

DEVELOPMENT OF PARTITIONING PROCESS IN JAERI

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ABSTRACT

One of the methods to manage HLLW generated from nuclear fuel reprocessing is to partition long-lived transuranic elements (TRU) and heat-generating nuclides such as Fr-90 and Cs-137 from HLLW, and then to transmute TRU to shorter-lived or stable nuclides by a fission process and to fix Sr-90 and Cs-137 in mineral-like stable compounds.

Since 1985, many efforts have been directed to developing an advanced partitioning process for separating elements in HLLW into four groups; TRU, Tc-platinum group metals (PGM), Sr-Cs and the other elements. The latest studies were focused on the separation of the TRU group, the pretreatment of HLLW for the TRU extraction and the separation of the Tc-PCM group.

Through these fundamental studies, the advanced partitioning process has been constructed and its effectiveness will be demonstrated with an actual HLLW in the near future.

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1. [introduction

Partitioning of nuclides such as transuranium elements (TRU), Tc-99, Sr-90 and Cs-137 in a high-level liquid waste (HLLW) generated in nuclear fuel reprocessing and transmutation of long-lived nuclides by nuclear reactions are expected to increase the efficiency of high-level waste disposal and will seek the utilization of existing resources in a spent fuel.

2. Progress of our research activity

From 1973 to 1984, a partitioning process was developed for separating elements in HLLW into three groups; TRU, Sr-Cs and others.

The process shown in Fig. 1 consists of three steps; the first is solvent extraction of U and Pu with tributylphosphate (TBP) and the second is solvent extraction of Am and Cm with diisodecylphosphoric acid (DIDPA), and the third is adsorptions of Sr and Cs with inorganic ion exchangers.

The three group partitioning process was demonstrated by using an actual HLLW and it was confirmed that more than 99.99% of Am and Cm could be extracted with DIDPA.

The preliminary assessment study indicated that the cost for the construction and the operation of a partitioning plant becomes less than 5% of that of a Purex plant, provided that the partitioning plant is operated in connection with the Purex plant.

After 1985, a four group partitioning process has been developed in which a step for separating Tc-platinum group metals (PGM) was developed in addition to the three group separation. The latest studies are focused on developing effective methods for (1) the separation of TRU, especially Np, (2) the separation of Am and Cm from rare earths, (3) the treatment of HLLW prior to the TRU extinction and (4) the separation of Tc-PGM group, especially Tc.

3. Separation of TRU, especially Np

Experiments on a counter-current continuous extraction using a miniature

mixer-settler were carried out to determine the conditions for extracting Np initially in a penta-valent state with diisodecylphosphoric acid (DIDPA), of which effectiveness for the complete extraction of Am, Cm and Pu was confirmed in the three group partitioning process, and experiments were carried out to make the behavior of other elements clearer in the extraction process.

Figure 2 shows the operating condition of a 16-stage miniature mixer-settler. In case (a), 7 stages were used for the Np extraction and in case (b) 14 stages were used. These mixer-settlers were operated at 25 or 45 C.

Table 1 shows the experimental condition and the percentage of Np extracted. The percentage was increased by raising temperature and by the addition of hydrogen peroxide. When a simulated HLLW was used as a feed solution, the Np extraction was further accelerated by a catalytic effect of some elements containing in the simulated waste.

As to the Runs No.14 and 15, concentration profiles of Np in the aqueous phase at the extraction stages are shown in Fig. 3. The rate of Np extraction was faster just after the points where hydrogen peroxide was added. The extraction rate became slow as the hydrogen peroxide was decomposed. When hydrogen peroxide was 're-added' so as to compensate for its decomposition, the extraction rate was increased again and more than 99.96% of Np was found to be extracted in the 14-stage extraction.

Table 2 shows the behavior of fission and corrosion products in the continuous center-current extraction under the experimental condition corresponding to Run No.10 shown in Table 1. It was confirmed that more than 99.99% of Nd, which was used as a stand-in for rare earths, Am and Cm, was recovered by back-extraction with 4 M nitric acid. Most of iron was extracted with DIDPA, but not back-extracted with 4 M nitric acid. Therefore, Fe could be separated from Nd with a decontamination factor of about 10. About 6% of Ru and 11% of Rh were extracted in this experiment. Their extraction behavior might be changed in a practical application because their chemical forms seem to differ in an actual HLLW. Almost all Cs and Sr were transferred to the raffinate fraction and Nd was found to be completely separated from these heat generating nuclides in HLLW.

Back-extraction behavior of Np and elements remaining in the DIDPA solvent was also studied with 0.8M oxalic acid solution. Fig. 4 shows the concentration profile of Np. More than 99.9% of Np was found to be

back-extracted with oxalic acid solution. About 97% of Fe was back-extracted together with Np. As for the other two extracted elements, about 98% of Rh could be back-extracted, but about 80% of Ru remained in the DIDPA solvent.

The present experiments on the counter current continuous extraction and back-extraction offered a promising prospect of separating TRU from HLLW by the DIDPA extraction process consisting of the three steps shown in Fig. 5; the first, simultaneous extraction of TRU with the DIDPA solvent, the second, back-extraction of tri-valent Am, Cm and rare earths with 4 M nitric acid, and the third, back-extraction of tetra-valent TRU, Np and Pu, with oxalic acid. In this **flowsheet**, it is assumed that Am and Cm are separated from rare earths by using a cation exchanger column.

4. Separation of Am and Cm from rare earths

In order to develop a more continuous process, we are now developing a preferential back-extraction of Am and Cm, leaving rare earths in the DIDPA solvent. Figure 6 shows the pH dependence of the distribution ratio of Am and Nd in the back-extraction from the DIDPA solvent with diethylenetriaminepentaacetic acid (DTPA). The separation factor between two elements became more than 10. Figure 7 shows the comparison of distribution ratio of Am with those of rare earths- The distribution ratio of Sm was the nearest to that of Am. In addition to these experiments, the change of pH caused by the extraction of ammonium ion was also experimented.

From these results we estimated the behavior of each element in continuous back-extraction. Table 3 shows the decontamination factor (DF) of rare earths from Am and Cm, and the concentration ratio of rare earths to Am and Cm. The DF of Sm is the lowest, but it reaches 90. On the condition that 99.99% of Am and Cm are recovered, the contamination of rare earths becomes about 10%. A continuous extraction is being studied to examine the actually obtainable DF.

When this method is applied to the separation of Am and Cm, the **flowsheet** will be modified as shown in Fig. 8. After the simultaneous extraction of TRU and rare earths, Am and Cm are preferentially back-extracted with DTPA and then rare earths are back-extracted with 4 M nitric acid.

5. Treatment of HLLW prior to the TRU extraction

Prior to the solvent extraction of TRU, nitric acid concentration of HLLW should be reduced from about 2 M to about 0.5 M by denigration. The

precipitation behavior of Pu, Np and Am during the denigration of HLLW with formic acid was studied by using a simulated HLLW.

Table 4 shows the relationship between pH and the percentage of TRU precipitated. The precipitated fractions of TRU increased with decreasing acidity of the denigrated HLLW. In denigration at $[\text{HCOOH}]/[\text{HNO}_3] = 1.5$, which was adopted in the partitioning process developed in our laboratory, the precipitated fractions of Np and Am were only 0.6% and 0.06%, respectively, whereas that of Pu was 93%. Pu was found to be coprecipitated with other elements such as Zr and Mo. Heating and reflux of HLLW also induced the formation of a precipitate including Pu. Therefore, the precipitations of Pu and a small amounts of Np and Am can not be avoided even if HLLW is not denigrated.

