

Fig. 10-7. Reduction of $Np(IV)$ by $DTPA$ in $0.1M$ HNO_3 solution. Conditions: $[DTPA] = 0.01M$, $[H_2O_2] = 0.01M$, $[Np(IV)] = 0.01M$, $[HNO_3] = 0.1M$. Reduction with $DTPA$ and H_2O_2 is shown as a solid line, with $DTPA$ as a dashed line, and with H_2O_2 as a dotted line.

CHAPTER IV

EFFECTS OF MONOISODECYLPHOSPHORIC ACID AND SOLVENT DEGRADATION BY RADIOLYSIS ON THE NEPTUNIUM EXTRACTION

The study reported in this chapter deals with the effects of monoisodecylphosphoric acid (MDPA) on the extraction of neptunium from HNO_3 solution by $DTPA$. The study is divided into two parts: the first part deals with the effects of MDPA on the extraction of neptunium by $DTPA$ and the second part deals with the effects of MDPA on the degradation of the solvent by radiolysis. The study is divided into two parts: the first part deals with the effects of MDPA on the extraction of neptunium by $DTPA$ and the second part deals with the effects of MDPA on the degradation of the solvent by radiolysis. The study is divided into two parts: the first part deals with the effects of MDPA on the extraction of neptunium by $DTPA$ and the second part deals with the effects of MDPA on the degradation of the solvent by radiolysis.

IV-1 INTRODUCTION

The studies described in the preceding chapters showed that DIDPA was a promising reagent for the Np extraction. The present chapter deals with the effects of radiolysis of DIDPA and impurities in DIDPA. These are essential for a successful partitioning of HLW.

By radiolysis, DIDPA is degraded to its monoester, MIDPA. The radiolysis also generates other miscellaneous materials such as alcohol, H_3PO_4 , nitrocompounds etc. Among these degradation products, MIDPA would be most influential. Tachimori et al.(77) found that distribution ratio of Am increased in the presence of MIDPA. Unavoidably MIDPA accompanies DIDPA not only as a major radiolysis product of DIDPA but also as an impurity formed during the synthesis of DIDPA.

In the studies described in the preceding chapters and also in the following chapters, DIDPA was used as received, which contained MIDPA as an impurity in a molar ratio of 0.077 to DIDPA. Therefore, a study must be carried out to know whether the results of these studies with unpurified DIDPA were seriously affected by MIDPA present as an impurity. It is necessary to define the tolerable range of the MIDPA concentration in the Np extraction; to what degree DIDPA should be purified or whether MIDPA should be added as one of the extractants. Influence of MIDPA on the back-extraction of Np with $H_2C_2O_4$ should also be examined. Section IV-2 of the present chapter describes the influence of MIDPA on Np separation by DIDPA extraction, including the back-extraction of Np with $H_2C_2O_4$.

In the following section, Section IV-3, the DIDPA solvents were irradiated with ^{60}Co γ -rays and the irradiated solvents were analyzed and used in the experiment on the Np extraction.

Two kinds of solvents were irradiated, solvents with and without TBP. These solvents were irradiated under two conditions, irradiation of solvent alone and

irradiation in the presence of aqueous phase of HNO_3 . Tachimori et al.⁽⁷⁷⁾ examined the radiolysis of DIDPA and its diluted solvent in the system without TBP. They mentioned that no MIDPA was detected in the solvent irradiated in the presence of HNO_3 using the analytical method of paper chromatography. In the present study, concentrations of acidic extractants were analyzed by potentiometric titration. Degradation of TBP in the solvent was estimated by comparison of analytical results on the irradiated solvents with and without TBP.

Using the irradiated solvents, Np initially in the pentavalent states was extracted in the presence and absence of H_2O_2 . The discussion was given to the change of the Np extraction rate with increasing the absorbed dose of the solvents. The result of the Np extraction with the irradiated solvents was compared with that of the extraction using mixed solvents of MIDPA and DIDPA.

IV-2 EFFECTS OF MONOISODECYLPHOSPHORIC ACID ON THE EXTRACTION OF NEPTUNIUM WITH DIISODECYLPHOSPHORIC ACID

EXPERIMENTAL

Reagents

The extractants, DIDPA and MIDPA, were obtained from Daihachi Chemical Co., Ltd. The unpurified DIDPA contains 90.4 % DIDPA, 4.4 % MIDPA (the molar ratio of MIDPA to DIDPA is 0.077) and 5.2 % neutral components (triisodecylphosphate and isodecylalcohol) by weight. The purification by the method of Peppard et al.⁽⁷²⁾ was not enough to remove all MIDPA. Two samples of purified DIDPA were made. One contained 92.7 % DIDPA, 1.7% MIDPA (the molar ratio was 0.029) and 5.6 % neutral components. The other contained 93.6 % DIDPA, 2.1 % MIDPA (the molar ratio was 0.036) and 4.3 % neutral components.

Commercially obtained MIDPA is a viscous and red colored liquid. It was treated by the following method. After the addition of ethanol to the MIDPA to make the alcohol concentration about 20 %, the mixture was shaken with the same volume of 0.5 M HNO_3 to remove H_3PO_4 . Ethanol is necessary for the phase separation. The MIDPA phase was then heated and stirred with 1/3 volume of 6 M HCl at 100 °C to convert any pyro esters to ortho esters. Heating was continued until the aqueous phase completely disappeared. The MIDPA thus treated was a transparent yellow liquid, and less viscous than the original liquid. It contained 62.0 % MIDPA, 37.1 % DIDPA and 0.9 % neutral components. The purification by the method of Peppard et al.⁽⁷²⁾ was found to be useless because of a very low yield (a few percentages) in spite of a good purity of the product.

The compositions of the extractants described above were determined by

alkalimetry⁽¹⁰⁵⁻¹⁰⁷⁾. A measured amount of extractant (about 0.1 g) was diluted with about 50 ml of 2-propanol and about 10 ml of deionized water, and then the resultant solution was titrated with a standard 0.1 M NaOH solution at about 40 °C. Two equivalence points could be determined from the titration curve. At the first equivalence point (pH 6.5-7), monobasic acids and the first protons of dibasic acids are neutralized. The second protons of the dibasic acids are neutralized at the second equivalence point (pH 10.5-11). The monobasic acids represent DIDPA, and dibasic acids represent MIDPA in the present analysis. Analytical random error of this alkalimetry was estimated to be ± 0.002 M.

To prepare the mixed solvents of various concentrations of DIDPA and MIDPA, suitable amounts of the extractants purified by the method mentioned above were weighed and mixed, and diluted with n-dodecane to make desired compositions. The standard concentration of the extractants is 0.5 M. Tributylphosphate was also added to the solvents to make its concentration 0.1 M. The solvent prepared in this way was pre-equilibrated with HNO₃ of which concentration was the same as that of the Np solution to be examined.

Solutions of Np(V) were prepared by the method of Srinivasan et al.⁽³⁰⁾ The concentration of Np in the experiments on the extraction rate was 1.0×10^{-4} M.

Procedure

Experiments on the extraction rate were carried out by the same procedure as described before. The temperature was kept at 25 °C in the present experiments. The Initial Rate Constant defined in Chapters II and III was used as a measure of the extraction rate.

Oxidation state of Np was determined by the spectrophotometric measurement described in Chapter II.

Back-extraction procedure is the same as in Chapter III, Section III-4.

RESULTS AND DISCUSSION

Effect on the Np extraction

Figure IV-1 shows the dependence of the Initial Rate Constant on the MIDPA concentration when the DIDPA concentration is kept constant (0.5 M). The extraction rate of initially Np(V) increased with the MIDPA concentration. The extent of this acceleration is larger in the absence of H₂O₂ than in its presence. For example, in the absence of H₂O₂, the Initial Rate Constant when [MIDPA] = 0.1 M is about 10 times larger than when [MIDPA] = 0 M. In the presence of 0.5 M H₂O₂, the Initial Rate Constant is only about twice larger by the same comparison.

The slopes of the curves in Fig. IV-1 do not change much when the MIDPA concentration approaches to 0 M. Hence, the Initial Rate Constant when [MIDPA] = 0 M can be easily obtained by extrapolation. They were 2.5×10^{-5} and $2.0 \times 10^{-3} \text{ s}^{-1}$, respectively in the absence and presence of H₂O₂. This result shows that there exists no essential difference between the extraction with the commercially available DIDPA that contains a small amount of MIDPA (0.039 M in 0.5 M DIDPA solution) and the extraction with pure DIDPA. The Initial Rate Constant is not extremely decreased even when MIDPA is removed completely from the solvent. This confirms that the results of the studies where DIDPA was used without purification were not seriously affected by MIDPA which was present as an impurity.

