (37)$$

where the prime denotes the derivative. In this case,

$$f(x) = (X_4)^2 - \frac{(X_3)^3(R+D_3) - (X_3)^2(Rx_3-y_3)}{kR\theta} \quad (38)$$

The derivative of Equation (38) is obtained with the help of Equation (36):

$$f'(x) = 2X_4 + \frac{3(X_3)^2(R+D_4) + 2X_3(Rx_3+y_3)(R+D_4)/(R+D_3)}{kR\theta} \quad (39)$$

In applying this method, a suitable initial value for X_4 is assumed and used to calculate X_3 , $f(X_4)$ and $f'(X_4)$ from Equations (36), (38), and (39). The values of X_4 , $f(X_4)$ and $f'(X_4)$ are substituted into Equation (37) to calculate an improved approximation for X_4 . The iteration proceeds until the difference between successive approximations is sufficiently small.

After X_3 and X_4 are calculated, the results (together with the calculated equilibrium aqueous phase concentrations of the other constituents) are compared with the values used in UCOR to obtain the equilibrium distribution ratios. If the difference exceeds an acceptable value, new distribution ratios are determined and the above calculation procedure repeated until the difference is sufficiently small. The calculation proceeds from stage to stage, starting with the first aqueous feed stage, until all stage concentrations for the time interval are determined. Control is then returned to the main program where a material balance test is made to determine the degree of approach to steady state. If the desired approach has not been achieved, the program returns to subroutine STAGES to calculate the stage concentration profile for the next time interval, using the equilibrium aqueous phase concentrations just calculated as the first approximations to be used in the new UCOR distribution ratio calculations.

The value of k used in the preceding equations is obtained from Equation (8), which in turn uses the value of k' determined by Equation (28). Changes in reactant concentrations used in Equation (8) are based on the stoichiometry of Equation (22), with one mole of HAN lost and two moles of HNO_3 formed per mole of Pu(IV) reduced. The values of k are readjusted after each pass through the UCOR subroutine.

SOLVENT EXTRACTION STUDIES

The solvent extraction studies of HAN partitioning included batch equilibration and single-stage continuous flow tests, as well as the 12-stage 1B contactor runs, and will be discussed in that order.

Batch Equilibration Studies

The results of batch equilibrium tests made during this program are summarized in Table 5. Although the tests were not made as a systematic study, the results show qualitatively that the factors favoring rapid Pu(IV) reduction in the aqueous phase kinetic studies also resulted in lower, more favorable distribution ratios (E_a^0) in the two-phase system. These factors include the temperature, the aqueous phase acidity, and the HAN concentration.

A fourth factor affecting the reduction rate, the degree of uranium and plutonium loading in the solvent, can be inferred from the data in Table 5. Although largely obscured by compensating variations in other parameters, the effect is shown to be significant by comparing the results of tests R-1, 2, and 3 with the results of tests S-1, 2, and 3. In the latter tests, the plutonium distribution ratio (E_a^0) remained almost constant while the acidity decreased by 20% and the uranium plus plutonium loading in the solvent decreased by 25%. A similar decrease in acidity in tests R-1, 2, and 3, but with no decrease in solvent loading, resulted in approximately a three-fold decrease in the plutonium distribution ratios.

The cause of the solvent loading effect can be explained by the following analysis. In the two-phase system, the solvent phase provides a reservoir of Pu(IV) for the reduction reaction in the aqueous phase. Thus, those factors that favor transfer of Pu(IV) from the solvent phase will result in higher Pu(IV)/Pu(III) ratios in the aqueous phase and, consequently, higher Pu(IV) reduction rates. These factors include high uranium-plutonium solvent loading, low aqueous phase acidity, and low aqueous phase nitrate salting strength.

The B series of tests was made to confirm the expected high Pu(IV) reduction rates at low acidities and to determine if dibutyl phosphate (DBP) would adversely affect the plutonium partitioning behavior. The results indicate that the reaction

TABLE 5
BATCH EQUILIBRATION DATA SUMMARY

Test No	Initial Feed Compositions M						Input (HAN)/(Pu)	A/O Volume Ratio	Temp C	Equilibrium Values			Contact Time, Min
	Aqueous			Organic (30 TBP)						% Solv Sat (a)	M HNO ₃ Aq (b)	Pu E _a ^(c)	
	HNO ₃	HAN	N ₂ H ₅ ⁺	U	Pu	HNO ₃							
B-1	0 30	0 32	0 10	0 25	0 0001	0 05	640	0 20	23	43	0 33	0 014	5
B-2 ^(d)	0 30	0 32	0 10	0 25	0 0012	0 05	53	0 20	23	43	0 33	0 009	5
B-3	0 30	0 32	0 10	0 25	0 0001	0 05	640	0 20	23	43	0 33	0 011	5
B-4 ^(d)	0 30	0 32	0 10	0 25	0 0012	0 05	53	0 20	23	43	0 33	0 010	5
B-5 ^(e)	0 30	0 15	0 09	0 25	0 0074	0 06	4 1	0 20	23	43	0 33	0 047	5
B-6 ^(e)	0 30	0 16	0 10	0 25	0 0074	0 06	4 3	0 20	23	43	0 33	0 012	5
S-1	0 71	0 23	0 077	0 267	0 0356	0 20	1 5	0 237	49	51	1 12	0 14	5
S-2	0 67	0 17	0 056	0 236	0 0310	0 18	1 5	0 276	48	44	0 98	0 13	5
S-3	0 68	0 14	0 049	0 206	0 0270	0 16	1 5	0 297	48	38	0 90	0 12	5
S-4	0 71	0 15	0 042	0 179	0 0230	0 15	2 0	0 313	48	33	0 87	0 089	5
S-5	0 43	0 23	0 077	0 338	0 0356	0 20	1 5	0 237	47	62	1 00	0 19 0 13 0 079	1 2 5
S-6	0 82	0 23	0 077	0 338	0 0344	0 12	1 6	0 237	48	62	1 05	0 25 0 17 0 086	1 2 5
S-7	0 76	0 17	0 056	0 326	0 0305	0 12	1 5	0 276	48	57	0 92	0 22 0 13 0 084	1 2 5
R-1	0 99	0 30	0 10	0 30	0 0382	0 10	2 0	0 25	50	56	1 23 ^(f)	0 14 0 10 0 072	4 10 5
R-2	0 99	0 30	0 10	0 30	0 0358	0 10	2 1	0 25	50	56	1 17 ^(f)	0 14 0 10 0 10	4 10 25
R-3	0 61	0 30	0 10	0 30	0 0386	0 15	1 9	0 25	50	56	0 94 ^(f)	0 046 0 039 0 027	3 10 25
R-4	0 20	0 30	0 10	0 30	0 0386	0 15	1 9	0 25	50	54	0 71 ^(f)	0 030 0 022 0 0095	3 10 25

(a) Percent solvent saturation (200)(L + P in solvent)/TBP calculated by SEPHIS computer code

(b) Calculated by SEPHIS computer code

(c) Plutonium organic/aqueous distribution ratio

(d) Organic feed also contained 0 002M dibutyl phosphate (DBP)

(e) Organic feed was a 1BL sample from Run 6 12 stage runs) This sample may have contained some U(VI)

(f) Analyzed

was essentially complete within 5 minutes with 0.3M HNO_3 at 23°C. The addition of DBP at 2 to 20 times the plutonium concentration had no effect. Only in one test (B-5) was an abnormally high distribution ratio obtained. The test was made to try to explain the high plutonium loss to the 1BU stream in a twelve-stage 1B contactor run (No. 6) which was later found to have Pu(VI) in the feed. It is possible, therefore, that the high distribution ratio in test B-5 was caused by Pu(VI) in the feed. A repeat of the test a day later, but with the same feed (Test B-6) gave a normal distribution ratio.

Single-Stage Continuous Flow Studies

The plutonium distribution ratios obtained with HAN in batch equilibrations will generally be lower than those obtained with comparable feed streams and contact times in a continuous flow system. This is readily explained by the inhibiting effect of Pu(III) on the reaction rates, as shown in Equation (7). The batch contact starts with no Pu(III) present and, consequently, has a high initial reduction rate. Plutonium reduction in the continuous flow case takes place at the steady state Pu(III) concentration and, thus, has the maximum Pu(III) inhibiting effect throughout the entire contact period.

This effect was examined by a series of tests in the single-stage flow apparatus shown in Figure 1, in which the feed streams were fed continuously to a heated, vigorously agitated contact vessel. The average aqueous phase residence time was varied from ~3 to ~30 min by continuously recycling a portion of the aqueous product stream; the average organic phase residence time was held constant at about 3 min. The flowsheet conditions and feed streams were identical to those used in batch contact tests R-1 through R-4 (Table 4). The results, together with the results of the corresponding batch contact tests, are shown in Figure 10.

The results show that the batch contacts gave distribution ratios ranging from 2 to 5-fold lower than obtained in the continuous flow tests. The difference increased with decreasing acidity.

The run conditions used in the continuous flow tests were used in the previously described computer program to check the accuracy of the computational model. The results, also plotted in Figure 10, were in fair to excellent

FIGURE 10. Effect of Aqueous Phase Residence Time on Stripping Plutonium(IV) from Solvent with Aqueous HAN-HNO₃ Solutions.

agreement with the experimental results. The largest discrepancies were obtained at aqueous phase acidities below 1M, where the distribution ratios were overestimated by 50 to 100%. Although better agreement between calculated and experimental results would be desirable, the direction of the difference should lead to conservative results with the computer program.

Twelve-Stage 1B Contactor Runs

The run conditions and partition performance of the 21 runs made in the 12-stage miniature 1B contactor are presented in Table 6. The flowsheet conditions used in these runs were similar to those presented in Figure 4 with appropriate variations made in the flow rates, feed compositions, etc., to test their effect on partition performance. All of the runs used 30% TBP-NPH except Runs 16, 17, and 17B, which used 15% TBP-NPH. Runs 1 and 2 used six partition and six scrub (uranium reextraction) stages, the remaining runs used eight partition and four scrub stages. All runs were made at $50 \pm 3^\circ\text{C}$. Flow rates were set to give an aqueous phase residence time of about 0.5 min. in the mixing zone of each partition stage.

Although an attempt was made initially to vary the flowsheet parameters systematically, the early results were somewhat discouraging. For example, increasing the HAN input from a slight stoichiometric excess in Run 1 to over 100% excess in Run 2 increased the Pu loss by 4 fold. A step-wise increase in the flow rates from Run 3 to Run 5 (at 33% increase per step) resulted initially in a 2-fold decrease in the Pu loss despite the shorter residence time. The effect of an increase in partition stages was ambiguous; a comparison of Runs 2 and 3 indicates a significant improvement in Pu losses, while a comparison of Runs 1 and 7 indicates a decrease in performance.

It became evident from these results that the flowsheet conditions were at a borderline at which even a minor deviation in some parameter could produce a significant effect on the plutonium losses. The suspect parameters were the solvent feed composition and the relative flow ratios in the partition and scrub sections. In combination, these parameters affect both the acidity and the solvent loading throughout the contactor, both factors in turn affecting

TABLE 6
TWELVE-STAGE 1B CONTRACTOR RUN SUMMARY

Temperature = 50 ± 3 C
Nitrogen atmosphere (air atmosphere in Run 9)

Run No	1	2	3	4	5	6	7	8	9 ^(c)	10 ^(c)
Partition/Scrub Stages	6/6	6/6	8/4	8/4	8/4	8/4	8/4	8/4	8/4	8/4
% TBP - NPH	30	30	30	30	30	30	30	30	30	30
Run Length, Hours	6 0	6 0	6 0	5 9	5 7	5 2	6 8	6 0	5 7	6 1
1BF M U	0 328	0 328	0 315	0 315	0 315	0 315	0 315	0 315	0 30	0 30
M Pu	0 0344	0 0332	0 0356	0 0347	0 0344	0 0367 ^(a)	0 0344	0 0342	0 0388	0 0379
M HNO ₃	0 15	0 14	0 14	0 14	0 12	0 15	0 16	0 17	0 19	0 24
Flow, ml/min	4 00	4 02	4 00	5 27	6 69	3 94	3 85	3 97	4 10	4 12
1BX M HNO ₃	0 25	0 30	0 30	0 30	0 30	0 30	0 30	0 30	0 33	0 34
M HAN	0 16	0 32	0 32	0 32	0 32	0 15	0 16	0 04	0 15	0 15
M N ₂ H ₅ NO ₃	0 10	0 10	0 10	0 10	0 10	0 09	0 10	0 10	0 11	0 10
M Fe(NO ₃) ₂	0	0	0	0	0	0	0	0	0	0
Flow, ml/min	0 99	0 95	0 94	1 35	1 69	0 97	0 95	2 01	1 00	1 00
Partition Contact Time, min /stage	0 53	0 53	0 53	0 40	0 31	0 53	0 54	0 42	0 51	0 51
1BS Flow, ml/min	0 97	0 96	0 95	1 24	1 68	1 01	1 00	1 49	1 00	1 00
1BP M Pu	0 14	0 14	0 16	0 15	0 15	0 11	0 14	0 073 ^(b)	0 15	0 14
M HNO ₃	0 78	0 89	1 00	0 99	0 91	0 84	0 98	0 63	1 05	0 98
M HAN	-	-	-	-	-	-	-	0	0 024	0 025
M N ₂ H ₅ NO ₃	-	-	-	-	-	-	-	0 075	0 056	0 059
Pu as % of 1BF	101	103	111	115	110	78	103	112	82	81
U as % of 1BF	0 0005	0 0002	0 0004	0 0005	0 0006	0 0085	2 1	0 0002	0 0060	0 0060
1BU M U (material balance)	0 27	0 27	0 26	0 26	0 25	0 25	0 22	0 24	0 24	0 24
M HNO ₃	0 054	0 071	0 055	0 051	0 054	0 060	0 059	0 045	0 072	0 073
M HN ₃	-	-	-	-	-	-	-	-	0 0027	0 0035
Pu as % of 1BF	1 9	7 7	0 16	0 072	0 34	26	4 2	0 0018	27	19
Flow Ratios 1BX/(1BF+1BS)	0 20	0 19	0 19	0 21	0 20	0 20	0 20	0 37	0 20	0 20
1BX/1BS	1 01	0 99	1 00	1 09	1 01	0 96	0 95	1 35	1 00	1 00
Input Mole Ratios										
H ⁺ Pu	1 14	2 25	2 11	2 36	2 35	1 00	1 15	0 59	0 94	0 96
N ₂ H ₅ ⁺ /Pu	0 71	0 70	0 66	0 74	0 73	0 60	0 72	1 48	0 67	0 64
Fe ²⁺ /Pu	0	0	0	0	0	0	0	0	0	0

(a) Approximately 30% of the plutonium was Pu(VI)

(b) Approximately 5% of the plutonium in the 1BP was Pu(IV)

(c) Open contactor vents in these runs allowed evaporation of about 10% of the aqueous flow

TABLE 6 (Cont'd)