The dissolution of the precipitate formed in the denigrated HLLW was also studied using oxalic acid to recover TRU from the precipitate and we found that the precipitate formed in 1 l of the simulated HLLW could be dissolved in a 800ml of 0.5M oxalic acid solution.

Filtration characteristic of the precipitate was also studied using a simulated HLLW. It was found that both precipitates formed by heating the HLLW under refluxing and by 'denigrating the HLLW which was previously heated under refluxing for long time could be easily filtered.

6. Separation of the Tc-PGM group, especially Tc

The separation of the Tc-PGM group, especially focusing on the Tc separation, was studied by using an active carbon column. Figure shows break-through curves of Tc and PGM when a simulated raffinate, which was generated in the TRU extraction with DIDPA, was poured into the column. Tc and Pd were effectively adsorbed on the column, but Rh was adsorbed only a little. The curve of Ru suggests the presence of several chemical species. Other elements including Sr and Cs were not adsorbed on the active carbon column.

Figure 10 shows the elution curves of Tc and PGM when an alkaline potassium thiocyanate solution was used as eluant. Complete elution of Tc was achieved, but it was very difficult to elute Pd quantitatively.

Summary of these results is shown in Table 5. More than 98% of Tc was recovered in the present method, adsorption on the active carbon column and elution with thiocyanate. Pd was also adsorbed completely, but only 18% was eluted. For the recycle use of the column, the elution of Pd and Ru should be studied.

7. Four group partitioning process

Through these fundamental studies, the four group partitioning process was constructed as shown in Fig. 11.

his process includes the two kinds of chemical methods for the Tc-PGM group separation. As to the precipitation method, we found that more than 95% of Tc and PGM could be precipitated when a simulated HLLW was denigrated with formic acid to reduce its acidity to above pH 2. However, this precipitation method was not applicable when a Rh and Pd concentration was lower than 0.005 M.

The four group partitioning process will be demonstrated with an actual HLLW at the NUCEF (Nuclear Fuel Cycle Safety Engineering Research Facility), which is under construction and comes into hot operation in 1994.

TABLE 1

Experimental condition of the continuous counter-current extraction of N_p and the ratio of N_p extracted

Run No.	Temp. ($^{\circ}C$)	Feed solution	Extracting stages	$[H_2O_2]$ in scrub(M)	H_2O_2 Addition Stage	H_2O_2 Addition Cone. (ff)	Extracted (%)
1	25	N_p alone	7	0			24.6
2	45	N_p alone	7	0			45.4
3	25	N_p alone	7	0.5			78.8
4	45	N_p alone	7	0.5		-	92.7
9	25	Sire. HLW	7	0.5			92.1
10	45	Sire. HLW	7	0.5			95.6
12	25	Sire. HLW	7	0.5	3	5.0	95.5
13	45	Sire, HLW	7	0.5	3	5.0	98.2
14	45	Sire. HLW	7	1.0	3	8:0	99.0
15	45	Sire. HLW	14	1.0	3 & 7	8,0	>99, 96

Table 2 Behavior of fission and corrosion products in the continuous counter-current extraction, carried out at Run No. 10

Percentage of each element. distributed in the three fractions

Element	Raffinate	Back-extracted fraction	Organic fraction
Na	>996	0.31	<0.1
Cr	>99.5	0.38	<0.1
Fe	0.13	0.1	99.77
Ni	>99.5	0.44	<0.1
Rb	>99.97	<0.02	<0.01
Cs	>99.99	<0.005	<0.002
Sr	>99.95	0.042	<0.004
Ba	>99.94	0.027	<0.04
Ru	93.53	0.98	5.49
Rh	88.30	1.86	9.84
Pd	>99.5	0.43	<0.02
Nd	0.002	>99.99	<0.006

Table 3 Separation of Am and Cm from RE.
 Preliminary Estimation of Decontamination Factor (DF)
 and Concentration Ratio of RE after Separation

Ele.	In ILLW ¹⁾		Cation Exchange ²⁾		Extraction	
	Conc. (mM)	Ratio ³⁾	DF	Ratio ⁴⁾	DF ⁵⁾	Ratio ⁴⁾
Am	3.07					
Cm	0.16	1.00		1.00		1.00
Y	10.36	3.21	>10 ⁶	<10 ⁻⁵	>10 ⁶	<10 ⁻⁵
La	17.53	5.43	>10 ⁶	<10 ⁻⁵	>10 ⁶	<10 ⁻⁵
Ce	33.80	10.46	>10 ⁶	<10 ⁻⁵	23000	0.0006
Pr	15.86	4.91	>10 ⁶	<10 ⁻⁵	2700	0.0018
Nd	55.62	17.22	>10 ⁶	<10 ⁻⁵	300	0.0574
Pm	0.52	0.16	>10 ⁶	<10 ⁻⁵	120	0.0013
Sm	11.17	3.46	>10 ⁶	<10 ⁻⁵	90	0.0384
Eu	1.83	0.57	>10 ³	<10 ⁻³	120	0.0048
Gd	1.23					
Tb-Er	0.05	0.40	3	0.13	260	0.0015
Total	148.0	45,82	(350)	0.13	(430)	o. 106

1) Calculated on condition that 0.5 m³ of ILLW is generated per t of spent fuel which is ironed up to 33000 MWD/t and reprocessed after 6-years cooling.

2) The method previously developed

3) Ratio of RE concentration to the total concentration of Am and Cm

4) The concentration ratio after separation

5) DF by the extraction is depend on the process condition. These value are obtained as typical ones by calculation on condition that 99,99 % of Am and Cm are recovered.

Table 4 pH and percentage of TRU precipitated during denitration of simulated HLLW

[HCOOH/HNO ₃]	pH	Percentage of TRU precipitated		
		Pu	Np	Am
0.0	-0.4	14	0.34	0.03
1.0	0.1	27	0.54	0.03
1.2	0.3	31	0.54	-
1.4	0.4	76	0.70	-
1.5	0.6	93	0.64	0.06
1.6	1	97	1.20	0.13
1.8	3	98	93	2.0
2.0	5	100	97	42

Table 5 Results of Experiment on Adsorption with Active Carbon and Elution with KSCN

Column: 1 g active carbon, 150 mm long, 7.5 mm diameter
 Feed : 0.5 M HNO₃ solution, 72 ml (50 % break through for Tc)
 Eluate: 2 M KSCN - 4 M NaOH solution, 40 ml
 Flow rate: 5 bed volumes/h both in adsorption and in elution

Element	Feed Cone. (M)	Adsorbed ¹⁾ (mM/g)	Ratio in each fraction (%)		
			Effluent	Eluate	Adsorbent)
Tc	0.0040	0.237	1	>98	<0.5
Ru	0.0085	0.262	51	41	8
Rh	0.0020	0.019	84	2	14
Pd	0.0045	0.269	0	18	82
Others ³⁾	0.534)	0	100	0	0

