

DEVELOPMENT OF PARTITIONING PROCESS IN JAERI

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1. INTRODUCTION

Present paper describes research and development works on the partitioning of high-level liquid waste (HLLW) which have been carried out in our laboratory.

One of the methods to manage HLLW generated from nuclear fuel reprocessing is to partition long-lived **transuranium** elements (**TRU**) and heat-generating **nuclides** such as **Sr-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. Partitioning methods have been developed based on such a strategy since 1973 in our laboratory.

2. THREE GROUPS SEPARATION

The partitioning process fractionating elements in HLLW into three groups, the **TRU** group, the **Sr-Cs** group and the other elements group, was constricted through many fundamental studies. Figure 1 shows the flow sheet which had been developed until 1984. Main characteristics of this flow sheet are as follows:

- (1) U and Pu are extracted with **tributyl phosphate (TBP)**.
- (2) Prior to solvent extraction of **TRU**, most of **Zr** and **Mo** are removed as precipitate by the denigration with formic acid.
- (3) **Am** and **Cm** are extracted with **diisodecyl phosphoric acid (DIDPA)** along with rare earths. A chemical structure of DIDPA is shown in Fig.2. The DIDPA solvent is very similar to D2EHPA solvent, and **TRU** is extracted by cation exchange reaction with hydrogen ion. Extracted **Am**, **Cm** and rare earths are back-extracted with 4 M nitric acid.
- (4) Separation of **Am** and **Cm** from a large amount of rare earths is carried out with pressurized cation exchanger column.
- (5) **Sr-90** and **Cs-137** are adsorbed on the inorganic exchangers of titanate acid and zeolite, respectively.

This process was demonstrated with an actual HLLW in 1983. We found that over 99.99% of **Am** and **Cm** could be extracted and confirmed the effectiveness of

the flow sheet shown in Fig.1.

3. FOUR GROUPS SEPARATION

In 1984, a preliminary assessment was carried out on the results of research and development, and a future plan was proposed to develop an advanced partitioning process fractionating elements into four groups. The Tc-noble metals group separation was newly added to the three groups separation. The latest study is especially focused on establishing an effective method for separating Np-237 and Tc-99, because these are regarded as hazardous nuclides in long-term environmental assessment of vitrified HLLW disposed in a deep geologic formation.

Table 1 shows the objective recovery of TRU from HLLW arising from spent uranium fuel burned up to 33,000MWD/MTU in PWR. In this table, two kinds of recovery are shown, one is determined from hazard index based on maximum permissible concentration (MPC), and the other based on annual limit on intake (ALI). The recovery was determined to make the hazard index of a vitrified HLLW after storage for 1000 years comparable to that for naturally occurring minerals containing 3% of U. If we adopt the hazard index based on ALI, Np will become one of the most important elements to be separated from HLLW.

3.1 METHOD OF Separating THE TRU GROUP

For the separation of Np as well as Pu, Am, and Cm, two kinds of separation methods of solvent extraction and precipitation have been developed.

Solvent Extraction Method

In the solvent extraction, the use of DIDPA has been studied. As the first step, the behavior of Np was measured in the three groups separation tested with actual HLLW. The results are shown in Fig.3. At the first step, 86% of Np was not extracted with TBP. It was suggested that most of Np was penta-valent state in a feed solution. At the following step, over 81% of Np was extracted with DIDPA, and was not back-extracted with 4M nitric acid. Most of Np remained in the DIDPA solvent.

In tracer experiments, we found that the tetra- and hexa-valent Np could be extracted rapidly and completely with DIDPA. In addition to those findings, the DIDPA solvent was found to have unique characteristics of extracting penta-valent Np even in a slow rate as shown in Fig.4. From the analysis of the oxidation state of Np in the organic phase, it was proved that the disproportionation of penta-valent Np was involved in the extraction.

In order to accelerate the extraction of Np, additional studies were undertaken, and we found hydrogen peroxide improved the extraction rate, as shown in Fig.5. The Np extracted into DIDPA from 0.5M nitric acid solution containing hydrogen peroxide was found to be in the **tetra-valent** state in the organic phase.

After batch experiments, the continuous extraction of **penta-valent** Np was studied with a mixer settler. Figure 6 shows the operating rendition of the mixer settler, which has 7 extracting stages, 4 scrubbing stages and 5 back-extracting stages. Hydrogen peroxide was added to the scrub solution and it was also poured into the number 3 stage.

Figure 7 shows the concentration profiles of Np in the aqueous phase at the extracting stages. Open circle, A, shows the result of the experiment without hydrogen peroxide. In experiment B, hydrogen peroxide was added to the scrub solution. The addition of hydrogen peroxide increased the recovery of Np from 45% to 93%. When a simulated HLLW was used as a feed solution, in the cases of C, D, and E, the recovery further increased. However, in experiment C, the extraction rate became slow at latter stages, number 3 to 1. This is due to the decomposition of hydrogen peroxide catalyzed by some elements in the simulated HLLW. Therefore, in experiment D, hydrogen peroxide was also poured into number 3 stage to compensate its decomposition. By this addition, the rate was increased again at the latter stages. In experiment E, concentration of hydrogen peroxide was increased and **99%** recovery was obtained.

Figure 8 shows the latest experimental result when the number of extraction stage was increased from 7 to 14. Over **99.96%** of Np was extracted.

Through these studies, we found that DID PA can extract not only tri-, **tetra-** and **hexa-valent TRU** but also **penta-valent TRU**, so that all of the alpha bearing **nuclides** in HLLW can be extracted by using DIDPA solvent.

Precipitation Method

In addition to the solvent extraction of Np, we studied on the **oxalate** precipitation of Np with the expectation of developing a more economical process for the separation of **TRU**.