In order to improve the extraction rate, MIDPA can be intentionally added to the solvent. However, even if the MIDPA concentration is increased up to 0.1 M, the Initial Rate Constant in the absence of H₂O₂ is smaller than the value in the presence of H₂O₂ and in the absence of MIDPA. To accelerate the Np extraction, therefore, the addition of H₂O₂ to the aqueous solution is more effective than the addition of MIDPA to the organic solution. As mentioned before, H₂O₂ is more favorable than MIDPA also in the back-extraction of Np.

Figure IV-2 shows the dependence of the Initial Rate Constant on the molar ratio of MIDPA to DIDPA. The sum of the two concentrations was kept constant, 0.5 M. This experiment was carried out with the intention of simulating the degraded solvents.

The Initial Rate Constant at MIDPA concentrations below 0.1 M were almost the same as the values in Fig. IV-1. This observation can be understood by considering that the DIDPA concentration is kept nearly constant when the MIDPA concentration is small. When the MIDPA concentration is increased, the rate of the Np extraction is influenced more by the increase of the MIDPA concentration than by the decrease of the DIDPA concentration. Thus, when the change of the extractant composition by radiolysis is considered, attention should be paid more to the increase of the MIDPA concentration than to the decrease of the DIDPA concentration.

The dependence of the Initial Rate Constant on the HNO_3 concentration is shown in Fig. IV-3. In the absence of H_2O_2 , the ratio of the Initial Rate Constant when $[\text{MIDPA}] = 0.1 \text{ M}$ to the Constant when $[\text{MIDPA}] = 0.017 \text{ M}$ was independent of the HNO_3 concentration. In the presence of $0.5 \text{ M H}_2\text{O}_2$, the same phenomenon was observed when the HNO_3 concentration is below 1 M . When the HNO_3 concentration exceeds 1 M , the difference of the Initial Rate Constant between 0.1 M MIDPA and 0.017 M is decreased, since the reduction of Np(V) with H_2O_2 in the aqueous phase appreciably contributes to the extraction at this acidity, as described in Chapter III.

The fact that the acceleration of the Np extraction by MIDPA is independent of the HNO_3 concentration suggests that the mechanism of the extraction with DIDPA is not changed by the increase in the MIDPA concentration. This was also supported by analyzing the oxidation state of Np in the organic phase. In the presence of H_2O_2 , Np extracted with $0.2 \text{ M MIDPA} - 0.3 \text{ M DIDPA}$ solution was found to be tetravalent. In the absence of H_2O_2 , 52.5 and 47.5 % of Np was tetravalent and hexavalent, respectively, which means that Np(V) disproportionated during the extraction. These observations are the same as those in the extraction with $0.039 \text{ M DIDPA} - 0.5 \text{ M}$

DIDPA solution described in Chapters II and III.

Thus, the extraction mechanism in the aspect of Np redox reactions does not change even when the MIDPA concentration is as high as 0.2 M . It can be considered that MIDPA accelerates the extraction because it release two hydrogen ions per one MIDPA molecule and makes a stronger complex with Np than DIDPA. It is not clear in the present experiments whether MIDPA shows a synergistic effect on the Np extraction with DIDPA. The extraction rate increased monotonously with MIDPA concentration in the examined range (Fig. IV-2).

Effect on the Np back-extraction

Although MIDPA gives favorable effect on the rate of the forward extraction, the increase in its concentration was found to be undesirable in the back-extraction of Np with $\text{H}_2\text{C}_2\text{O}_4$. As shown in Fig. IV-4, distribution ratio (D) increases with MIDPA concentration, which means that Np is less back-extracted with increasing MIDPA concentration. The influence of MIDPA should be taken into account particularly in the back-extraction process. The tolerable concentration of MIDPA is determined by the condition of the back-extraction process.

Figure IV-4 also shows that Np extracted from the solution containing H_2O_2 has a smaller D than Np extracted from the solution without H_2O_2 . This is due to the fact that D of Np(IV) is smaller than D of Np(VI) , which was mentioned in Section III-4. Table IV-1 shows the results of the oxidation state analysis after back-extraction. Distribution ratios of Np(IV) and Np(VI) were found 8.0 and 15.7, respectively, in the system of $0.2 \text{ M MIDPA} - 0.3 \text{ M DIDPA} - 0.1 \text{ M TBP}$ solution and $0.7 \text{ M H}_2\text{C}_2\text{O}_4$ solution.

Table IV-1 also shows that the sum of the Np(IV) in the organic and aqueous phases was still 49 % of the total Np. Therefore, the change of Np oxidation state could not be observed in the back-extraction.

Figure IV-5 shows the dependence of D for the back-extraction on the $\text{H}_2\text{C}_2\text{O}_4$ concentration. In this experiment, Np was extracted with 0.1 M MIDPA - 0.4 M DIDPA solution from 0.5 M HNO_3 solution containing 0.5 M H_2O_2 . Neptunium was tetravalent in the organic phase. The slope of the straight line was -2.5, which was the same as in the back-extraction from 0.039 M MIDPA - 0.5 M DIDPA - 0.1 M TBP with 0.5 M to 1 M $\text{H}_2\text{C}_2\text{O}_4$ shown in Section III-4, Fig. III-9. The change in the concentration ratio of MIDPA to DIDPA does not alter the dependence of D on the $\text{H}_2\text{C}_2\text{O}_4$ concentration at least in the $\text{H}_2\text{C}_2\text{O}_4$ concentration region of 0.5 M to 1 M.

The tolerable concentration of MIDPA in the back-extraction process can be estimated using the data shown in Figs. IV-4 and IV-5. It is preferable to increase the $\text{H}_2\text{C}_2\text{O}_4$ concentration, but there is the limit of solubility. Maximum applicable concentration of $\text{H}_2\text{C}_2\text{O}_4$ is 1 M at room temperature. If the back-extraction process can be designed when $D = 1$ using 1 M $\text{H}_2\text{C}_2\text{O}_4$ solution, 0.1 M MIDPA is tolerable, which is easily found from the data plotted in Fig. IV-5. If it is necessary to decrease D to 0.5, the tolerable concentration is 0.066 M, which was estimated as follows. When $D = 0.5$ at 1 M $\text{H}_2\text{C}_2\text{O}_4$, $D = 2.8$ at 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ in the back-extraction of Np from the same organic phase, which was calculated by using the -2.5 power dependence on the $\text{H}_2\text{C}_2\text{O}_4$ concentration. The MIDPA concentration that gives 2.9 of D at 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ is 0.066 M, which was obtained from the plot in Fig. IV-4.

Thus, the MIDPA concentration is restricted by the back-extraction step, but the limit is not so small. The concentration, 0.066 M, would serve as the measure of the recycle use of the solvent. The increase of the MIDPA concentration by radiolysis and the absorbed dose that gives 0.066 M MIDPA will be described in the following section.

IV-3 RADIOLYSIS OF DIISODECYLPHOSPHORIC ACID AND ITS EFFECT ON THE NEPTUNIUM EXTRACTION

EXPERIMENTAL

Reagents

Solutions of Np(V) were prepared by removing Np(VI) and Np(IV) through DIDPA extraction from a stock solution where Np was almost pentavalent. Distribution ratios of Np(VI) and Np(IV) are large enough to permit their removal through one batchwise extraction as described in Chapter II. The concentration of Np in extraction rate experiments was 1.8×10^{-4} M.

The extractant, DIDPA, was used without further purification. Each of DIDPA and TBP was taken from the same stock as in the experiments in the preceding section. These extractants were diluted with n-dodecane (n-dodecane 97.8 %, n-undecane 1.7 %, n-tridecane 0.5 %). Initial concentrations of DIDPA and TBP were 0.5 M and 0.1 M, respectively.

Irradiation

A solvent was irradiated with ^{60}Co γ -rays at a dose rate of 14-33 kGy/h at room temperature, in a glass flask plugged with quartz wool. The four kinds of irradiated solvents, shown as symbols A-D in Table IV-2, were used in Np extraction experiments. Solvents C and D were irradiated in stationary contact with the same volume of 0.5 M HNO_3 , while solvent and HNO_3 phase were vigorously stirred before irradiation. For Solvent E, organic and aqueous phases were continuously stirred during the irradiation. Only two samples in Solvent E were obtained because of the radiation damage of the stirrer. They were not used in the Np extraction experiments,

but their degradation was analyzed and compared with that of Solvent D. The aqueous phases in Solvents C, D and E were separated from the solvents soon after the irradiation without further stirring.

Table IV-3 shows absorbed dose of the solvents. Hereafter, the irradiated solvents are represented by the combination of the alphabetical symbol in Table IV-2 and the number in Table IV-3, such as A-1, B-2, etc.