1) Amount of the element adsorbed before elution

2) Ratio of the element remaining in active carbon after elution

3) Na, Cs, Rb, Sr, Ba, Cr, Fe and Ni

4) Total concentration of the above 8 elements

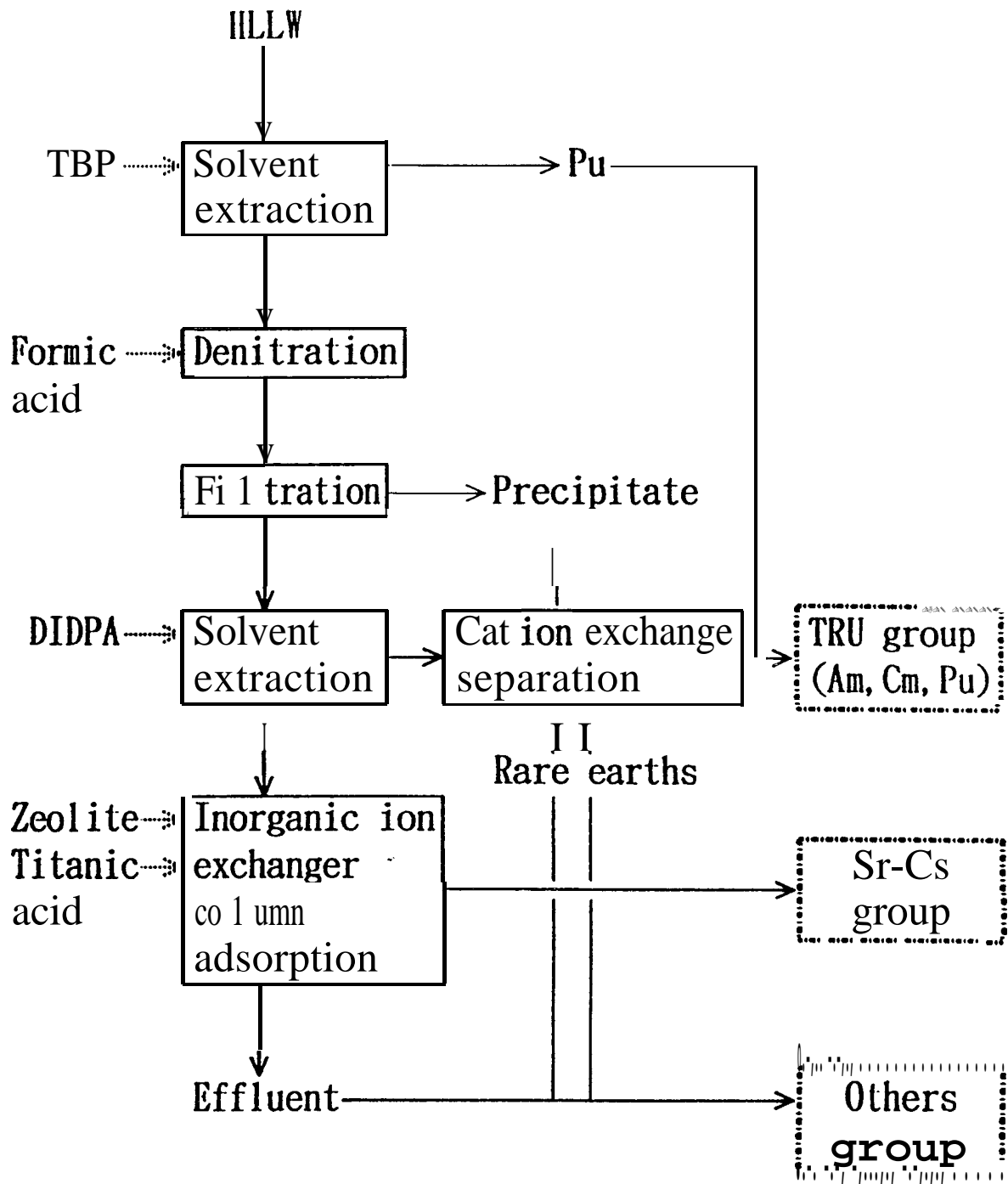


Fig.1 Three group partitioning process demonstrated with actual HLLW

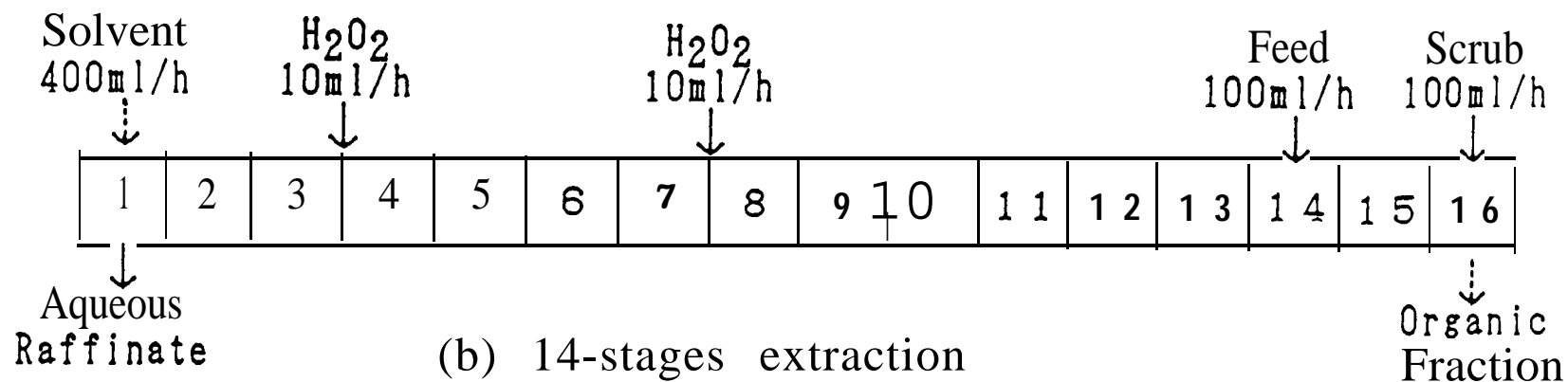
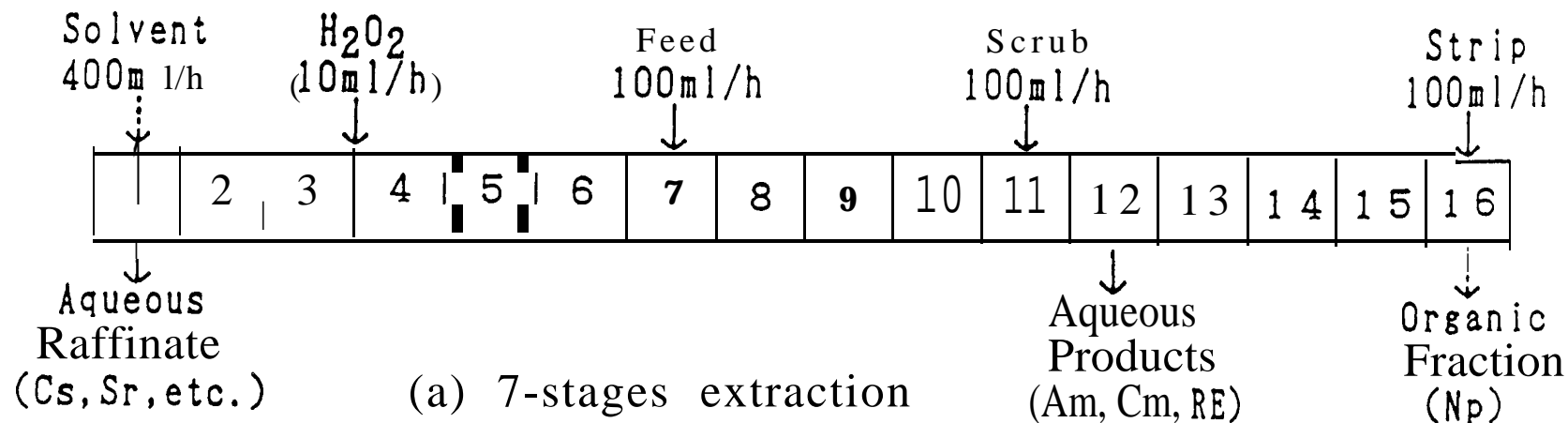