At first, a preliminary fundamental study was carried out with the simulated HLLW containing Nd, Sr and Cs. As shown in Fig.9, over **99.9940** of Nd, used as a representative of Am, Cm and rare earths, was found to be precipitated by the addition of crystalline oxalic acid into the simulated HLLW of **2 M** nitric acid. In this method, **coprecipitated** fractions of Sr and Cs could be reduced to about **470**.

A fundamental study was continued with simulated HLLW containing Np-237. Figure 10 shows the precipitated fraction of Np in various valence state when the crystalline oxalic acid was added to the simulated HLLW containing Nd, Sr and Cs. The initial concentration of oxalic acid was 0.5M in the solution. Tetra-valent Np was precipitated quantitatively, while penta-valent Np, which is more common in HLLW, was precipitated in only about 35% yield.

Therefore, experiments were focused on the precipitation behavior of penta-valent Np and how to increase the precipitation yield. Figure 11 shows that the precipitated fraction of Np increases with the chemical constituents of simulated HLLW from 3 to 14 components, and it increases with elapsed time and goes up to over 99% after treating the 14 component HLLW for 2 hours. However, long treatment will be difficult in practical application, because of extremely high radiation and heat generation of HLLW.

To overcome this difficulty, the reduction of penta-valent Np to tetra-valent under the coexistence of oxalic acid was examined with several reductants as shown in Fig.12, and ascorbic acid was found to be effective for the quantitative precipitation of Np within 5 minutes even at room temperature as shown in the case of C.

Figure 13 shows the precipitation behavior of fission produced elements when oxalic acid was directly added to the simulated HLLW. As shown in the cases of B and C, over 90% of Sr and Ba were precipitated, and the precipitation of these elements was found to be influenced by Zr and or Mo concentrations in HLLW. Therefore, the method of adding oxalic acid into the filtrate after removing Zr and Mo as precipitate by denigrating the simulated HLLW was studied. From experimental results shown in Fig. 14, we found that the precipitated fractions of Sr and Ba could be suppressed to about 10%, and 0.4 M oxalic acid was enough to quantitative precipitation of the TRU group.

3.2 METHOD OF SEPARATING TC

For the separation of Tc, two kinds of separation methods of precipitation and adsorption have been developed.

At first, we examined the possibility of separating Tc as precipitate by the denigration of HLLW.

Precipitation Method

Figure 15 shows the precipitation behavior of Tc when the simulated HLLW containing Tc-99 was denigrated with formic acid under reflux condition for 3 hours. The precipitated fraction of Tc became over 95% at pH ranges above 2.0, which was attainable when the concentration ratio of formic acid to nitric

acid was over 1.8. However, the precipitation of Tc was found to be quite difficult when the concentrations of Rh and Pd were lower than 0.005 M. Tc was coprecipitated along with noble metals group. Therefore, another separation method was also developed, and we found activated carbon had a possibility in practical application.

Adsorption Method

Figure 16 shows the relationship between the distribution coefficient of Tc and nitric acid concentration when 2.5 weight percent of activated carbon was added in the nitric acid solution containing only trace amounts of Tc and the resultant mixture was shaken for 1 hour at 25 C. The open circle in the figure is for the direct use of the activated carbon commercially obtained and the closed circle for the use of the activated carbon previously conditioned with 4 M nitric acid, where the preconditioning of activated carbon was carried out under the estimation of its recycle use. The distribution coefficient of Tc for the activated carbon previously conditioned was generally lower by about a half of that for the activated carbon of direct use. Anyhow, the distribution coefficient was found to exceed 100 at the nitric acid concentrations lower than 0.5 M. The distribution coefficient varied in inverse proportion to nitrate ion concentration, and the adsorption mechanism of Tc could be explained simply by anion exchange of pertechnetate ion.

The elution of Tc adsorbed on the activated carbon was also examined, and we found thiocyanate was superior to nitric acid or nitrate as eluent. Figure 17 shows that the distribution coefficient of Tc depends sensitively on pH in the presence of potassium thiocyanate. The distribution coefficient exceeds 10 to 50 below pH 2 and becomes less than 10 above pH 4. This large difference was found to be due to the change of the chemical form of Tc. We found over 99% of Tc adsorbed on the activated carbon could be eluted with 4 M sodium hydroxide solution containing 2 M potassium thiocyanate.

3.3 ADVANCED PARTITIONING PROCESS

Through these fundamental studies, the advanced partitioning process was presented as shown in Fig.18. This process, including the two kinds of chemical methods for the TRU group and the Tc-noble metals group separations, will be demonstrated with an actual HLLW in the near future. Of course, a part of this process can be used for the separation of only the TRU group from HLLW.

4. CONCLUSIONS

- (1) Fundamental studies especially focused on the separations of Np and Tc have been earned out.
- (2) For the TRU separation by solvent extraction, DIDPA proved excellent for extracting not only **tetra-** and **hexa-valent** TRU but also **penta-valent** TRU under the coexistence of hydrogen peroxide.
- (3) For the TRU separation by precipitation, the addition of oxalic acid into the filtrate after removing Zr and Mo by the denigration of HLLW was useful in suppressing Sr contamination.
- (4) For the Tc separation, the denigration with formic acid was effective in precipitating Tc along with noble metals.
- (5) Adsorption with activated carbon was also effective for quantitative separation of Tc. Over **99%** of Tc could be **eluted** with alkaline thiocyanate solution.
- (6) Through these fundamental studies, the advanced partitioning process was presented.