Temperature 50 + 3°C

Nitrogen atmosphere

Two-part runs (14 and 17) were made without intervening shutdown

Vertical arrow ↑ indicates trend of increasing concentrations

Run No	11	12	13	14A	14B	15	16	17A	17B	18	19
Partition/Scrub Stages	8/4	8/4	8/4	8/4	8/4	8/4	8/4	8/4	8/4	8/4	8/4
% TBP - NPH	30	30	30	30	30	30	15	15	15	30	30
Run Length, Hours	5 7	4 5	5 8	3 0	2 4	5 5	5 5	3 0	2 5	7 0	7 0
<u>1BF</u> <u>M U</u>	0 30	0 30	0 30	0 30	0 30	0 30	0 14	0 14	0 14	0 30	0 30
<u>M Pu</u>	0 0374	0 0385	0 0399	0 0397	0 0397	0 0394	0 0167	0 0170	0 0170	0 0387	0 0388
<u>M HNO₃</u>	0 18	0 14	0 18	0 19	0 19	0 19	0 11	0 10	0 10	0 13	0 13
Flow, ml/min	4 01	4 04	4 00	4 00	4 00	4 03	4 12	4 05	3 82	4 09	4 09
<u>1BX</u> <u>M HNO₃</u>	0 32	0 35	0 32	0 33	0 38	0 40	0 33	0 37	0 37	0 38	0 34
<u>M HAN</u>	0	0 31	0	0	0 15	0 55	0 22	0 32	0 32	0 33	0 24
<u>M N₂H₅NO₃</u>	0 12	0	0 31	0 29	0 30	0 11	0 11	0 11	0 11	0 12	0 10
<u>M Fe(NO₃)₂</u>	0 22	0	0	0 022	0 018	0	0	0	0	0	0
Flow, ml/min	0 98	0 96	1 00	0 97	0 97	0 97	0 66	0 43	0 43	0 98	1 30
Partition Contact Time, min /stage	0 52	0 52	0 52	0 52	0 52	0 53	0 53	0 56	0 58	0 56	0 48
<u>1BS</u> Flow, ml/min	1 04	1 04	1 03	1 03	1 03	0 95	1 04	1 04	1 04	0 53	1 07
<u>1BP</u> <u>M Pu</u>	0 15	0 004(e)	0 11	0 13	0 16	0 15	0 10	0 09+	0 11+	0 16	0 12
<u>M HNO₃</u>	0 68	0 90	0 90	0 86	0 94	1 06	0 93	-	1 03	0 81	0 73
<u>M HAN</u>	0	0	0	0	<0 01	0 37	0 105	-	0 19	0 096	0 115
<u>M N₂H₅NO₃</u>	0 02(d)	0	0 18	0 14	0 19	0 044	0 092	-	0 081	0 079	0 078
Pu as % of 1BF	100	2 5(e)	68	79	98	92	100	56+	74+	100	98
U as % of 1BF	0 0096	-	-	-	-	0 0087	0 10	-	-	0 23(h)	0 011
<u>1BU</u> <u>M U (material balance)</u>	0 24	0 24	0 24	0 24	0 24	0 24	0 11	0 11	0 11	0 27	0 24
<u>M HNO₃</u>	0 060	0 09	0 05	0 055	0 072	0 09	0 025	-	0 031	0 06	0 05
<u>M HN₃</u>	0 0046	0(f)	0 0012	0 0017	0 0037	0 0050	0 0007	-	0 0012	0 0034	0 0025
Pu as % of 1BF	<7x10 ⁻⁵	131(e)	30	18	5+(g)	10+	0 00019	0 0007+	0 0055+	0 0021+	0 00044
Flow Ratios 1BX/(1BF+1BS)	0 19	0 19	0 20	0 19	0 19	0 19	0 13	0 084	0 088	0 21	0 25
1BX/1BS	0 94	0 92	0 97	0 94	0 94	1 02	0 63	0 41	0 41	1 85	1 21
<u>Input Mole Ratios</u>											
HAN/Pu	0	1 91	0	0	0 92	3 36	2 07	2 00	2 12	2 04	1 99
N ₂ H ₅ ⁺ /Pu	0 78	0	1 94	1 77	1 83	0 67	1 01	0 67	0 72	0 76	0 80
Fe ⁺⁺ /Pu	1 44	0	0	~0 13	~0 11	0	0	0	0	0	0

(d) 0 17M Fe⁺⁺ found in the 1BP 20 minutes after sampling High loss of N₂H₅⁺ attributed to reduction of Fe(III)

(e) Partition failure started 3 hours after run started Sample results were obtained 1 5 hours later

(f) 0 0082M HNO₂ found in 1BU after 4 hours Pu was 240 of 1BF Pu at this time (~ 1 hour after start of partition failure

(g) Plutonium loss decreased sharply after addition of HAN but was increasing slowly at the end of the run

(h) May be analytical error, uranium losses were 0 035 and 0 023 after 2 and 4 hours, respectively

the mean plutonium distribution ratio*.

In order to strip the plutonium quantitatively from the solvent phase, it is essential that the mean plutonium distribution ratio in each stage be less than the net aqueous-to-organic flow ratio in that stage. Failure to achieve this will lead to a flowsheet "pinch" and result in excessive internal reflux of the plutonium and, most generally, a significant increase in the plutonium loss. Thus, the most probable explanation of the erratic results in the early runs is the presence of a flowsheet pinch; and, indeed, computer simulation runs, described later, confirmed that a pinch had occurred.

The results of Run 8 demonstrated that the suspected flowsheet pinch could be alleviated. In this run, the net A/O flow ratio in the partition section was increased from a normal 0.2 to 0.37 by doubling the 1BX flow. The resulting plutonium loss to the 1BU stream was only 0.002%, a factor of 40 lower than obtained on the best previous run. This outstanding performance was obtained with the addition of only 60% of the HAN required according to the stoichiometry of Reaction (22). Very little of the plutonium was stripped as Pu(IV), however. Only 5% of the plutonium in the 1BP product was analyzed as Pu(IV) within minutes after the sample was taken. An overall material balance for the run showed that 1.2 moles of Pu(III) were formed per mole of HAN plus hydrazine destroyed. This stoichiometry indicates that Reaction (23) must have occurred to an appreciable extent at the low HAN/Pu input mole ratio.

Although Run 8 gave a low plutonium loss, it was not entirely successful. The use of a low scrub flow (1BS) resulted in the loss of 2.1% of the input uranium to the plutonium product stream. This performance shows that the interaction between the 1BX, 1BF, and 1BS flows and the product losses is complex. A low 1BS flow can cause internal uranium reflux, increase the solvent loading, and thus decrease the plutonium loss through improved reduction kinetics. However, if the 1BS flow is too low, the uranium loss to the 1BP may be excessive. A high 1BS flow will insure good uranium reextraction but may dilute

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* The mean plutonium distribution ratio is that determined by both Pu(IV) and Pu(III) species. Although the distribution ratio of each of these is nearly independent of contact time, the resultant ratio determined by both species will vary with the aqueous phase residence time.

the solvent loading to the extent that the plutonium reduction kinetics are unfavorable, and high plutonium losses may result.

At this point in the program, the reaction mechanism studies, previously described, were initiated and eventually led to the selection of the run conditions used successfully in Runs 16 through 19. The first three of these runs used a 15% TBP flowsheet with the 1BF feed composition adjusted accordingly. Two flowsheet conditions were used, differing primarily in the net A/O flow ratio in the partition section of the contactor. Run 16, with a flow ratio of 0.13, had the lowest plutonium loss (0.0002%) of the entire HAN run series. Runs 17A and 17B (A/O = 0.08-0.09 in the partition section) also had low losses, but the runs were short and probably had not reached steady state. The excellent performance with 15% TBP can be attributed to the lower Pu(IV) distribution ratio, the effect being similar to that obtained with 30% TBP at high solvent loadings (low "free" TBP concentration).

Runs 18 and 19 used flowsheet conditions predicted by an early version of the modified SEPHIS code to provide relief from the flowsheet pinch encountered in the earlier 30% TBP runs. Run 18 accomplished this with a 47% reduction in the 1BS flow. The resulting Pu loss was 0.002% but was still increasing slowly at the end of the run. The uranium losses were erratic, with successive losses of 0.035, 0.023, and 0.23% obtained. Run 19 was made with the normal 1BS flow but a 30% increase in 1BX flow. Steady plutonium and uranium losses of 0.0004 and 0.01% respectively, were obtained throughout the seven hour run.

The results of the last five runs confirmed that excellent partitioning is attainable with both 15 and 30% TBP flowsheets. Perhaps the most important parameter affecting the performance was the solvent loading or free TBP concentration. Other factors, such as the aqueous phase acid and nitrate concentrations, are also important but were not extensively investigated.

The adverse effect of increased nitrate concentration was indirectly determined in Run 15. This run contained nearly twice the normal HAN concentration to examine the effect of a high HAN/Pu mole ratio on the Pu loss. The results are compared with those of similar runs at low HAN/Pu ratios in Table 7.

TABLE 7
EFFECT OF HAN AND NITRATE CONCENTRATION
ON PU PARTITION LOSSES

Run No.	Input HAN/Pu mole Ratio	Aqueous Phase Nitrate, M		%Pu loss
		1BX	Stage 8 (Estimated)	
7	1.15	0.56	1.9	4.2
3	2.11	0.72	2.1	0.07
15	3.36	1.06	2.5	~10

These results are not necessarily a definitive measure of the nitrate effect because of the pinching flowsheet conditions previously discussed. However, other workers have also reported an adverse effect of excessive HAN on reductive plutonium stripping, attributed to the added nitrate salting effect on Pu(IV) extraction.⁽¹⁰⁾

A number of additional runs were made to examine specialized facets of the partitioning process. In common with most of the early runs, the results may be colored by flowsheet pinching, and only limited comments will be made.

1. The 1BF in Run 6 contained ~30% Pu(VI). Nearly one fourth of the plutonium was unstripped, but similar performance was obtained in Runs 9 and 10 with comparable flowsheet conditions except for the absence of Pu(VI) (mole ratio of HAN/total Pu = 0.94 to 1.0).
2. Runs 9 and 10 were made to compare the effect of air and nitrogen atmospheres on the plutonium losses. Comparable losses were obtained; but, unfortunately, a low HAN/Pu ratio was used, and the results were inconclusive.
3. Run 11 was a control run with hydrazine-stabilized ferrous nitrate reductant ($\text{Fe}^{++}/\text{Pu} = 1.44$). The plutonium loss was $<7 \times 10^{-5}\%$, at least three to six-fold lower than obtained in the best 15 and 30% TBP runs with HAN. A major loss of hydrazine in this run (0.65 moles/mole Pu) indicated that iron participated in a catalytic reaction between hydrazine and plutonium.

4. Run 12 was a HAN run made without hydrazine stabilization. A complete partition failure occurred during this run, beginning about three hours after the start of the run.
5. Run 13 was made with hydrazine as the sole reductant at an input $\text{N}_2\text{H}_5^+/\text{Pu}$ mole ratio of 1.9. A 30% plutonium loss was obtained.
6. Run 14A was similar to Run 13 but with 0.022M Fe^{++} added to the 1BX as a potential catalyst ($\text{Fe}^{++}/\text{Pu} = 0.13$). The plutonium loss decreased to 18%.
7. Run 14B was a continuation of Run 14A with 0.15M HAN added to the hydrazine and iron already in the 1BX. The plutonium loss dropped sharply to 2.5% but increased slowly over the next two hours to 5.4%. (The total run time for Runs 14A and 14B was only 6 hours, probably insufficient to attain steady state profiles in either run).

The results of these miscellaneous tests indicate that the presence of hydrazine is essential to prevent total reoxidation of the plutonium, that hydrazine also contributes to the partitioning of plutonium, and that iron catalysis at low Fe/Pu ratios is relatively ineffective.

Reaction Stoichiometry in 12-Stage Contactor Runs

Effluent streams of several runs were analyzed for HAN, hydrazine, and hydrazoic acid to determine the overall reaction stoichiometry. The results are presented in Table 8.

The reactant stoichiometry ratios based on the 1BP plutonium content indicate that about 1.3 moles of HAN plus hydrazine were used up per mole of plutonium product. However, the formation of hydrazoic acid indicates that some of the hydrazine was used up in a side reaction with HNO_2 .

The nitrous acid most probably was formed by reoxidation of Pu(III) in the solvent phase. This reaction has been studied by several workers, ^(53,54) who show that the rate of Pu(III) reoxidation is proportional to the nitric acid content of the solvent phase. A logical inference is that one or more of the following reactions takes place in the solvent phase:

TABLE 8
REACTION STOICHIOMETRY OBTAINED IN 12-STATE 1B CONTACTOR RUNS

Run No.	Mole Ratios, Δ Reactant/Pu(III) in 1BP Stream					Net Δ Reductant ^(c) Total Pu(III) formed
	HAN	$N_2H_5^+$	Total Reductant	(a) HN_3	(b) Pu(III)	
8	(0.53)	0.29	0.82	---	---	---
9	0.98	0.43	1.41	0.105	1.21	1.08
10	1.0	0.37	1.37	0.142	1.28	0.96
11 ^(d)	0	0.65	0.98	0.155	1.31	0.63
12 ^(e)	78	0	78	0	---	---
13 ^(f)	0	1.20	1.20	0.056	1.11	1.03
14A ^{(f)(g)}	0	1.10	1.2-1.3	0.067	1.13	~1.04
14B ^(g)	0.85	0.62	1.5-1.6	0.118	1.24	~1.16
15	1.24	0.45	1.69	0.170	1.34	1.13
16	1.02	0.084	1.10	0.052	1.10	0.95
17B ^(h)	1.16	0.24	1.40	0.12	~1.24	~1.03
18	1.45	0.27	1.73	0.099	1.20	1.36
19	1.07	0.17	1.24	0.082	1.16	0.99

(a) Based on HN_3 content in 1BU stream.

(b) Total Pu(III) formed corrected for reoxidation loss, which was based on the assumption that hydrazoic acid formation is an indirect measure of the extent of Pu(III) reoxidation. See text.

(c) Based on total calculated Pu(III) formed, including the calculated reoxidation loss. The net reductant utilization was corrected for $N_2H_5^+$ reaction with HNO_2 to form HN_3 .

(d) 1BX Contained 0.22M Fe^{++}

(e) No hydrazine in 1BX.

(f) No HAN in 1BX.

(g) 1BX Contained ~0.02M Fe^{++}

(h) Run not at steady state.

With the solvent phase in intimate contact with the IBX stream, most of the HNO_2 formed will react with hydrazine (when present in excess) to form hydrazoic acid, according to the reaction:

The HN_3 is extractable in TBP^(3,19) and could conceivably react further with HNO_2 in the solvent phase; however, the solvent phase reaction, if it occurs, is slow. ⁽⁵³⁾

If the presence of hydrazine essentially limits the reoxidation reaction to that of Equation (42), 0.5 moles of HNO_2 , and subsequently 0.5 moles of HN_3 , will be formed by reoxidation of each mole of Pu(III). The reactant stoichiometry ratios of the IB contactor runs were recalculated according to this assumption to include the added Pu(III) and the loss of hydrazine consumed to form the HN_3 . The results, shown in the last column of Table 8, indicate that the expected 1/1 reductant stoichiometry was closely approached in most of the runs examined. The results with excess HAN indicate that HAN accounted for about 92% of the total reduction.