Fig. 2 Operating condition of the mixer-settler

Solvent: 0.5 M DIDPA, 0.1 M TBP in n-dodecane

Feed : 0.5 M HNO₃, NP alone or simulated HLW

Scrub : 0.5 M HNO₃, [H₂O₂] = 0, 0.5, 1.0 M

Strip : 4.0 M HNO₃

H₂O₂ solution: 0.5 M HNO₃, [H₂O₂] = 0, 5.0, 8.0 M

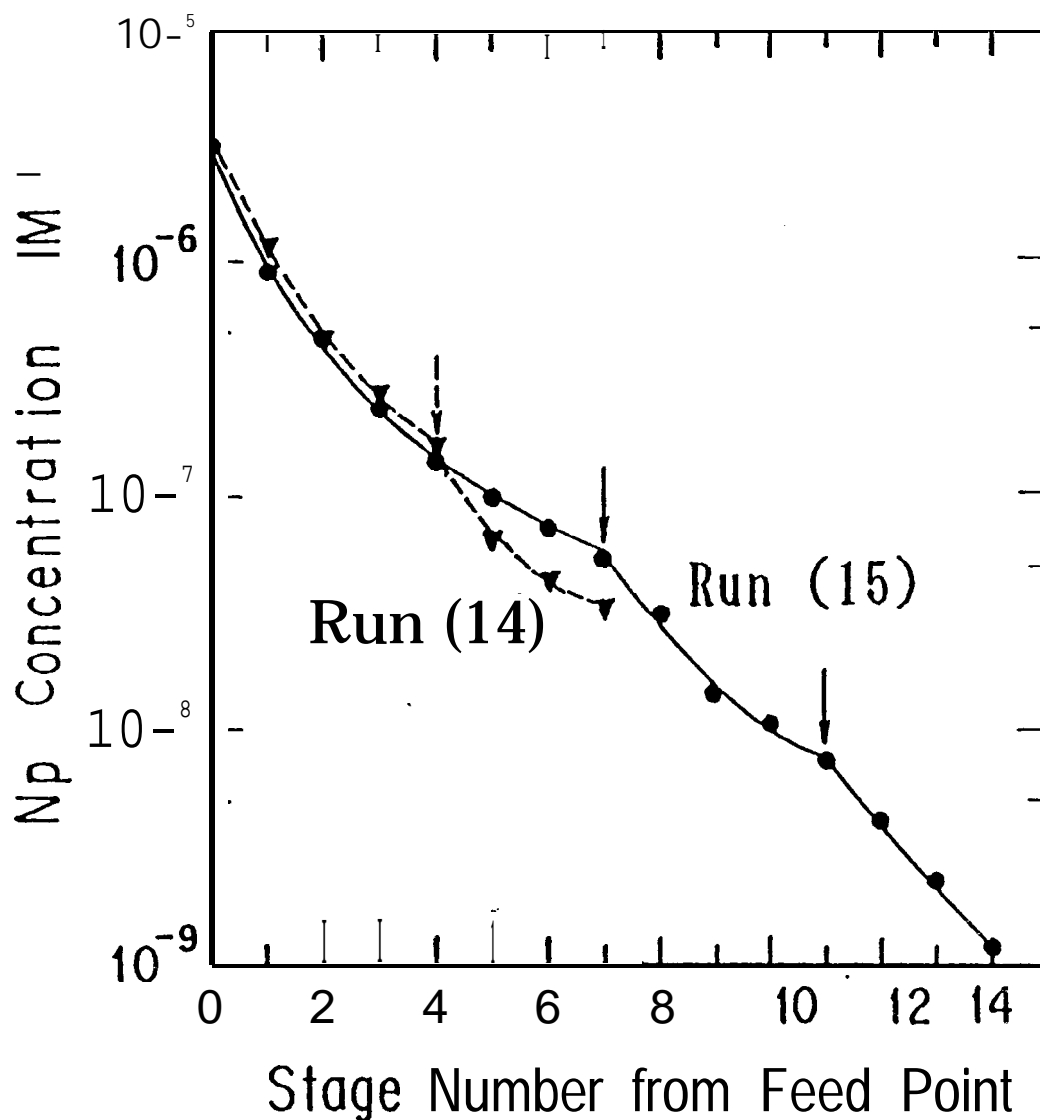


Fig. 3 Concentration profile of Np in aqueous phase at the extraction section. 45 °C
 Downward arrows show the points where H₂O₂ is added.