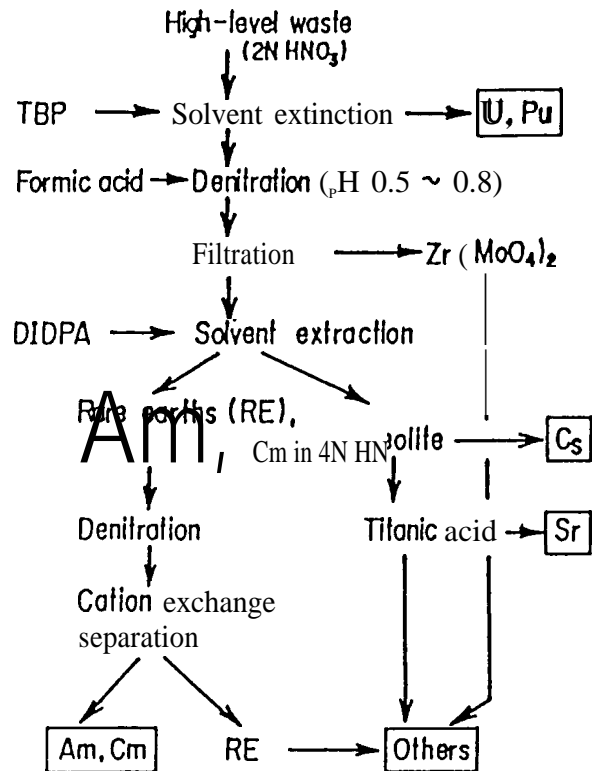


Fig. 1 Chemical flow sheet for the three groups separation of HLLW

DEHPA	di(2-ethylhexyl) phosphoric acid	$\begin{array}{c} \text{C}_8\text{H}_{17}\text{O} \\ \diagdown \quad \diagup \\ \text{P} \\ \diagup \quad \diagdown \\ \text{C}_8\text{H}_{17}\text{O} \quad \text{O} \quad \text{H}^+ \end{array}$
DIDPA	di-isodecylphosphoric acid	$\begin{array}{c} \text{C}_{10}\text{H}_{21}\text{O} \\ \diagdown \quad \diagup \\ \text{P} \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_{21}\text{O} \quad \text{O} \quad \text{H}^+ \end{array}$

Fig.2 Chemical structure of organic solvents

Table 1 Objective recovery of TRU from HLLW

Element	Recovery based on MPC ^a	Recovery based on ALI ^b
Np	90 x	99.95 %
Pu	99 %	99.9 %
Am	99.9 x	99.99 %
Cm	99.9 %	99.9 %