In the present study, G-value (the number of atoms or molecules which are degraded or produced per 100 eV of absorbed energy) was obtained, which is a familiar means in evaluating the radiolysis. Calculation is based on the energy absorbed by the whole of solvent unless otherwise noted.

Analysis

Acidic extractants and H_3PO_4 in solvents were analyzed by alkalimetry as described in the preceding section. In the present titration, 1 ml of the solvent was taken, and the concentrations of monobasic and dibasic acids were determined. The monobasic acids represent DIDPA and dibutylphosphoric acid (DBP), and dibasic acids represent MIDPA, monobutylphosphoric acid (MBP) and H_3PO_4 in the present experiment. Although H_3PO_4 is a tribasic acid by definition, it behaves like a dibasic acid in titration to give only two equivalence points. The titration curve for H_3PO_4 was found almost the same as for MIDPA. Analytical random error of this alkalimetry was ± 0.002 M.

Each irradiated solvent was analyzed by the alkalimetry twice; one was for untreated solvent and the other was for the solvent washed with 0.5 M HNO_3 . Papers on TBP degradation described that distribution ratio of DBP in the unionized form between 20% TBP-kerosene and water was about $10^{(108)}$, while almost MBP was washed out by acidic solution^(108,109). Distribution ratio of H_3PO_4 was found to be less than 0.01 between 0.5 M DIDPA in n-dodecane and 0.5 M HNO_3 solution

regardless of the presence of 0.1 M TBP. Therefore, MBP and H_3PO_4 were removed from the solvent by the washing while DBP remained in the solvent. Because of the long chain of alkyl group, MIDPA also remains in the solvent.

Concentration of H_3PO_4 in the aqueous solution was determined by spectrophotometric phosphomolybdate method⁽¹¹⁰⁾. Two kinds of solutions were analyzed: the irradiated aqueous phase and the washing solution mentioned above. Concentration of HNO_3 in the irradiated aqueous phase was also determined by alkalimetry.

Neptunium Extraction

Experimental procedure for Np extraction and the method of evaluating the extraction rate were the same as described before. Temperature was kept at 25 °C during the extraction.

RESULTS AND DISCUSSION

Radiolysis of Solvents

Table IV-4 shows the result of the analysis of the solvent irradiated alone. A difference in dibasic acid concentration between before and after washing gives the concentrations of MBP and H_3PO_4 in the solvent. This difference was not distinct since a small amount of H_3PO_4 was produced. For Solvent A-4, which contained 0.008 M H_3PO_4 , however, the difference agreed with the H_3PO_4 concentration analyzed. Production of MBP in Solvent B was found to be very small (less than analytical error) from the comparison of this difference for Solvent B with that for Solvent A.

A good agreement was obtained in dibasic acid concentration after washing between Solvents A and B. It can be considered that these values directly show the

MIDPA concentrations.

The sum of the acid concentrations for Solvent A decreased with increasing absorbed dose. This suggests that the extractants, DIDPA and MIDPA, changed to some materials which cannot be detected by the method employed in the present work. The color of the solvent also changed gradually from very light yellow to yellowish red with increasing absorbed dose. For Solvent B, the sum was not decreased because of the production of DBP.

Figure IV-6 shows the decrease of monobasic acid concentration with increasing absorbed dose. The decrease for Solvent B was obviously slow, which was due to the degradation of TBP to DBP. From the result for Solvent A which does not contain TBP, G-value for DIDPA degradation was found to be 0.47.

Figure IV-7 shows the increase of the difference in monobasic acid concentration between Solvents B and A. All the points except one lay on a straight line. Regarding that this increase indicates the production of DBP, its G-value is found to be 0.14 from the slope of the line. This value is smaller than that for DIDPA degradation, but it cannot be concluded only from this comparison that TBP is more stable to radiation than DIDPA in the solvent, because G-value was calculated based on the energy absorbed by the whole of the solvent and the concentration of TBP is lower than that of DIDPA. To obtain the G-value based on the energy absorbed by the extractant itself, original G-value was divided by the electron fraction for the extractant: 0.258 for DIDPA and 0.032 for TBP. From this conversion of G-value, 1.8 was obtained for DIDPA degradation and 4.4 for DBP production. (DBP production must be a little smaller than TBP degradation.) The comparison of the stability to radiation cannot be achieved also from these values because there is the energy transfer between the diluent and the extractant. Tachimori et al.⁽⁷⁷⁾ stated that G-value for MIDPA production was 1.1 when undiluted DIDPA was irradiated. Various papers^(109,111,112) presented around 2.0 as G-value for DBP production in undiluted TBP. It can be considered that

DIDPA is not less stable than TBP, at least.

From Fig. IV-7, the concentration of DBP produced can be estimated for each absorbed dose. Table IV-5 shows the concentrations of extractants and H_3PO_4 in Solvents A and B derived by this estimation.

Table IV-6 shows the result of the analysis of the solvent irradiated in the presence of HNO_3 . On this condition, many miscellaneous materials were produced by radiolysis in which HNO_3 participated. Therefore, the result in Table IV-6 cannot be well interpreted like the result in Table IV-4 for the solvent irradiated in the absence of HNO_3 . It is difficult, in particular, to reveal the reason for changes in the concentrations of mono- and dibasic acids after washing. Chemical form of degraded products may be changed by washing with 0.5 M HNO_3 .

Figure IV-8 shows the decrease of monobasic acid concentration with increasing absorbed dose after washing. Difference caused by the presence of TBP in Fig. IV-8 was smaller than in Fig. IV-6, but this does not directly indicate that an amount of DBP produced in Solvent D is smaller than that in Solvent C because the production of the dibasic acid in Solvent D was greater than in Solvent C, as shown in Table IV-6. More DIDPA must have been degraded in Solvent D. Some papers^(109,113) showed that the presence of HNO_3 in the organic phase decreased the production of DBP by radiolysis when n-dodecane is used as a diluent. Such effect of HNO_3 , however, could not be observed from the analysis employed in the present study. The more specific technique such as gas or liquid chromatography should be employed to analyze the DBP concentrations in the solvents irradiated in contact with HNO_3 .

From Fig. IV-8, G-value for DIDPA degradation in Solvent C was found to be 0.78. This value was 1.7 times larger than in Solvent A which was irradiated in the absence of HNO_3 .

Concentration of dibasic acid was plotted in Fig. IV-9 against absorbed dose. Plots below 1 MGy in Fig. IV-9 make a straight line for each solvent. The slopes of

the lines were found to be 0.037 M/MGy for Solvents A and B, 0.042 for Solvent C and 0.053 for Solvent D. The increase of the dibasic acid concentration with absorbed dose for Solvent D was much greater than for Solvent C. This difference does not indicate the production of MBP since the plotted data was for the solvent after washing, where MBP must be removed from the solvent. The cause of the difference was not clear and the composition of the dibasic acids in Solvent D could not be determined by the analysis employed in the present study. All the dibasic acids in Fig. IV-9 were, therefore, regarded as MIDPA considering that the dibasic acids have the same function for the Np extraction as MIDPA.

As described in the preceding section, the tolerable concentration of MIDPA in the back-extraction of Np with $H_2C_2O_4$ is 0.066 M at lowest and this would serve as the measure of the recycle use of the solvent. Figure IV-9 showed that the MIDPA concentration increased to 0.066 M from 0.039 M when the absorption dose increased to more than 0.5 MGy in the Solvent D.

Tachimori et al.⁽¹¹⁴⁾ estimated that the solvent absorbs 10 Wh/l per one passage through the partitioning process when HLW is cooled for 150 days after reactor discharge. This value corresponds to 45 kGy when the specific gravity of the solvent is 0.8, and is lower than 1/10 of the 0.5 MGy. Tachimori et al. also showed the dependence of the absorbed dose on the cooling time of HLW. When HLW is cooled for five years, which is more realistic length in the present situation of the nuclear fuel cycle, the absorbed dose decreases to 4 kGy. In their calculation, the number of the extraction stages was only four. The Np extraction must require more stages. Even when the number of stages should be increased five times, the absorbed dose of the solvent is 20 kGy, which is 1/25 of the 0.5 MGy. The DIDPA solvent would be able to be used 25 times at least without washing for the MIDPA removal from the aspect of the Np back-extraction.

Comparison of Solvent E which was continuously stirred with 0.5 M HNO_3

during the irradiation to Solvent D was found to be the following; for the increase of dibasic acid concentration shown in Fig. IV-9, the slope for Solvent D was 0.053 M/MGy, while that for Solvent E was 0.055 M/MGy, which was 3.6 % increase. The same comparison between Solvents B and D shows 43 % increase. The difference between the irradiations with and without stirring the solvent and aqueous phase of HNO_3 was, therefore, smaller than that between the irradiations in stationary contact with HNO_3 and its absence. This finding indicates the validity of the extraction experiment using the solvent irradiated in the presence of HNO_3 without stirring.