Run (14) (7-stares) : 99.0 % recovery

run (15) (14-stages): over 99.96 % recovery

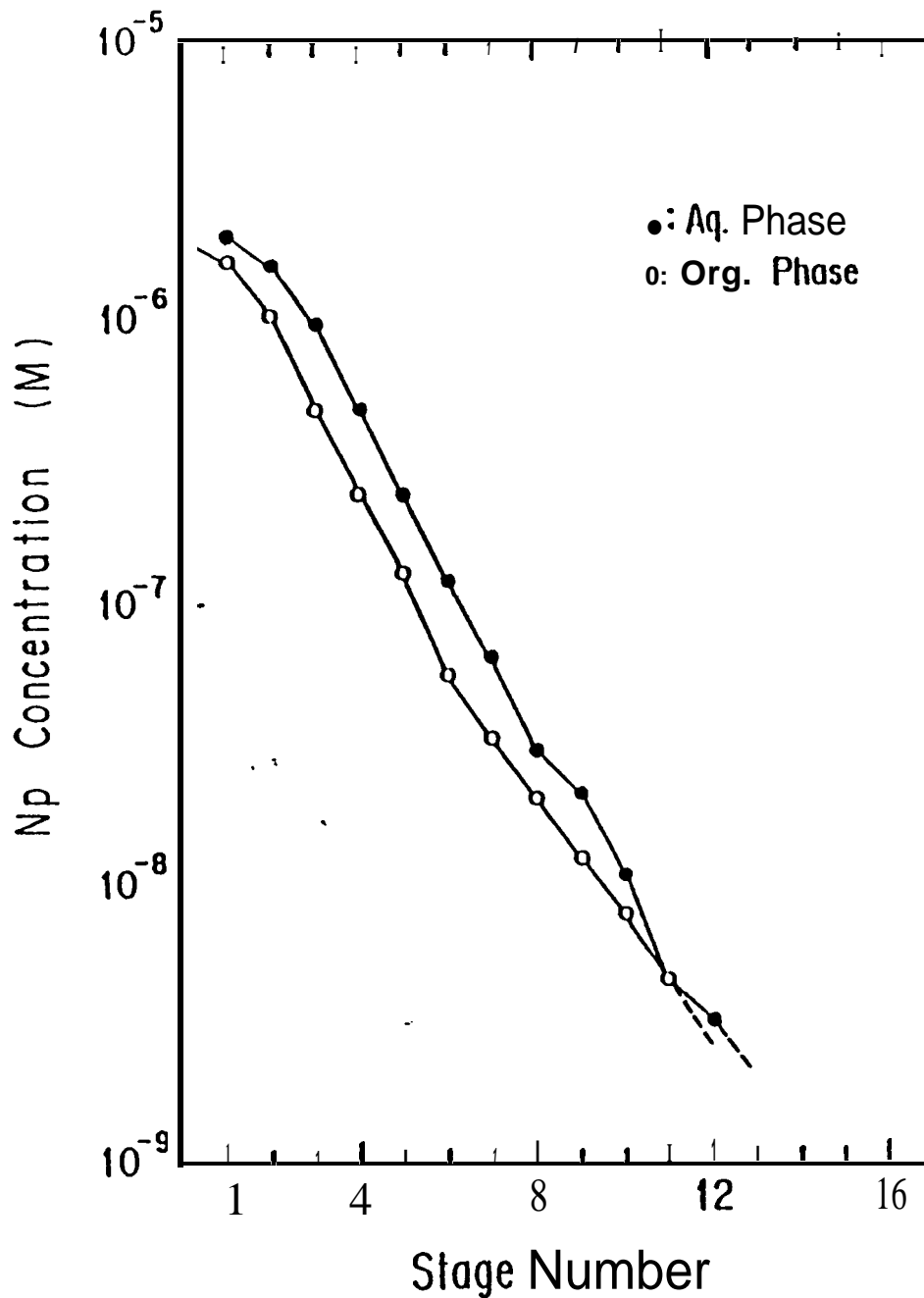


Fig.4 concentration profile of N_P in the 10-stages back-extraction with oxalic acid at 25°C
 Feed: the solvent containing $2 \times 10^{-6} \text{ M } N_P$
 Strip: 0.8 M oxalic acid

Over **99.9 %** of N_P was recovered.