^a Recovery was determined from hazard index based on MPC

^b Recovery was determined from hazard index based on ALI

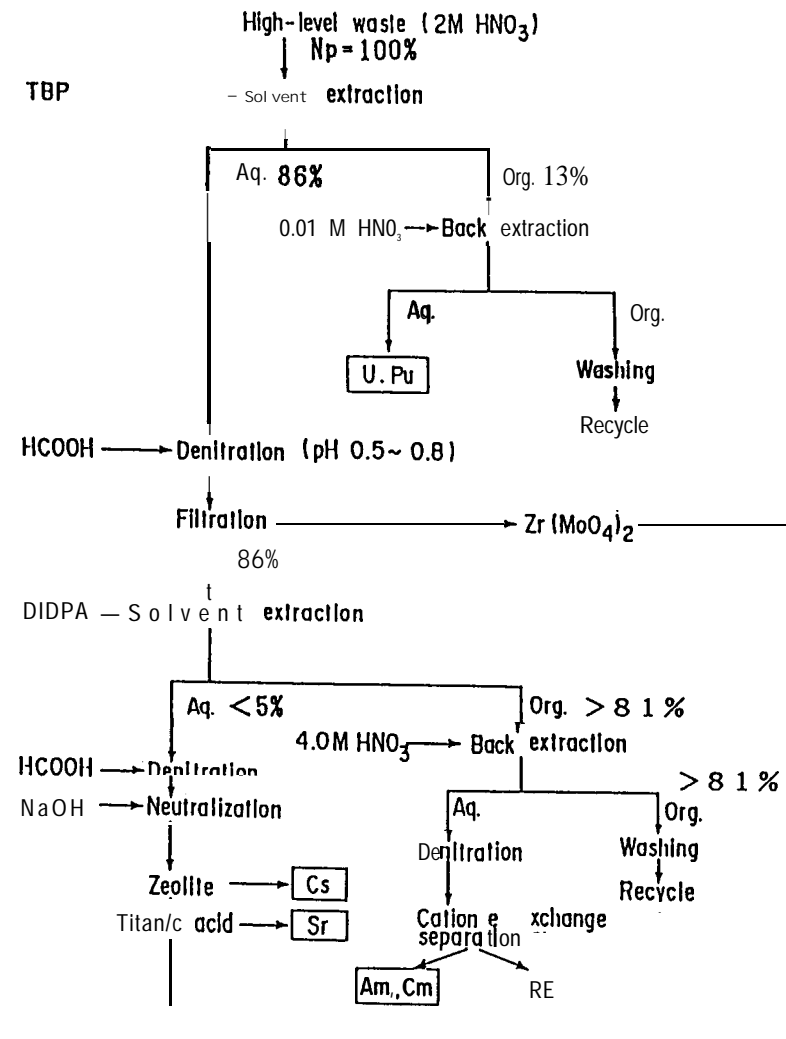


Fig. 3 Behavior of Np in the partitioning process of the three groups separation

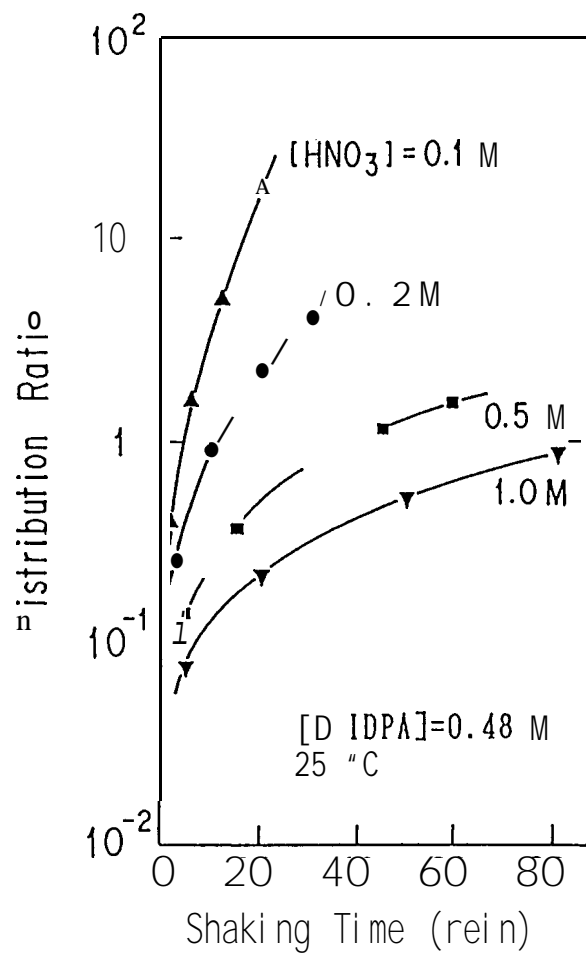


Fig. 4 Dependence of nitric acid concentration on the extraction of penta-valent Np with DIDPA in n-dodecane

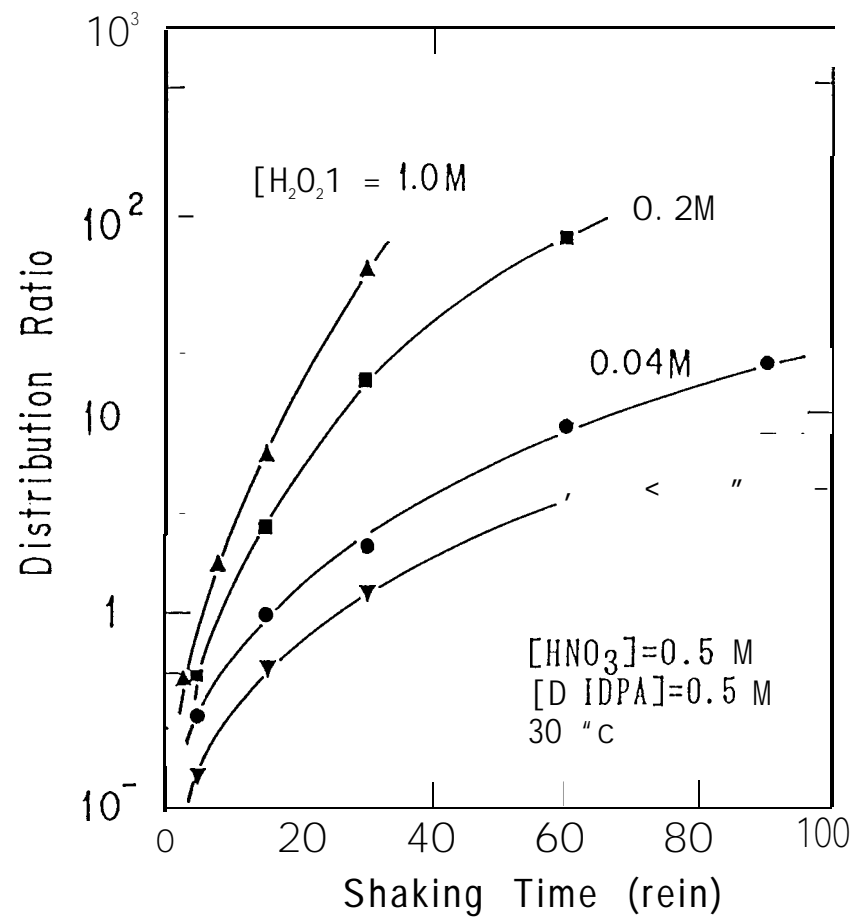


Fig. 5 Effect of hydrogen peroxide on the extraction of penta-valent Np with DIDPA

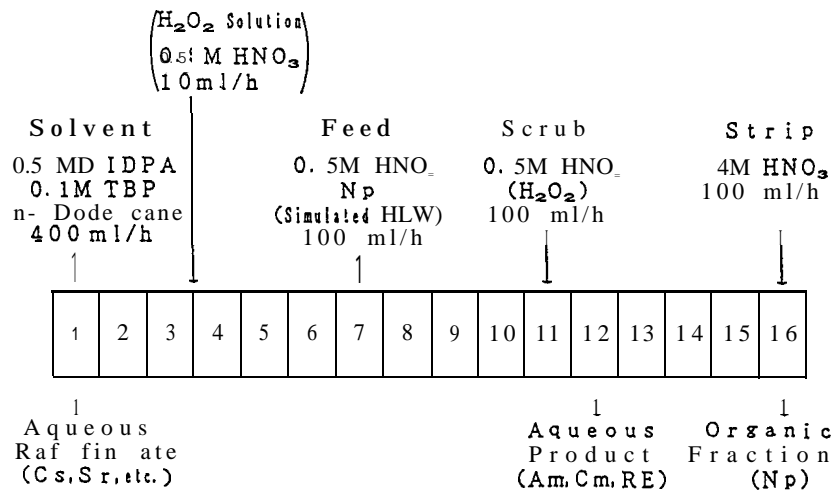


Fig. 6 Operating condition of mixer settler for the extraction of penta-valent Np