The hydrazoic acid/Pu(III) ratios from Table 8 were plotted against the average scrub section solvent phase nitric acid concentration (calculated by the SEPHIS code) in Figure 11. The data as plotted indicate an almost linear HN_3 dependency on the solvent acidity. Surprisingly, the data also show that the amount of HN_3 formed depended on the reductant used. Although further work should be done to confirm this trend, it appears that the faster reductants generate more HN_3 in hydrazine stabilized systems. Twice as much HN_3 (per mole

HEDL 7503-96.2

FIGURE 11. Effect of 1B Scrub Section Solvent Phase Acidity on Formation of Hydrazoic Acid.

Pu(III) product) was formed with HAN-hydrazine than with hydrazine alone, and the amount was increased by another 30% with Fe(II)-hydrazine.

The Fe(II)-hydrazine run demonstrated another unexpected effect. The overall stoichiometry of this run indicated that a net of only 23% of the Fe(II) was oxidized in reducing plutonium [0.33 moles/mole Pu(III)], but about 80 to 90% of the hydrazine was destroyed. Although the Fe(II)-Pu(IV) reaction is much faster than the hydrazine-Pu(IV) reaction, the iron catalytic effect previously described resulted in a greater net utilization of hydrazine than Fe(II). Failure to recognize this effect with hydrazine-stabilized ferrous nitrate flowsheets could result in an unexpected loss of the holding reductant. Autocatalytic reactions, such as those described in Equations (40) - (45), would then quickly oxidize the Pu(III) and any remaining Fe(II). This effect may have contributed to partition failure in a Hanford Purex Plant test with Fe(II)-hydrazine reductant.⁽¹⁾

Extraction Performance of Plutonium Product

Extraction studies with the plutonium product (1BP) from Runs 16 and 18 confirmed that the HAN treatment had no adverse effect on subsequent purification steps. In these tests, portions of the 1BP stream were treated with NaNO_2 to destroy the reductant and to oxidize the Pu(III) to Pu(IV). After acidification to 4M HNO_3 , the resulting aqueous phases were extracted repeatedly with equal volumes of 30% TBP. The unextracted plutonium after three contacts was 0.05% for the Run 16 1BP and 0.01% for the Run 18 1BP. A fourth contact reduced the plutonium content of the Run 18 1BP to less than 0.001% of that in the starting solution.

Six-Stage 1B Contactor Runs (Partition Only)

A series of 30% TBP 1B partition runs with HAN reductant has been reported earlier.⁽⁴⁹⁾ The runs were made in a six-stage centrifugal contactor of the same design as that used in the current program. The flowsheets were similar except for the absence of the scrub section and 1BS flow, the use of a slightly lower temperature, and the use of about 4-fold lower plutonium concentrations in the early study. The solvent had radiation exposures up to 1.6 W-hr/liter prior to extraction of the plutonium, but the partition performance appeared

to be unaffected. Because of the relevance of the early results to the present study, they are summarized in Table 9.

The primary variable studied in these early runs was the input reductant/plutonium mole ratio. A plot of the plutonium losses to the 1BU stream as a function of this variable is presented in Figure 12. The results show the expected improvement in plutonium loss with increased HAN input. The data also show that a significant, nearly 10-fold improvement was obtained by lowering the 1BP acidity from ~ 1.12 to $0.98M$ HNO_3 . The addition of $0.01M$ ferrous nitrate had little or no effect on the losses (HAN/Fe^{++} mole ratio = 6). Data scattering was not as severe as in the 12-stage runs, suggesting that the absence of the scrub section provided more consistent performance. However, the generally high losses indicate that flowsheet pinching still occurred.

Computer Simulation of Multistage 1B Contactor Runs

The flowsheet conditions used in both the 12-stage and 6-stage 1B contactor runs were used as input to the modified SEPHIS computer program to evaluate the applicability of the program to flowsheet development. In programming the computer, the stage volume was set at 3 ml, the volume of the mixing section only; and hydrazine nitrate was added as an inert salt nitrate. Small amounts of $Fe(II)$, if present with HAN, were treated as HAN input. The phase ratio in the mixing section was assumed to be equal to the input flow ratio, and no plutonium reduction was assumed to occur in the centrifuge section of the contactor. Stages were considered to be 100% efficient with respect to mass transfer.

The comparative results of the computer simulation are presented in Table 10. With only a few exceptions, the computer results agree quite well with the experimental values. Most of the major discrepancies in plutonium losses can be explained by non-achievement of steady state in the experimental runs. This was particularly true in Runs 14B, 17A, and 17B, which had run lengths of only 2.5 hours rather than the normal six hours. Run 18 lasted seven hours, but both the 1BU plutonium loss and the aqueous phase plutonium concentration leaving the sixth stage increased steadily throughout the run with little sign of leveling off.

TABLE 9
SIX-STAGE 1B CONTACTOR RUN SUMMARY

Temperature = 45°C, air atmosphere
30% TBP-n-dodecane (irradiated to 0.2 to 1.6 W-hr/liter just prior to extraction)
6 Partition stages, no scrub stages (1BS flow = 0)
Uranium and nitric acid concentrations calculated by SEPHis computer code.

Run No.	CL-3	CL-4	CL-5	CL-6	CL-7	CL-8	CL-9 (b)	CL-10	CL-11	CL-12	CL-13 (c)	CL-14 (c)
Run Length, hours	5.8	5.5	4.3	4.1	6.2	4.2	5.0 (a)	5.1	4.0 (a)	6.1	5.0	4.0 (a)
1BF: M U	0.29	0.29	0.31	0.30	0.31	0.31	0.31	0.30	0.30	0.34	0.34	0.34
M Pu	0.0083	0.0083	0.0087	0.0085	0.0088	0.0087	0.0087	0.0087	0.0084	0.0096	0.0096	0.0096
M HNO ₃	0.19	0.19	0.17	0.18	0.17	0.17	0.17	0.18	0.18	0.15	0.15	0.15
Flow, ml/min.	4.14	4.17	4.10	4.10	4.11	4.13	4.13	4.13	4.13	4.16	4.17	4.17
1BX: M HNO ₃	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
M HAN	0.030	0.030	0.050	0.050	0.050	0.070	0.070	0.060	0.060	0.050	0.050	0.050
M N ₂ H ₅ NO ₃	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
M Fe(NO ₃) ₂	0	0	0	0	0	0	0	0.010	0.010	0	0	0
Flow, ml/min.	0.78	0.79	0.78	0.78	0.75	0.79	0.79	0.79	0.79	0.82	0.81	0.81
Partition contact time, min./stage	0.64	0.63	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.63	0.63	0.63
1BP: M U	0.15	0.14	0.16	0.15	0.16	0.16	0.16	0.14	0.14	0.23	0.22	0.22
M Pu	0.041	0.038	0.041	0.044	0.047	0.043	0.040	0.040	0.036	0.045	0.045	0.043
M HNO ₃	1.14	1.13	1.10	1.13	1.11	1.10	1.10	1.13	1.13	0.97	0.98	0.98
U as % of 1BF	9.8	9.7	10.2	9.6	9.8	10.2	10.1	9.5	9.4	13.7	13.3	13.3
Pu as % of 1BF	97	91	93	103	102	99	90	94	86	95	94	90
1BU: M U	0.27	0.27	0.28	0.28	0.29	0.28	0.28	0.28	0.28	0.30	0.30	0.30
M HNO ₃	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02
Pu as % of 1BF	10.1	14.0	1.6	1.6	3.5	0.59	0.13	0.25	0.32	0.45	0.59	0.36
Flow Ratio, 1BX/1BF	0.19	0.19	0.19	0.19	0.18	0.19	0.19	0.19	0.19	0.20	0.19	0.19
Input Mole Ratios: HAN/Pu	0.68	0.68	1.09	1.13	1.05	1.52	1.52	1.37	1.37	1.02	1.01	1.01
N ₂ H ₅ ⁺ /Pu	2.2	2.3	2.2	2.2	2.1	2.2	2.2	2.3	2.3	2.0	2.0	2.0
Fe ³⁺ /Pu	0	0	0	0	0	0	0	0.22	0.22	0	0	0

Notes (a) Continuation of preceding run without shutdown.
(b) Solvent also contained 0.03 M I₂.

(c) Solvent also contained ~0.0007 M dimethyl sulfate, which appeared to cause some Pu precipitation in the 1BU.

FIGURE 12. Effect of HAN/Plutonium Mole Ratio on Six-Stage Contactor Plutonium Losses

TABLE 10

COMPARISON OF ACTUAL CONTACTOR PERFORMANCE WITH SEPHIS-CALCULATED PERFORMANCE

12-Stage Runs

Run No.	1BU Stream				1BP Stream				Pu Reflux,	
	% Pu		M HNO ₃		% U		M HNO ₃		Stage 6 Aq./1BP	
	Actual	SEPHIS	Actual	SEPHIS	Actual	SEPHIS	Actual	SEPHIS	Actual	SEPHIS
1	1.9	7.7	0.054	0.038	5x10 ⁻⁴	5x10 ⁻⁵	0.78	0.82	-	1.17
2	7.7	2.3	0.071	0.046	2x10 ⁻⁴	2x10 ⁻⁶	0.89	0.89	-	1.16
3	0.16	0.27	0.055	0.042	4x10 ⁻⁴	3x10 ⁻⁴	1.00	0.95	-	1.09
4	0.072	0.080	0.051	0.036	5x10 ⁻⁴	6x10 ⁻⁴	0.99	0.91	1.03	1.08
5	0.34	0.22	0.054	0.039	6x10 ⁻⁴	5x10 ⁻⁴	0.91	0.85	1.12	1.08
7	4.2	6.3	0.059	0.046	0.0053	0.0011	0.98	0.96	1.19	1.20
8	0.0018	15	0.045	0.036	2.1	7.8	0.63	0.60	0.74	1.53
9	27	21	0.072	0.054	2x10 ⁻⁴	8x10 ⁻⁴	1.05	1.06	1.27	1.24
10	19	23	0.073	0.055	0.0060	3x10 ⁻⁴	0.98	1.26	1.24	1.24
11	<7x10 ⁻⁵	2.3x10 ⁻⁷	0.060	0.039	0.0096	2x10 ⁻⁴	0.68	0.83	1.22	0.013
12	131(a)	3.3	0.090	0.057	-	4x10 ⁻⁴	0.90	0.93	25(a)	1.13
14B(b)	>5(c)	34	0.072	0.067	-	2x10 ⁻⁴	0.94	1.02	-	1.21
15	>10(c)	8.7	0.090	0.084	0.0087	2x10 ⁻⁵	1.06	1.04	1.27	1.11
16	0.00019	8.2x10 ⁻⁶	0.025	0.016	0.10	0.0049	0.93	1.07	0.48	0.93
17A	>0.0007(c)	16	-	0.037	-	7x10 ⁻⁵	-	1.11	-	1.13
17B	>0.0055(c)	11	0.031	0.036	-	7x10 ⁻⁵	1.03	1.09	-	1.13
18	>0.0021(c)	0.23	0.060	0.046	0.02-0.2	0.0059	0.81	1.00	≥0.61	1.04
19	0.00044	0.00012	0.050	0.036	0.011	0.0046	0.73	0.83	0.44	0.87
6-Stage Runs (Partition Only)										
CL-3	10	22	-	0.029	7.8	9.8	-	1.14	-	-
CL-4	14	22	-	0.029	-	9.7	-	1.13	-	-
CL-5	1.6	1.6	-	0.027	-	10.2	-	1.10	-	-
CL-6	1.6	1.8	-	0.028	-	9.6	-	1.13	-	-
CL-7	3.5	3.2	-	0.027	-	9.8	-	1.11	-	-
CL-8	0.59	0.060	-	0.026	-	10.2	-	1.10	-	-
CL-9	0.13	0.062	-	0.026	-	10.1	-	1.10	-	-
CL-10(b)	0.25	0.082	-	0.027	-	9.4	-	1.13	-	-
CL-11(b)	0.32	0.082	-	0.027	-	9.4	-	1.13	-	-
CL-12	0.45	0.21	-	0.024	13.7	13.7	-	0.97	-	-
CL-13	0.59	0.39	-	0.025	-	13.3	-	0.98	-	-
CL-14	0.36	0.39	-	0.025	-	13.3	-	0.98	-	-
(a) Partition failure										
(b) A small amount of Fe(II) in the 1BX was treated as HAN in the SEPHIS calculations.										
(c) Not at steady state. Plutonium losses were still increasing slowly at the end of the run.										

Run 8 was made with a substoichiometric amount of HAN and a flow ratio that produced an abnormally low nitric acid profile. As previously discussed, the plutonium reduction was unusual for this run, with much more plutonium reduced than could be accounted for by a 1-to-1 HAN/plutonium reductant stoichiometry. The low acid concentration prevailing in most of the partition section (less than $0.4M$ HNO_3 , aqueous, up to the feed stage by SEPHIS calculation) and elevated temperature would also favor plutonium disproportionation, which would result in lower plutonium distribution ratios and lower losses.

The observed and calculated uranium losses were also in reasonably good agreement, considering the magnifying effect of minor errors in the distribution ratios on the calculated losses during reextraction, the assumption of 100% stage efficiency, and the poor accuracy of uranium analyses at low concentrations.

The nitric acid calculations consistently underestimated the acid concentrations in the 1BU but were generally in good agreement with the 1BP analyses. It is possible that the correlation used for nitric acid equilibrium calculations needs a small adjustment; however, the discrepancy might also be due to difficulties in determining the free acid concentration at the high U/HNO_3 ratios found in the 1BU.

The plutonium reflux ratios presented in the final columns are a measure of internal consistency. These ratios are based on the plutonium concentration in the aqueous phase leaving stage 6. They do not necessarily represent the maximum plutonium reflux, but should be close for the higher-loss runs. According to the SEPHIS results, the maximum reflux ratio (defined as the maximum aqueous phase plutonium concentration in the contactor divided by the 1BP plutonium concentration) usually occurred at stage 7 but could occur as high as stage 5 with high plutonium losses or as low as the 1BF feed stage with low losses. The agreement between calculated and measured reflux was good except in those runs with unusually low losses. In those cases, SEPHIS overestimated the reflux ratio by as much as a factor of two. Run 11 with Fe(II)-hydrazine reduction, was an exception to this rule; in this use the actual reflux ratio at stage six was nearly 100 times the calculated ratio. This undoubtedly arises because of the simplifying assumptions used in ferrous reduction calculations.

