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CALCULATION CODE REPROSY-P FOR PROCESS
STUDIES ON Pu PURIFICATION WITH TBP

October 1975

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Calculation code; REPROSY-P for
process studies on Pu purification with TBP

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To evaluate the plutonium purification process with tributyl phosphate (TBP), the calculation code; REPROSY-P for TBP-HNO₃-Pu system, has been prepared on the basis of a batchwise counter-current extraction cascade model.

With the code, the concentration profiles under transient or steady state condition and the number of theoretical stages required, can be calculated for a given process condition.

Empirical distribution equations, distribution data of plutonium and the detailed calculation program, are described.

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TBPによるPu精製工程用の計算コード; REPROSY-P

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TBPによるPu精製工程を検討するため、TBP-HNO₃-Pu系の計算コード(REPROSY-P)を多段回分向流抽出の原理に基づいて作成した。

このコードは、定常あるいは非定常状態にある濃度分布および所要理論段数を与えられたフローシート条件から求めることができる。

この報告は、使用したPuの分配データとその数式化、計算プログラムを含む計算コードの詳細をまとめたものである。

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1. Introduction

A solvent extraction process of the Purex type is the only practical method at present for the reprocessing of irradiated fuels.

It is a typical multi-component system involving tri-n-butyl phosphate (TBP), nitric acid, uranium, plutonium and fission products.

These multi-component problems are intractable except with the use of a digital computer and/or an experimental proving test. The latter technique is, however, very laborious and time-consuming.

As the first stage in the use of a computer for solving multi-component extraction problems, a calculation code was prepared for the system TBP-HNO₃-Pu, employing the model of a batchwise counter-current extraction cascade. The concentration profiles and the numbers of theoretical stages required under transient or steady state conditions, can be computed for a given process condition.

The validity of the calculation programme was proven through the comparison with experimental results, and its application example to the calculation of plutonium purification process was shown in the JAERI Reprocessing Test Plant. Their results have already been reported⁽¹⁾.

In the present paper, are presented the complete calculation programme together with summarized distribution data and the formation of empirical equations used in the programming.

This code is named "REPROSY-P" (REprocessing PROcess StudY-Pu) and is usable to the conditions with low concentration of plutonium below several grams of Pu/l where its loading effect could be negligible.

Some calculation codes for reprocessing flowsheets have been prepared by Olander⁽²⁾ and Burton & Mills⁽³⁾. It seems that they use a conventional trial and error technique similar to that employed in the graphical approach on an operating diagram. By this method, it is difficult to evaluate transient phenomena.

The present calculation code, based on the model of a batchwise counter-current extraction cascade, is very simple for programming and covers the extraction, scrubbing and stripping processes under transient or steady state conditions.

At ORNL of the U.S.A.⁽⁴⁾, the same type of calculation programme as that of the present paper is being prepared with a view to evaluating chemical flowsheets for a FBR spent fuel.

2. Fundamental Data of Plutonium Distribution

Representative data of plutonium distribution for a given condition are necessary in forming empirical distribution equations required for programming a calculation code.

Distribution data of plutonium in the system of HNO_3 -U-TBP, which have so far been published, are summarized here to obtain a standard distribution curves and to derive their numerical expressions.

Some distribution data obtained by the present authors, (experimental conditions are shown in Appendix I), are also added to the published data and representative empirical equations are proposed for the plutonium distribution.

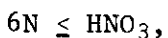
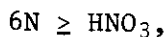
Concentration of plutonium is limited within a few grammes of Pu/l which does not apparently affect the extraction of foreign elements and the concentration of TBP. These limitations are acceptable in the standard Purex process for reprocessing of the irradiated fuel with low burn-up.

2.1 System of TBP- HNO_3 -Pu

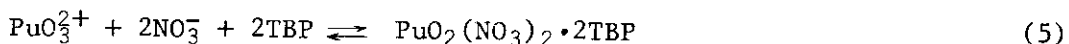
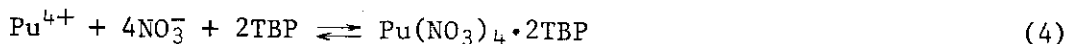
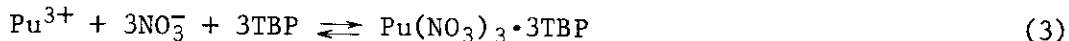
The distribution data of plutonium in the system of 30 v/o TBP- HNO_3 are summarized in Fig. 1. The published data are well fitted each other and also with the results obtained by the present authors.

These extractions are expressed by the following competition reactions.

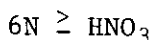
- Extraction of nitric acid,



- Extraction of plutonium,



- Formation of acidic plutonium nitrate



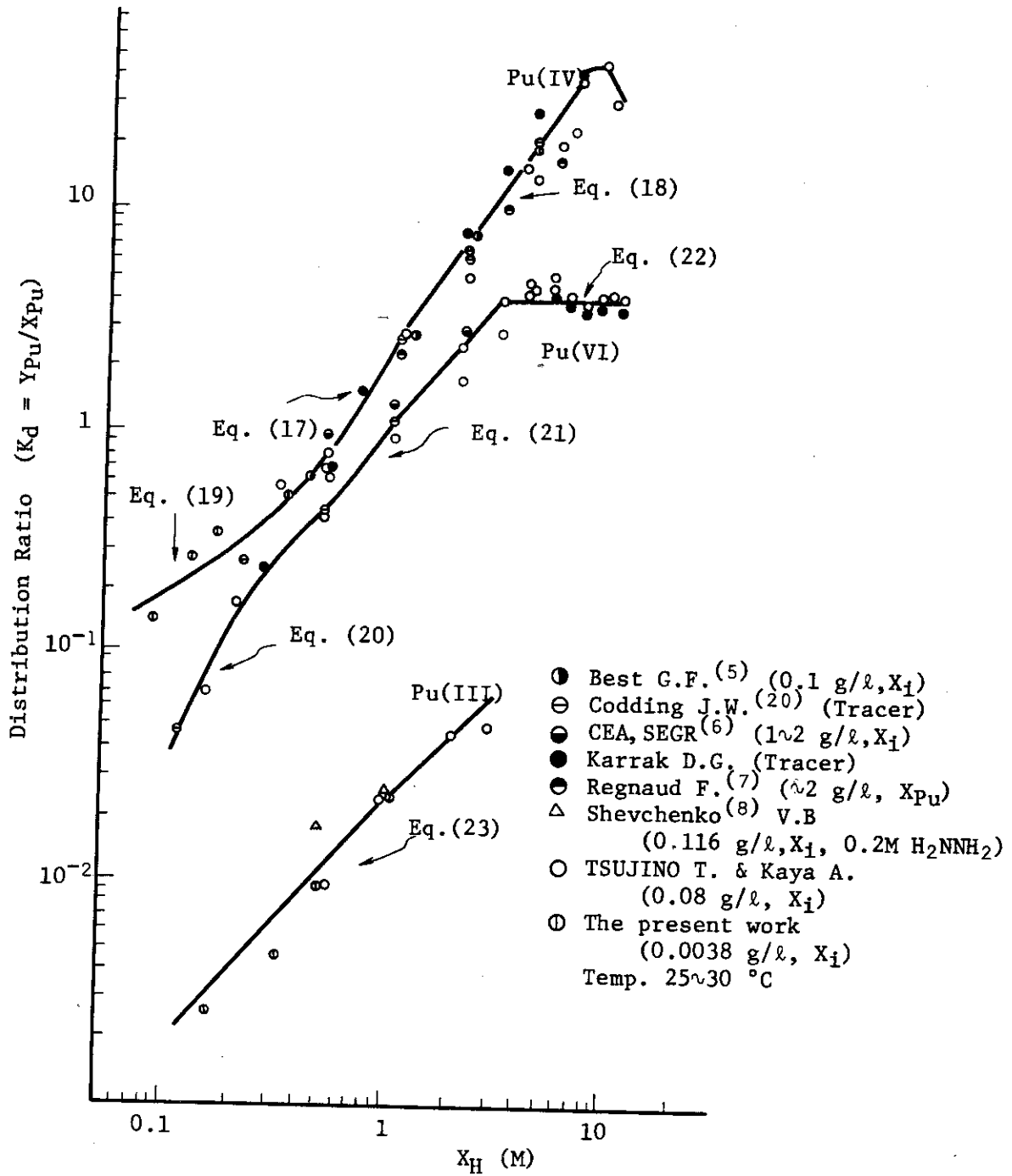


Fig. 1 Summarized Distribution Data of Plutonium in HNO_3 -30 v/o TBP

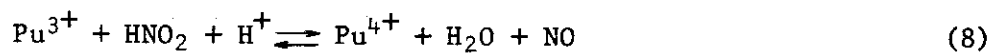
As shown in Appendix Fig. 1, the constant K_d of Pu(III) is not obtained⁽⁹⁾ because the oxidation of Pu(III) proceeds in the system of nitric acid.

The oxidation reaction of Pu(III) is explained by the auto-catalysis with nitrite as follows⁽¹⁰⁾;

(slow reaction)



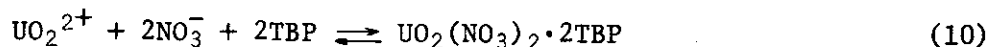
(fast reaction)



These reaction rates increase with increasing nitric acid concentration.

2.2 System of TBP-HNO₃-U(VI)-Pu

As shown in Figs. 2 through 5, the distribution ratios of plutonium decrease with increasing uranyl concentration according to the competition reactions of Eqs. (3) through (5) and (10).



The large dispersion of the published data is seen from Appendix Fig. 2 even under the constant condition. The standard equilibrium curves could not, therefore, be decided in this system.

In the present work, the data of plutonium by Coddling J.W. et al.⁽²⁰⁾ are representatively taken. Because they studied systematically in the widest range of uranium loading among the published data. The uranium distribution data by Coddling J.W. et al.⁽²⁰⁾ and Sakakura M.⁽²¹⁾ were also used for the parameteric conversions.

The Pu(IV) data arranged with the parameters of organic loading of uranium (y_U) and aqueous composition (x_U, x_H), are shown in Figs. 2 and 3, respectively.

The distribution data of Pu(III) and Pu(VI) are shown in Figs. 4 and 5, respectively.