Figure IV-10 shows the production of H_3PO_4 by irradiation. From the slopes of the lines shown in Fig. IV-10, G-values for H_3PO_4 production below 0.5 MGy were found to be 0.033 for Solvents A and B, 0.18 for Solvent C, 0.16 for Solvent D and 0.32 for Solvent E. Presence of HNO_3 increased H_3PO_4 production by a factor of five. Accordingly, the effect of HNO_3 on the H_3PO_4 production was found greater than on the DIDPA degradation and the MIDPA production. Continuous stirring of the solvent and the aqueous phase of HNO_3 increased the G-value of H_3PO_4 production by the further factor of two.

Presence of H_3PO_4 in the aqueous phase may decrease the extraction rate for Np by making a complex with Np. However, it is not necessary to consider the accumulation of H_3PO_4 in the separation process because it does not remain in the organic phase even if the solvent was recycled without clean-up.

Concentration of HNO_3 in the aqueous phase which had been contacting with the solvent during the irradiation was also analyzed and the result was shown in Table IV-7. Accuracy of the analysis became poorer with increasing absorbed dose because of the contamination with dibasic acids (particularly for Solvent D), but there was no difference between Solvents C and D. From the result for Solvent C, G-value for HNO_3 degradation was found to be 1.4, which was much larger than for DIDPA degradation.

Extraction of Np with the Irradiated Solvent

This sub-section describes the results of the experiments on the extraction of Np initially in the pentavalent state with the irradiated solvent. Figure IV-11 shows the Initial Rate Constant for Np extraction from 0.5 M HNO_3 solution without H_2O_2 . The rate of the extraction with the solvent irradiated alone (A and B) increased with absorbed dose. It was considered that the increase of MIDPA concentration by radiolysis accelerated the extraction.

On the other hand, when the solvent was irradiated in the presence of HNO_3 , this acceleration disappeared. The extraction rate changed very little or decreased. These phenomena are considered to be caused by many miscellaneous products by radiolysis in which HNO_3 participated. If H_3PO_4 were responsible for the disappearance of the acceleration by MIDPA, much effect should have been observed in the extraction with Solvents A and B, because they contained higher concentration of H_3PO_4 than Solvents C and D, as shown in Tables IV-4 and IV-6. Most of H_3PO_4 in Solvents C and D had moved to aqueous phase during the irradiation.

In any event, it is difficult to apply the extraction of initially Np(V) with DIDPA without addition of H_2O_2 to a partitioning process because of its slow rate. Much attention should be paid to the extraction from the solution containing H_2O_2 , described below.

Figure IV-12 shows the rate constant of Np extraction with the irradiated TBP-free solvent from a solution containing 0.5 M HNO_3 and 0.5 M H_2O_2 . The extraction rate increased with absorbed dose in the region below 1 MGy, regardless of the presence or absence of HNO_3 in the solvent irradiation. In this respect, the addition of H_2O_2 depresses the influence of HNO_3 -participating radiolysis products. When the solvent absorbed higher dose, the extraction rate decreased, but the rate of the extraction with the solvent that absorbed 2 MGy in the presence of HNO_3 was still comparable to that with the non-irradiated solvent.

Figure IV-13 shows the result of the Np extraction with the irradiated solvent containing TBP. The presence of TBP in the solvent decreased the change of the extraction rate caused by solvent degradation. The similar effect was found also in the extraction from the solution which did not contain H_2O_2 , as shown in Fig. IV-11.

Figure IV-13 also showed that the rate of Np extraction was almost the same as that with the non-irradiated solvent until the absorbed dose of the solvent increased to 0.5 MGy. The dose of 0.5 MGy corresponds to the more than 25 times recycle use of the solvent in an actual partitioning plant, as described before. Consequently, it was confirmed that the radiolysis of the solvent gave practically no influence on the extraction of Np in an actual process.

Figure IV-14 shows the comparison of the present work using the irradiated solvents with the work using mixed solvents of MIDPA and DIDPA which were described in the preceding section. In this figure, the rate constants were plotted against MIDPA concentration. Symbol ■ connected by a solid line shows the results of the experiments described in the preceding section using the solvent containing MIDPA, DIDPA and 0.1 M TBP, where the sum of the concentrations of MIDPA and DIDPA was maintained at 0.5 M. Plots for Solvent B (symbol ▼) lay well on the solid line in the MIDPA concentration region below 0.08 M (Absorbed dose was lower than 1 MGy). It was thus found that the rate of Np extraction was determined by the concentration of MIDPA produced by radiolysis when the solvent was irradiated with lower dose than 1 MGy in the absence of HNO_3 .

With Solvent B, however, the rate decreased apart from the solid line when absorbed dose increased to 2 MGy. Most of the plots for Solvent D (symbol ▽) did not lie on the solid line, either. When the solvent was irradiated in the presence of HNO_3 , the extraction rate cannot be evaluated only by the MIDPA concentration. The other radiolysis products were considered to influence the extraction.

If all of the radiolysis products were identified and their influences on the Np

extraction were examined individually, discussion could be given more quantitatively. Such a study, however, has little importance because the radiolysis of the DIDPA solvent does not cause a serious problem in the Np extraction as found in the present study.

IV-4 CONCLUSION

The extraction of Np initially in the pentavalent state with DIDPA was found to be accelerated by MIDPA. Even if MIDPA is produced by the radiolysis of DIDPA, it would give no deleterious influence on the extraction step for Np. To improve the extraction rate, MIDPA can be intentionally added. However, it was found that the addition of H_2O_2 is more effective and reasonable than the addition of MIDPA.

The extraction rate of Np is not extremely decreased even when MIDPA is removed completely from the solvent. This confirms that the results of the studies where DIDPA was used without purification were not seriously affected by MIDPA which was present as an impurity in a molar ratio of 0.077.

In the back-extraction of Np with $H_2C_2O_4$, the increase of the MIDPA concentration is undesirable. The tolerable concentration, however, was found to be as high as 0.066 M.

Radiolysis of 0.5 M DIDPA in n-dodecane with and without addition of 0.1 M TBP was studied by irradiating with ^{60}Co γ -rays in the presence or absence of HNO_3 . As a result, G-values for DIDPA degradation and for DBP production were found to be 0.47 and 0.14, respectively, for the solvent irradiated in the absence of HNO_3 . The G-values based on the energy absorbed by the each extractant were 1.8 for DIDPA degradation and 4.4 for the DBP production. It can be considered that DIDPA is not less stable than TBP, at least.

The increase of the MIDPA concentration to 0.066 M from 0.039 M required the absorption dose of 0.5 MGy. The dose of 0.5 MGy corresponds to the more than 25 times recycle use of the solvent in an actual partitioning plant. The DIDPA solvent would be able to be used without washing for the MIDPA removal from the aspect of the Np back-extraction.

In the experiment on the extraction of Np initially in the pentavalent state with the

irradiated solvents, it was found that both the presence of TBP in the solvent and the addition of H_2O_2 to the aqueous solution depress the change of the extraction rate caused by the solvent degradation. The rate was not always determined by the concentration of MIDPA formed by radiolysis. In particular, HNO_3 -participating radiolysis products appeared influential when the solvent was irradiated in the presence of HNO_3 . Even in this case, however, the rate of the Np extraction did not change until the absorbed dose increased to 0.5 MGy. The radiolysis of the DIDPA solvent give practically no influence also on the forward-extraction of Np.

In an actual separation process, Np is extracted in a radiation field. On such condition, radicals produced by radiation might directly interact with Np and the extraction rate might be changed. It seems necessary to carry out the experiment on the Np extraction using an actual high-level waste.

Table IV-1 Oxidation State of Np after Back-extraction with $H_2C_2O_4$.