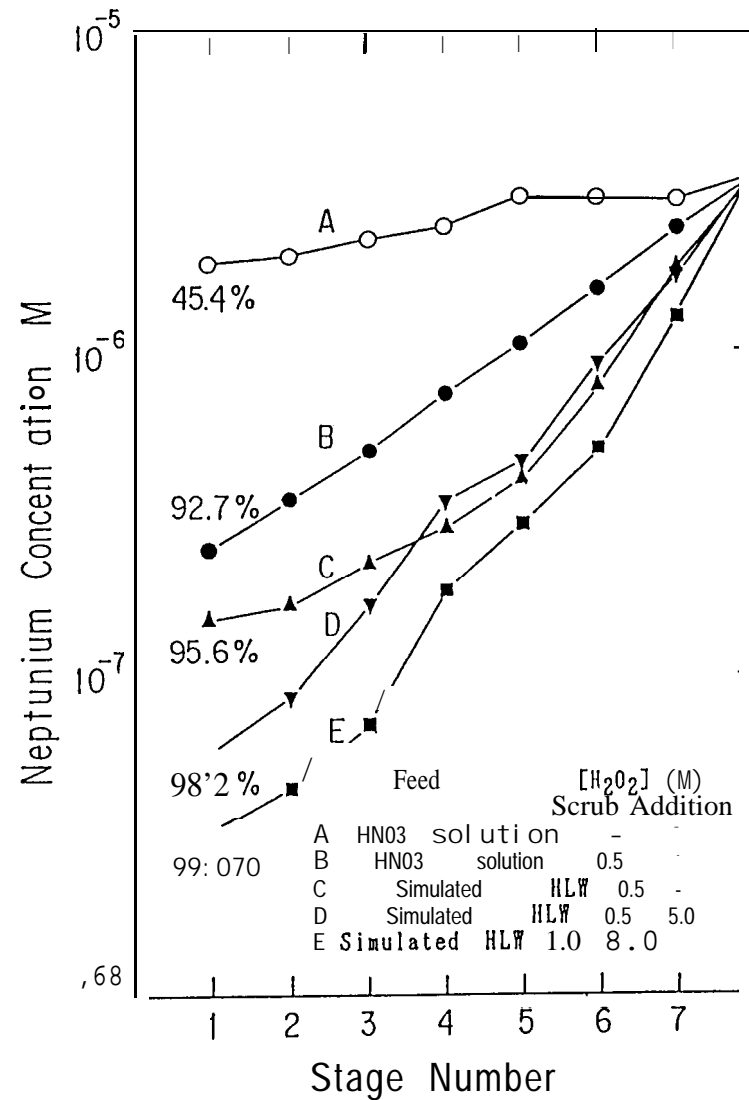


Fig.7 Concentration profiles of Np in aqueous phase at extraction stages
Percent values show the ratio of Np extracted

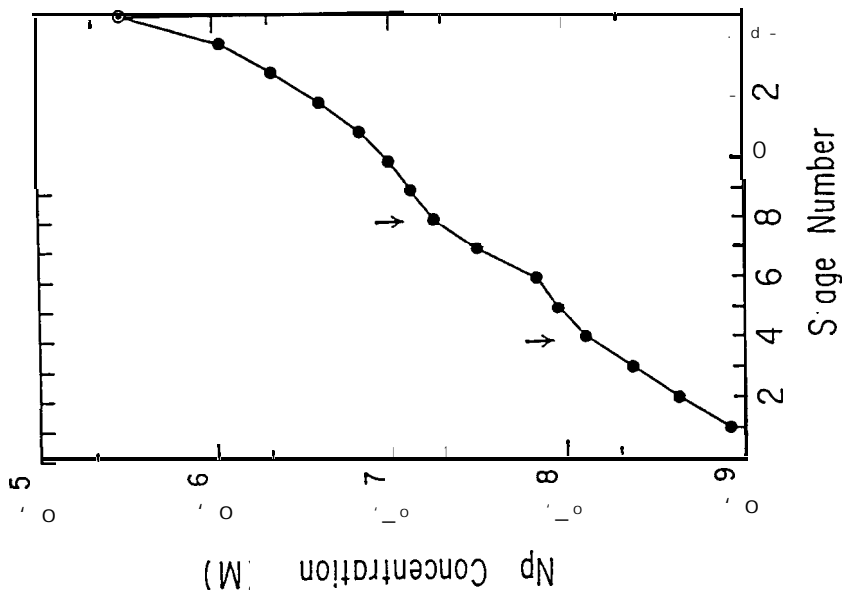


Fig. 8 Concentration profile of Np in aqueous phase at extraction stages
 Feed: simulated HLLW, Scrub: 1.0 M hydrogen peroxide - 0.5 M nitric acid, 8 M hydrogen peroxide was added to two positions of extraction stages, Operating condition: 45°C

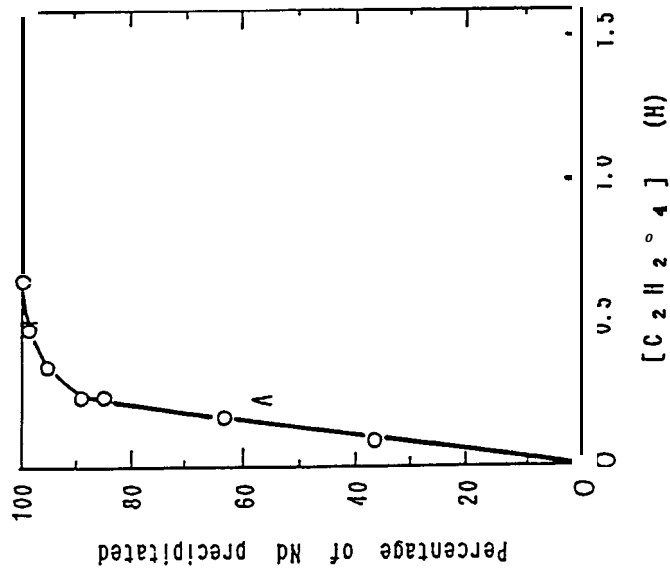


Fig. 9 Effect of oxalic acid concentration on the precipitation of Np in three component system at 25°C