In these figures, the loading effect of uranium is clearly shown. Much less data for Pu(III) and Pu(VI) than those for Pu(IV) are available

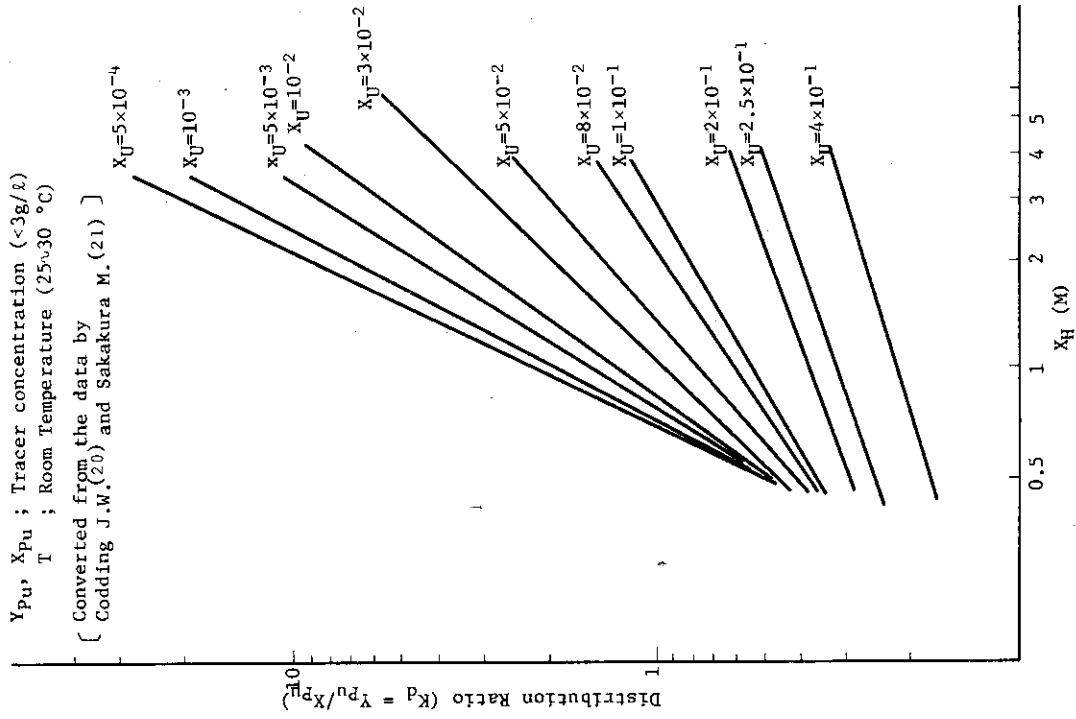


Fig. 3 Effect of Uranium co-existence on the Distribution Ratio of Plutonium (IV) in the HNO_3 -30 v/o TBP

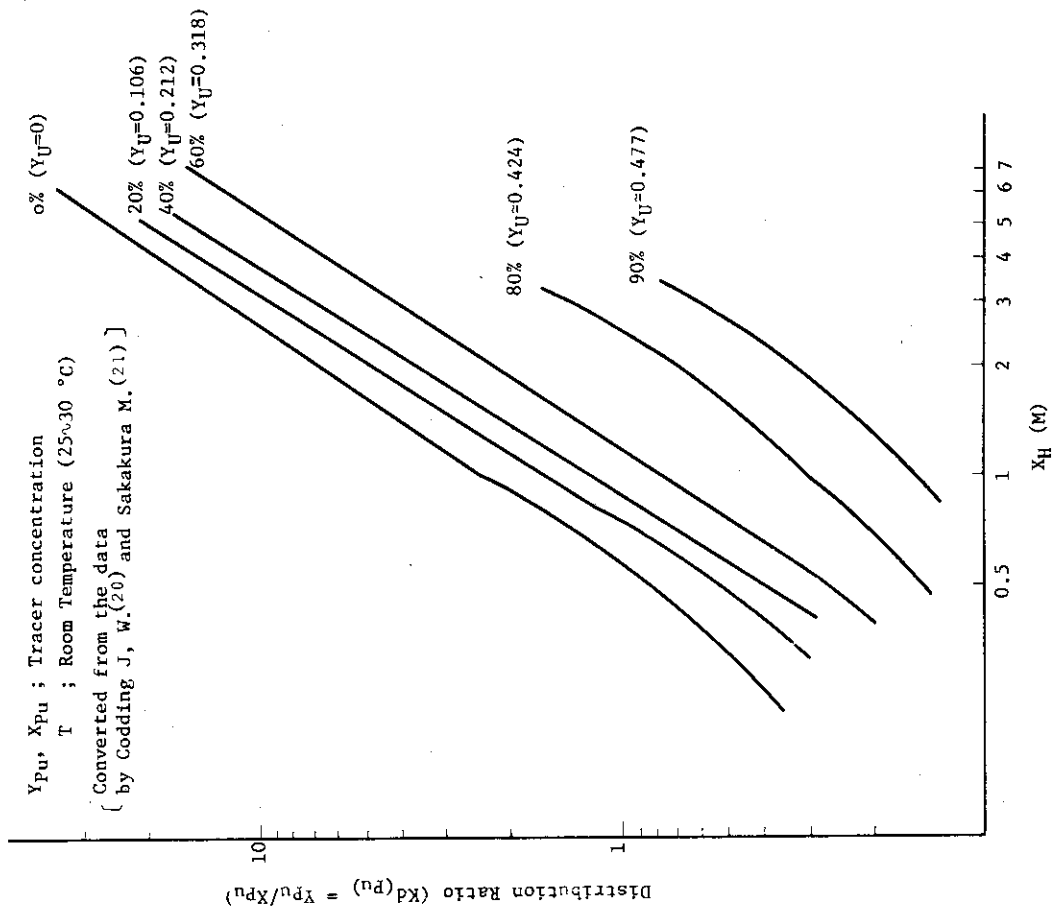


Fig. 2 Effect of Uranium Saturation on the Distribution Ratio of Plutonium (IV) in the HNO_3 -30 v/o TBP

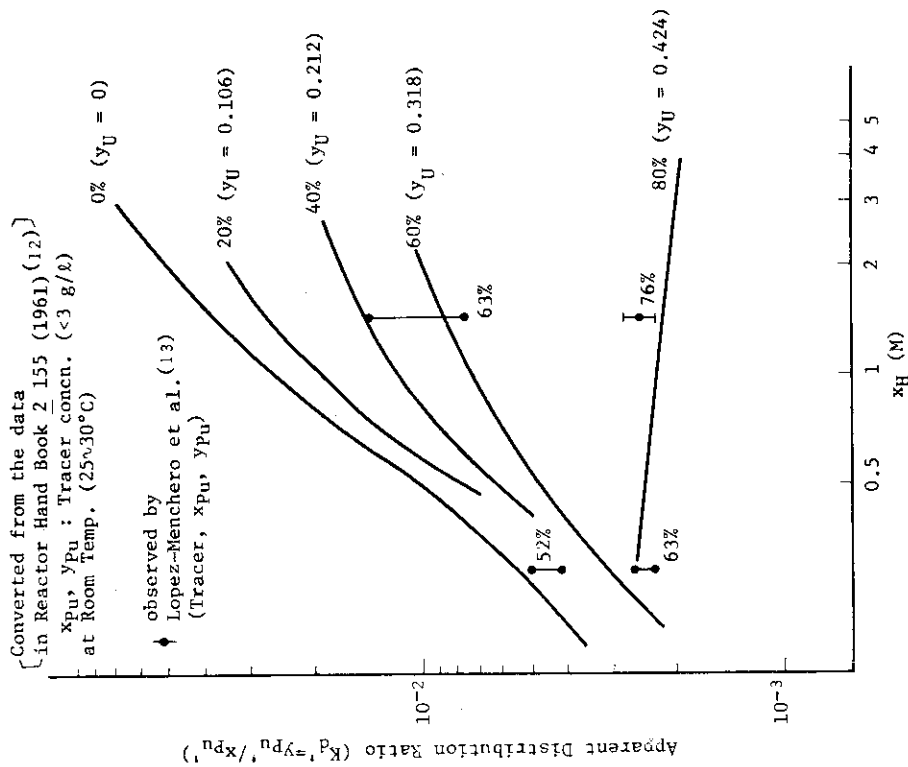


Fig. 4 Effect of Uranium Saturation on the Distribution Ratio of Plutonium (III) in the HNO₃-30 v/o TBP

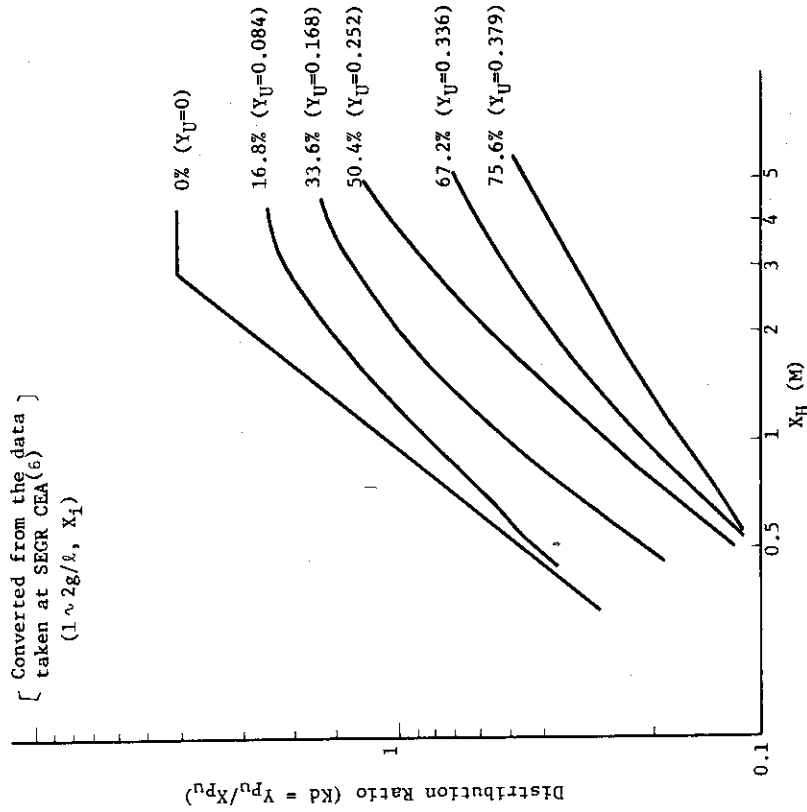


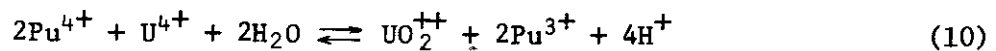
Fig. 5 Effect of Uranium Saturation on the Distribution Ratio of Plutonium (VI) in the HNO₃-30 v/o TBP

and it is necessary to accumulate much more data to find a standard equilibrium curve.