Extraction -				
Organic phase : 0.2 M MIDPA - 0.3 M DIDPA - 0.1 M TBP				
Aqueous phase : 0.5 M HNO_3 solution without H_2O_2				
Back-extraction -				
Organic phase : Prepared by the above extraction				
Aqueous phase : 0.7 M $H_2C_2O_4$ solution				
	Np(IV)		Np(VI)	
	Concentration (M)	Ratio (%)	Concentration (M)	Ratio (%)
Organic phase	1.20×10^{-3}	47.5	1.32×10^{-3}	52.4
Aqueous phase	1.50×10^{-4}	64.1	8.41×10^{-5}	35.9
Total	1.35×10^{-3}	49.1	1.40×10^{-3}	50.9
Distribution ratio	8.0		15.7	

Table IV-2 List of Irradiated Solvents

[DIDPA] = 0.5 M, [TBP] = 0.1 M

Symbol	Solvent Composition	Condition of Irradiation
A	DIDPA	solvent alone
B	DIDPA - TBP	solvent alone
C	DIDPA	in stationary contact with 0.5 M HNO ₃
D	DIDPA - TBP	in stationary contact with 0.5 M HNO ₃
E	DIDPA - TBP	continuously stirred with 0.5 M HNO ₃

Table IV-3 Absorbed Dose of Irradiated Solvents

Number	Absorbed Dose (MGy)
0	0
1	0.238
2	0.561
3	1.11
4	2.16

Table IV-4 Results of Analysis of the Solvents Irradiated Alone

No.	before washing			after washing			
	monobasic acid	dibasic acid	sum	monobasic acid	dibasic acid	H ₃ PO ₄	sum
A-0	0.513	0.037	0.550	0.508	0.037	0.00031	0.545
A-1	0.502	0.046	0.548	0.501	0.045	0.00105	0.547
A-2	0.492	0.055	0.547	0.488	0.056	0.00179	0.546
A-3	0.460	0.081	0.541	0.455	0.079	0.00478	0.539
A-4	0.429	0.105	0.534	0.424	0.097	0.00794	0.529
B-0	0.511	0.036	0.547	0.510	0.038	0.00029	0.548
B-1	0.503	0.044	0.547	0.503	0.046	0.00084	0.550
B-2	0.497	0.059	0.547	0.497	0.056	0.00157	0.555
B-3	0.475	0.078	0.553	0.478	0.079	0.00361	0.561
B-4	0.455	0.108	0.563	0.448	0.098	0.00799	0.554

Table IV-5 Composition of the Solvents Irradiated Alone

No.	DIDPA	MIDPA	H ₃ PO ₄	DBP
A-0	0.508	0.037	0.00031	-
A-1	0.501	0.045	0.00105	-
A-2	0.488	0.056	0.00179	-
A-3	0.455	0.079	0.00478	-
A-4	0.424	0.097	0.00794	-
B-0	0.510	0.038	0.00029	0
B-1	0.500	0.046	0.00084	0.003
B-2	0.490	0.056	0.00157	0.007
B-3	0.465	0.079	0.00361	0.013
B-4	0.422	0.098	0.00799	0.026

Table IV-6 Results of Analysis of the Solvents Irradiated in the Presence of Aqueous Phase of HNO₃

No.	before washing		after washing				sum
	monobasic acid	dibasic acid	monobasic acid	dibasic acid	H ₃ PO ₄		
					solvent	aq.phase*	
C-0	0.513	0.037	0.508	0.037	0.00031	-	0.545
C-1	0.500	0.047	0.493	0.048	0.00072	0.00334	0.545
C-2	0.475	0.060	0.475	0.059	0.00112	0.00707	0.542
C-3	0.434	0.088	0.435	0.085	0.00141	0.0170	0.538
C-4	0.365	0.1019	0.385	0.109	0.00193	0.0395	0.535
D-0	0.511	0.036	0.510	0.038	0.00029	-	0.548
D-1	0.497	0.051	0.497	0.051	0.00064	0.00267	0.551
D-2	0.479	0.065	0.480	0.065	0.00099	0.00651	0.553
D-3	0.438	0.098	0.442	0.098	0.00147	0.0161	0.558
D-4	0.374	0.130	0.386	0.125	0.00181	0.0377	0.551
E-1	0.500	0.049	0.494	0.051	0.00037	0.00610	0.551
E-2	0.477	0.068	0.471	0.069	0.00056	0.0145	0.555

*) Aqueous phase of HNO₃ which coexisted with solvent during irradiation

Table IV-7 Concentration of HNO₃ in the Aqueous Solution which Coexisted with the Solvent during the Irradiation

Number	Solvent C	Solvent D
0	0.506	0.506
1	0.47	0.49
2	0.43	0.4
3	0.34	0.3
4	<0.1	<0.1

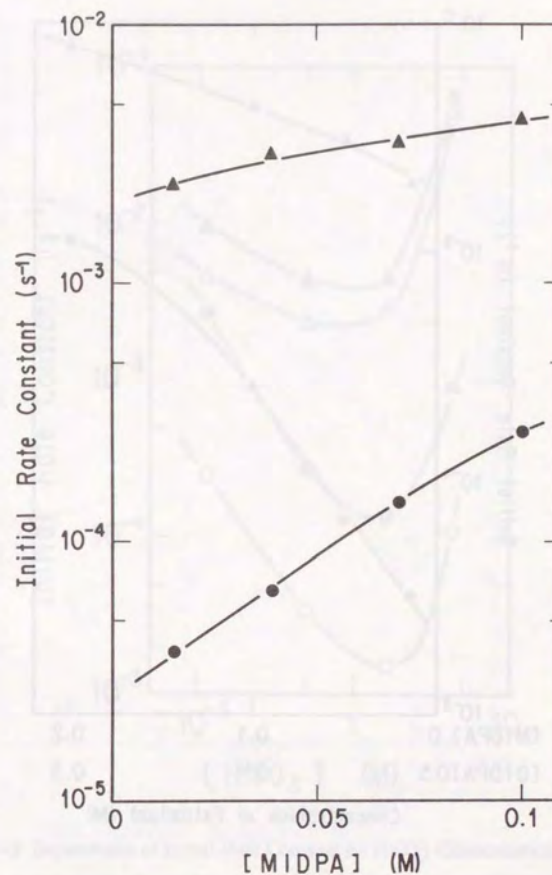


Fig. IV-1 Dependence of Initial Rate Constant on MIDPA Concentration.

[DIDPA] = 0.5 M, [TBP] = 0.1 M, [HNO₃] = 0.5 M, 25 °C

● : [H₂O₂] = 0 M, ▲ : [H₂O₂] = 0.5 M

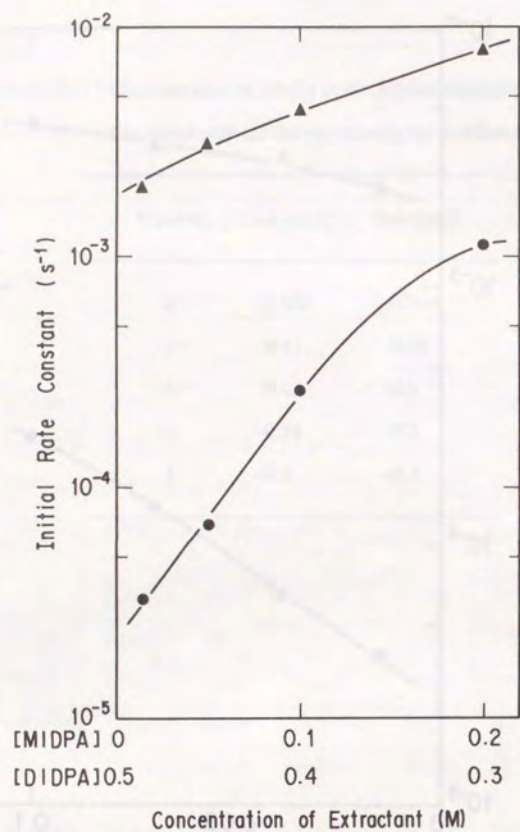


Fig. IV-2 Dependence of Initial Rate Constant on Molar Ratio of MIDPA to DIDPA.

[DIDPA] + [MIDPA] = 0.5 M, [TBP] = 0.1 M, [HNO₃] = 0.5 M, 25 °C

● : [H₂O₂] = 0 M, ▲ : [H₂O₂] = 0.5 M

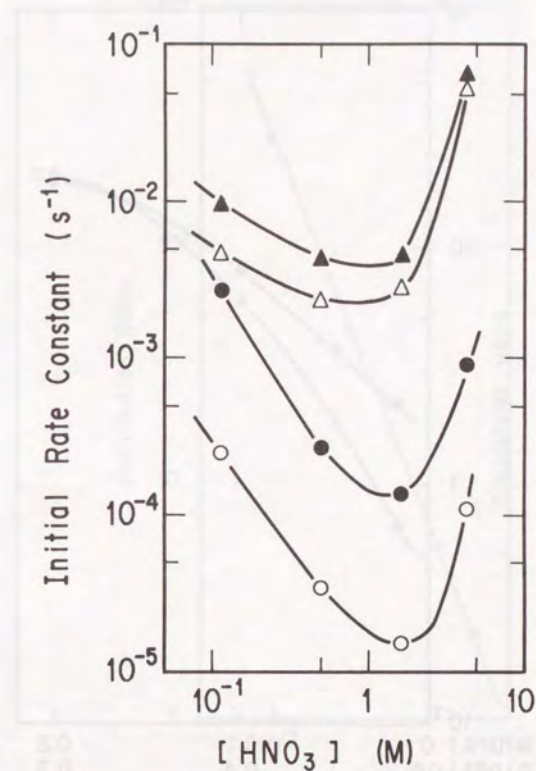


Fig. IV-3 Dependence of Initial Rate Constant on HNO₃ Concentration.