On balance, it can be concluded that the modified SEPHIS program provided a reasonably good approximation of the performance obtained in the laboratory contactors. It still remains to be proved that it will simulate the performance of other contactors equally well. The program has been used to calculate the HAN reduction performance in two successful applications of HAN in Hanford pulse columns.^(1,8c) In both cases, the program predicted low losses; however, these applications employed low acid flowsheet conditions and high aqueous phase residence times which would favor calculation of low losses even if the computational model were incorrect.

Perhaps the biggest limitation to the use of SEPHIS in partitioning calculations is the lack of correlations to account for reoxidation of plutonium in the solvent and for the reactions of hydrazine with Pu(IV), Fe(III), and nitrous acid. Until such correlations are developed, it should be used cautiously in flowsheet development. Perhaps the best use of SEPHIS is to determine the general feasibility of a given flowsheet and to investigate the relative effects of various flowsheet parameters on product recovery, plutonium reflux, etc. The following examples illustrate this use of the SEPHIS program.

Parametric Studies of 1B Contactor Partitioning with HAN

Several parametric studies were made with the modified SEPHIS code to determine the effect of flowsheet and contactor variables on the predicted performance of the 12-stage contactor. The assumptions and flowsheet conditions used, except for the parameter under study, were similar to those used in the preceding discussion; the temperature was set at 50°C.

The results of varying the HAN concentration and the stage volumes are presented in Figure 13. The results show that plutonium losses are minimized at an input HAN/Pu mole ratio of 3, a confirmation of the experimental results of Patigny, et al.⁽¹⁰⁾ The stage volume (aqueous phase residence time) had a major effect on plutonium losses. The losses decreased about 4 to 9-fold with each doubling of the stage volume from 1.5 to 12 ml (aqueous phase contact times increasing from 0.26 to 2.1 minutes per stage in the partition section).

The results of two parametric studies showing the effects of relative 1BX and 1BS flows and of minor changes in 1BF composition are combined in Figure 14.

HEDL 7503-96.11

FIGURE 13. Effect of HAN Concentration and Stage Volume on SEPHIS-Calculated Uranium and Plutonium Losses.

FIGURE 14. Effect of Feed Composition and Flow Ratios on SEPHEX-Calculated Uranium and Plutonium Losses.

In these calculations, the 1BX contained 0.3M HNO_3 plus sufficient HAN and hydrazine to give input mole ratios of $\text{HAN}/\text{Pu} = 2$ and $\text{N}_2\text{H}_5^+/\text{Pu} = 0.5$. The 1BX and 1BS flows were varied independently while holding the 1BF flow at 4 ml/min and the stage volumes at 3 ml. The results were first plotted to show the effect of varying flows on uranium and plutonium losses. The data were then cross plotted, as shown, to indicate the threshold 1BS/1BF and 1BX/1BF flow ratios that would yield plutonium and uranium losses of less than 10^{-4} and $10^{-2}\%$, respectively. The shaded areas between the two sets of curves represent the operating range where the plutonium and uranium losses should not exceed those limits.

The limiting conditions for the two different feeds differ only slightly at high 1BS/1BF, 1BX/1BF flow ratios; but the more saturated feed would provide greater rangeability at low flow ratios. The operable range would be broadened by increasing the stage volume or decreasing the flow ratios, in effect increasing the aqueous phase residence time.

The flow ratios used in Runs 18 and 19 are superimposed on Figure 14. The graph predicts that losses for Run 19 would have met the arbitrary loss criteria for either feed composition. The predicted plutonium loss in Run 18 would have been acceptable with the high saturation feed but too high with the low saturation feed; the predicted uranium loss would have been borderline for either feed.

The effect on losses of changing the 1BF feed point in the 12-stage contactor is shown in Figure 15. The results of this example show a near balance of uranium and plutonium losses with 6 partition and 6 scrub stages. The plutonium losses decreased by a factor of 30 with each additional partition stage while the uranium losses decreased by a factor of 7.4 with each additional scrub stage. The flowsheet conditions used in this calculation were similar to those used in the preceding parametric study; the 1BX/1BF and 1BS/1BF flow ratios were 0.45 and 0.525, respectively.

FIGURE 15. Effect of IBF Feed Point on SEPHIS-Calculated Uranium and Plutonium Losses.

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APPENDIX

TABLE A-1:	DATA CARD FORMATS FOR SEPHIS PROGRAMMING	<u>PAGE</u> A-3
TABLE A-2:	REVISED SEPHIS COMPUTER CODE LISTING	A-6
TABLE A-3:	EXAMPLE OUTPUT FROM THE SEPHIS COMPUTER CODE (12-STAGE RUNS 3 AND 19)	A-23

A-2

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TABLE A-1

DATA CARD FORMATS FOR SEPHIS PROGRAMMINGPROBLEM CARD

Variable Name	Column Field	Description	Field Format
TITLE	1-36	Problem title	6A6
CTBP	37-40	Volume fraction TBP in dry solvent	F4.0
NTOST	41-42	Number of stages (25 maximum)	I2
IPRO	43-44	0 for a zero initial profile (25°C) 1 for a non-zero initial profile (profile cards must be provided for each stage)	I2
IRATIO	45-46	0 if phase ratio equals flow ratio 1 if phase ratio does not equal flow ratio (usually true; Phase Ratio cards required)	I2
ICALC	47-48	0 to calculate shut-down transient to zero uranium and plutonium concentrations 1 for start-up or interruptive transient calculation	I2
IOUT	49-50	0 for no outgoing streams other than end streams 1 if there are outgoing streams in addition to normal end streams	I2
IVOL	51-52	0 if all stage volumes are equal 1 if stage volumes are unequal but vary according to total flow 2 if stage volumes are unequal and not flow related (Stage Volume cards required) 3 if stage volumes are equal and specified (options 2 or 3 must be used with HAN reductant)	I2
IPR	53-54	0 to print transient results for every time interval 1 to print only last time interval -1 to print every 20th time interval	I2
IPNCH	55-56	0 if no punched card output is desired 1 to punch final profile concentrations and temperatures according to Profile Card format	I2
IRED	57-58	0 no reductant 1 $\text{Fe}(\text{NO}_3)_2$ reductant -1 HAN reductant	I2

FEED STREAM CARDS (One card required for each feed stream)

Variable Name	Column Field	Description	Field Format
I	1-4	Stage number that feed enters	I4
JHAS	5-8	0 (or -1) for an organic feed 1 for aqueous feed	I4
FDRT	9-16	Feed rate in relative volume units	F8.0
CON1	17-24	Uranium concentration, <u>M</u>	F8.0
CON2	25-32	Plutonium(IV) concentration, <u>M</u>	F8.0
CON3	33-40	Nitric acid concentration, <u>M</u>	F8.0
TEMP	41-48	Temperature, °C (not needed if temperature is 25°C)	F8.0
INDEX	49-52	0 for last card 1 if more cards of this type follow	I4
CON4	53-60	Plutonium(III) concentration, <u>M</u>	F8.0
CON5	61-68	Reductant concentration, <u>M</u>	F8.0
CON6	69-76	<u>M</u> nitrate from inextractable salts (does not include nitrate from reductant.)	F8.0

PROFILE CARDS (Used only for a non-zero initial profile. One card required
for each stage.)

X(1,J,1)	1-8	<u>M</u> U, aqueous	F8.0
X(2,J,1)	9-16	<u>M</u> Pu(IV), aqueous	F8.0
X(3,J,1)	17-24	<u>M</u> HNO ₃ , aqueous	F8.0
Y(1,J,1)	25-32	<u>M</u> U, organic	F8.0
Y(2,J,1)	33-40	<u>M</u> Pu(IV), organic	F8.0
Y(3,J,1)	41-48	<u>M</u> HNO ₃ , organic	F8.0
TPROF(J,1)	49-56	Temperature, °C (not needed for 25°C profile)	F8.0
X(4,J,1)	57-64	<u>M</u> Pu(III), aqueous	F8.0
X(5,J,1)	65-72	<u>M</u> reductant, aqueous	F8.0
X(6,J,1)	73-80	<u>M</u> NO ₃ ⁻ from inextractable salts, excluding reductants.	F8.0

OUT CARDS (Used only if there are outgoing streams in addition to the end streams. One card required for each extra out stream.)

Variable Name	Column Field	Description	Field Format
I	1-4	Stage number that stream leaves	I4
JHAS	5-8	0 if an organic stream 1 if an aqueous stream	I4
OTRT	9-16	Flow rate in solute-free volume units*	F8.0
INDEX	17-20	0 for last card 1 if more cards of this type follow	I4

PHASE RATIO CARDS (Used only if phase ratio and flow ratios are not equal. One card needed for each region of constant phase ratio starting with stage 1.)

I	1-8	Number of stages having ratio shown	I8
RATIO	9-16	Phase ratio, A/O	F8.0

STAGE VOLUME CARDS (Used only if IVOL options 2 or 3 are specified on the problem card. Only STVOL (1) is required for IVOL = 3; one value for each stage for IVOL = 2. Several cards may be required.)

STVOL (1)	1-8	Volume of Stage 1	F8.0
STVOL (2)	9-16	Volume of Stage 2.	F8.0
"	"	"	"
"	"	"	"
STVOL (10)	72-80	Volume of Stage 10	F8.0

CONTINUATION CARD

ICHNGE	1-2	0 if a complete set of cards for a new case follow 1 if a second case follows involving only a change in feed streams** 2 if no cases follow	I2
ICALC	3-4	0 for shut-down calculation 1 for continuation to a new steady-state profile	I2
IOUT	5-6	0 if no extra outgoing streams 1 for outgoing streams in addition to end streams	I2
IPNCH	7-8	0 for no punched card output 1 to punch final profile conditions	I2

* Aqueous flow out = (flow in) (1-0.0724 M Pu (IV)-0.0309M H⁺-0.1M Pu(III)-0.04M reductant-0.03M inextractable salt nitrate).

** For ICHNGE = 1, the CONTINUATION CARD must be followed, in order, by FEED STREAM and OUT CARDS, one card for each feed and extra outgoing stream used in the next case, and a second CONTINUATION CARD. The initial profile will be that calculated for the preceding case.

TABLE A-2

REVISED SEPHIS COMPUTER CODE LISTING

PROGRAM SEPHIS

01/21/75

PAGE 1

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PROGRAM SEPHIS(INPLT,OUTPLT,PUNCH)
CCC
C PROGRAM SEPHIS (HFOL VERSION BY G.L.RICHARDSON). REVISED 8-17-73 TO INCLUDE
C THE EFFECT OF HYDROXYLAMINE AND FERROUS NITRATE PL REDUCTION REACTIONS.
5 C REVISED 5/74 BY ARMC TO REDUCE CORE STORAGE.
C HYDROXYLAMINE CORRELATION REVISED 1/75.
C
C TRANSIENT STAGE CALCULATIONS FOR PUREX SOLVENT EXTRACTION PROCESS.
C CALCULATIONS VALID FOR 3 TRANSFERRING COMPONENTS. INCLUDES SALTING
10 C EFFECT FROM NON-TRANSFERRING NITRATE SALTS. PLUTONIUM PARTITION
C CALCULATIONS WITH FERROUS OR HYDROXYLAMINE NITRATE (HAN) REDUCTANTS
C CAN BE MADE WITH THE APPROPRIATE IRED OPTION
C COMPONENT 1 = URANIUM COMPONENT 4 = PLUTONIUM (III)
C COMPONENT 2 = PLUTONIUM (IV) COMPONENT 5 = REDUCTANT CLARITY
15 C COMPONENT 3 = NITRIC ACID COMPONENT 6 = INERT SALT NITRATE
C (INERT SALT NITRATE INCLUDES NITRATES FROM ALL NON-TRANSFERRING SALTS
C EXCEPT THOSE INTRODUCED WITH PLUTONIUM REDUCTANTS.)
C STAGE VOLUMES EQUAL UNLESS NOTED OTHERWISE.
CCC
20 DIMENSION TITLE(6),SOLIN(5),SOLOUT(5),ACUT(25),COUT(25),DF(3),
1ACOUT(25),CROUT(25)
COMMON/MPFS/NTOST,AFDRT(25),CFDRT(25)
COMMON/MPS/IFR0,X(6,25,2),Y(4,25,2),XFF(6,25),YFD(4,25),TPROF(25,2
1),AFDTEM(25),OFDTEM(25)
25 COMMON/MP/IRATIO,ICUT,ICHNGE,RCYC(25),ALVPT(25),OLVPT(25)
COMMON/MPF/2(25),O(25),RATIO(25),RCYCA(25),RCYCC(25),STVOL(25),IVOL
COMMON/MS/COLUM(25),AR(25),CF(25),AI(25),OT(25)
COMMON/MSU/ARY(6),UTRY(6),CTEM,TO,IRED
C
30 C READ 900, TITLE,CTEM,NTOST,IFR0,IRATIO,ICALC,ICUT,IVOL,IFA,IPNCH,
1IRED
C
C TITLE IS THE PROGRAM TITLE. 35 SPACES ARE ALLOWED.
C CTEM = VOLUME FRACTION OF DRY TSP
35 C NTOST = TOTAL NUMBER OF STAGES. MUST NOT EXCEED 24
C IFR0 = 0 FOR A ZERO INITIAL CONCENTRATION PROFILE
C 1 FOR A NON-ZERO INITIAL PROFILE
C IRATIO = 0 IF PHASE RATIO = FLOW RATIO
C 1 IF PHASE RATIO CARDS FOLLOW
40 C ICALC = 0 FOR SHUT-DOWN CALCULATIONS (NO L OR PU IN FEED STREAMS)
C 1 FOR START-UP OR INTERRUPTION
C ICUT = 0 IF THERE ARE NO EXTRA OUTGOING STREAMS
C 1 IF THERE ARE OUT GOING STREAMS IN ADDITION TO END STREAMS.
45 C IVOL = 0 IF STAGE VOLUMES ARE ALL EQUAL
C 1 IF STAGE VOLUMES ARE UNEQUAL BUT ACCORDING TO TOTAL FLOW
C 2 IF STAGE VOLUMES ARE INDEPENDENTLY UNEQUAL
C 3 IF STAGE VOLUMES ARE EQUAL AND SPECIFIED. (OPTIONS 2 OR 3
-- --
C SHOULD BE USED FOR HAN CALCULATIONS TO CORRECT FOR STAGE
C RESIDENCE TIME.)
50 C IFR = 0 TO PRINT OUT ALL TIME INTERVALS
C 1 TO PRINT ONLY LAST INTERVAL
C -1 TO PRINT EVERY 20TH TIME INTERVAL
C IPNCH = 0 IF NO PUNCHED CARD OUTPUT DESIRED
C 1 FOR FINAL PROFILE OUTPUT ON PUNCHED CARDS
55 C IRED = 0 FOR NO PL REDUCTANT
C 1 FOR FERROUS NITRATE REDUCTANT
C -1 FOR HYDROXYLAMINE NITRATE REDUCTANT