2.3 System of TBP-HNO₃-U(IV)-Pu

As shown in Appendix Fig. 3, Pu(IV) is reduced to Pu(III) by uranous nitrate. Below 2N of nitric acid concentration, Pu(IV) is completely reduced and the apparent distribution ratio (K_d') in the presence of U(IV) is partially oxidized to Pu(IV) as indicated in Appendix Fig. 1 and higher K_d' is observed than that of Pu(III).

The reduction reaction of Pu(IV) with U(IV) is proposed by Newtron J.W.⁽¹⁴⁾ as;



These oxidation-reduction mechanism, kinetics and application to actual process performance have been reviewed by one of the present authors⁽¹⁵⁾.

3. Numerical Expression of Plutonium Distribution

Based on the summarized distribution data which are shown above, standard distribution equations for 30 v/o TBP were derived for preparing a calculation code. The principle for the derivation is an empirical modification of the mass action law.

The uranium distribution equations have already been reported by Coddling J.W. et al.⁽²⁰⁾ and Sakakura M.⁽²¹⁾ with the view of flowsheet calculation.

The distribution equations for plutonium have been proposed for 20 v/o TBP by Ochsenfeld W. et al.⁽¹⁸⁾;

$$\bar{K}_{Pu} = -0.43 + 3.11\mu^{-1} + 1.79\mu^{-2} \quad (12)$$

where, $\mu = [H^+] + 10[Pu]$

$$\bar{K}_{Pu} = 12.163 = 9.033\mu + 2.230\mu^2 - 0.163\mu^3 \quad (13)$$

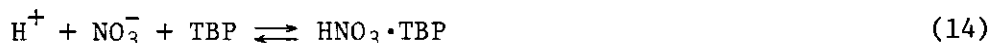
where, $\mu = [H^+] + 3[U] + 10[Pu]$

These semi-empirical equations are derived based on the ion-strength theory.

3.1 System of TBP-HNO₃-Pu

1) HNO₃

It is well known that extraction of nitric acid with TBP is expressed by;



Utilizing the mass action law to Eq. (14) and correcting the apparent equilibrium constant K_H' with aqueous concentration of nitric acid, the following distribution equations were made and they have been proven in the actual computer calculation for the present authors' process study⁽¹⁶⁾.

$$\text{in } 0 \leq y_H \leq 0.5;$$

$$K_H' = -0.375y_H + 0.350 \quad (15)$$

$$\text{in } 0.5 \leq y_H \leq 1;$$

$$K_H' = 0.165 \quad (16)$$

where, $K_H' = y_H / (x_H \cdot x_{NO_3^-} \cdot y_{TBP})$

x and y denote the molar concentration in aqueous and organic phase, respectively.

It is also found that these semi-theoretical equations could actually be used in the presence of low concentration of plutonium (below 3 g/l).

2) Pu(IV)

The actual distribution data graphically presented in Fig. 1, are directly expressed by the following empirical Eqs. (17)(18) and they have also been proven in the flowsheet calculation except for the low concentration of nitric acid below 0.2 N.

$$\begin{aligned} &\text{in } 0.2 \leq x_H \leq 1.5, \\ &\log K_d = 1.635 \log x_H + 0.413 \end{aligned} \quad (17)$$

$$\begin{aligned} &\text{in } 1.5 \leq x_H \leq 4 \text{ or } 6, \\ &\log K_d = 1.31 \log x_H + 0.468 \end{aligned} \quad (18)$$

For the low acidity data of plutonium taken in the present work, the distribution equation is also shown by;

$$\begin{aligned} &\text{in } 0.05 \leq x_H \leq 0.2 ; \\ &\log K_d = 0.319 \log x_H - 0.507 \end{aligned} \quad (19)$$

As shown in Fig. 1, Eq. (18) could be extended to the nitric acid concentration of 6 N.

3) Pu(VI)

By the same principle as above, the empirical distribution equations for Pu(VI) are expressed as follows;

$$\begin{aligned} &\text{in } 0.1 \leq x_H \leq 0.2, \\ &\log K_d = 0.292 \log x_H - 0.592 \end{aligned} \quad (20)$$

$$\begin{aligned} &\text{in } 0.2 \leq x_H \leq 3, \\ &\log K_d = 1.205 \log x_H + 0.048 \end{aligned} \quad (21)$$

$$\begin{aligned} \text{in } 3 \leq x_H \leq 8 \\ K_d = 4.2 \end{aligned} \quad (22)$$

4) Pu(III)

The empirical equation for Pu(III) is also given by;

$$\begin{aligned} \text{in } 0.1 \leq x_H \leq 3 \\ \log K_d = 1.02 \log x_H - 1.68 \end{aligned} \quad (23)$$

It is noted that all the empirical equations which are proposed above, are available only for the low concentration of plutonium below 3 g/l in the system of 30 v/o TBP-HNO₃.

3.2 System of TBP-HNO₃-U-Pu

1) Pu(IV)

It is well known that extraction of Pu(IV) with TBP is expressed by Eq. (4).

Assuming all the activity coefficients are unity and uranyl nitrate, plutonium nitrate and nitric acid dissociate completely, the mass action law for Eq. (4) is shown by;

$$\tilde{K}_{Pu} = K_d(Pu) / [2x_U + x_H]^n [T_1 - 2y_U - y_H]^m \quad (24)$$

where, \tilde{K} and K_d are the apparent (or average) equilibrium constant and the distribution ratio, respectively.

T_1 is initial molar concentration of TBP. m and n show solvation number and number of nitrate dependency, respectively. (theoretically $m=2$, $n=4$ in Eq. (24) for the extraction of Pu(IV))

This equation is applicable when the plutonium concentration is so low that plutonium does not affect the distribution of uranium and nitric acid. (below several g/l)

The actual distribution of Pu(IV) could be expressed by Eq. (24) where \tilde{K} , n and m values correct with aqueous and organic phase compositions. The empirical constant corrected are summarized in Tables 1 and 2, which are obtained from the data in Figs. 2 and 3.

Table 1. Empirical constants in Eq. (24) for Pu(IV) distribution (parameter of aqueous compositions)

Aqueous compositions		\tilde{K}_{Pu}	n	m
x_H, x_U	$N = 2x_U + x_H$			
$x_H \leq 9.6$ $0.001 < x_U < 0.1$	($N < 1$)	2.2	2.2	2.0
$0.6 \leq x_H \leq 4$ $0.001 < x_U < 0.1$	($N > 1$)	2.2	3.5	2.0
$0.6 \leq x_H \leq 4$ $0.1 \leq x_U < 0.6$	$N < 2.7$	1.5	3.4	2.0
	$N > 2.7$	0.8	4.0	2.0

$$y_0 = 1.09 \text{ (30 w/o TBP)}$$

It is estimated that the calculated values include the higher CV (Coefficient of variation) with the higher loading of uranium. (to $\pm 10\%$) As the published data disperse in the wide range as shown in Appendix Fig. 2, it is noted that the calculated values are only one example, which is acceptable at present, and much data are further necessary to obtain precise values.

2) Pu(III)

The extraction of Pu(III) in the presence of U(VI) is important in the separation of uranium/plutonium.

According to the same principle as above, empirical distribution equations for Pu(III), were obtained from the data in Fig. 4.

Extraction of Pu(III) with TBP is shown by Eq. (3) and its mass action law is also expressed by Eq. (24), where $m=3$ is utilized in spite of $m=2$ in the extraction of Pu(IV).

Table 2. Empirical constants in Eq. (24) for Pu(IV) distribution (parameter of organic composition)

Organic compositions		\tilde{K}_{Pu}	n	m
y_H, y_U	T_f			
$y_H \leq 0.1$ $0.1 \leq y_U \leq 0.32$	-	5.2	4.0	2.5
$0.1 < y_H \leq 0.62$ $0.1 \leq y_U \leq 0.32$	$T_f < 0.28$	3.7	4.0	2.9
	$0.18 < T_f \leq 0.28$	1.15	4.0	2.0
$0.01 \leq y_H < 0.3$ $0.32 < y_U \leq 0.5$	$0.1 < T_f < 0.18$	3.8	4.0	2.7
	$T_f < 0.1$	0.75	4.0	2.0

$$T_f = y_0 - 2y_U - y_H, \quad y_0 = 1.09 \text{ (30 v/o TBP)}$$

The apparent distribution of Pu(III) in the presence of uranium is, therefore, expressed by Eq. (25);

$$\tilde{K}_{Pu} = K_d / [2x_U + x_H]^2 [T_f - 2y_U - y_H]^3 \quad (25)$$

where, \tilde{K}_{Pu} varies empirically with the aqueous concentration of nitric acid x_H as shown in Eq. (26).

$$\tilde{K}_{Pu} = e^{-1.3x_H^{-1.6}} \quad (26)$$

Combining Eqs. (25) and (26), the actual distribution equation for Pu(III) in the presence of uranium is obtained as,

$$K_d(\text{Pu(III)}) = e^{-1.3x_H^{-1.6}} [2x_U + x_H]^2 [T_f - 2y_U - y_H]^3 \quad (27)$$

This empirical equation is usable under the following conditions;

$$\begin{aligned} 0 < x_{Pu} < 0.02, \\ 0.5 \leq x_H \leq 3 \\ 0.005 \leq x_U \leq 0.4 \end{aligned}$$

or

$$\begin{aligned} 0.01 \leq y_H \leq 0.53 \\ 0.106 \leq y_U \leq 0.424 \text{ (80\% saturation)} \end{aligned}$$

In the calculated values by Eq. (27), large CV (up to 20%) is included.

3) Pu(VI)

If the valency of plutonium is well adjusted, the extraction behavior of Pu(VI) is not so important in an ordinary Purex process that the mathematical expression is abbreviated in the present paper.

4. Principle in Programming Calculation Code

4.1 Batchwise counter-current extraction cascade

A principal flowchart on batchwise extraction cascade, which is used in programming, is given in Fig. 6.