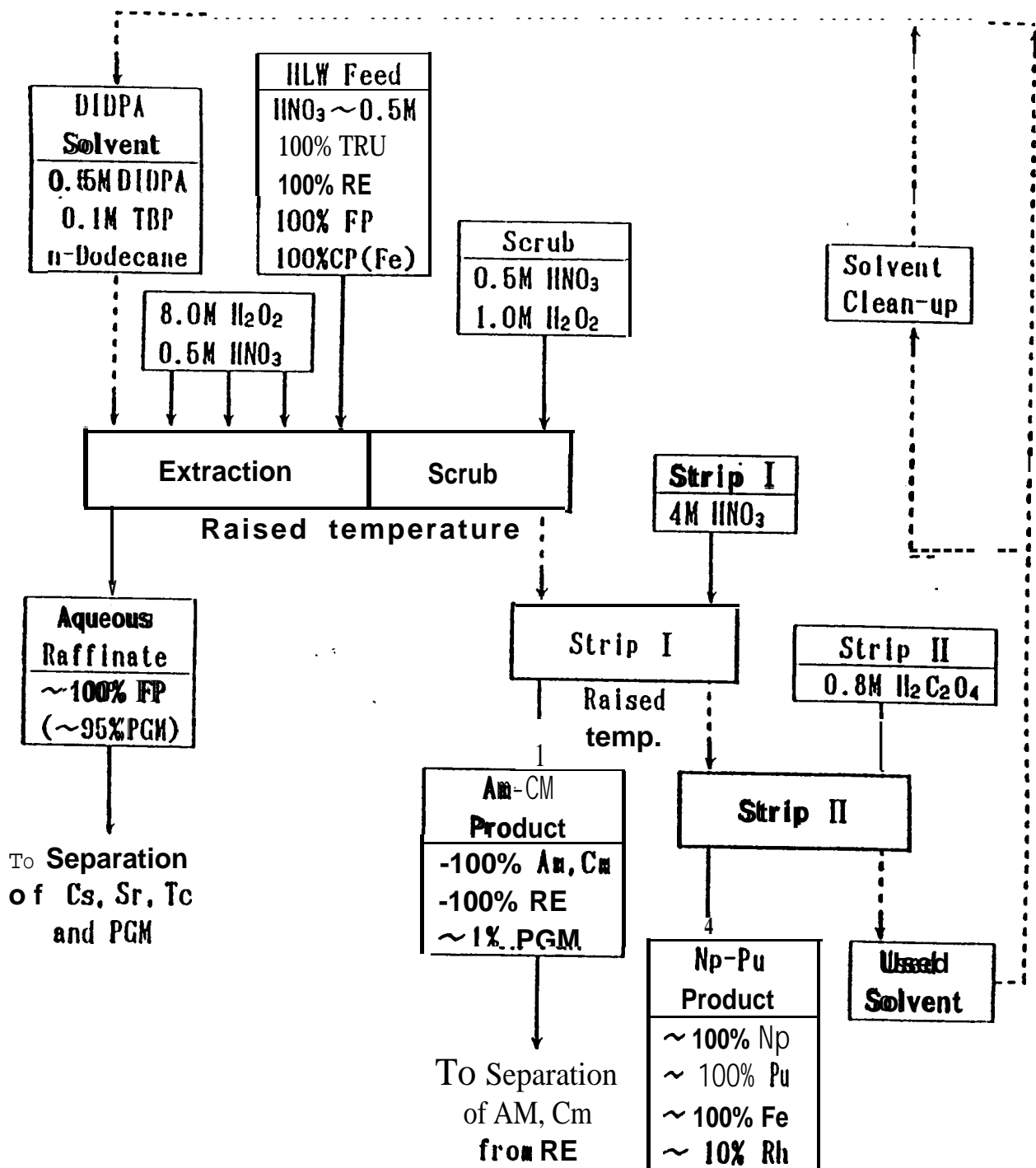


Fig. 5 Process Flowsheet for TRU Separation by Extraction with DIDPA

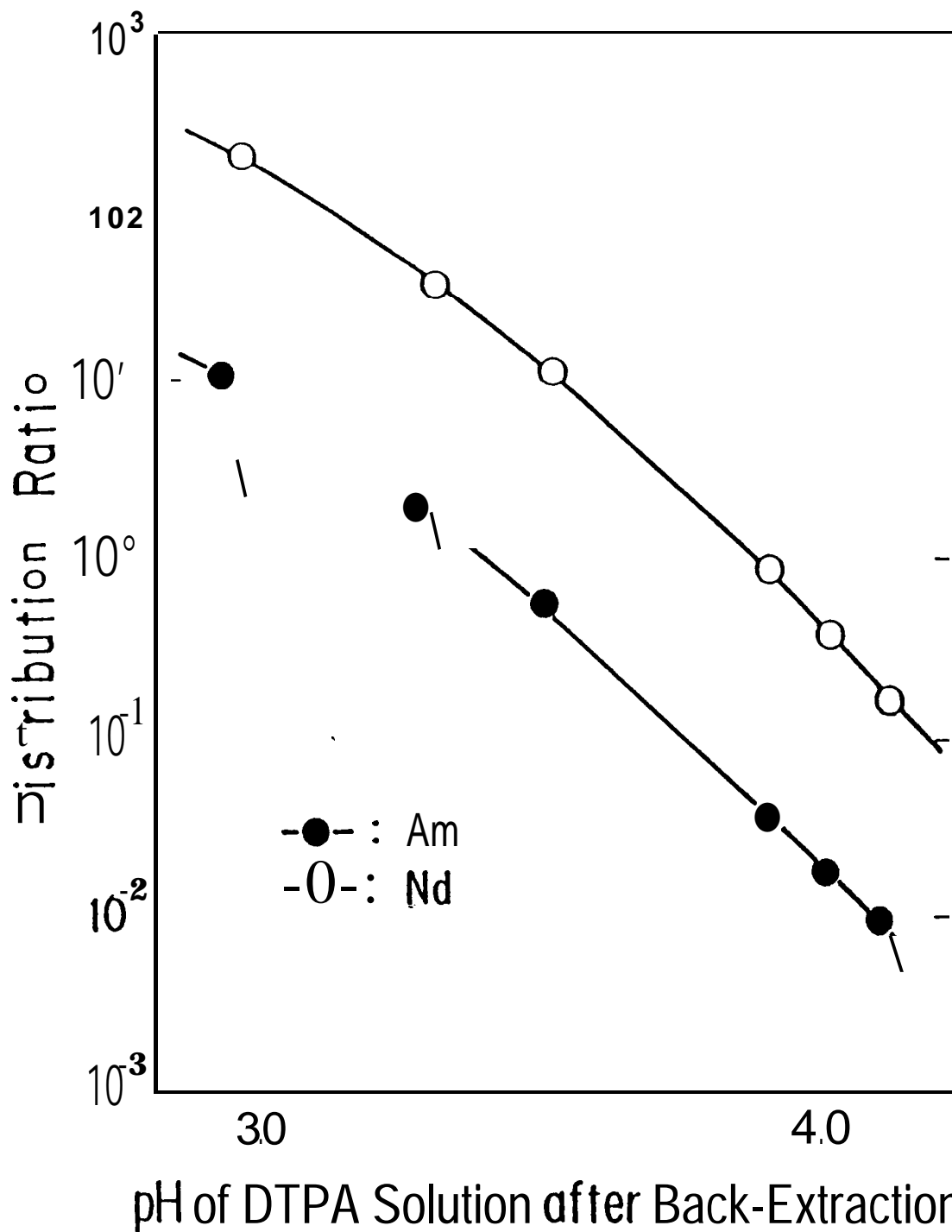


Fig. 6 pH Dependence of Distribution Ratio of Am and Rare Earths in Back-Extraction from DIDPA with DTPA