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```

C
60      DO 20 KO = 1,2
          DO 20 J=1,NTCST
            TPROF(J,KO) = 25.0
            STVOL(J) = 0.0
            DO 18 I=1,4
              Y(I,J,KO) = 0.0
65      18 CONTINUE
          DO 20 I=1,6
            X(I,J,KO) = 0.0
70      20 CONTINUE
          DO 23 I=1,3
            UF(I) = 0.0
75      23 CONTINUE
            ICHNGE = 0
          25 DO 30 J=1,NTCST
            CUJUM(J) = 0.0
            A(J) = 0.0
            O(J) = 0.0
            AFDRT(J) = 0.0
            OFDRT(J) = 0.0
            ALVHT(J) = 0.0
            ULVHT(J) = 0.0
            AFDTEM(J) = 25.0
            OFDTEM(J) = 25.0
80      30 CONTINUE
          DO 40 J=1,NTCST
            DO 35 I=1,4
              YFD(I,J) = 0.0
85      35 CONTINUE
          DO 40 I=1,6
            XFD(I,J) = 0.0
90      40 CONTINUE
            CALL PROFIL
C
C PROFIL SETS INITIAL CONCENTRATIONS FOR TIME ZERO, ALSO DEFINES FEED STREAMS
C
95      PRINT 910, TITLE
          PRINT 920
          DO 50 I=1,NTCST
            IF (AFDRT(I)) 50,50,45
100      45 PRINT 930,I,XFD(1,I),XFD(2,I),XFD(3,I),XFD(6,I),AFDRT(I),AFDTEM,I
            IF (XFD(5,I)) 452,452,449
            IF (IHEC) 450,452,451
            449 PRINT 931,XFL(5,I)
            450 PRINT 931,XFL(5,I)
            GO TO 452
            451 PRINT 932,XFD(5,I)
105      452 DENOMA = 1.0-0.0/24*AFD(1,I)-0.13*XFD(2,I)-0.0309*XFD(3,I)
            1=0.1*XFD(4,I)-0.040*XFD(5,I)-0.03*XFD(6,I)
            AFDRT(I) = AFDRT(I)*DENOMA
            DO 46 J=1,6
              XFD(J,I) = XFD(J,I)/DENOMA
110      46 CONTINUE
          50 CONTINUE
            TO = 3.65145 * CTBP
C
C TO IS MOLARITY OF DRY, SOLUTE-FREE TRP

```

```

115      US = 0.5*TC/(1.0+0.046*TC)
      PUS=0.5*TO/(1.0+0.07*TO)
      C
      C US,PUS,AND HS ARE MOLARITIES OF U,PU,AND HNO3 REQUIRED TO SATURATE THE TBP
      C WO*WC, AND WCM ARE CALCULATED WATER CONCENTRATIONS IN THE TBP PHASE
120      C
      DO 60 I=1,NTCST
      IF(IPRC.EQ.0.AND.1CHNGF.EQ.0)*X(3,I,1)=XFD(3,I)
      IF(OFDRT(I))60,60,55
125      55 PRINT 935,CTBP,I,YFD(1,I),YFD(2,I),YFD(3,I),OFDRT(I),OFDTEM(I)
      WO=(3.95-0.0144*OFDTEM(I))*CTBP**1.65
      HS= TC*(1.0-0.00609*WO)/(1.0+0.043*TC)
      WC = WC*(1.0-YFD(1,I)/US-YFD(2,I)/PUS-0.65*YFD(3,I)/HS)
      DENOMC=1.0-0.092*YFD(1,I)-0.14*YFD(2,I)-0.043*YFD(3,I)-0.0174*WC
      OFDRT(I) =CFLRT(I)*DENOMC
130      DO 56 J=1,3
      YFD(J,I) = YFD(J,I)/DENOMC
      56 CONTINUE
      60 CONTINUE
      C
135      C FEED CONCENTRATIONS AND VOLUMES ARE NOW ON A SOLUTE-FREE BASIS
      C
      CALL FLOWS
      C
      C FLOWS SETS ALL INTERSTAGE FLOW RATES, DEFINES OUTGOING STREAMS AND FLOW
140      C RATIOS, AND CALCULATES NECESSARY RECYCLE FLOWS
      C
      65 IF(IOUT) 800,800,70
      70 PRINT 930
      DO 75 I=1,NTCST
      IF(ALVRT(I))75,75,72
145      72 PRINT 960,I,ALVRT(I)
      75 CONTINUE
      DO 80 I=1,NTCST
      IF(OLVRT(I))80,80,77
150      77 PRINT 940,I,OLVRT(I)
      80 CONTINUE
      800 IF(1CHNGE)81,81,86
      81 IF(IPRC)91,91,82
      82 PRINT 970
155      DO 90 J=1,NTOST
      PRINT 980,J,X(1,J,1),X(2,J,1),X(3,J,1),Y(1,J,1),Y(2,J,1),Y(3,J,1)
      1,TPROF(J,1)
      DENOMA=1.0-0.0724*X(1,J,1)-0.13*X(2,J,1)-0.0309*X(3,J,1)
      1=0.10*X(4,J,1)-0.040*X(5,J,1)-0.030*X(6,J,1)
160      WO = (3.95 - 0.0144*TPROF(J,1))*CTBP**1.65
      HS= TO*(1.0-0.00609*WO)/(1.0+0.043*TO)
      WC=WO*(1.0-Y(1,J,1)/US-Y(2,J,1)/PUS-0.65*Y(3,J,1)/HS)
      DENOMC=1.0-0.092*Y(1,J,1)-0.14*Y(2,J,1)-0.043*Y(3,J,1)-0.0174*WC
      DO 85 I = 1,4
165      Y(I,J,1)=Y(I,J,1)/DENOMC
      85 CONTINUE
      DO 90 I=1,6
      X(I,J,1)=X(I,J,1)/DENOMA
      90 CONTINUE
170      86 CONTINUE
      IF(1CHNGE.EQ.1)PRINT 985

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```

C
C PROFILE CONCENTRATIONS ARE NOW ON SOLUTE-FREE BASIS
C
175 91 IF (RATIO) 100,100,92
    92 PRINT 995
    93 DO 99 I=1,NTOST
        IF (I-1) 94,94,95
    94 RATIO = RAJO(I)
    180 NST = I
        IF (I-NTOST) 95,98,98
    95 IF (RATIO-RAIC(I)) 96,97,96
    96 IK = I-1
        PRINT 996,NST,IK,RATIO
    185 GO TO 94
    97 IF (I-NTOST) 99,98,98
    98 PRINT 996,NST,I,RATIO
    99 CONTINUE
        GO TO 101
    190 100 PRINT 997
        GO TO 93
    101 PRINT 998
C
C A AND O ARE AQUEOUS AND ORGANIC INTERSTAGE FLOWS
195 C AA AND OC ARE TOTAL AQUEOUS AND ORGANIC FLOWS LEAVING A STAGE
    C AR AND OR ARE AQUEOUS AND ORGANIC RECYCLE FLOWS TO FILL A STAGE
    C RCYCA AND RCYCO ARE AQUEOUS AND ORGANIC RECYCLE TO SATISFY PHASE RATIO
    C AT AND OT ARE TOTAL AQUEOUS AND ORGANIC FLOWS WITHIN A STAGE
    C TT IS TOTAL FLOW WITHIN A STAGE
200 C
    DO 105 I=1,NTOST
        AA = ALVRT(I) + A(I)
        OO = OLVRT(I) + O(I)
        RATIO = AA/OC
    205 AR(I) = RCY(I)*RATIO/(1.0+RATIO)
        OR(I) = RCY(I)/(1.0+RAIC(I))
        AT(I) = AA + AR(I) + RCYCA(I)
        OT(I) = OO + OR(I) + RCYCO(I)
        TT = AT(I) + OT(I)
    210 PRINT 999,I,RATIO,AA,AR(I),RCYCA(I),AT(I),OO,OR(I),
        RCYCO(I),OT(I),TT,STVOL(I)
    105 CONTINUE
    110 PRINT 1000
        N = 100
    215 ICEN = 0
        BUF = 0.
        CDF = 0.
        UDF = 0.10
    220 DO 1101 I = 1,5
        SOLIN(I) = 0.0
        SOLOUT(I) = 0.
    1101 CONTINUE
        DO 1102 I=1,4
    225 DO 1102 J=1,NTOST
        SOLIN(I)=SCLIN(I)+AFDWT(J)*XFD(I,J)+CFDRT(J)*YFC(I,J)
    1102 CONTINUE
        DO 1103 J = 1,NTOST
        SOLIN(5) = SCLIN(5) + AFDWT(J)*XFD(5,J)

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230      1103 CONTINUE
          SOLIN(2) = SCLIN(2) + SOLIN(4)
          SPH = 0.399*CTBP + 0.375*(1.0 - CTBP)

          111 K=1
          112 CALL STAGES(SPH)
235      C
          C STAGES PERFORMS STAGE CALCULATIONS FOR EACH TIME INTERVAL
          C
          DO 115 J = 1,NTOST
            TPROF(J,1) = TPROF(J,2)
240          DO 113 I = 1,6
            113 X(I,J,1) = X(I,J,2)
            DO 114 I = 1,4
            114 Y(I,J,1) = Y(I,J,2)
            115 CONTINUE
245          IF (ICEN) 120,120,125
            120 IF (K-NTOST) 500,125,125
            125 IF (ICALC) 130,130,150
          C
          C FOR SHUTDOWN, IALC=0, TEST FOR COMPONENTS 1 AND 2 = 0, NOT COMPONENT 3
250      C
          DO 140 J=1,NTOST
            IF (X(1,J,1)-0.000001) 135,135,500
            135 IF (Y(1,J,1)-0.000001) 136,136,500
            136 IF (X(2,J,1)-0.000001) 137,137,500
255          137 IF (Y(2,J,1)-0.000001) 140,140,500
            140 CONTINUE
            GO TO 700
            DO 165 I=1,4
              SOLOUT(I) = A(NTOST)*X(I,NTOST,1) + O(I)*Y(I,1,1)
260              DO 165 J=1,NTOST
                SOLOUT(I) = SOLOUT(I) + ALVRT(J)*X(I,J,1) + CLVRT(J)*Y(I,J,1)
              165 CONTINUE
              IF (TREC) 166,169,168
              166 SOLOUT(5) = A(NTOST)*X(5,NTOST,1)
265              DO 167 J = 1,NTOST
                SOLOUT(5) = SOLOUT(5) + ALVRT(J)*X(5,J,1)
              167 CONTINUE
              DHAN = SOLIN(5) - SOLOUT(5)
              SOLOUT(3) = SOLOUT(3) - 2.*DHAN
270              168 SOLOUT(2) = SOLOUT(2) + SOLOUT(4)
              169 DO 170 I=1,3
                IF (SOLIN(I)) 1691,1691,1692
              1691 DF(I) = 0.
              GO TO 170
275              1692 CONTINUE
              DF(I) = ABS((SOLIN(I)-SOLOUT(I))/SOLIN(I))
              170 CONTINUE
              ADF = AMAX1(DF(1),DF(2),DF(3))
              DADF = ABS(ADF-BDF)
280              IF (DABCF-1.0E-10) 171,171,175
              171 CDF = ADF
              GO TO 700
              175 BDF = ADF
              IF (ICEN.GE.4.AND.DCF.LT.0.005) DCF=0.01
285              IF (ADF.GT.CDF) GO TO 500

```

```

      IF (DDF = 0.10) 190,180,180
180  JK=K+100*ICEN
      PDF = 100. * (1.0-DDF)
      DDF = 0.05
290  GO TO 500
      IF (DDF=0.05) 210,200,200
200  JJK=K+100*ICEN
      PPDF = 100. * (1.0-DDF)
      DDF = 0.010
295  GO TO 500
      IF (ICFN) 220,220,700
220  IF (DDF = 0.010) 240,230,230
230  JJJK=K+100*ICEN
      PPPDF = 100.*(1.0 - DDF)
300  DDF = 0.005
      GO TO 500
      IF (ICEN) 250,250,700
250  IF (DDF = 0.005) 260,260,260
260  JJJJK=K+100*ICEN
      PPPPDF = 100.*(1.0-DDF)
305  DDF = 0.001
      GO TO 500
500  CONTINUE
      IF (IPK) 531,502,530
502  DO 505 J=1,N10ST
310  DENA=1.0+0.0724*X(1,J,2)+0.13*X(2,J,2)+0.0309*X(3,J,2)+0.10*X(4,J,
      12)+0.040*X(5,J,2)+0.030*X(6,J,2)
      X(2,J,2) = X(2,J,2) + X(4,J,2)
      Y(2,J,2) = Y(2,J,2) + Y(4,J,2)
      WUM=(4.2-0.015*TPROF(J,2))*(1.-2.*(Y(1,J,2)+Y(2,J,2)))/
315  170-0.6*Y(3,J,2)/T0)*CTRP**1.69
      DENO=1.0+0.092*Y(1,J,2)+0.14*Y(2,J,2)+0.043*Y(3,J,2)+0.0174*WOM
      AQOUT(J)=(A(J)+ALVRT(J))*DENA
      OOUT(J)=(O(J)+OLVRT(J))*DENO
      IF (IOUT) 504,504,503
320  503 AQOUT(J)=-ALVRT(J)*DENA
      ORGOUT(J)=-OLVRT(J)*DENO
      DO 505 I=1,5
      X(I,J,2) = X(I,J,2)/DENA
      Y(I,J,2) = Y(I,J,2)/DENO
325  505 CONTINUE
      IF (K.EG.1.OR.K.FG.M) PRINT 1050
      DO 525 J=1,N10ST
      IF (J-1) 506,506,520
330  506 L=K+100*ICEN
      PRINT 1100,L,J,(X(I,J,2),I=1,3),(Y(I,J,2),I=1,3),CCDUM(J),AQOUT(J),
      10OUT(J),TPROF(J,2)
      GO TO 524
      IF (OLVRT(J).GT.0) PRINT 1610,ORGOUT(J)
      PRINT 1150 , J,(X(I,J,2),I=1,3),(Y(I,J,2),I=1,3),CCDUM(J),AQOUT(J),
335  10OUT(J),TPROF(J,2)
      524 IF (ALVRT(J).GT.0) PRINT 1600,AQOUT(J)
      525 CONTINUE
      GO TO 536
340  530 IF (K-M) 536,502,502
      531 IF (K-M) 532,502,502
      532 IF (K-20) 536,502,533
      533 IF (K-40) 536,502,534

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534 IF (K-60) 536,502,535
535 IF (K-80) 536,502,536
345 536 K=K+1
      IF (K.LE.M) GO TO 112
      IF (ICALC.FQ.0) GO TO 541
      APDF = 100.*(1.) - ALF)
      PRINT 1300, APDF
350      IF (DDF.LT.0.1) PRINT 1400,PLF,JK
      IF (DDF.LT.0.05) PRINT 1400,PPDF,JJK
      IF (DDF.LT.0.01) PRINT 1400,PPPDF,JJJK
      IF (DDF.LT.0.005) PRINT 1400,PPPPDF,JJJJK
      IF (ICLT.GT.0) PRINT 1650
355      IF (ADF-CDF) 541,540,541
      540 PRINT 1666
      541 IF (M-100) 542,560,560
      542 PRINT 1670,SCLIN(1),SOLOUT(1)
      PRINT 1680,SCLIN(2),SOLOUT(2)
360      IF (IRED.NE.0) PRINT 1685,SOLIN(4),SOLOUT(4)
      IF (IRED.LT.0) SOL(UT(3) = SCLOUT(3) + 2.*DHAN
      PRINT 1690,SCLIN(3),SOLOUT(3)
      IF (IRED.LT.0) PRINT 1693,SCLIN(5),SOLOUT(5)
      TIMINT = STVCL(1)/(AT(1) + OT(1))
365      IF (IVCI.GE.2) PRINT 1695,TIMINT