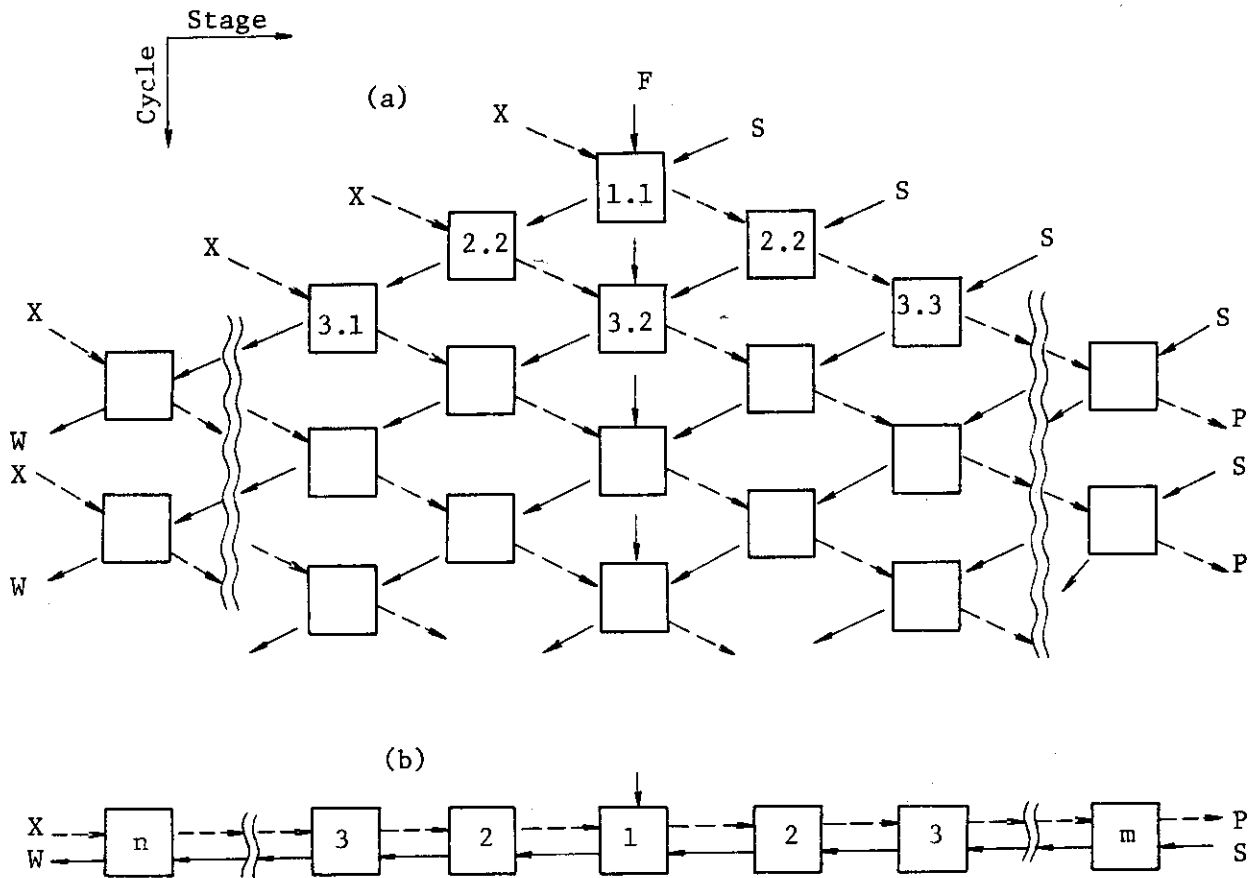


Fig. 6 Principle of Batchwise Counter-Current Extraction Cascade.

At the beginning, given volumes of feed solution (F), extraction solvent (X) and scrubbing or stripping solution (S) are mixed in the vessel (1.1). After an equilibrium, aqueous phase (expressed by rigid line) and organic phase (by dashed line) are respectively sent to the next vessels (2.1 and 2.2). The X and S are added respectively to these vessels and extractions are repeated. After a stationary state is reached by repeating these batchwise fractional extractions, the multistage counter-current extraction shown in Fig. 6-(b) is equivalent to the bottom of the flow scheme (a).

Giving the required stages n and m , output concentrations (W, P) and concentration profiles in the bank are determined under the transient or steady state.

The theory and detailed description have been reported by Scheibel⁽²²⁾ and Peppard et al.⁽²³⁾.

4.2 Stage efficiency

In the present work, a single stage efficiency EF is defined by Eq. (28) to simulate an actual partition in the bank.

$$\left. \begin{aligned} EF &= |y/y^*|_x \quad (\text{Extraction}) \\ EF &= |y^*/y|_x \quad (\text{Scrubbing \& stripping}) \end{aligned} \right\} \dots (28)$$

where, y^* , y are the organic molar concentration under equilibrium and in an actual partition, respectively at constant aqueous concentration of x .

For the actual simulation, y^* defined by Eq. (28), is employed instead of y in the equations (15) ~ (24).

4.3 Mass balance

As shown in Fig. 7, input at k -stage is expressed by the following equations assuming no volume change in the process.

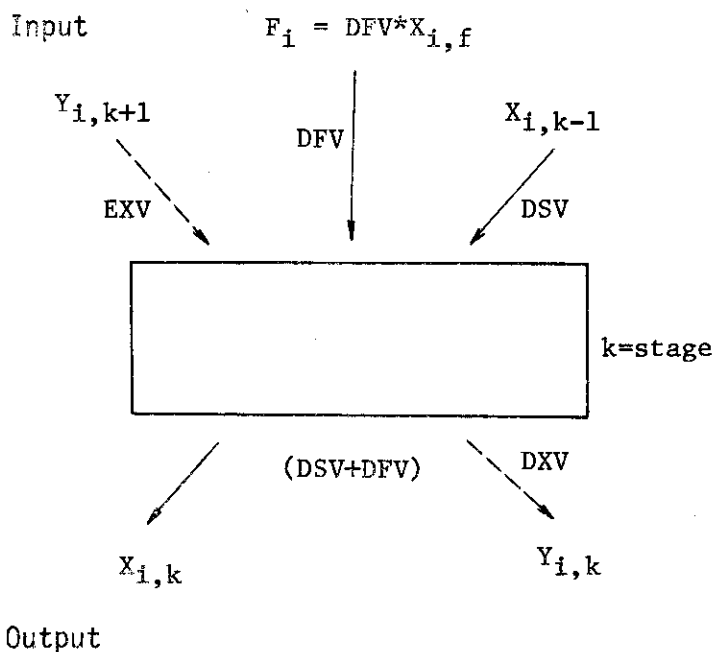


Fig. 7 Material Balance of i -species at k stage

(Extraction)

$$E_{i,k} = (DSV+DFV) \cdot x_{i,k-1} + DXV \cdot y_{i,k+1}$$

(Feed)

$$E_{i,k} = DSV \cdot x_{i,k-1} + DXV \cdot y_{k,k+1} + F_i$$

$$F_i = DVF \cdot x_{i,f}$$

(Scrubbing)

$$E_{i,k} = DSV \cdot x_{i,k-1} + DXV \cdot y_{i,k+1}$$

(Stripping)

$$E_{i,k} = DSV \cdot x_{i,k-1} + DXV \cdot y_{i,k+1}$$

} (29)

where, the notations of these symbols are summarized in Appendix II.

The input $E_{i,k}$ is partitioned between aqueous and organic phases according to;

$$f_i(x_{i,k}, y_{i,k}, (EF)_i) = E_{i,k} \dots \dots \dots (30)$$

where, $f_i(x_i, y_i)$ is the equilibrium equation and $f_i(x_i, y_i, (EF)_i)$ denotes partition equations for i-species as Eqs. (15) ~ (19). $x_{i,k}$ and $y_{i,k}$ are outputs from k-stage.

5. Calculation Programme

Based on the above distribution / mass balance equation and the counter-current extraction model, a computing code is programmed according to the flow chart shown in Fig. 8 whose symbols are given in Appendix II.

In the main routine, initial conditions and printing format are set and cycle numbers are then controled and fixed.

In the subroutine 1, the fixed site is distinguished whether it belongs to extraction, feed or scrubbing section and partition of nitric acid is at first calculated by solving the cubic or the fourth power equation through the Newton-Raphson Process.

In the subroutine 2, partition of plutonium is finally computed by solving the logarithmic equations which are obtained from Eqs. (17~19) and (28~30).

Above calculations are repeated for all the stages under consideration and the results are printed out in the form of Fig. 1(a).

The programme, which is named REPROSY-P (REprocessing PROcess Study-Pu), is written in FORTRAN IV for IBM 7044 available at the JAERI, computing center. The complete programme is shown in Table 3.

The typical print-out for the extraction bank of Pu(2A) is shown in Table 4 where calculating condition has already been reported⁽¹⁾.

Calculation time is within 20 sec. for one run of the standard flowsheets, as shown in Table 5.