Org. : 0.5 M DIDPA - 0.1 M TBP in n-dodecane

Aq. : 0.05 M DTPA - 1 M Lactic acid - NH₄OH

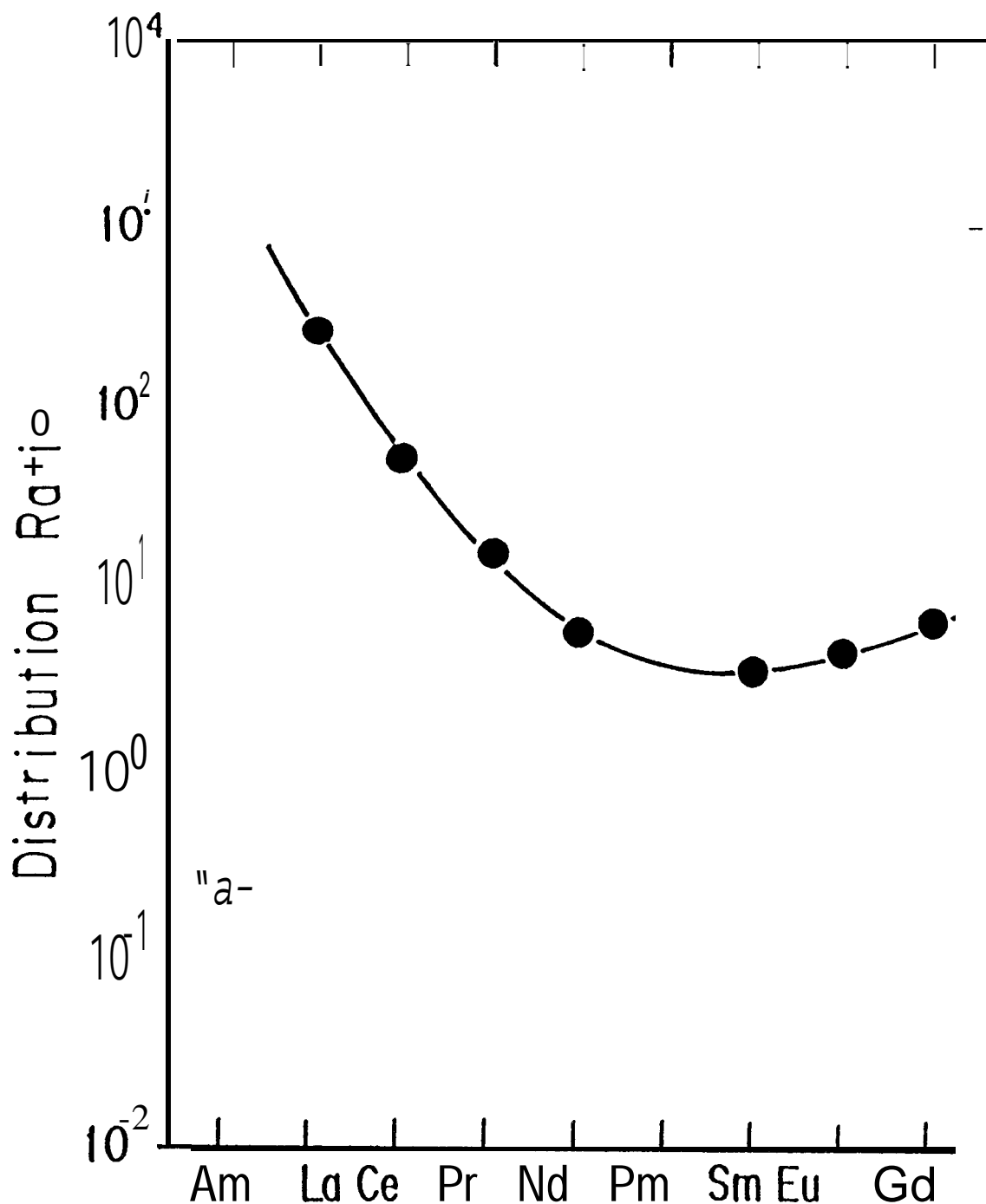


Fig. 7 Comparison of Am Distribution Ratio with That of Rare Earths

org. : 0.5 M DIDPA - 0.1 M TBP in n-dodecane

Aq. : 0.05 M DTPA - 1 M Lactic acid - NH_4OH ,
pH 3.6 after back-extraction

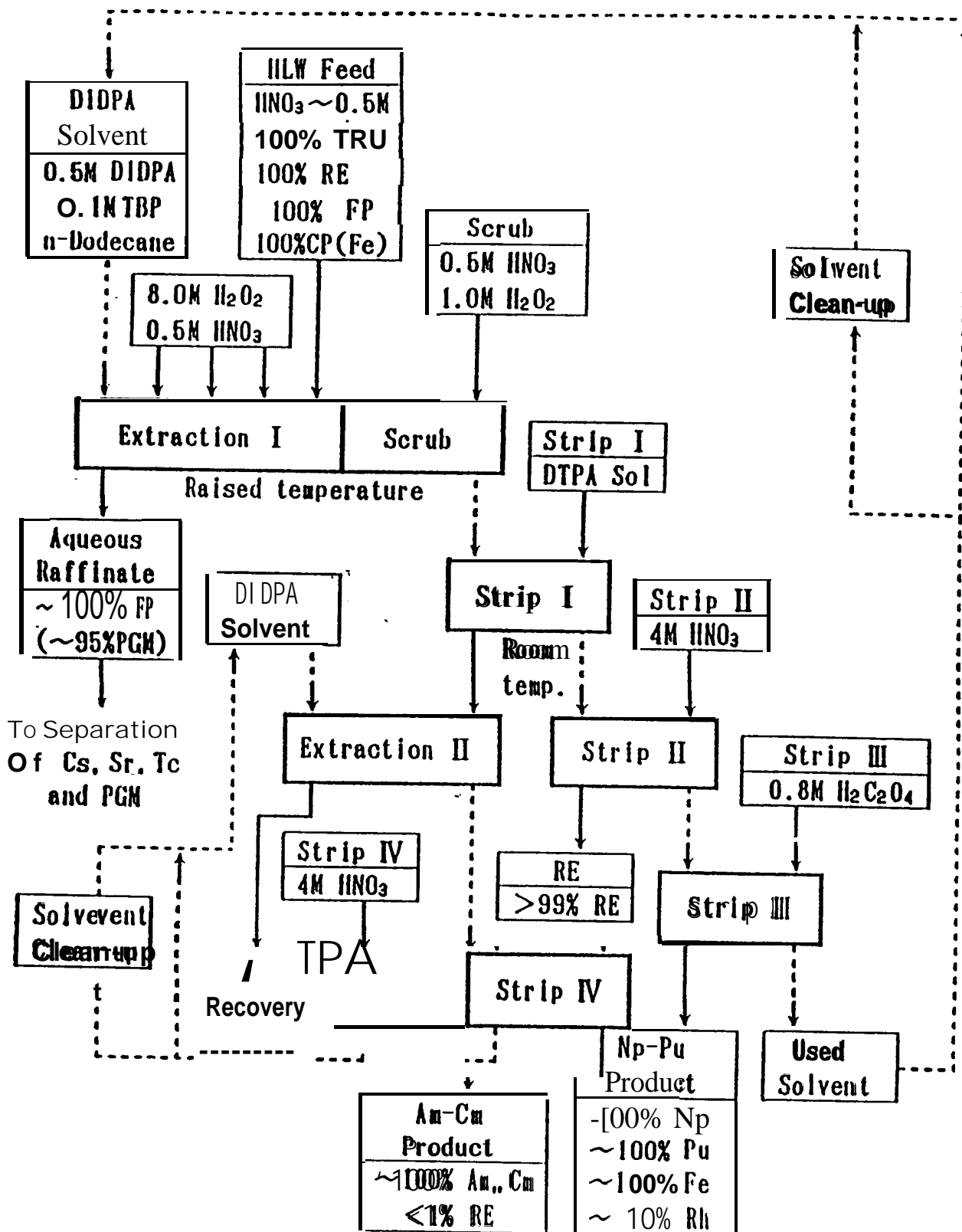


Fig. 8 Process Flowsheet for TRU Separation by Extraction with DIDPA Followed by Selective Back-Extract ion

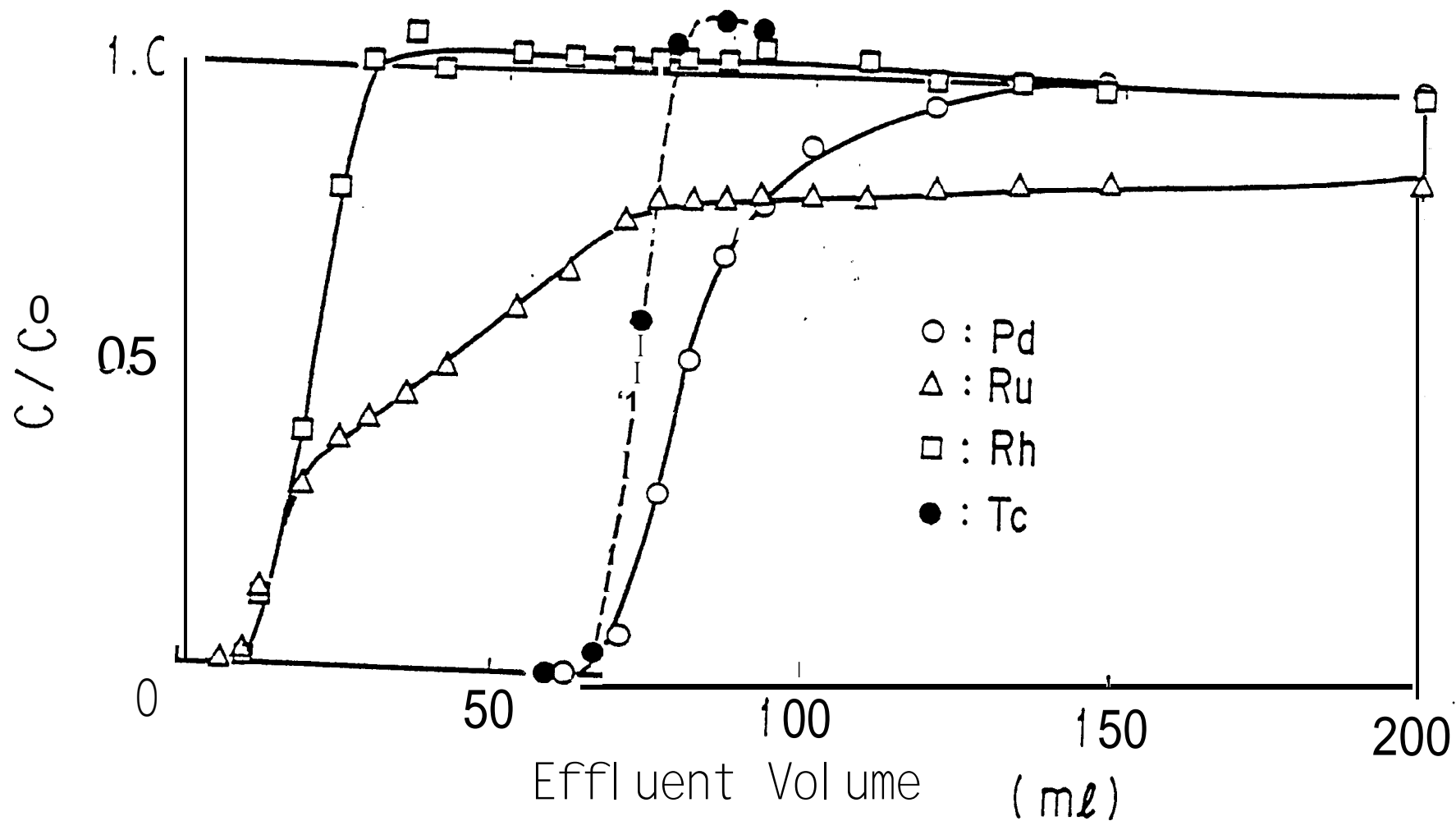


Fig. 9 Break Through Curves of Tc and PGM in Adsorption with an Active Carbon Column

Column: 1 g active carbon, 150 mm long, 7.5 mm diameter
 Feed : 0.5 M HN_3 solution, 5 bed volumes/h