      IF (IPACH) 551,551,543
543 DO 550 J = 1,NTOST
      X(2,J,2) = Y(2,J,2) - X(4,J,2)
      PUNCH 1450,(X(I,J,2),I=1,3),(Y(I,J,2),I=1,3),TPROF(J,2),(X(I,J,2),
      I=4,6)
550 CONTINUE
551 READ 1500,ICHNGE,ICALC,ICUT,IPNCH
C
375 C ICHNGE = 0 IF NEXT CASE IS NEW
C      1 IF NEXT CASE INVOLVES ONLY A CHANGE IN FEED FLOWS, COMP. AND TEMP
C      2 STOP
C IF ICHNGE = 1, NEW FEED STREAM AND OUT CARDS ARE REQUIRED FOR EACH
C FEED AND EXIT STREAM, EVEN IF NO CHANGE IS MADE. NO PROFILE CARDS
380 C ARE REQUIRED.
C
      IF (ICHNGE-1) 600,602,601
560 CONTINUE
      ICEN = ICEN + 1
385      IF (ICEN.EQ.15) GO TO 542
      GO TO 111
600 GO TO 2
601 STOP
602 IPRO = 0
390 C
C INITIAL PROFILE IS SET AS THAT AT END OF LAST CALCULATION.
C
      GO TO 25
700 M = K
      GO TO 500
- 395 - - -
900 FORMAT(6A6,F4.0,5I2)
910 FORMAT(75H1CALCULATIONS FOR A SOLVENT EXTRACTION PROCESS HAVING 3
      1 INTERACTING SOLUTES,16X,6A6)
920 FORMAT(27H0FEED STREAM DATA:      ,6X,5HSTAGE,3X,7HURANIUM,5X,

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400      19HPLUTONIUM,6X,4HNO3,6X,10H SALT NO3 ,3X,9HFLOW RATE,6X,4HTEMP/34
      2X,3HNO3,5X,5H (M) ,8X,5H (M) ,9X,3H(M),9X,3H(M),6X,11H(VOL.UNIT),
      35X,5HDEG C/)
      930 FORMAT(24X,6HAGUEOUS ,14,4(3X,1PF10.3),3X,1PE9.3,3X,0PF7.1)
      931 FORMAT(39X,1H(,1PE9.3, 35H M HYDROXYLAMINE NITRATE ADDED TO EFFC))
405      932 FORMAT(39X,1H(,1PE9.3, 33H M FERROUS NITRATE ADDED TO EFFC))
      935 FORMAT(19X,2PF6.1,7H % TRP ,14,3(3X,1PF10.3),16X,1PF9.3,3X,0PF7.1)
      940 FORMAT(37H ORGANIC STREAM REMOVED AT STAGE,13,9H. FLOW =,1PE9.3,
      128H (SOLUTE-FREE VOLUME UNITS).)
      950 FORMAT(1H0)
410      960 FORMAT(37H AGUEOUS STREAM REMOVED AT STAGE,13,9H. FLOW =,1PE9.3,
      128H (SOLUTE-FREE VOLUME UNITS).)
      970 FORMAT(25H0LON-ZERO INITIAL PROFILE,8X,5HSTAGE,13X,13HAQUEOUS PHA
      15E,26X,13HORGANIC PHASE ,14X,3HNO3,6X,7HURANIUM,4X,9HPLU
      2TONIUM,6X,4HNO3,8X,7HURANIUM,5X,9HPLUTONIUM,6X,4HNO3,7X,4HTEMP/
415      031X,9H(OUTFLOW),3X,3H(M),10X,3H(M),10X,3H(M),10X,3H(M),10X,3H(M),1
      40X,3H(M),7X,5HDEG C/)
      980 FORMAT(32X,14,6(3X,1PF10.4),3X,0PF6.1)
      985 FORMAT(53H0INITIAL PROFILE SAME AS THAT AT END OF PRECEDING RUN)
      995 FORMAT(40H0PHASE RATIOS DO NOT EQUAL FLOW RATIOS: ,
420      13X,9HSTAGE NO.,2X,15H0/0 PHASE RATIO/)
      996 FORMAT(40X,14,3H -,14,4X,1PE10.3)
      997 FORMAT(32H0PHASE RATIOS EQUAL FLOW RATIOS: ,11X,9HSTAGE NO.,2X
      1,15H0/0 PHASE RATIO/)
      998 FORMAT(75H0STAGE FLOWS (SOLUTE-FREE VOLUMES):/34X,13HAQUEOUS PHA
425      15E,32X,13HORGANIC PHASE,18X,7H0VFRALL/22X,4HFLOW,4X,20HRECYCLE 2
      2HRECYCLE 1,4X,5HTOTAL,8X,4HFLOW,4X,20HRECYCLE 2 HRECYCLE 1,4X,5HTOT
      3AL,7X,5HTOTAL/13H STAGE FLOW,8X,6HOUT OF,4X,7H10 FILL,3X,9HFOR P
      4HASE,3X,7HAQUEOUS,6X,6HOUT OF,4X,7HTO FILL,3X,9HFOR PHASE,3X,7HCRG
430      5ANIC,6X,5HSTAGE/3X,3HNO3,3X,5HURATIO,7X,5HSTAGE,6X,5HSTAGE,6X,5HURAT
      610,6X,4HFLOW,8X,5HSTAGE,6X,5HSTAGE,6X,5HURATIO,6X,4HFLOW,8X,4HFLOW,
      75X,9HSTAGE VOL/)
      999 FORMAT(15,2X,1PE9.3,1X,4(2X,1PE9.3),1X,4(2X,1PE9.3),3X,1PE9.3,2X,
      11PF9.3)
      1000 FORMAT(27H1TRANSIENT BEHAVIOR RESULTS,10X,49HSOLUTE CONCENTRATION
435      15 IN EFFLUENT FROM EACH STAGE)
      1050 FORMAT(1H0,24X,20HAQUEOUS PHASE VALUES,14X,21H ORGANIC PHASE VALU
      1ES/7H TIME,13X,30HURANIUM PLUTONIUM HNO3,6X,30HURANIUM
      2 PLUTONIUM HNO3,3X,6HITERA-,5X,8HFLOW OUT,10X,4HTEMP/9H INTE
      3RVAL,2X,5HSTAGE,6X,3H(M),9X,3H(M),4X,3H(M),9X,3H(M),9X,3H(M),9X,3H
440      4(M),4X,5HTIONS,3X,7HAQUEOUS,3X,7HORGANIC,4X,5HDEG C)
      1100 FORMAT(1H0,2X,14,4X,14,1X,6(3X,1PE9.3),2X,0PF4.0, 2(2X,1PE9.3),
      12X,0PF5.1)
      1150 FORMAT(11X,14,1X,6(3X,1PE9.3),2X,0PF4.0, 2(2X,1PE9.3),
      12X,0PF6.1)
445      1250 FORMAT(10FF,6)
      1300 FORMAT(1H0,F7.2,52H PERCENT OF STEADY STATE BY OVERALL MATERIAL BA
      1LANCE)
      1400 FORMAT(1H ,F6.1,2X,43HPERCENT OF STEADY STATE AFTER TIME INTERVAL
      1,I6)
450      1500 FORMAT(4I2)
      1600 FORMAT(14X,34H* * * * *,47X,1PE10.3)
      1610 FORMAT(14X,1H*,44X,25H* * * * *,22X,1PE10.3)
      1650 FORMAT(1H0," * SIDE STREAM REMOVED FROM INTERSTAGE FLOW BETWEEN
      1THE INDICATED STAGES.")
455      1666 FORMAT(1H0,"CALCULATION TERMINATED BY CONVERGENCE AT INDICATED * S
      1STEADY STATE.")

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1670 FORMAT(1H0,25HTOTAL MOLES URANIUM IN: ,1PE11.4,6H, OUT:,E11.4)
1680 FORMAT(1H ,25HTOTAL MOLES PLUTONIUM IN:,1PE11.4,6H, OUT:,E11.4)
1685 FORMAT(1H ,25HTOTAL MOLES PU(III) IN: ,1PE11.4,6H, OUT:,E11.4)
460 1690 FORMAT(1H ,25HTOTAL MOLES HNO3 IN: ,1PE11.4,6H, OUT:,E11.4)
1693 FORMAT(1H ,25HTOTAL MOLES HAN IN: ,1PE11.4,6H, OUT:,E11.4)
1695 FORMAT(1H0,22HMINUTES/TIME INTERVAL:,F7.3)
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END

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SUBROUTINE PROFIL
COMMON/MPS/NTOST,AFDRT(25),CFDRT(25)
COMMON/MPS/IFRO,X(6,25,2),Y(4,25,2),XFR(6,25),YFD(4,25),TPROF(25,2
1),AFDTEM(25),CFDTEM(25)

5      C
C      C
C      C      DEFINE FEED STREAMS
C      I = STAGE NUMBER THAT FEED ENTERS      JHAS = 1 FOR AQUEOUS FEED
C      FDRT = FEED FLOW RATE (VOLUME UNITS)      0 FOR ORGANIC FEED
C      CON1 = URANIUM CONTENT IN MOLARITY      INDEX = 1 IF MORE FEED CARDS FOLLOW
10     C      CON2 = PLUTONIUM CONTENT IN MOLARITY      0 FOR LAST CARD
C      CON3 = ACID MOLARITY      TEMP = TEMPERATURE IN DEGREES C
C      CON4 = PLUTONIUM(III) MOLARITY
C      CON5 = REDUCTANT MOLARITY
C      CON6 = NITRATE MOLARITY FROM ALL NON-EXTRACTABLE SALTS EXCEPT ACTIVE
15     C      REDUCTANTS.
C
C      10 READ 800,I,JHAS,FDRT,CON1,CON2,CON3,TEMP,INDEX,CON4,CON5,CON6
C      IF (CON1.EQ.0) CON1 = 0.
C      IF (CON2.EQ.0) CON2 = 0.
20     C      IF (CON3.EQ.0) CON3 = 0.
C      IF (JHAS) 20,20,30
C      OFDRT(I) = FDRT
C      IF (TEMP.EQ.0.) GO TO 21
C      OFDTEM(I) = TEMP
25     C      21 YFD(1,I) = CON1
C      YFD(2,I) = CON2
C      YFD(3,I) = CON3
C      IF (CON4.NE.0.) YFD(4,I) = CON4
C      GO TO 40
30     C      30 AFDRT(I) = FDRT
C      IF (TEMP.EQ.0.) GO TO 31
C      AFDTEM(I) = TEMP
C      31 XFD(1,I) = CON1
C      XFD(2,I) = CON2
35     C      XFD(3,I) = CON3
C      IF (CON4.NE.0.) XFD(4,I) = CON4
C      IF (CON5.NE.0.) XFD(5,I) = CON5
C      IF (CON6.NE.0.) XFD(6,I) = CON6
40     C      IF (INDEX)50,50,10
C      50 IF (IFRO)55,55,70
C      55 DO 57 J = 1,NTOST
C      TPROF(J,1) = AFDTEM(I)
C      57 CONTINUE
C      60 RETURN
45     C      70 DO 100 J=1,NTOST
C
C      C      FOR IFRO = 0, THE ZERO PROFILE IS ALREADY IN X AND Y ARRAYS
C      C      FOR A NON-ZERO INITIAL PROFILE, VALUES ARE NOW READ
C
50     C      READ 810,(X(I,J,1),I=1,3),(Y(I,J,1),I=1,3),TPROF(J,1),(X(I,J,1),I=
C      14,6)
C      IF (TPROF(J,1).EQ.0.) TPROF(J,1)=25.0
C      100 CONTINUE
C      GO TO 60
55     C      800 FORMAT (2I4,5F8.0,I4,3F8.0)
C      810 FORMAT(10F8.0)
C      END

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SUBROUTINE FLOWS
COMMON/MPFC/NTOST,AFDRT(25),CFDRT(25)
COMMON/MF/IRATIO,IOUT,ICHAGE,RCYC(25),ALVRT(25),CLVRT(25)
COMMON/MFS/A(25),O(25),RATIO(25),RCYCA(25),RCYCO(25),STVOL(25),TVOL

5      C
C      DEFINE OUTGOING STREAMS OTHER THAN AQUEOUS WAFERATE AND ORGANIC PRODUCT
C      I = STAGE NUMBER THAT STREAM LEAVES JFAS = 1 FOR AQUEOUS STREAM
C      INDEX = 1 IF MORE CARDS FOLLOW          U FOR ORGANIC STREAM
C      0 FOR LAST CARD          OTAT = EXIT FLOW RATE (VOLUME UNITS)
10     C (FLOWS GIVEN IN SOLUTE-FREE VOLUME UNITS)
C
      IF(IOUT)50,50,10
      10 HEAD 700,T,JFAS,OTAT,INDEX
      IF(JFAS)20,20,30
15     20 OLVRT(I) = OTAT
      GO TO 40
      30 ALVRT(I) = OTAT
      40 IF(INDEX)50,50,10
      50 DO 100 I=1,NTOST
      IF(I-1)60,60,70
20     60 A(I) = AFDRT(I)-ALVRT(I)
      65 O(NTOST) = OFDRT(NTOST)-CLVRT(NTOST)
      GO TO 100
      70 A(I) = A(I-1)+AFDRT(I)-ALVRT(I)
      NST = NTOST+1-I
      O(NST) = O(NST+1)+OFDRT(NST)-OLVRT(NST)
25     100 CONTINUE
C
C      THE INTERSTAGE FLOWS ARE NOW SET
30     C
C      DEFINE PHASE RATIOS
C
      DO 150 I=1,NTOST
      RCYCA(I) = 0.0
      RCYCO(I) = 0.0
35     150 CONTINUE
      FLOMAX = 0.0
      K = 1
      IF(IRATIO)200,200,300
40     200 DO 250 I=1,NTOST
      RATIO(I) = (ALVRT(I)+A(I))/(OLVRT(I)+O(I))
      250 CONTINUE
      GO TO 310
      300 IF(ICHAGE) 301,301,320
45     301 HEAD 710,I,RATIO
C
C      I = NUMBER OF STAGES HAVING THE PHASE RATIO SHOWN
C
      I = K + I - 1
50     C
C      CALCULATE NECESSARY RECYCLE FLOWS
C      TYPE 1 IS RECYCLE OF ONE PHASE ONLY, TO SATISFY PHASE RATIO
C      USED WHEN IRATIO = 1
C      TYPE 2 IS RECYCLE OF BOTH PHASES WITH PHASE RATIO RATIO(I)
55     C      TO ALLOW TOTAL STAGE FLOW TO EQUAL FLOMAX
C      USED WHEN IVCI = 0.2
C      RECYCLE VOLUMES AND RATIOS ARE SOLUTE-FREE VALUES