[TBP] = 0.1 M, 25 °C

● : [MIDPA] = 0.1 M, [DIDPA] = 0.4 M, [H₂O₂] = 0 M

▲ : [MIDPA] = 0.1 M, [DIDPA] = 0.4 M, [H₂O₂] = 0.5 M

○ : [MIDPA] = 0.017 M, [DIDPA] = 0.483 M, [H₂O₂] = 0 M

△ : [MIDPA] = 0.017 M, [DIDPA] = 0.483 M, [H₂O₂] = 0.5 M

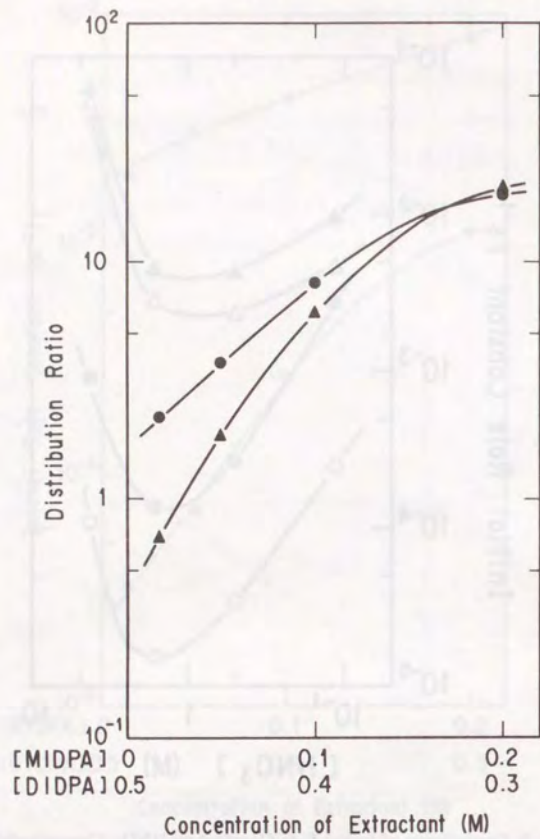


Fig. IV-4 Dependence of Distribution Ratio for Back-Extraction on Molar Ratio of MIDPA to DIDPA.

Extraction condition : [TBP] = 0.1 M, [HNO₃] = 0.5 M, 25 °C
 ● : [H₂O₂] = 0 M, ▲ : [H₂O₂] = 0.5 M
 Back-extraction condition : [H₂C₂O₄] = 0.5 M

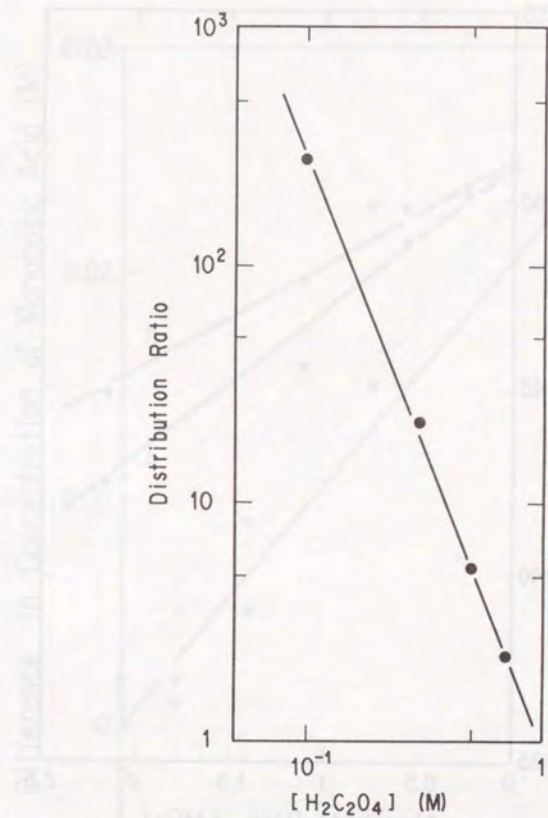


Fig. IV-5 Dependence of Distribution Ratio in the Back-Extraction of Np(IV) on the H₂C₂O₄ Concentration.

Extraction condition: [MIDPA] = 0.1 M, [DIDPA] = 0.4 M, [TBP] = 0.1 M,
 [HNO₃] = 0.5 M, [H₂O₂] = 0.5 M

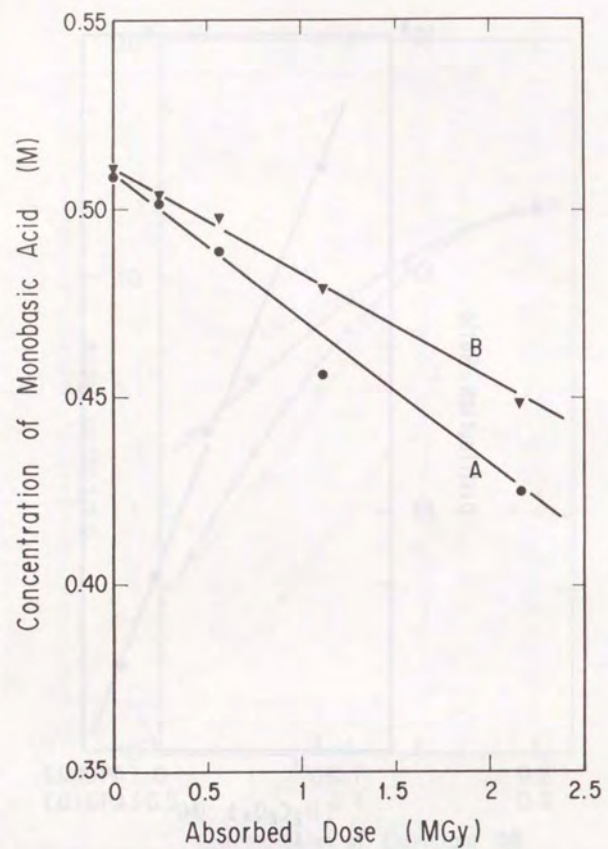


Fig. IV-6 Concentration of Monobasic Acid in the Solvents Irradiated Alone.

● : Solvent A which does not contain TBP

▼ : Solvent B which contains TBP

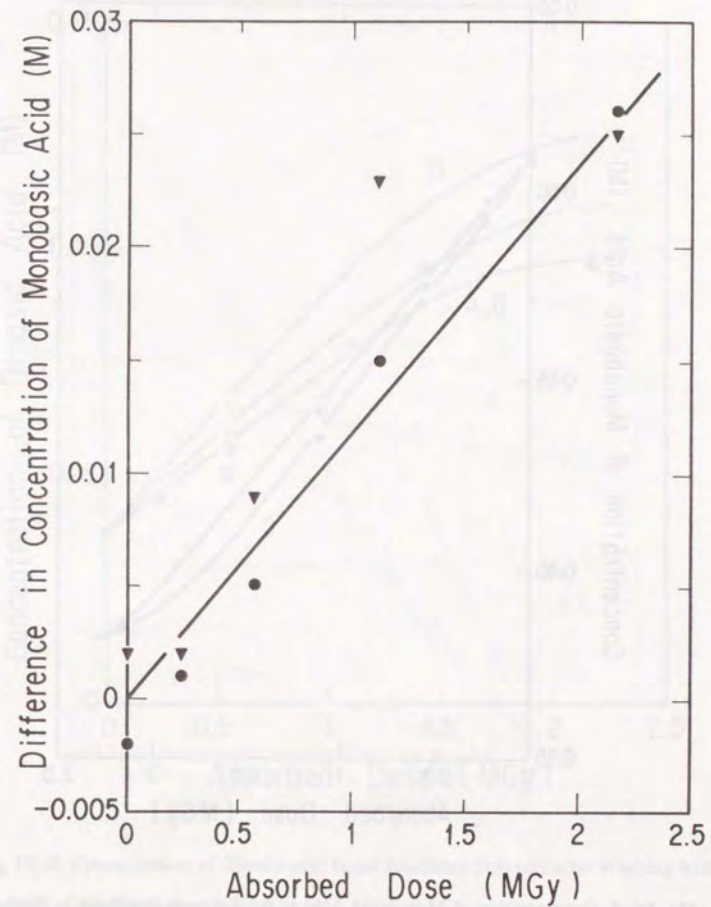


Fig. IV-7 Difference in Concentration of Monobasic Acid between Solvents A and B.