Table 5 Calculation time required for one run⁽¹⁾

	Extraction (2A)	Stripping (2B)
Total time	18 sec	10.8 sec
Execution	1.8	2.5
Printing	16.2	7.5
Stage Nos.	(extraction) n=10 (scrubbing) m=7	m=12

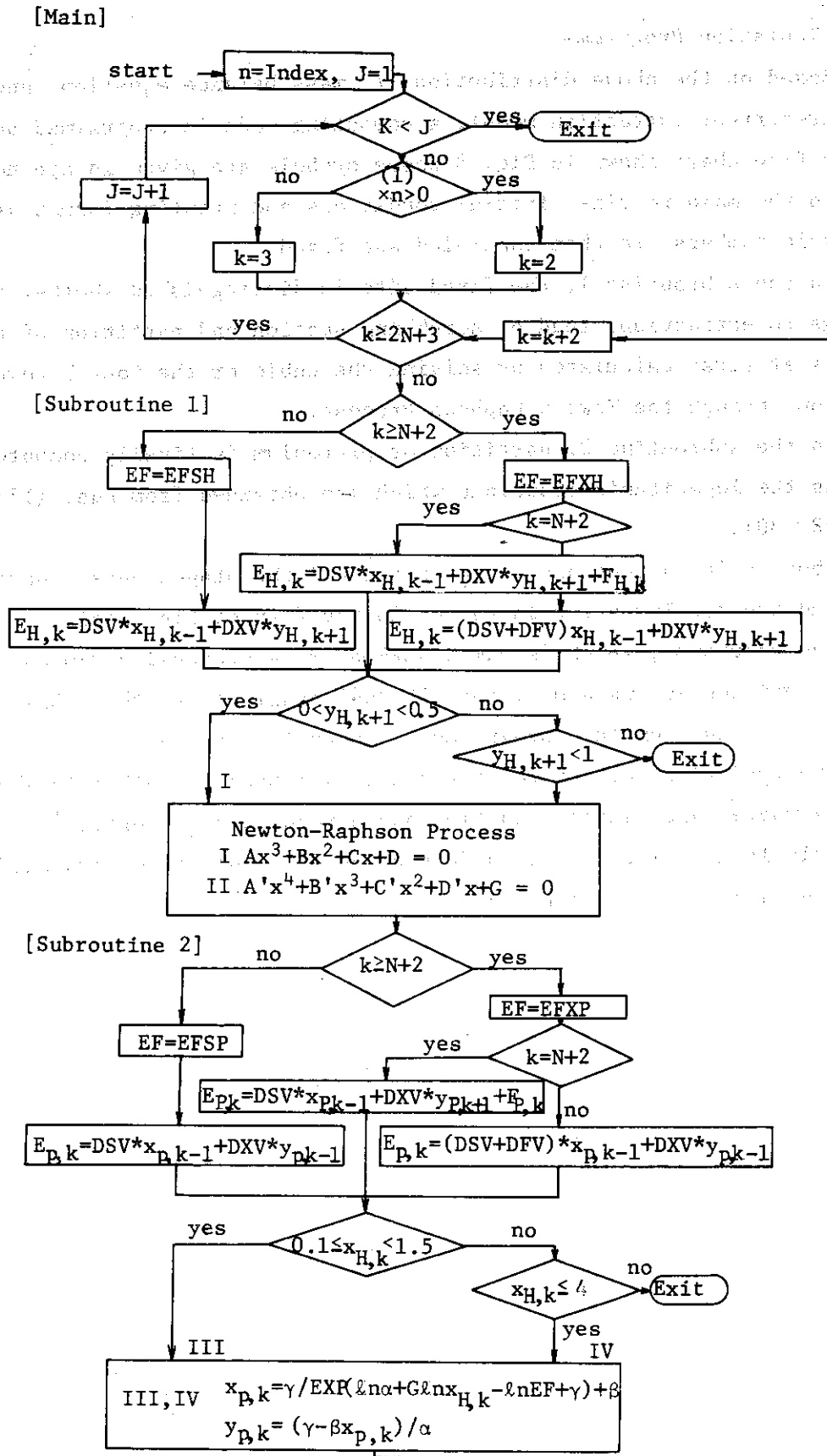


Fig. 8 Calculation Flow chart for REPROSY-P

Table 3 Complete Programme of REPROSY-P

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REPROSY-P /T.TSUJINO /2453          FORTRAN SOURCE LIST
ISN      SOURCE STATEMENT

0 $IBFTC MAIN
C      REPROCESSING PROCESS STUDY-P *SAISHORI T.TSUJINO
C      (HNO3)-PU-TBP-PARTITION      KEISAN SENTA A.KOHSAKA
1      COMMON      AQUAS(30),ORGAN(30),AQ(30),OG(30),N,DSV,DFV,DXV,DSN,
1          1      DFN,DXN,DSP,DFP,DXP,C1,C2,C3,C4,C5,C6,C7,C8,C9,EFXH,
2          2      EFSH,EFXP,EFSP,UPSIL
C          * INPUT DATA
2      READ (5,3001)DSV,DFV,DXV,DSN,DFN,DXN,DSP,DFP,DXP,C1,C2,C3,C4,C5,
1          1      C6,C7,C8,C9
3      READ (5,3002)N,NSTAGE,UPSIL
6      1000 READ (5,3001)EFXH,EFSH,EFXP,EFSP
7      3001 FORMAT(8E9.5)
10     3002 FORMAT(2I2,E9.5)
C          *SETTING OF INTEGER
11     N1=N+1
12     N2=N+2
13     N3=N+3
14     MM=2*N+1
15     NN=2*N+2
16     INDEX=-1
17     M=N-1
C          *PREPARATION
20     DO 100 I=1,N1
21         AQUAS(I)=DSN
22         ORGAN(I)=0.
23         AQ(I)=DSP
24         OG(I)=0.
25         J=I+N2
26         AQUAS(J)=0.
27         ORGAN(J)=DXN
30         AQ(J)=0.
31     100     OG(IJ)=DXP
C          *CALCULATION OF THE DELTA PART
C
33     WRITE (6,4001)
34     4001 FORMAT(1 H1)
C
35     DO 300 I=1,M
36         M1=N3-I
37         M2=N1+I
40     DO 10 K=M1,M2,2
41         CALL NEWTON (K,X,Y)
42         AQUAS(K)=X
43         ORGAN(K)=Y
44         CALL FUN(K,S,T)
45         AQ(K)=S
46     10     OG(K)=T
50     INDEX=(-1)*INDEX
51     IF (INDEX) 1,1,2
52     1 WRITE(6,5001) (AQUAS(L),L=3,MM,2)
57     WRITE(6,5001) (ORGAN(L),L=3,MM,2)
64     WRITE(6,5001) (AQ(L),L=3,MM,2)
71     WRITE(6,5001) (OG(L),L=3,MM,2)
76     WRITE(6,5003)
77     GO TO 300

```

Table 3 (continued)

REPROSY-P	/T.TSUJINO /2453	FORTRAN SOURCE LIST MAIN
ISN	SOURCE STATEMENT	
100	2 WRITE(6,5002) (AQUAS(L),L=2,NN,2)	
105	WRITE(6,5002) (ORGAN(L),L=2,NN,2)	
112	WRITE(6,5002) (AQ(L),L=2,NN,2)	
117	WRITE(6,5002) (OG(L),L=2,NN,2)	
124	WRITE(6,5003)	
125	300 CONTINUE	
127	5001 FORMAT(11X,8E14.3)	
130	5002 FORMAT(4X,9E14.3)	
131	5003 FORMAT(1H)	
	C	*CALCULATION OF EACH STAGE
	C	
132	DO 400 I=1,NSTAGE	
133	INDEX=(-1)*INDEX	
134	IF (INDEX) 5,5,6	
135	5 DC 20 K=3,MM,2	
136	CALL NEWTON (K,X,Y)	
137	AQUAS(K)=X	
140	ORGAN(K)=Y	
141	CALL FUN(K,S,T)	
142	AQ(K)=S	
143	20 OG(K)=T	
145	WRITE (6,5001) (AQUAS(L),L=3,MM,2)	
152	WRITE (6,5001) (ORGAN(L),L=3,MM,2)	
157	WRITE(6,5001) (AQ(L),L=3,MM,2)	
164	WRITE(6,5001) (OG(L),L=3,MM,2)	
171	WRITET(6,5003)	
172	GOTO 400	
	C	
173	6 DO 40 K=2,NN,2	
174	CALL NEWTON (K,X,Y)	
175	AQUAS(K)=X	
176	ORGAN(K)=Y	
177	CALL FUN(K,S,T)	
200	AQ(K)=S	
201	40 OG(K)=T	
203	WRITE (6,5002) (AQUAS(L),L=2,NN,2)	
210	WRITE (6,5002) (ORGAN(L),L=2,NN,2)	
215	WRITE(6,5002) (AQ(L),L=2,NN,2)	
222	WRITE(6,5002) (OG(L),L=2,NN,2)	
227	WRITE(6,5003)	
230	400 CONTINUE	
232	GO TO 1000	
233		END

Table 3 (continued)