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C
60      DO 305 J=K,1
          RAIO(J) = RATIO
          305 CONTINUE
          IF (I-NTOST) 306,320,320
          306 K = I + 1
          GO TO 300
65      310 IF (IVOL-1) 315,340,315
          315 DO 317 I=1,NTOST
              FLOTOT = ALVRT(I) + A(I) + CLVRT(I) + C(I)
              RECY(I) = FLOTOT
              FLOMAX = AMAX1(FLOTOT,FLCMAX)
70      317 CONTINUE
          IF (IVOL-1) 340,360,400
          320 DO 330 I=1,NTOST
              AFL = ALVRT(I) + A(I)
              OFL = CLVRT(I) + C(I)
              FLOTOT = AFL + OFL
              RFL = AFL/OFL
              IF (RFL-RAIC(I)) 322,325,323
          322 FLOTOT = FLOTOT*(RAIO(I)+1.0)/(RFL+1.0)
              RECYCA(I) = FLOTOT - AFL - OFL
              GO TO 325
          323 FLOTOT = FLOTOT*RFL*(RAIC(I)+1.0)/(RAIC(I)*(RFL+1.0))
              RECYCO(I) = FLOTOT - AFL - OFL
          325 RECY(I) = FLOTOT
              FLOMAX = AMAX1(FLOTOT,FLCMAX)
          330 CONTINUE
35      C
          C FLOMAX CONTAINS THE LARGEST TOTAL FLOW FROM A STAGE - STAGES HAVING A
          C TOTAL FLOW LESS THAN FLOMAX MUST EXHIBIT RECYCLE
          C OF TYPE ?
90      C
          IF (IVOL-1) 340,360,400
          340 DO 350 I=1,NTOST
              RECY(I) = FLCMAX - RECY(I)
          350 CONTINUE
          RETURN
95      360 DO 370 I=1,NTOST
              RECY(I) = 0.0
          370 CONTINUE
          RETURN
100     400 IF (ICHNGE) 410,410,415
          410 IF (IVOL-2) 413,413,411
          411 HEAD 715,VCL
              DO 412 I = 1,NTOST
                  STVOL(I) = VCL
105     412 CONTINUE
              GO TO 415
          413 HEAD 720,(STVOL(I),I=1,NTOST)
C
C STAGE VOLUMES ARE SOLUTE-FREE VOLUMES
C
110     415 TIMIN = 0.0
          DO 420 I=1,NTOST
              RECY(I) = RECY(I)/STVOL(I)
              TIMIN = AMAX1(RECY(I),TIMIN)

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SUBROUTINE FLOWS

01/21/75

PAGE 3

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115      420 CONTINUE
          FLOMAX = TIMIN
          DO 430 I = 1,NTOST
            RECY(I) = (FLOMAX - RECY(I))*STVOL(I)
          430 CONTINUE
120      RETURN
          700 FORMAT (2I4,F8.0,I4)
          710 FORMAT (I8,F8.0)
          715 FORMAT (F8.0)
          720 FORMAT (10F8.0)
125      END
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SUBROUTINE STAGES(SPH)
  DIMENSION AIN(6),OIN(6),TSIN(6)
  COMMON/MPFS/NTOST,AFDRT(25),CFDRT(25)
  COMMON/MPF/IFRO,X(6,25,2),Y(4,25,2),XFR(6,25),YFD(4,25),TPHOF(25,2
5  1),AFDTEM(25),CFDTEM(25)
  COMMON/MFS/A(25),O(25),RAIO(25),PCYCA(25),RCYCO(25),STVOL(25),TVOL
  COMMON/MS/COGUP(25),AR(25),CR(25),AT(25),OT(25)
  COMMON/MSU/ARY(6),DTRY(6),CTEP,T0,JREC
10  C PERFORM STAGE CALCULATIONS FOR CURRENT TIME INTERVAL - CONSIDER
  C INPUTS FROM ADJACENT STAGES, FEED STREAMS, AND MOST IMPORTANTLY
  C RECYCLE WITHIN THE STAGE - RECYCLE A RESULT OF STAGE FLOW BEING
  C LESS THAN FLOMAX (TYPE 2) AND PHASE RATIO NOT EQUAL TO FLOW
  C RATIO (TYPE 1)
15  C
      K = 2
      KK = 1
      DO 130 J=1,NTOST
      JJ = J-1
      JJJ = J+1
20  5 DO 20 I = 1,4
      IF (J=NTOST) 10,15,15
      OIN(I) = (OFDRT(J)*YFD(I,J) + (OR(J)+RCYCO(J))*Y(I,J,KK) + O(JJJ)*Y(I,
10  JJJ,KK))/OT(J)
      GO TO 20
25  15 OIN(I) = (OFDRT(J) * YFD(I,J) + (OR(J)+RCYCO(J))*Y(I,J,KK))/OT(J)
      20 CONTINUE
      OIN(5) = 0.
      OIN(6) = 0.
30  DO 40 I=1,6
      IF (JJ) 25,25,30
      AIN(I) = (AFDRT(J)*XFD(I,J) + (AR(J)+RCYCA(J))*X(I,J,KK))/AT(J)
      GO TO 35
35  30 AIN(I) = (AFDRT(J)*XFD(I,J) + (AR(J)+RCYCA(J))*X(I,J,KK) + A(JJ)*X(I,JJ,
      KK))/AT(J)
      35 TSIN(I) = AIN(I)*RAIO(J)+OIN(I)
      ARY(I) = X(I,J,KK)
      DTRY(I) = 0.
      40 CONTINUE
      ARY(5) = AIN(5)
      ARY(6) = AIN(6)
      IF (JREC) 405,405,400
40  400 TPU4=TSIN(2)-TSIN(5)
      IF (TPU4.LT.0.) TPU4 = 0.
45  DPU3 = TSIN(2) - TPU4
      TSIN(2) = TPU4
      TSIN(4) = TSIN(4) + DPU3
      TSIN(5) = TSIN(5) - DPU3
      TSIN(6) = TSIN(6) + 3.*DPU3
50  405 CONTINUE
      IF (J-1) 410,410,415
      410 AHTIN=AFDRT(J)*AFDTEM(J) + (AR(J)+RCYCA(J))*TPHOF(J,KK)
      GO TO 420
415 415 AHTIN=AFDRT(J)*AFDTEM(J) + (AR(J)+RCYCA(J))*TPHOF(J,KK) + A(JJ)*TPHOF
55  1(JJ,KK)
      420 IF (J=NTOST) 425,430,430
      425 OHTIN=SPH*(OFDRT(J)*OFDTEM(J) + (OR(J)+RCYCO(J))*TPHOF(J,KK) + O(JJJ)

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      1*TPPOF(JJJ,KK))
      GO TO 435
60      430 OHTIN=SPH*(OFDRT(J)*OFDTEM(J)+(OR(J)+R(YCO(J))*TPHCF(J,KK))
      435 TPROF(J,K)=(AHTIN+OHTIN)/(AT(J)+SPH*CT(J))
      TEMPC=TPROF(J,K)
      TEMPRK = 1000./(TEMPC + 273.16)
      DRT = TEMPRK - 3.3539
65      IF(IRED)440,445,445
      440 HKA = 40000.*EXP(-2.7*TEMPRK)
      HKB = 6.0E42*EXP(-28.5*TEMPRK)
      TPU4 = TSIN(2)
      TH = TSIN(3)
70      TPU3 = TSIN(4)
      THAN = TSIN(5)
      445 CONTINUE
      XPU3 = 0.
      XPU4 = 0.
75      HANK = 0.
      DPU3 = 0.
      CCD = 0.001
      41 MCK = 0
      42 MDEX = 0
80      C
      C MCK IS THE ITERATION COUNTER
      C MDEX IS THE FIT COUNTER
      C
      CALL UCOR(DRT,TEMPC)
85      C
      C UCOR CALCULATES DISTRIBUTION RATIOS (DTRY) FOR EACH TRIAL AQUEOUS PHASE
      C COMPOSITION (ARY) AT THE STAGE EQUILIBRIUM TEMPERATURE (TEMPC)
      C
      DO 43 I=1,6
90      X(I,J,K) = TSIN(I)/(HAIO(J) + DTRY(I))
      IF(X(I,J,2).LT.1.0E-40) X(I,J,2) = 0.0
      43 CONTINUE
      IF(THAN-1.0E-20)60,60,45
      45 IF(IRED)50,60,60
95      50 XPU4=X(2,J,K)
      IF(XPL4.LT.1.0E-50) GO TO 60
      DO 501 I = 2,5
      IF(MCK.EQ.0) X(I,J,K) = ARY(I)
      501 CONTINUE
100      N = 0
      5002 TNV=2.*X(1,J,K)+4.*X(2,J,K)+X(3,J,K)+3.*X(4,J,K)+X(5,J,K)+X(6,J,K)
      HANK = HKB*X(5,J,2)**2/(X(3,J,2)**4*(1. + HKA*TNV)**2)
      IF(IVOL.GE.2)HANK=HANK*STVOL(J)/(AT(J)+CT(J))
      51 XPU3=(TPU3+TPU4-XPU4*(RAIO(J)+DTRY(2)))/(RAIO(J)+DTRY(4))
105      IF(XPU3.LT.1.0E-30) XPU3 = 1.0E-30
      FX4=XPU4-XPU4*(XPU3*XPU3*(RAIO(J)+DTRY(4))-XPL3*XPU3*TPU3)
      1/(RAIO(J)+HANK)
      DX4=2.*XPL4+(3.*XPU3*XPL3*(HAIO(J)+DTRY(2))-2.*XPL3*(RAIO(J)+DTRY
      1(2))*TPU3/(RAIO(J)+DTRY(4)))/(RAIO(J)+HANK)
110      XNPU4 = XPL4-FX4/DFX4
      DIF = ABS((XPU4-XNPU4)/XPU4)
      XPU4 = XNPU4
      N = N+1
      IF(DIF.LT.CCL.OR.N.GT.50) GO TO 52

```

```

115      GO TO 51
      52 TPU3N = XPL3 * (KA10(J) + DTRY(4))
      DPU3 = TPU3N - TPU3
      IF (MCK.GT.0) DPU3 = (DPU3+DPL3X)/2.
      IF (DPU3.GT.THAN) DPU3 = TSIN(5)/2.
120      DPU3X = DPL3
      TSIN(2) = TPL4 - DPU3
      TSIN(3) = TH + 2.*DPU3
      TSIN(4) = TPL3 + DPU3
      TSIN(5) = THAN - DPU3
125      DO 53 I = 2,5
      X(I,J,K) = TSIN(I)/(KA10(J) + DTRY(I))
      53 CONTINUE
      60 DO 70 I = 1,6
      IF (X(I,J,2)-1.0E-40) 70,70,44
130      44 D1 = (X(I,J,K)-ARY(I))/X(I,J,K)
      DIF = ABS(D1)
      ARY(I) = X(I,J,K)
      IF (DIF.LE.CCD) GO TO 70
135      68 MDEX = MDEX + 1
      70 CONTINUE
      MCK = MCK + 1
      IF (MCK.EQ.20) GO TO 78
      77 IF (MDEX) 78,78,42
      78 DO 80 I = 1,4
140      Y(I,J,K) = X(I,J,K)*DTRY(I)
      80 CONTINUE
      CODUM(J) = MCK
      130 CONTINUE
140      RETURN
145      END

```