● : before washing, ▼ : after washing

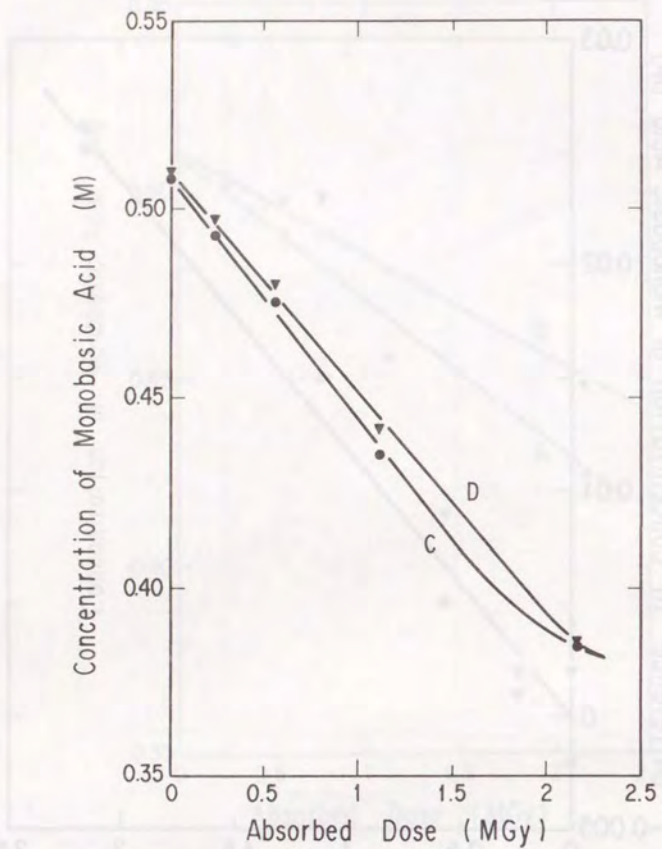


Fig. IV-8 Concentration of Monobasic Acid in the Solvents Irradiated in Stationary Contact with 0.5 M HNO₃.

● : Solvent C which does not contain TBP
 ▼ : Solvent D which contains TBP

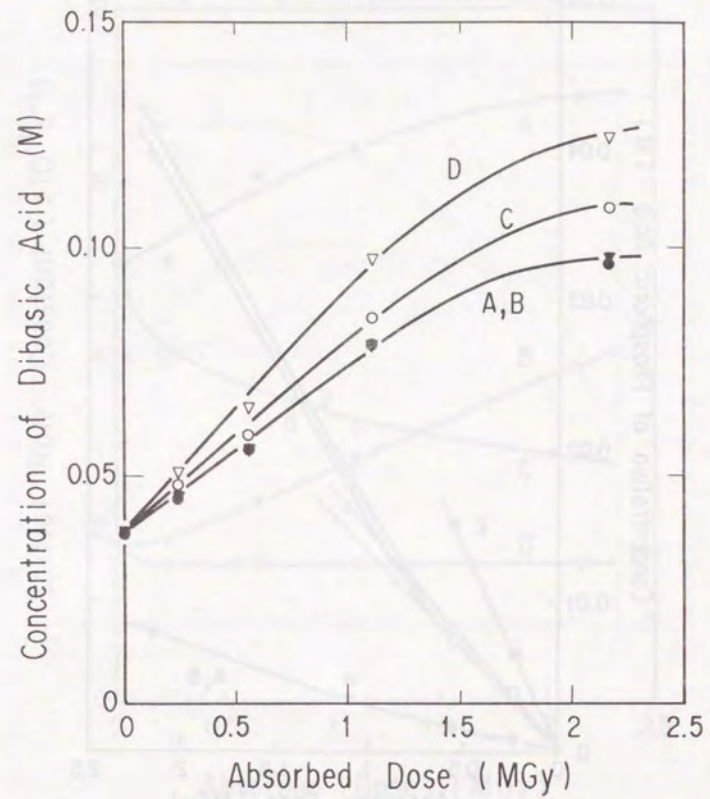


Fig. IV-9 Concentration of Dibasic acid in the Irradiated Solvents after Washing with 0.5 M HNO₃.

● : Solvent A ▼ : Solvent B ○ : Solvent C ▽ : Solvent D

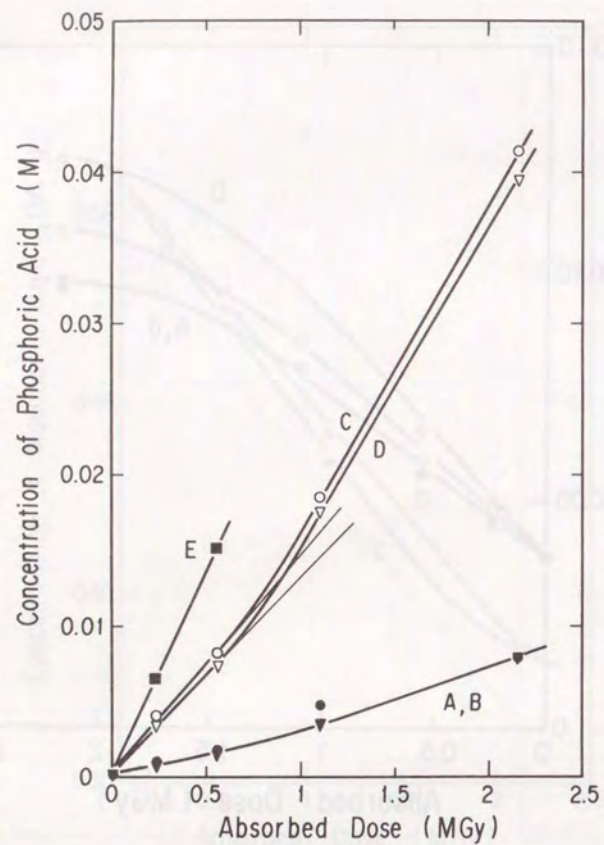


Fig. IV-10 Increase of the Sum of the H_3PO_4 Concentrations in the Washing Solution and the Irradiated solution.

● : for Solvent A ▼ : for Solvent B ○ : for Solvent C
 ▼ : for Solvent D ■ : for Solvent E

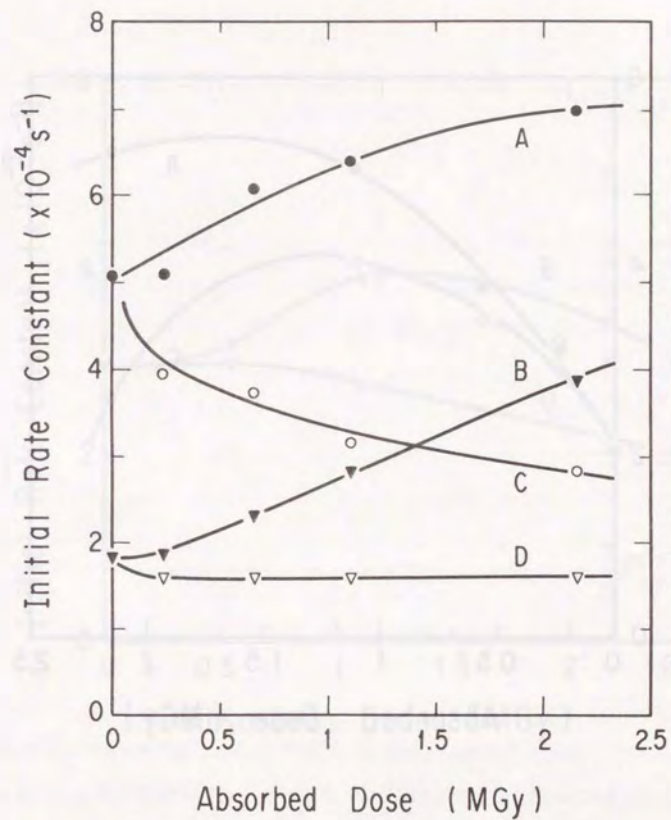


Fig. IV-11 Change of Neptunium Extraction Rate with Solvent Irradiation.