```

REPROGSY-P /T.TSUJINO /72453          FORTRAN SOURCE LIST
ISN          SOURCE STATEMENT

0 $IBFTC SUB1
C REPROCESSING PROCESS STUDY-P, SUB-I
1 SUBROUTINE NEWTON (K,X,Y)
2 COMMON /AQUAS(30),ORGAN(30),AQ(30),OG(30),N,DSV,DFV,DXV,DSN,
   1 DFN,DXN,DSP,DFP,DXP,C1,C2,C3,C4,C5,C6,C7,C8,C9,EFXH,
   2 EFSH,EFXP,EFSF,UPSIL
3 XN=C5
4 ALPHA=DXV
5 IF (K-N-2) 1,2,3
6 1 E=DSV*AQUAS(K-1)+DXV*ORGAN(K+1)
7 C=DSV
10 BETA=E
11 EF=EFSH
12 GO TO 100
13 2 E=DSV*AQUAS(K-1)+DXV*ORGAN(K+1)+DFV*DFN
14 C=DSV+DFV
15 BETA=E
16 EF=EFSH
17 GO TO 100
20 3 E=(DFV+DSV)*AQUAS(K-1)+DXV*ORGAN(K+1)
21 C=DSV+DFV
22 BETA=E
23 EF=EFSH
C *CALCULATION OF THE ROOT
24 100 IF (ORGAN(K+1)-0.5) 4,5,5
25 4 FX=C3*EF*C**2*XN**4-C*(2.*C3*EF*BETA-ALPHA*(C2*C3+C4))*XN**3
   1+(C3*EF*BETA**2-ALPHA*BETA*(C2*C3+C4)+(ALPHA**2*C4*C2)/EF)*XN**2
   2+ALPHA*C*XN-ALPHA*BETA
26 FD=4.*C3*EF*C**2*XN**3-3.*C*(2.*C3*EF*BETA-ALPHA*(C2*C3+C4))*XN**2
   1+2.*(C3*EF*BETA**2-ALPHA*BETA*(C2*C3+C4)+(ALPHA**2*C4*C2)/EF)*XN
   2+ALPHA*C
27 D=FX/FD
30 IF (ABS(D)-UPSIL) 7,7,6
31 6 XN=XN-D
32 GO TO 4
33 7 X=XN
34 GO TO 12
35 5 IF (ORGAN(K+1)-1.) 9,9,8
36 9 FX=C1*C*XN**3+C1*(C2*ALPHA/EF-BETA)*XN**2+C*XN-BETA
37 FD=3.*C1*C*XN**2+2.*C1*(C2*ALPHA/EF-BETA)*XN+C
40 D=FX/FD
41 IF (ABS(D)-UPSIL) 11,11,10
42 10 XN=XN-D
43 GO TO 9
44 11 X=XN
45 12 IF (K-N-2) 13,14,14
46 13 Y=(E-DSV*XN)/DXV
47 RETURN
50 14 Y=(E-(DSV+DFV)*XN)/DXV
51 RETURN
52 8 CALL EXIT
53

```

END

Table 3 (continued)

REPROSY-P	/T.TSUJINO	/2453	FORTRAN SOURCE LIST
ISN	SOURCE STATEMENT		
0	\$IBFTC	SUB2	
	C	REPROCESSING PROCESS STUDY-P, SUB-2	
1		SUBROUTINE FUN (K,S,T)	
2		COMMON AQUAS(30),ORGAN(30),AQ(30),OG(30),N,DSV,DFV,DXV,DSN, DFN,DXN,DSP,DFP,DXP,C1,C2,C3,C4,C5,C6,C7,C8,C9,EFXH, EFSH,EFXP,EFSP,UPSIL	
3		XN=AQUAS(K)	
4		ALPHA=DXV	
5		IF (K-N-2) 1,2,3	
6	1	EP=CSV*AQ(K-1)+DXV*OG(K+1)	
7		C=CSV	
10		GAMMA=EP	
11		EF=EFSP	
12		GO TO 100	
13	2	EP=DSV*AQ(K-1)+DXV*OG(K+1)+DFV*DFP	
14		C=CSV+DFV	
15		GAMMA=EP	
16		EF=EFXP	
17		GO TO 100	
20	3	EP=(DFV+DSV)*AQ(K-1)+DXV*OG(K+1)	
21		C=DFV+DSV	
22		GAMMA=EP	
23		EF=EFXP	
	C	*CALCULATION OF THE ROOT	
24	100	IF (AQUAS(K)-1.5) 4,5,5	
25	4	G=C6	
26		H=C7	
27		GO TO 7	
30	5	IF (AQUAS(K)-4.) 6,6,11	
31	6	G=C8	
32		H=C9	
33	7	XP=GAMMA/(C+(ALPHA*XN**G*EXP(2.303*H))/EF)	
34		S=XP	
35	8	IF (K-N-2) 9,10,10	
36	9	T=(EP-CSV*XP)/DXV	
37		RETURN	
40	10	T=(EP-(CSV+DFV)*XP)/DXV	
41		RETURN	
42	11	CALL EXIT	
43		END	

Table 4 Typical Print-out for 2A-Bank, EFXH=EFSH=EFXP=EFSP=1.00

0.990E 00	0.990E 00	0.990E 00	0.990E 00	0.291E 01	0.	0.	0.
0.	0.	0.	0.	0.578E 00	0.	0.	0.
0.	0.	0.	0.	0.122E 03	0.	0.	0.
0.	0.	0.	0.	0.185E 04	0.	0.	0.
0.990E 00	0.990E 00	0.990E 00	0.990E 00	0.162E 01	0.273E 01	0.	0.
0.	0.	0.	0.	0.330E 00	0.557E 00	0.	0.
0.	0.	0.	0.	0.284E 03	0.262E 02	0.	0.
0.	0.	0.	0.	0.135E 04	0.286E 03	0.	0.
0.990E 00	0.990E 00	0.990E 00	0.990E 00	0.115E 01	0.315E 01	0.	0.
0.	0.	0.	0.	0.269E 00	0.535E 00	0.	0.
0.	0.	0.	0.	0.573E 03	0.136E 03	0.605E 01	0.
0.	0.	0.	0.	0.121E 04	0.179E 04	0.605E 02	0.
0.990E 00	0.990E 00	0.106E 01	0.185E 01	0.310E 01	0.238E 01	0.	0.
0.	0.	0.	0.	0.243E 00	0.396E 00	0.513E 00	0.
0.	0.	0.	0.	0.375E 03	0.276E 03	0.150E 01	0.
0.	0.	0.	0.	0.106E 04	0.183E 04	0.137E 02	0.
0.990E 00	0.990E 00	0.102E 01	0.129E 01	0.321E 01	0.305E 01	0.	0.
0.	0.	0.	0.	0.305E 00	0.661E 00	0.489E 00	0.
0.	0.	0.	0.	0.348E 03	0.139E 03	0.647E 01	0.
0.	0.	0.	0.	0.925E 03	0.179E 04	0.821E 02	0.330E 01
0.990E 00	0.100E 01	0.113E 01	0.196E 01	0.320E 01	0.302E 01	0.206E 01	0.
0.	0.	0.	0.	0.228E 00	0.423E 00	0.588E 00	0.465E 00
0.	0.	0.	0.	0.310E 03	0.548E 03	0.146E 01	0.113E 00
0.	0.	0.	0.	0.804E 03	0.172E 04	0.409E 03	0.183E 02
0.990E 00	0.990E 00	0.105E 01	0.137E 01	0.323E 01	0.317E 01	0.298E 01	0.
0.	0.	0.	0.	0.236E 00	0.327E 00	0.679E 00	0.439E 00
0.	0.	0.	0.	0.212E 03	0.573E 03	0.140E 03	0.343E 00
0.	0.	0.	0.	0.698E 03	0.161E 04	0.191E 04	0.891E 02
0.992E 00	0.102E 01	0.118E 01	0.202E 01	0.323E 01	0.314E 01	0.294E 01	0.177E 01
0.226E 00	0.233E 00	0.277E 00	0.437E 00	0.688E 00	0.673E 00	0.578E 00	0.412E 00
0.237E 03	0.562E 03	0.585E 03	0.270E 03	0.306E 02	0.150E 01	0.840E 01	0.111E 01
0.605E 03	0.150E 04	0.196E 04	0.198E 04	0.417E 03	0.198E 02	0.101E 01	0.693E 01
0.991E 00	0.108E 01	0.143E 01	0.324E 01	0.322E 01	0.311E 01	0.288E 01	0.165E 01
0.225E 00	0.229E 00	0.252E 00	0.340E 00	0.690E 00	0.687E 00	0.575E 00	0.388E 00
0.208E 03	0.532E 03	0.658E 03	0.440E 03	0.140E 03	0.672E 01	0.345E 00	0.218E 01
0.525E 03	0.138E 04	0.195E 04	0.209E 04	0.192E 04	0.914E 02	0.256E 00	0.218E 01
0.995E 00	0.109E 01	0.122E 01	0.205E 01	0.324E 01	0.321E 01	0.308E 01	0.282E 01
0.227E 00	0.238E 00	0.288E 00	0.447E 00	0.690E 00	0.686E 00	0.568E 00	0.388E 00
0.495E 03	0.687E 03	0.579E 03	0.268E 03	0.307E 02	0.149E 01	0.814E 01	0.604E 02
0.127E 04	0.189E 04	0.207E 04	0.198E 04	0.419E 03	0.202E 02	0.105E 01	0.691E 01
0.993E 00	0.111E 01	0.147E 01	0.324E 01	0.323E 01	0.321E 01	0.305E 01	0.264E 01
0.225E 00	0.259E 00	0.340E 00	0.691E 00	0.690E 00	0.685E 00	0.560E 00	0.347E 00