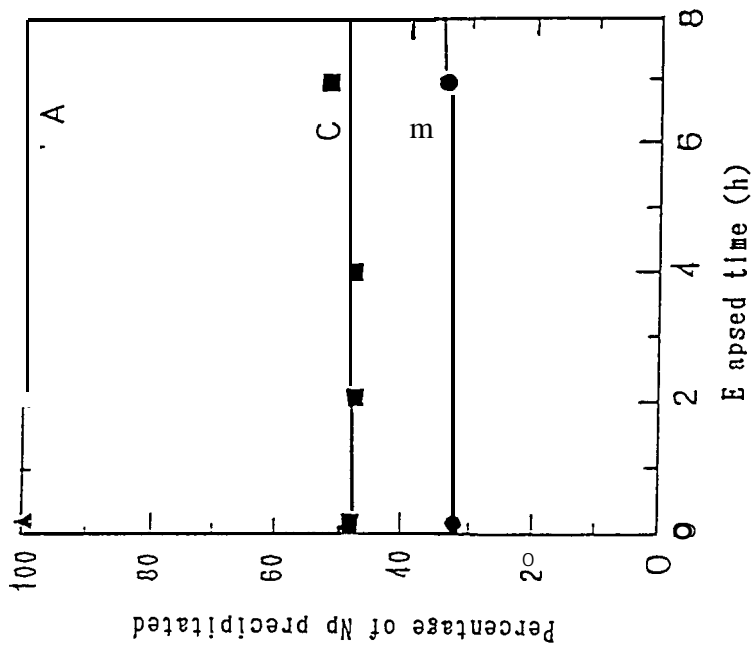


Fig. 10 Effect of Np valence state on the precipitation of Np
 Oxalic acid: 0.5 M, Temp.: 25°C,
 Np conc.: 30 mg/l
 A) Tetra-valent Np in three components system
 B) Penta-valent Np in three components system
 C) Hexa-valent Np in three components system

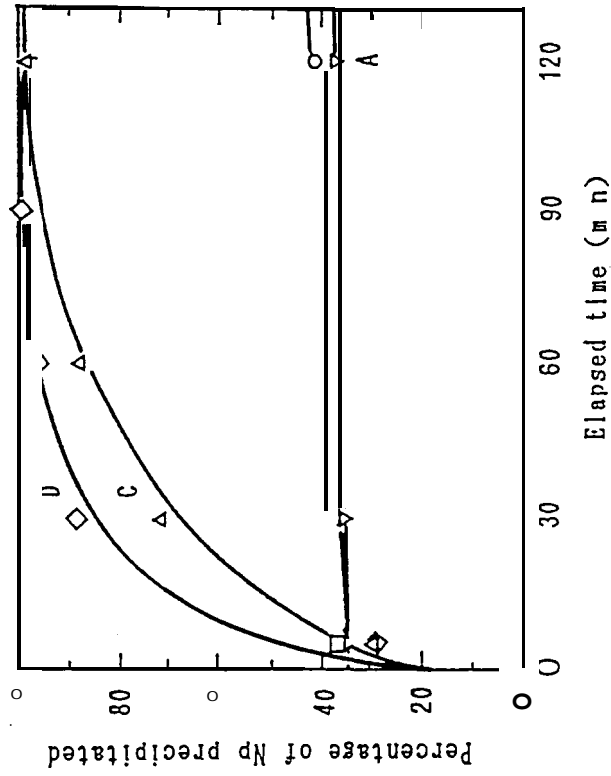


Fig. 11 Effect of elemental constituents in simulated HLLW on the precipitation of Np
 Oxalic acid: 0.5 M, Temp.: 25°C,
 Np conc.: 30 mg/l
 A) 1 component system: Nd
 B) 3 components system: Nd, Sr, Cs
 C) 12 components system: Nd, Sr, Cs, Fe, Cr, Ni, Na, Mo, Ba, Rb, Zr, Te
 D) 14 components system: 12 components, Rh, Pd

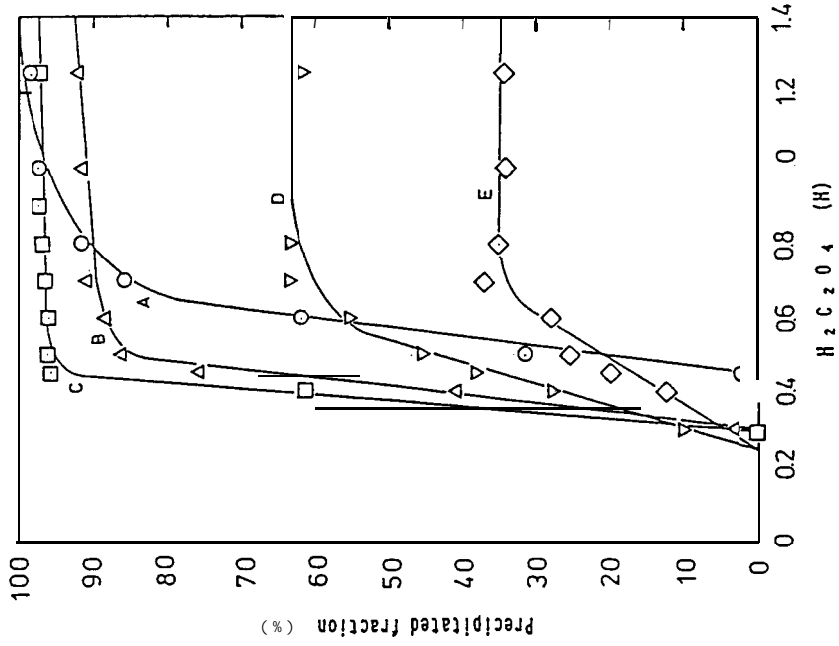


Fig. 13 Effect of oxalic acid concentration on the precipitation of several constituents in the 15 components system
 Temp.: 25 °C, Elapsed time: 30 min
 A) Nd, B) Sr, C) Ba, D) Zr, E) Rh