```

SUBROUTINE UCOR(DMT,TEMPC)
COMMON/MSU/ARY(6),DTRY(6),CTEP,TO,JRED

```

```

C UCOR RETURNS A VALUE OF THE DISTRIBUTION COEFFICIENT = Y/X FOR EACH
C VALUE OF X TRIED
C

```

```

F=CTEP
DO 5 I = 1,4
IF (ARY(I).LT.0.) ARY(I)=0.
5 CONTINUE
JAM = ARY(1)
PUAM = ARY(2)
HAM = ARY(3)
PU3AM = ARY(4)
REDM = ARY(5)
IF (JRED.EQ.0) REDM = 0.
SNITH = ARY(6)
TNM=HAM+SNITH+REDM+2.*(UAM+PLAM)+3.*PU3AM
IF (JRED.EQ.1) TNM = TNM + REDM
IF (TNM.LE.0.) TNM = 1.
UK = 3.7*TNM**1.57 + 1.4*TNM**3.9 + 0.011*TNM**7.3
UK = UK*(4.*F**(-0.17) - 3.)
PUK = UK*(.20 + .55*F**1.25 + .0074*TNM**2)
HK1 = 0.135*TNM**0.82 + 0.0052*TNM**3.44
IF (F.LT.1.) HK1 = HK1*(1. - 0.54*EXP(-15.*F))
IF (TEMPC.NE.25.) UK = UK*EXP(2.5*DMT)
IF (TEMPC.NE.25.) PUK = PUK*EXP(-.2*DMT)
IF (TEMPC.NE.25.) HK1 = HK1*EXP(0.34*DMT)
HK2 = HK1
PU3K=0.04*TNM**1.8+0.000156*F*TNM**7
A=2.*(UK*UAM+PUK*PUAM+HK2*HAM+PU3K*PU3AM)
B = HK1*HAM + 1.
C = -TC
IF (A) 10,10,20
10 TF = TC
GO TO 30
20 TF = (-B + SGRT(B**2 - 4.*A*C))/(2.*A)
30 CONTINUE
DTRY(1) = UK*TF**2
DTRY(2) = PUK*TF**2
DTRY(3) = HK1*TF + HK2*TF**2
DTRY(4) = PU3K*TF**2
50 RETURN
END

```

TABLE A-3

EXAMPLE OUTPUT FROM THE SEPHIS COMPUTER CODE (12-STAGE RUNS 3 AND 19)

CALCULATIONS FOR A SOLVENT EXTRACTION PROCESS HAVING 3 INTERACTING SOLUTES							IB GLOVERCK RUN NO. 3				
FEED STREAM DATA:		STAGE NO.	URANIUM (M)	PLUTONIUM (M)	HNO3 (M)	SALT NO3 (M)	FLOW RATE (VOL. UNITS)	TEMP DEG C			
AQUEOUS		1	0.	0.	3.000E-01	1.000E-01	9.400E-01	55.0			
(3.200E-01 M HYDROXYLAMINE NITRATE ADDED TO FEED)											
30.0 * TRP		8	3.150E-01	3.560E-02	1.340E-01		4.000E+00	25.0			
30.0 * THP		12	0.	0.	0.		9.500E-01	25.0			
PHASE RATIOS EQUAL FLOW RATIOS:			STAGE NO.		A/O PHASE RATIO						
			1 - 8		1.941E-01						
			9 - 12		1.001E+00						
STAGE FLOWS (SOLUTE-FREE VOLUMES):											
STAGE NO.	FLOW RATIO	FLOW OUT OF STAGE	AQUEOUS PHASE		TOTAL AQUEOUS FLOW	FLOW OUT OF STAGE	ORGANIC PHASE		TOTAL ORGANIC FLOW	OVERALL TOTAL STAGE FLOW	STAGE VOL
			RECYCLE 2 TO FILL STAGE	RECYCLE 1 FOR PHASE RATIO			RECYCLE 2 TO FILL STAGE	RECYCLE 1 FOR PHASE RATIO			
1	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
2	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
3	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
4	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
5	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
6	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
7	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
8	1.941E-01	9.164E-01	0.	0.	9.164E-01	4.721E+00	0.	0.	4.721E+00	5.637E+00	3.000E+00
9	1.001E+00	9.164E-01	1.904E+00	0.	2.820E+00	5.154E-01	1.904E+00	0.	2.817E+00	5.637E+00	3.000E+00
10	1.001E+00	9.164E-01	1.904E+00	0.	2.820E+00	5.154E-01	1.904E+00	0.	2.817E+00	5.637E+00	3.000E+00
11	1.001E+00	9.164E-01	1.904E+00	0.	2.820E+00	5.154E-01	1.904E+00	0.	2.817E+00	5.637E+00	3.000E+00
12	1.001E+00	9.164E-01	1.904E+00	0.	2.820E+00	5.154E-01	1.904E+00	0.	2.817E+00	5.637E+00	3.000E+00

TRANSIENT BEHAVIOR RESULTS

SOLUTE CONCENTRATIONS IN EFFLUENT FROM EACH STAGE

TIME INTERVAL	STAGE	AQUEOUS PHASE VALUES			ORGANIC PHASE VALUES			ITERA- TIONS	FLOW OUT		TEMP DEG C
		URANIUM (M)	PLUTONIUM (M)	HNO3 (M)	URANIUM (M)	PLUTONIUM (M)	HNO3 (M)		AQUEOUS	ORGANIC	
100	1	1.549E-01	4.074E-03	3.688E-01	2.594E-01	6.104E-05	4.063E-02	5.	9.531E-01	4.863E+00	53.0
	2	1.570E-01	2.997E-02	5.130E-01	2.807E-01	8.376E-04	5.370E-02	7.	9.553E-01	4.874E+00	53.0
	3	1.248E-01	7.936E-02	5.794E-01	2.900E-01	6.186E-03	7.434E-02	8.	9.654E-01	4.882E+00	53.0
	4	1.039E-01	1.181E-01	7.992E-01	2.734E-01	1.578E-02	9.013E-02	8.	9.702E-01	4.888E+00	53.0
	5	9.210E-02	1.425E-01	8.884E-01	2.685E-01	2.387E-02	1.014E-01	6.	9.735E-01	4.894E+00	53.0
	6	8.508E-02	1.555E-01	9.890E-01	2.654E-01	2.871E-02	1.112E-01	5.	9.768E-01	4.898E+00	53.0
	7	7.883E-02	1.617E-01	1.066E+00	2.642E-01	3.149E-02	1.231E-01	4.	9.788E-01	4.901E+00	53.0
	8	7.241E-02	1.587E-01	1.211E+00	2.627E-01	3.279E-02	1.404E-01	3.	9.835E-01	4.905E+00	53.0
	9	7.372E-03	1.521E-01	1.263E+00	7.299E-02	1.735E-02	2.898E-01	1.	9.794E-01	4.404E-01	53.0
	10	5.953E-04	1.508E-01	1.252E+00	7.522E-03	9.999E-03	3.410E-01	1.	9.783E-01	4.366E-01	53.0
	11	4.906E-05	1.500E-01	1.188E+00	6.070E-04	8.845E-03	3.293E-01	2.	9.762E-01	4.355E-01	53.0
	12	4.624E-06	1.431E-01	9.457E-01	4.788E-05	8.002E-03	2.806E-01	2.	9.679E-01	4.328E-01	53.0

97.48 PERCENT OF STEADY STATE BY OVERALL MATERIAL BALANCE

90.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 50

95.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 78

TIME INTERVAL	STAGE	AQUEOUS PHASE VALUES			ORGANIC PHASE VALUES			ITERA- TIONS	FLOW OUT		TEMP DEG C
		URANIUM (M)	PLUTONIUM (M)	HNO3 (M)	URANIUM (M)	PLUTONIUM (M)	HNO3 (M)		AQUEOUS	ORGANIC	
126	1	1.534E-01	5.179E-03	3.752E-01	2.592E-01	8.017E-05	4.147E-02	5.	9.533E-01	4.863E+00	53.0
	2	1.529E-01	3.494E-02	5.270E-01	2.801E-01	1.087E-03	5.559E-02	7.	9.556E-01	4.875E+00	53.0
	3	1.219E-01	8.439E-02	6.998E-01	2.791E-01	7.023E-03	7.589E-02	8.	9.658E-01	4.882E+00	53.0
	4	1.019E-01	1.221E-01	8.062E-01	2.726E-01	1.678E-02	9.121E-02	7.	9.706E-01	4.889E+00	53.0
	5	9.131E-02	1.450E-01	8.923E-01	2.682E-01	2.444E-02	1.020E-01	6.	9.741E-01	4.894E+00	53.0
	6	8.451E-02	1.575E-01	9.719E-01	2.657E-01	2.903E-02	1.117E-01	5.	9.770E-01	4.898E+00	53.0
	7	7.841E-02	1.632E-01	1.068E+00	2.640E-01	3.163E-02	1.235E-01	4.	9.800E-01	4.901E+00	53.0
	8	7.207E-02	1.607E-01	1.212E+00	2.626E-01	3.284E-02	1.407E-01	3.	9.837E-01	4.905E+00	53.0
	9	7.280E-03	1.537E-01	1.265E+00	7.260E-02	1.741E-02	2.909E-01	1.	9.755E-01	4.404E-01	53.0
	10	5.828E-04	1.526E-01	1.255E+00	7.415E-03	1.005E-02	3.422E-01	1.	9.785E-01	4.366E-01	53.0
	11	4.754E-05	1.520E-01	1.190E+00	5.925E-04	8.981E-03	3.305E-01	1.	9.764E-01	4.356E-01	53.0
	12	4.428E-06	1.453E-01	9.483E-01	4.430E-05	8.210E-03	2.618E-01	2.	9.681E-01	4.329E-01	53.0

99.02 PERCENT OF STEADY STATE BY OVERALL MATERIAL BALANCE

90.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 50

95.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 78

TOTAL MOLES URANIUM IN: 1.2600E+00, OUT: 1.2606E+00
 TOTAL MOLES PLUTONIUM IN: 1.4240E-01, OUT: 1.4101E-01
 TOTAL MOLES PU(III) IN: 0., OUT: 1.4095E-01
 TOTAL MOLES HNO3 IN: 8.3800E-01, OUT: 1.1197E+00
 TOTAL MOLES HAN IN: 3.0080E-01, OUT: 1.5947E-01

MINUTES/TIME INTERVAL: .532

CALCULATIONS FOR A SOLVENT EXTRACTION PROCESS HAVING 3 INTERACTING SOLUTES

IN GLOVEBOX RUN NO. 19

FED STREAM DATA:	STAGE NO.	URANIUM (M)	PLUTONIUM (M)	HNO ₃ (M)	SALT NO ₃ (M)	FLOW RATE (VOL. LITS)	TEMP DEG C
AQUEOUS	1	0.	0.	3.400E-01	9.800E-02	1.30 E+00	50.0
30.0 % THP	8	(2.431E-01) M HYDROXYLAMINE NITRATE ADDED TO FEED	3.800E-02	1.300E-01		4.00E+00	50.0
30.0 % THP	12	0.	0.	0.		1.07 E+00	50.0

PHASE RATIOS EQUAL FLOW RATIOS:

STAGE NO. #/O PHASE RATIO

1 - 8 2.575E-01
9 - 12 1.227E+00

STAGE FLOWS (SOLUTE-FREE VOLUMES):

STAGE NO.	FLOW RATIO	AQUEOUS PHASE				ORGANIC PHASE				OVERALL	
		FLOW OUT OF STAGE	RECYCLE 2 TO FILL STAGE	RECYCLE 1 FOR PHASE RATIO	TOTAL AQUEOUS FLOW	FLOW OUT OF STAGE	RECYCLE 2 TO FILL STAGE	RECYCLE 1 FOR PHASE RATIO	TOTAL ORGANIC FLOW	TOTAL STAGE FLOW	STAGE VOL
1	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
2	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
3	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
4	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
5	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
6	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
7	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
8	2.575E-01	1.270E+00	0.	0.	1.270E+00	4.931E+00	0.	0.	4.931E+00	6.201E+00	3.000E+00
9	1.227E+00	1.270E+00	2.147E+00	0.	3.417E+00	1.035E+00	1.745E+00	0.	2.784E+00	6.201E+00	3.000E+00
10	1.227E+00	1.270E+00	2.147E+00	0.	3.417E+00	1.035E+00	1.745E+00	0.	2.784E+00	6.201E+00	3.000E+00
11	1.227E+00	1.270E+00	2.147E+00	0.	3.417E+00	1.035E+00	1.745E+00	0.	2.784E+00	6.201E+00	3.000E+00
12	1.227E+00	1.270E+00	2.147E+00	0.	3.417E+00	1.035E+00	1.745E+00	0.	2.784E+00	6.201E+00	3.000E+00

TRANSIENT BEHAVIOR RESULTS

SOLUTE CONCENTRATIONS IN EFFLUENT FROM EACH STAGE

TIME INTERVAL	STAGE	AQUEOUS PHASE VALUES			ORGANIC PHASE VALUES			ITERA- TIONS	FLOW OUT		TEMP DEG C
		URANIUM (M)	PLUTONIUM (M)	HNO3 (M)	URANIUM (M)	PLUTONIUM (M)	HNO3 (M)		AQUEOUS	ORGANIC	
100	1	1.550E-01	2.845E-06	3.253E-01	2.422E-01	4.462E-08	3.551E-02	2.	1.314E+00	3.072E+00	50.0
	2	1.971E-01	6.981E-05	3.347E-01	2.732E-01	7.567E-07	3.256E-02	2.	1.315E+00	3.044E+00	50.0
	3	2.036E-01	1.542E-03	3.727E-01	2.836E-01	1.073E-05	3.544E-02	4.	1.321E+00	3.049E+00	50.0
	4	1.840E-01	1.656E-02	4.615E-01	2.846E-01	3.945E-04	4.491E-02	7.	1.324E+00	3.092E+00	50.0
	5	1.455E-01	5.962E-02	5.474E-01	2.796E-01	4.354E-03	6.168E-02	6.	1.330E+00	3.095E+00	50.0
	6	1.160E-01	1.022E-01	7.153E-01	2.696E-01	1.552E-02	7.752E-02	7.	1.337E+00	3.102E+00	50.0
	7	1.004E-01	1.277E-01	8.224E-01	2.616E-01	2.070E-02	9.066E-02	8.	1.342E+00	3.109E+00	50.0
	8	8.836E-02	1.341E-01	9.761E-01	2.570E-01	4.302E-02	1.004E-01	5.	1.348E+00	3.115E+00	50.0
	9	1.700E-02	1.261E-01	1.028E+00	1.081E-01	2.151E-02	2.000E-01	2.	1.341E+00	1.063E+00	50.0
	10	2.357E-03	1.235E-01	1.031E+00	2.109E-02	1.006E-02	2.579E-01	1.	1.340E+00	1.057E+00	50.0
	11	3.110E-04	1.226E-01	9.461E-01	2.888E-03	7.188E-03	2.611E-01	1.	1.338E+00	1.055E+00	50.0
	12	4.289E-05	1.165E-01	8.306E-01	3.358E-04	5.929E-03	2.154E-01	2.	1.330E+00	1.053E+00	50.0

99.31 PERCENT OF STEADY STATE BY OVERALL MATERIAL BALANCE

90.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 38

95.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 45

99.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 89

TIME INTERVAL	STAGE	AQUEOUS PHASE VALUES			ORGANIC PHASE VALUES			ITERA- TIONS	FLOW OUT		TEMP DEG C
		URANIUM (M)	PLUTONIUM (M)	HNO3 (M)	URANIUM (M)	PLUTONIUM (M)	HNO3 (M)		AQUEOUS	ORGANIC	
110	1	1.549E-01	3.039E-06	3.254E-01	2.421E-01	3.722E-08	3.564E-02	2.	1.314E+00	3.072E+00	50.0
	2	1.968E-01	7.492E-05	3.353E-01	2.737E-01	8.132E-07	3.273E-02	2.	1.315E+00	3.044E+00	50.0
	3	2.025E-01	1.626E-03	3.740E-01	2.835E-01	1.990E-05	3.553E-02	4.	1.321E+00	3.049E+00	50.0
	4	1.831E-01	1.717E-02	4.642E-01	2.846E-01	4.182E-04	4.524E-02	7.	1.324E+00	3.092E+00	50.0
	5	1.448E-01	6.042E-02	5.998E-01	2.794E-01	4.319E-03	6.222E-02	8.	1.330E+00	3.096E+00	50.0
	6	1.166E-01	1.028E-01	7.173E-01	2.694E-01	1.575E-02	7.781E-02	7.	1.337E+00	3.102E+00	50.0
	7	1.006E-01	1.280E-01	8.236E-01	2.615E-01	2.701E-02	9.082E-02	6.	1.342E+00	3.109E+00	50.0
	8	8.826E-02	1.343E-01	9.770E-01	2.569E-01	3.367E-02	1.006E-01	5.	1.348E+00	3.115E+00	50.0
	9	1.701E-02	1.263E-01	1.029E+00	1.079E-01	2.154E-02	2.003E-01	2.	1.341E+00	1.063E+00	50.0
	10	2.346E-03	1.237E-01	1.032E+00	2.100E-02	1.008E-02	2.582E-01	1.	1.340E+00	1.047E+00	50.0
	11	3.082E-04	1.228E-01	9.574E-01	2.867E-03	7.200E-03	2.615E-01	1.	1.338E+00	1.055E+00	50.0
	12	4.240E-05	1.187E-01	8.317E-01	3.325E-04	5.944E-03	2.162E-01	1.	1.330E+00	1.053E+00	50.0

99.51 PERCENT OF STEADY STATE BY OVERALL MATERIAL BALANCE

90.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 38

95.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 45

99.0 PERCENT OF STEADY STATE AFTER TIME INTERVAL 89

TOTAL MOLES URANIUM IN: 1.2270E+00, OUT: 1.2279E+00
 TOTAL MOLES PLUTONIUM IN: 1.5869E-01, OUT: 1.5791E-01
 TOTAL MOLES PU(III) IN: 0., OUT: 1.5788E-01
 TOTAL MOLES HNO3 IN: 9.7370E-01, OUT: 1.2870E+00
 TOTAL MOLES H2O IN: 3.1590E-01, OUT: 1.5794E-01

MINUTES/TIME INTERVAL: .484

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