0.432E 03	0.685E 03	0.675E 03	0.422E 03	0.140E 03	0.673E 01	0.200E 01	0.135E 02
0.110E 04	0.181E 04	0.208E 04	0.205E 04	0.192E 04	0.920E 02	0.253E 00	0.141E 01
0.100E 01	0.105E 01	0.125E 01	0.208E 01	0.324E 01	0.323E 01	0.320E 01	0.302E 01
0.228E 00	0.243E 00	0.296E 00	0.453E 00	0.691E 00	0.689E 00	0.564E 00	0.388E 00
0.668E 03	0.729E 03	0.762E 03	0.253E 03	0.308E 02	0.148E 01	0.760E 01	0.479E 02
0.172E 04	0.206E 04	0.209E 04	0.198E 04	0.420E 03	0.202E 02	0.103E 01	0.597E 01
0.995E 00	0.102E 01	0.113E 01	0.150E 01	0.324E 01	0.323E 01	0.319E 01	0.283E 01
0.227E 00	0.234E 00	0.265E 00	0.356E 00	0.691E 00	0.689E 00	0.568E 00	0.388E 00

Table 4 (continued)

0.582E 03	0.754E 03	0.666E 03	0.408E 03	0.140E 03	0.670E 01	0.328E 00	0.175E-01	0.993E-03
0.149E 04	0.202E 04	0.212E 04	0.204E 04	0.192E 04	0.919E 02	0.448E 01	0.235E 00	0.114E-01
0.101E 01	0.107E 01	0.127E 01	0.210E 01	0.324E 01	0.324E 01	0.323E 01	0.316E 01	
0.230E 00	0.247E 00	0.302E 00	0.457E 00	0.891E 00	0.690E 00	0.689E 00	0.676E 00	
0.748E 03	0.735E 03	0.544E 03	0.255E 03	0.305E 02	0.147E 01	0.733E-01	0.394E-02	
0.196E 04	0.212E 04	0.209E 04	0.198E 04	0.419E 03	0.202E 02	0.100E 01	0.521E-01	
0.997E 00	0.163E 01	0.115E 01	0.152E 01	0.325E 01	0.324E 01	0.323E 01	0.323E 01	0.296E 01
0.227E 00	0.237E 00	0.270E 00	0.361E 00	0.692E 00	0.690E 00	0.688E 00	0.685E 00	0.581E 00
0.660E 03	0.775E 03	0.551E 03	0.800E 03	0.139E 03	0.668E 01	0.324E 00	0.778E-03	
0.170E 04	0.211E 04	0.212E 04	0.203E 04	0.191E 04	0.917E 02	0.444E 01	0.223E 00	0.948E-02
0.101E 01	0.108E 01	0.129E 01	0.211E 01	0.325E 01	0.324E 01	0.324E 01	0.319E 01	
0.231E 00	0.250E 00	0.306E 00	0.461E 00	0.692E 00	0.691E 00	0.690E 00	0.682E 00	
0.782E 03	0.728E 03	0.530E 03	0.252E 03	0.304E 02	0.146E 01	0.716E-01	0.356E-02	
0.206E 04	0.214E 04	0.208E 04	0.197E 04	0.418E 03	0.201E 02	0.981E 00	0.479E-01	
0.999E 00	0.104E 01	0.117E 01	0.154E 01	0.325E 01	0.324E 01	0.324E 01	0.300E 01	
0.228E 00	0.239E 00	0.274E 00	0.365E 00	0.692E 00	0.691E 00	0.690E 00	0.585E 00	
0.694E 03	0.776E 03	0.636E 03	0.393E 03	0.139E 03	0.665E 01	0.321E 00	0.696E-03	
0.179E 04	0.214E 04	0.211E 04	0.203E 04	0.191E 04	0.914E 02	0.441E 01	0.216E 00	0.860E-02
0.102E 01	0.109E 01	0.131E 01	0.212E 01	0.325E 01	0.325E 01	0.324E 01	0.320E 01	
0.233E 00	0.253E 00	0.310E 00	0.464E 00	0.692E 00	0.692E 00	0.691E 00	0.684E 00	
0.791E 03	0.714E 03	0.518E 03	0.250E 03	0.304E 02	0.145E 01	0.705E-01	0.338E-02	
0.210E 04	0.214E 04	0.207E 04	0.197E 04	0.418E 03	0.200E 02	0.967E 00	0.457E-01	
0.100E 01	0.105E 01	0.118E 01	0.155E 01	0.325E 01	0.325E 01	0.324E 01	0.301E 01	
0.228E 00	0.241E 00	0.277E 00	0.368E 00	0.692E 00	0.692E 00	0.691E 00	0.587E 00	
0.705E 03	0.768E 03	0.624E 03	0.387E 03	0.683E 01	0.318E 00	0.154E-01	0.658E-03	
0.183E 04	0.215E 04	0.211E 04	0.202E 04	0.191E 04	0.912E 02	0.438E 01	0.211E 00	0.818E-02
0.102E 01	0.110E 01	0.132E 01	0.213E 01	0.325E 01	0.325E 01	0.325E 01	0.321E 01	
0.234E 00	0.256E 00	0.313E 00	0.466E 00	0.692E 00	0.692E 00	0.691E 00	0.685E 00	
0.791E 03	0.704E 03	0.508E 03	0.249E 03	0.303E 02	0.145E 01	0.697E-01	0.329E-02	
0.211E 04	0.213E 04	0.206E 04	0.197E 04	0.417E 03	0.199E 02	0.957E 00	0.445E-01	
0.100E 01	0.105E 01	0.119E 01	0.156E 01	0.325E 01	0.325E 01	0.325E 01	0.301E 01	
0.225E 00	0.243E 00	0.280E 00	0.370E 00	0.692E 00	0.692E 00	0.692E 00	0.587E 00	
0.707E 03	0.760E 03	0.613E 03	0.383E 03	0.139E 03	0.661E 01	0.316E 00	0.638E-03	
0.184E 04	0.214E 04	0.210E 04	0.202E 04	0.191E 04	0.910E 02	0.435E 01	0.208E 00	0.795E-02
0.102E 01	0.111E 01	0.133E 01	0.214E 01	0.325E 01	0.325E 01	0.325E 01	0.321E 01	AR (HNO ₃)
0.235E 00	0.258E 00	0.316E 00	0.468E 00	0.692E 00	0.692E 00	0.692E 00	0.686E 00	OR (HNO ₃)
0.786E 03	0.694E 03	0.501E 03	0.247E 03	0.303E 02	0.144E 01	0.691E-01	0.323E-02	AR (H ₂)
0.211E 04	0.213E 04	0.206E 04	0.196E 04	0.417E 03	0.199E 02	0.950E 00	0.437E-01	OR (H ₂)

END-OF-DATA ENCOUNTERED ON SYSTEM INPUT FILE.

Stage 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

Scrubbing Feed Extraction

6. Conclusions

The distribution data of plutonium, under low concentration below several g/l, which have been published so far and have newly been obtained, are summarized for the system of 30 v/o TBP-HNO₃-U.

For the system without uranium, much data have been published and representative distribution curves and equations are obtained.

For the system with uranium, the published data disperses widely even under the constant condition and only acceptable curves and numerical equations are expressed based upon the mass action law.

In the present paper, the distribution data for only low concentration of plutonium, where loading effect is negligible, are summarized. Further experiments must be awaited for high concentration of plutonium with various concentration of TBP which will become necessary in an aqueous reprocessing of fast breeder reactor fuels. The exact plutonium distribution data in the system with large quantities of uranium, are not enough to determine the representative distribution curves even for low concentration of plutonium.