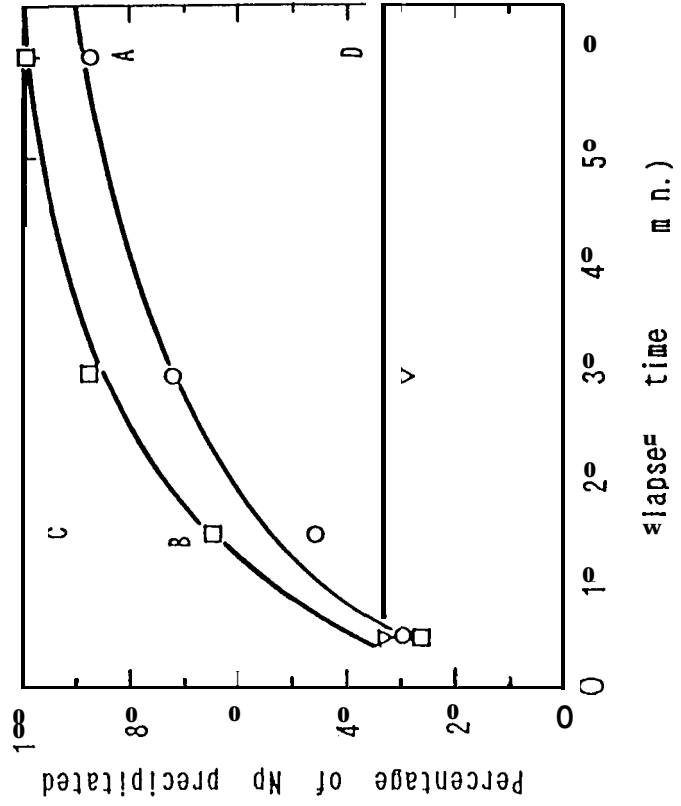


Fig. 12 Effect of reductant on the precipitation of Np in the 12 components system
 Oxalic acid: 1.0 M, Temp.: 25 °C,
 Np conc.: 66 mg/l
 A) No reductant
 B) Hydrochloric hydroxylamine: 0.017 M
 C) Ascorbic acid: 0.017 M
 D) Hydrogen peroxide: 0.017 M

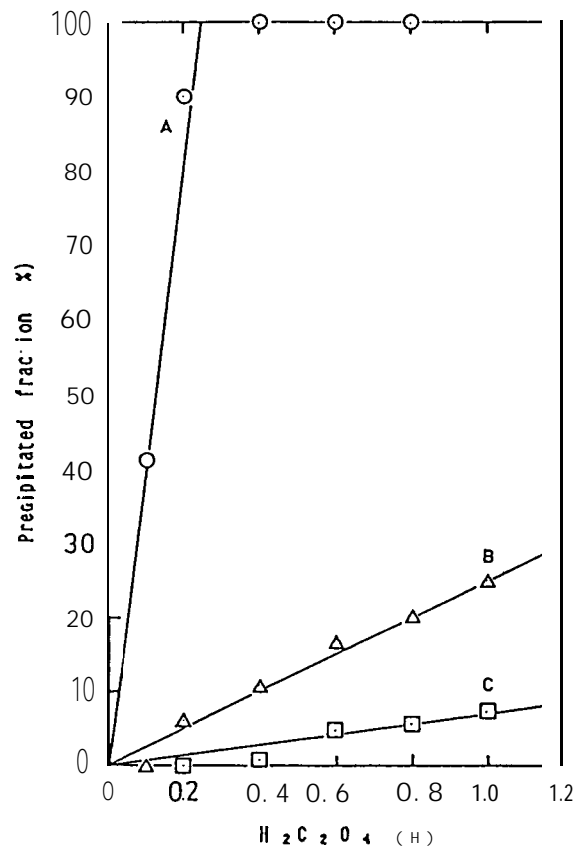


Fig. 14 Effect of oxalic acid concentration on the precipitation of several constituents remaining in the filtrate after denigration of the 15 components system solution
A) Nd, B) Sr, C) Cs