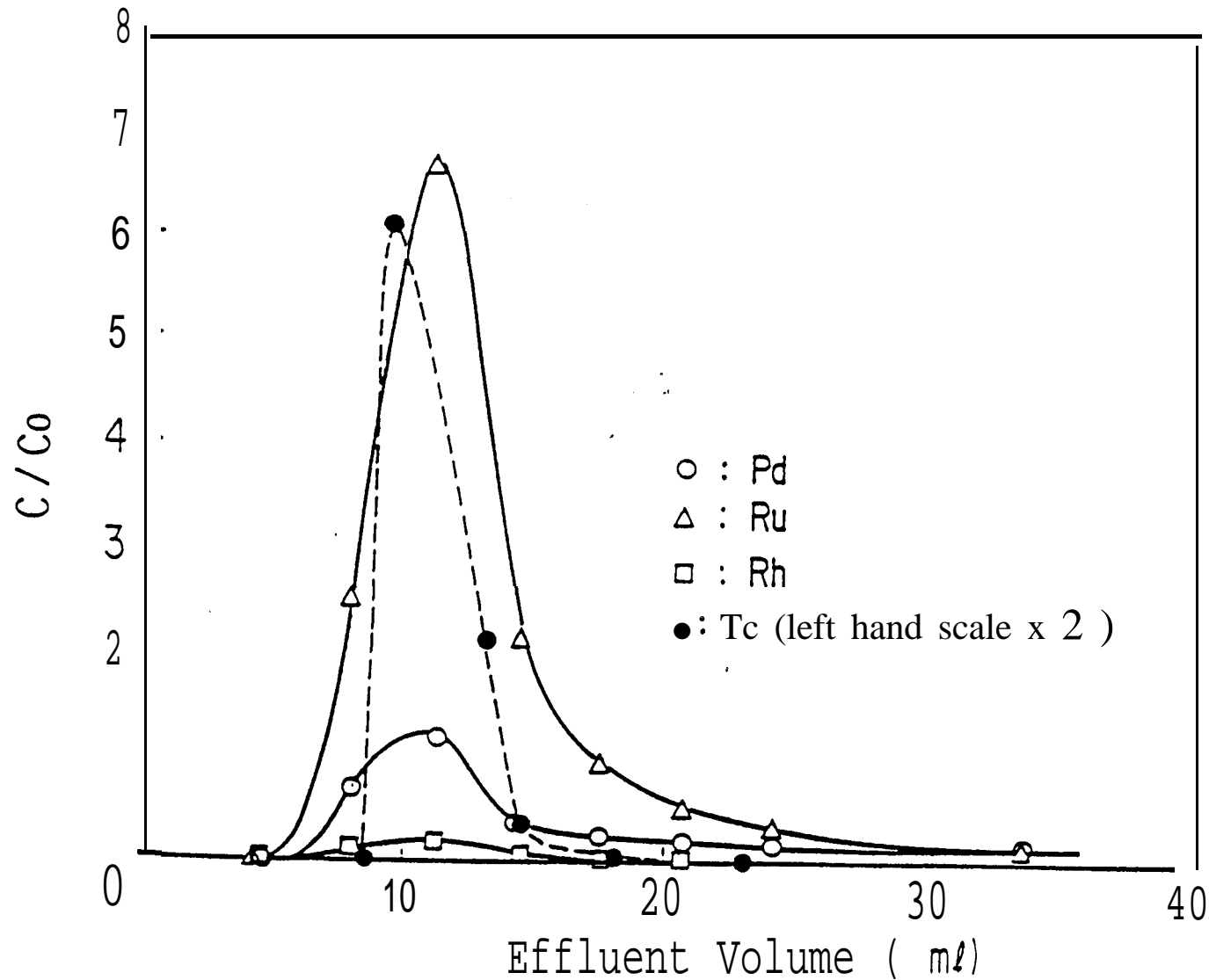


Fig.10 Elution of Tc and PGM from the Active Carbon Column
 with an Alkaline KSCN Solution
 Column: Obtained by the adsorption experiments shown in
 the preceding figure
 Eluate: 2 M KSCN - 4 M NaOH solution, 5 bed volumes/h

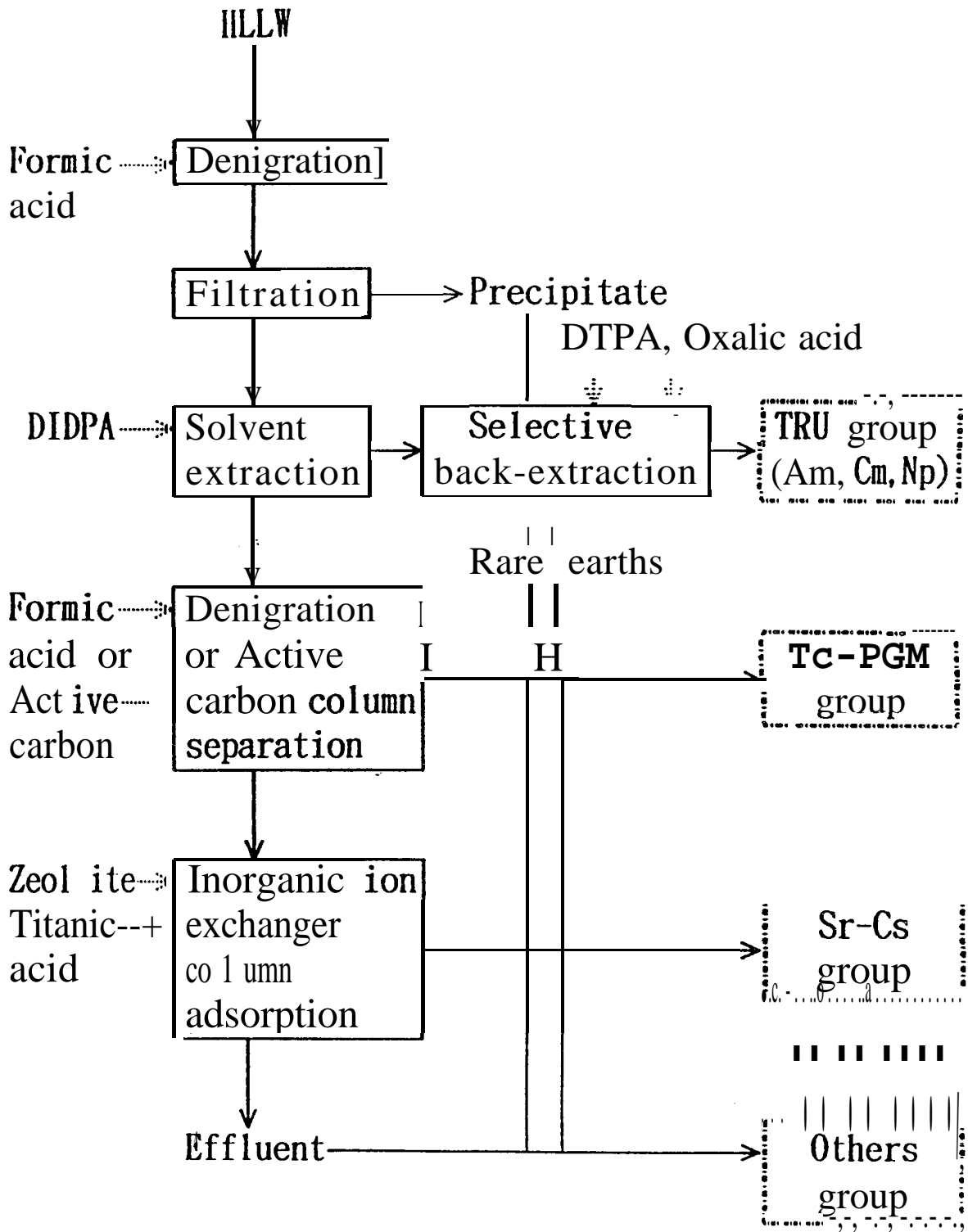


Fig. 11 Four group partitioning process