A calculation code for the system of TBP-HNO₃-Pu is programmed for evaluating the plutonium purification process with TBP. Theoretical stages required and concentration profiles under steady or transient state for nitric acid and plutonium, can be computed under a given condition.

Calculation completes within 20 sec. for one run, including printing time.

In the present work, three component system of TBP-HNO₃-Pu of standard flowsheets is studied and only purification process of plutonium could be analyzed with dilute plutonium concentration.

In order to cover all the reprocessing process, it must further be extended to three component system of concentrated plutonium, four component system of TBP-HNO₃-Pu-U and finally to the multicomponent system of TBP-HNO₃-Pu-U-F.Ps. (fission products)

The attempt for the first two is undertaken by the Reprocessing Group of PNC (Japan)⁽²⁴⁾ based on the present study.

Further study must also be done for solving the tailing phenomenon in dilute concentration of plutonium and for deriving kinetic equations for the plutonium reduction separation with uranous nitrate.

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Symbols

- Letters

- CV ; coefficient of variation (%)
 EF ; single stage efficiency defined by Eq. (28)
 K' ; apparent equilibrium constant
 \bar{K} ; average "
 N ; total concentration of nitrate ion
 = $2x_U + x_H$
 T_f ; concentration of free TBP
 = $T_i - 2y_U - y_H$
 T_i ; initial concentration of TBP
 k_d ; distribution-ratio = (y/x)
 k_d' ; apparent distribution ratio
 m ; solvation number
 n ; number of nitrate ion dependency
 x ; molar concentration in aqueous phase
 y ; molar concentration in organic phase

- Roman numerals indicate valencies.

- (III) ; tri-valence
 (IV) ; tetra-valence
 (VI) ; hexa-valence

- Suffixes

- f ; free
 H ; nitric acid
 i ; initial
 NO₃⁻ ; nitrate ion
 Pu ; plutonium
 U ; uranium

Other Symbols are shown Appendix II.

References

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Appendix I Experimental conditions for measuring distribution ratio of plutonium

1.1 Chemicals

- 1) Plutonium was purified by an ordinary anion-exchange procedure. Pu(III) was arranged by the reduction of Pu with uranous nitrite. Pu(IV) was obtained by the oxidation of Pu(III) with sodium nitrite. The valency adjusted was confirmed by a spectro-photometry.
- 2) Uranyl nitrate was used of the first grade reagent. Uranous nitrate was obtained by an electrolysis of uranyl nitrate in the system of $\text{HNO}_3\text{-H}_2\text{NNH}_2$.
- 3) Other reagents as nitric acid were extra-pure reagents.
- 4) TBP (Tri-n-butyl phosphate), which satisfies the specification of the JAERI, Reprocessing Test Plant, was used without further purification. Dodecane as a diluent, which passed the specification of the French CEA, was imported from France (Progil).

1.2 Experimental Procedure

An equal volume of 30 v/o TBP/dodecane, which was pre-equilibrated with a nitric acid solution under consideration, and of aqueous solution containing nitric acid, plutonium, uranium and/or other reagents, were shaken for 1 to 2 minutes to attain an equilibrium.

After the phase separation (10 mins. of settling), analytical samples were taken from both the organic and aqueous phases.

Elapsed time dependency after settling was also followed when necessary.

All the extractions were performed at room temperature. ($\sim 25^\circ\text{C}$)

1.3 Analytical Method

The concentration of plutonium was determined by α -counting.

Nitric acid was analyzed by the titration with sodium hydroxide.

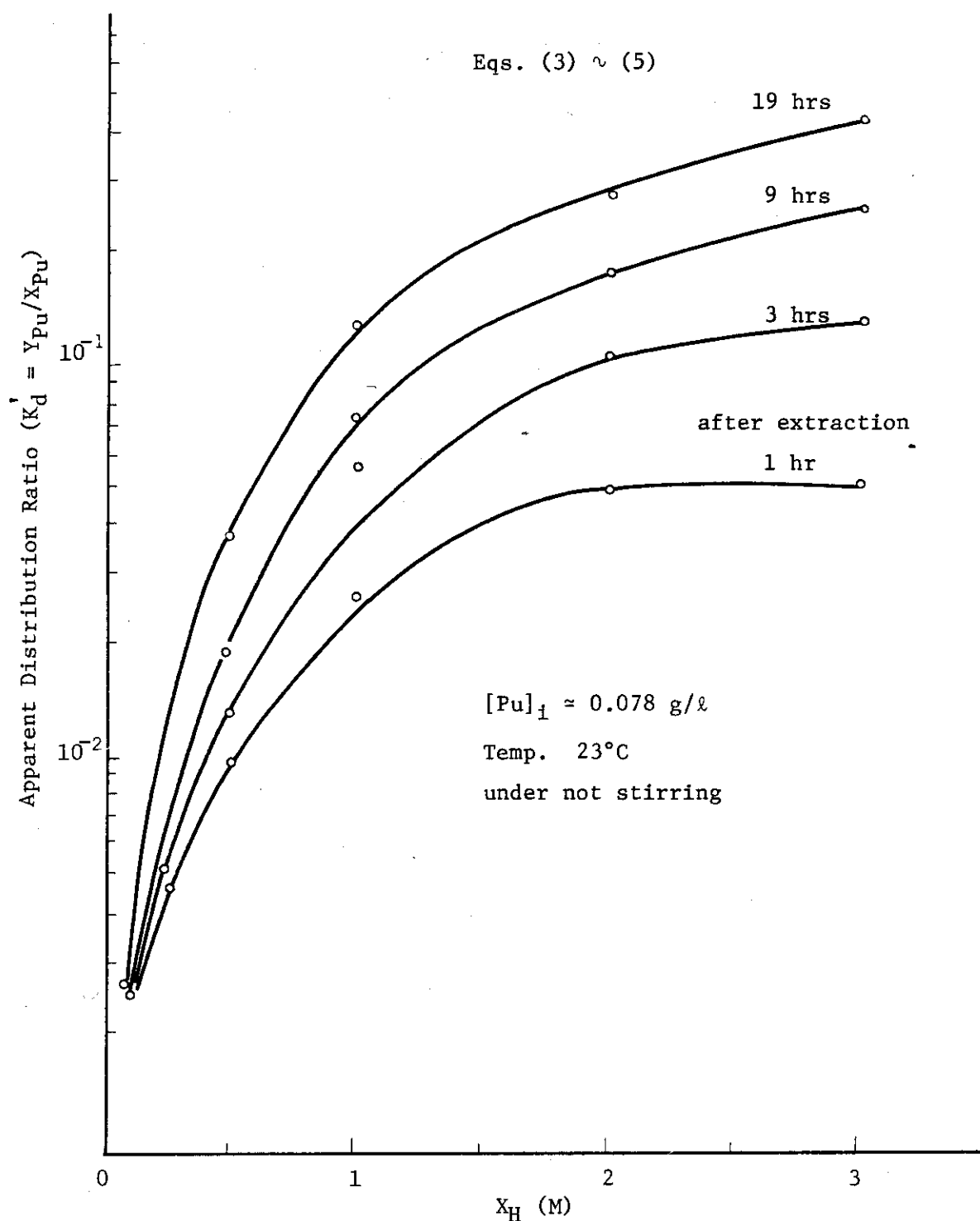
Uranium was determined by the spectrophotometry with hydrogen peroxide.

Appendix II Keys for the Material Balance (Fig. 7)
and the Flow Chart (Fig. 8)

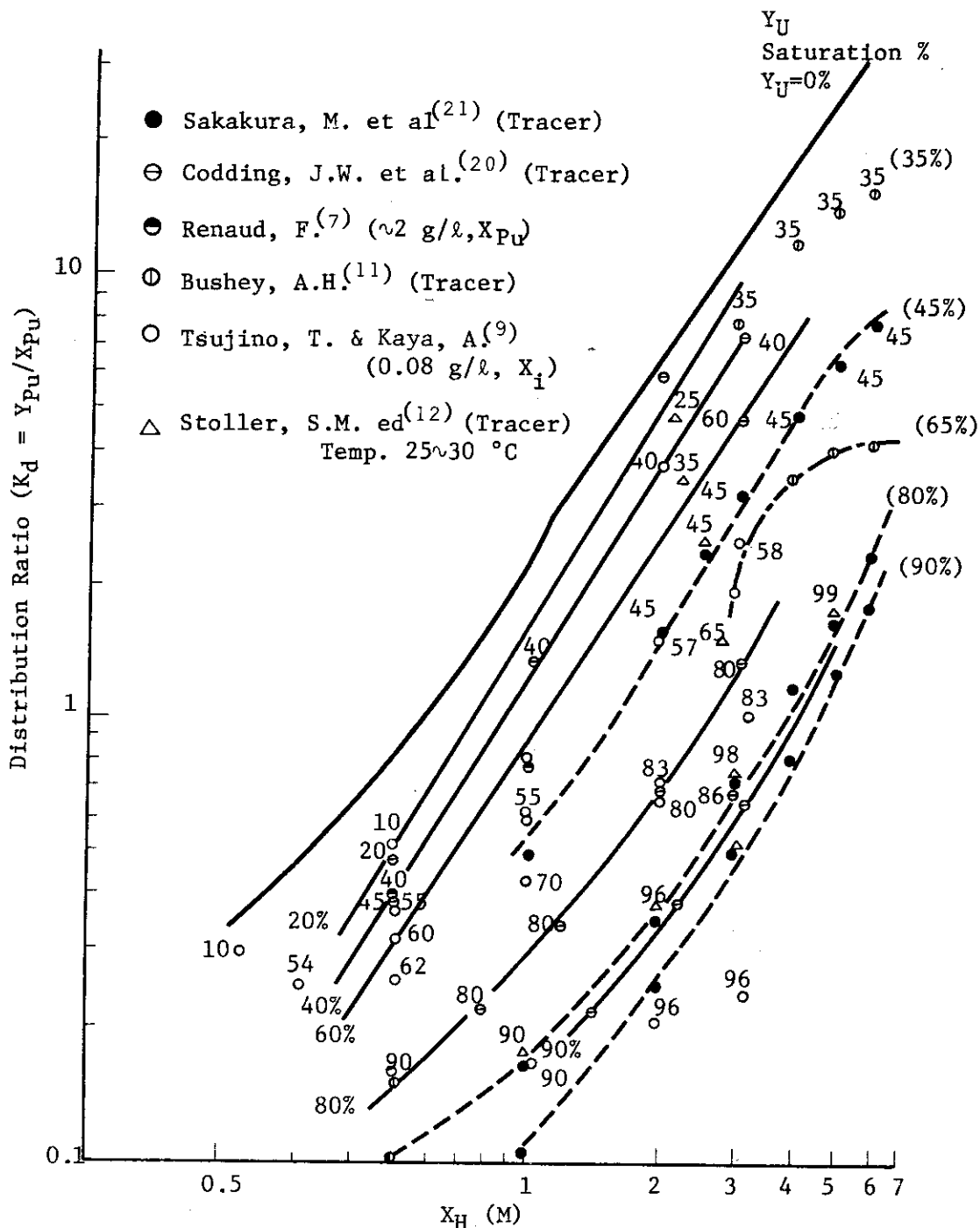
A, B, C, D	; Coefficients for Eq. (I)
A', B', C', D'	; " for Eq. (II)
DFV	; Flow rate of feed solution
DSV	; " of scrubbing solution
DXV	; " of solvent
E	; Total contents in the system (Material Balance)
EF	; Stage efficiency
EFSH	; " in scrubbing section for HNO ₃
EFSP	; " in " for Pu
EFXH	; " in feed and extraction section for HNO ₃
EFXP	; " for Pu
F	; Feed content $DFV \times x_{i,f}$
G	; Coefficients for Eq. (II) and (III) (IV)
J	; Index for cycle no.
K	; Cycle no.
N	; Index for stage no.
k	; Stage no.
n	; Index
x	; mol-concentration in aqueous phase
y	; " in organic phase
$\alpha, \beta, \gamma,$; Coefficient for Eq. (III) (IV)

Suffix

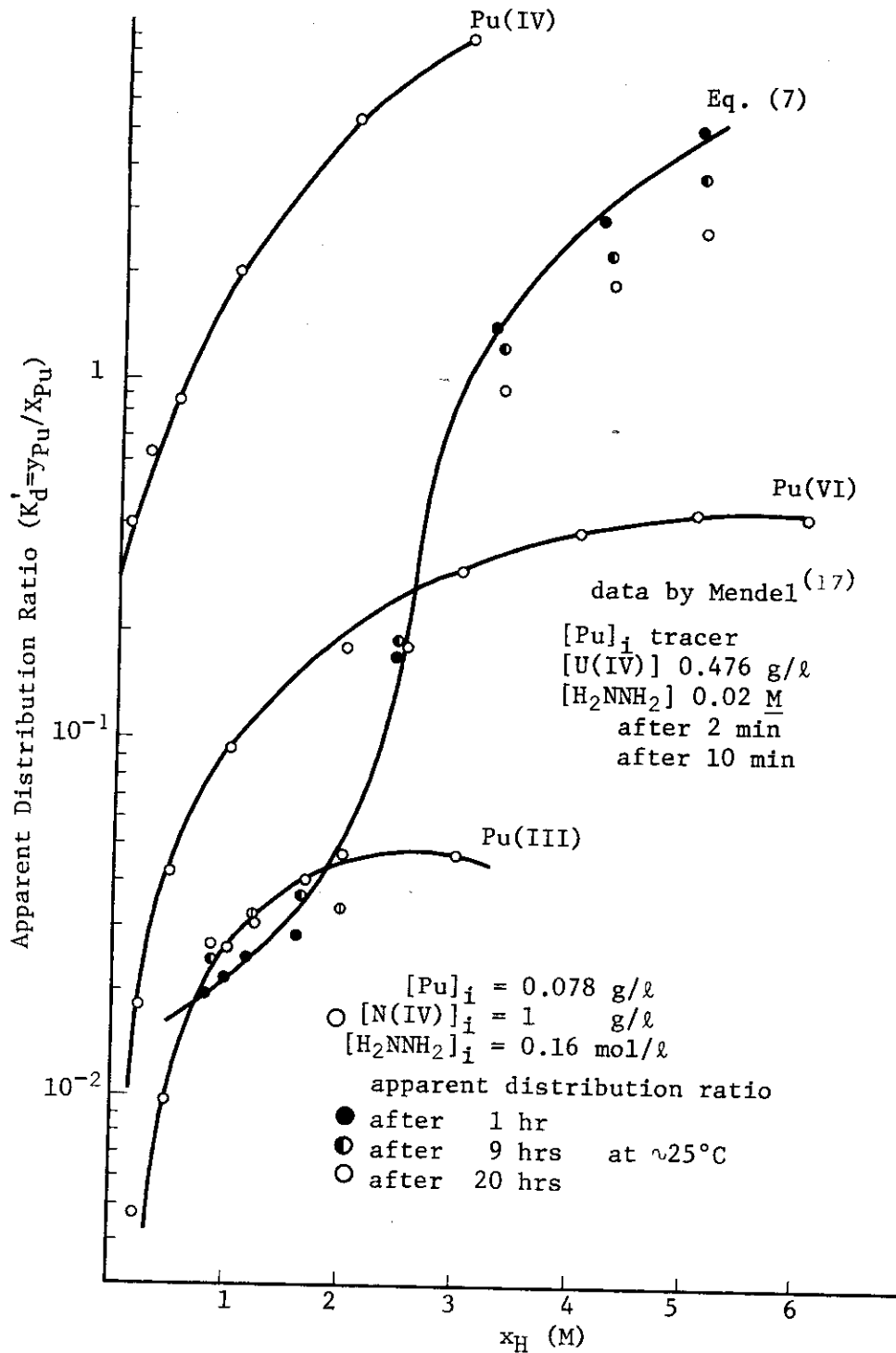
H	; for HNO ₃
P	; for Pu
f	; feed
i	; i-species
k	; k-stage



Appendix Fig. 1 Apparent Distribution Ratio of Plutonium (III) in the HNO_3 -30 v/o TBP⁽⁹⁾



Appendix Fig. 2 Summarized Distribution Data of Plutonium (IV) in the HNO₃-UO₂(NO₃)₂-30 v/o TBP



Appendix Fig. 3 Reduction of Pu(IV) with U(IV) in the HNO₃-30 v/o TBP⁽⁹⁾