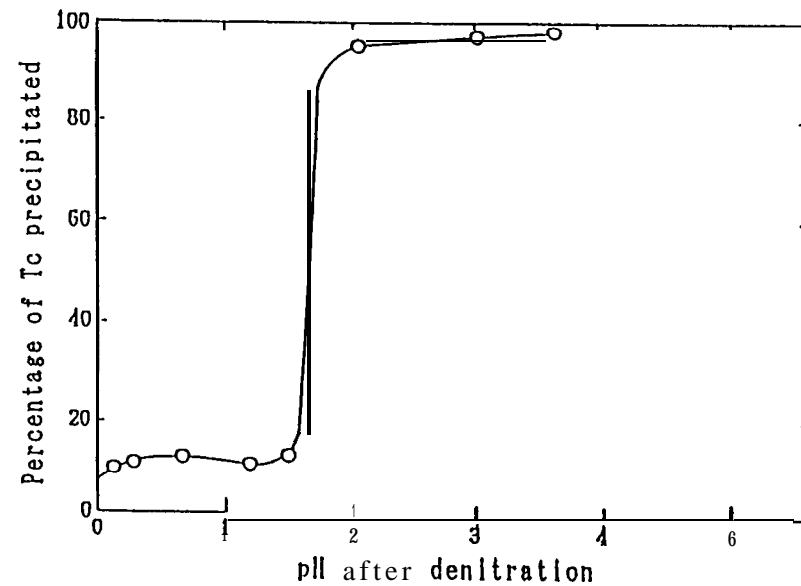


Fig. 15 Precipitation of Tc by denigration of simulated HLLW with formic acid

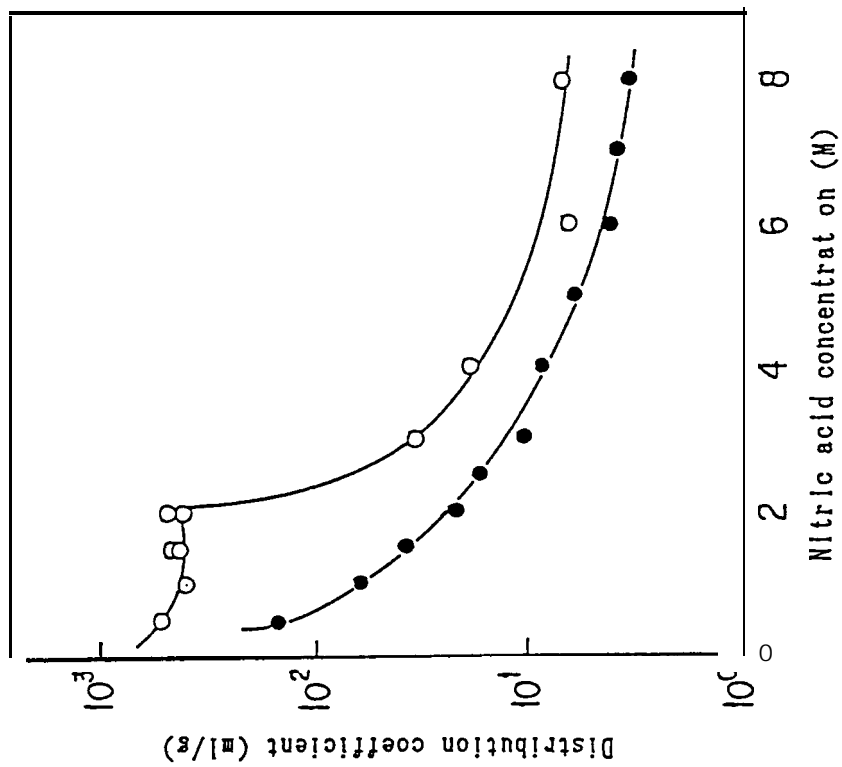


Fig. 16 Adsorption characteristic of Tc on activated carbon
 Open circle is for activated carbon of direct use. Closed circle is for activated carbon previously conditioned with 4 M nitric acid

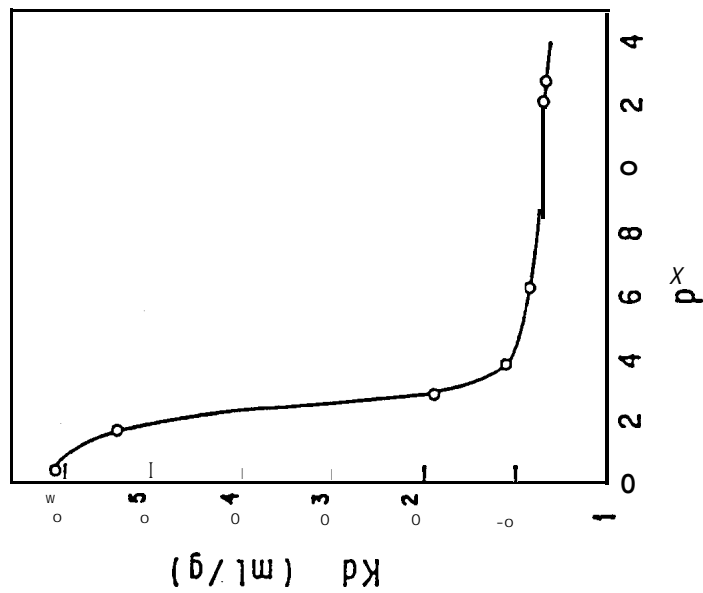


Fig. 17 Dependence of K_d on equilibrium pH (2 M KSCN present)

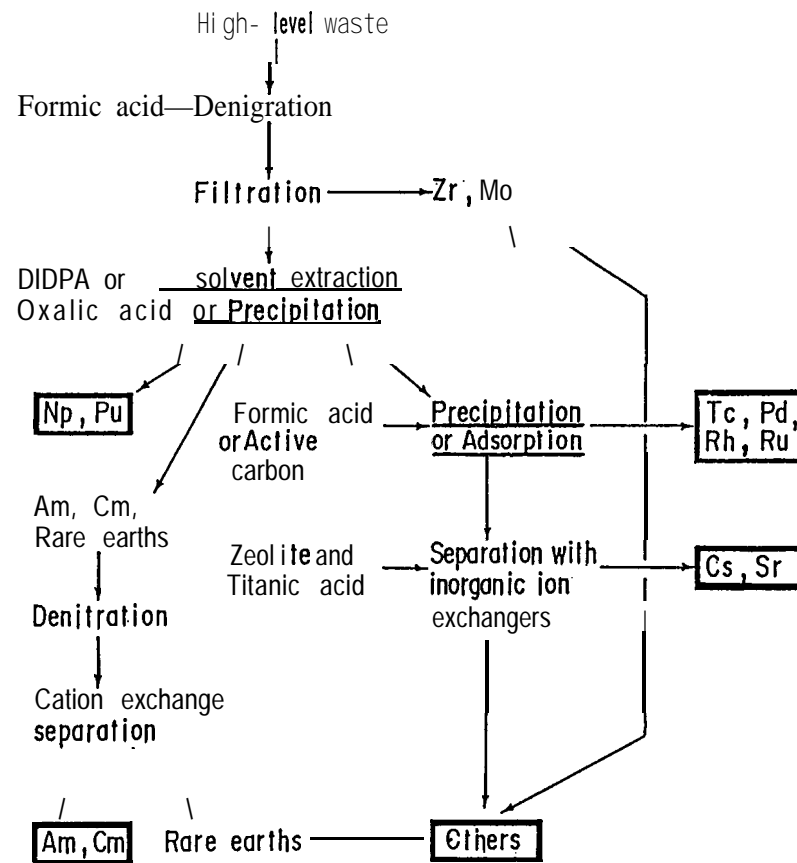


Fig. 18 Chemical flow sheet for the four groups separation of HLLW