Aqueous Phase : Np(V) in 0.5 M HNO_3 solution.
 Organic Phase ● : Solvent A ○ : Solvent C
 ▼ : Solvent B ▼ : Solvent D

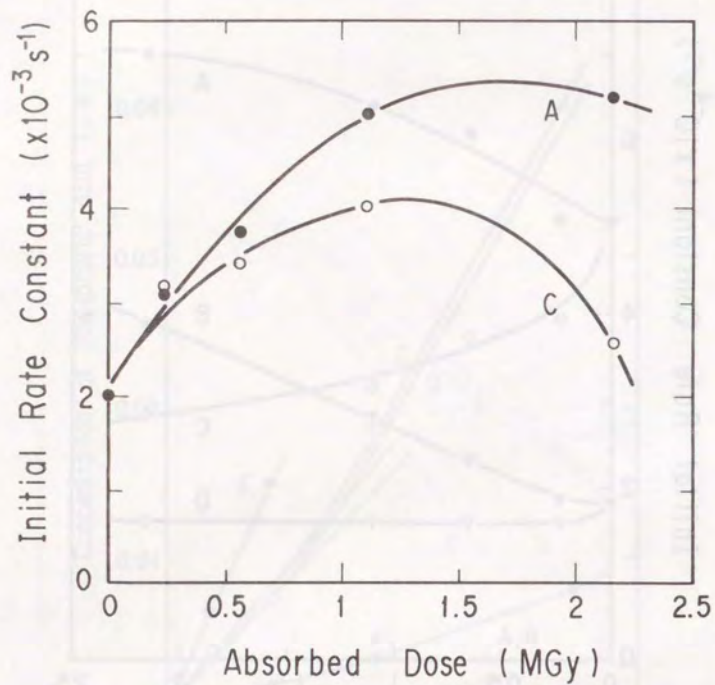


Fig. IV-12 Change of Neptunium Extraction Rate with Solvent Irradiation.

Aqueous Phase : Np(V) in 0.5 M H_2O_2 and 0.5 M HNO_3 solution

Organic Phase : Irradiated Solvent which does not contain TBP

● : Solvent A, ○ : Solvent C

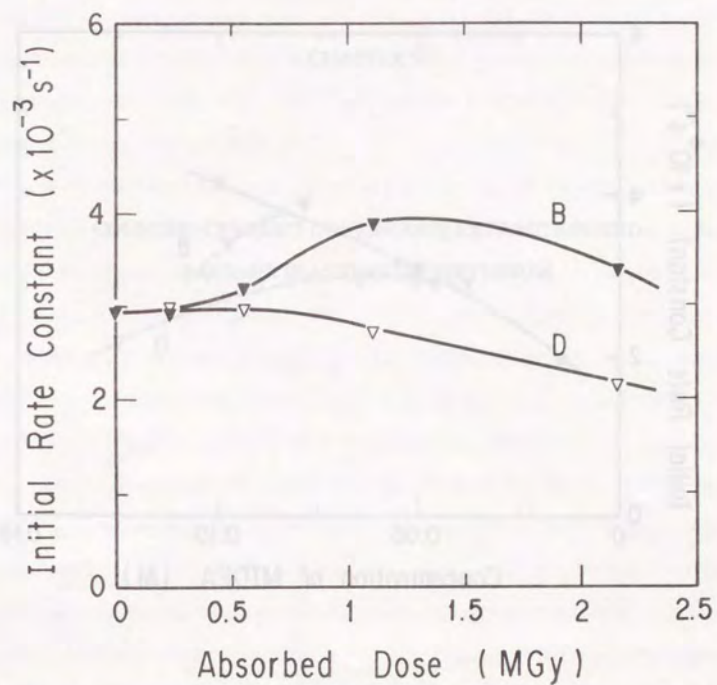


Fig. IV-13 Change of Neptunium Extraction Rate with Solvent Irradiation.

Aqueous Phase : Np(V) in 0.5 M H_2O_2 and 0.5 M HNO_3 solution

Organic Phase : Irradiated Solvent which contains TBP

▼ : Solvent B, ▽ : Solvent D

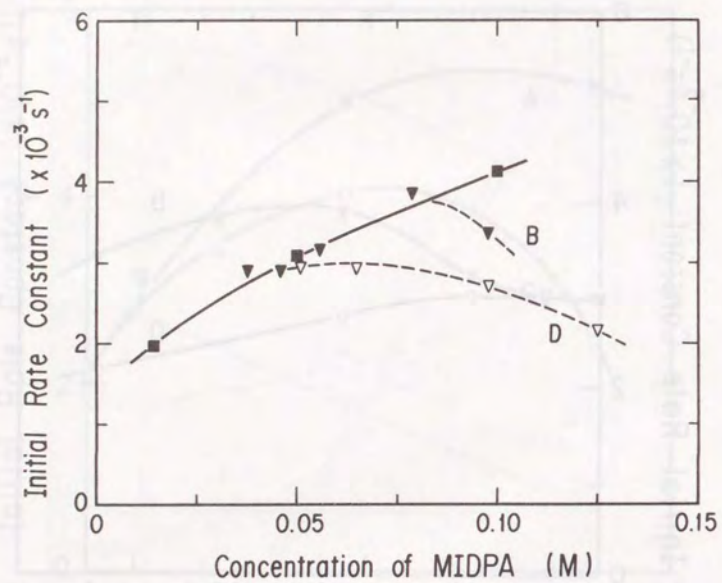


Fig. IV-14 Rates of Neptunium Extraction with Irradiated Solvent and with Mixed Solvent of MIDPA and DIDPA, Plotted Against MIDPA Concentration.
 Aqueous Phase : Np(V) in 0.5 M H₂O₂ and 0.5 M HNO₃ solution
 Organic Phase
 ▼ : Irradiated Solvent B ▽ : Irradiated Solvent D
 ■ : Mixed Solvent, [MIDPA]+[DIDPA]= 0.5 M, [TBP]= 0.1 M

COUNTER-CURRENT CONTINUOUS EXTRACTION AND
 BACK-EXTRACTION OF NEPTUNIUM

V-1 INTRODUCTION

The previous chapters dealt with the results and discussion of batchwise experiments on extraction of Np with DIDPA. They showed that Np initially in the pentavalent state could be extracted with DIDPA without adjustment of the Np oxidation state before extraction.

In the usual extraction, which is governed by distribution ratio at equilibrium, we can predict the behavior of an individual element in an actual separation process, i.e., the counter-current continuous extraction process, using the data of distribution ratios obtained through batchwise experiments under various conditions. However, the extraction rate should be considered in the Np extraction with DIDPA. In this case, it is necessary to perform experiments on counter-current continuous extraction and examine the ratio of Np extracted which is actually obtainable there.

The present chapter describes the results of the studies on the counter-current continuous extraction of Np(V) with DIDPA from a simulated HLW using a miniature mixer-settler. Batchwise extraction was also performed, keeping the initial condition the same as in the continuous extraction, in order to examine whether it is possible to make an estimate of the Np behavior in continuous extraction from the results of batchwise extraction. Then, the operating condition of a continuous extractor for the Np separation is discussed from a viewpoint of the application to an actual plant.

The Np extracted with DIDPA in the presence of H_2O_2 is in the pentavalent state in the organic phase, as shown in Chapter III, Section III-4. The Np(IV) can be back-extracted with $H_2C_2O_4$ without the change of the Np oxidation state. Continuous back-extraction of Np was also performed and the results are described in the present chapter.

EXPERIMENTAL

Reagents

A stored ²³⁷Np solution was used without adjustment of the Np oxidation state. In this solution, more than 98% of Np was pentavalent, which was verified by spectrophotometry.

Table V-1 shows the composition of the simulated HLW used in the continuous experiment. Concentrations of the elements except Np were calculated and estimated on condition that 1 m³ of HLW was produced by reprocessing 1 ton of spent fuel burned up to 28,000 MWd/t. Three other major elements in HLW, Zr, Mo and Te, were not added because they are to be separated as precipitates at the denitration step before the extraction step⁽⁷⁵⁾. Nevertheless, the simulated HLW was first prepared as 2 M HNO₃ solution and then it was denitrated with formic acid. After denitration, the concentration of HNO₃ in the simulated HLW was adjusted to 0.5 M. Finally, Np(V) was added to it.

The extractant, DIDPA, was used without further purification. n-Dodecane was used as a diluent. Tributylphosphate was also added to the solvent.

Procedure

A 16-stage miniature mixer-settler was set in a thermostatted air bath. The settler volume was 49 ml and the mixer volume was practically 7 ml. The operating conditions are shown in Fig. V-1 (a) and (b). The condition shown in Fig. V-1 (a) is the same as that in the partitioning process studied for the separation of Am and Cm at JAERI⁽⁸⁾, except for the addition of H₂O₂.

A preliminary experiment showed that 4-hour operation of the mixer-settler was enough to reach equilibrium. In the present experiments, the extractor was operated for 5 to 7 hours.

RESULTS AND DISCUSSION

Table V-2 shows the experimental conditions of the continuous extraction. The ratio of Np extracted was also shown as one of the results.

Figure V-2 shows concentration profiles of Np in the Run No. 4 as a typical case. The Np concentrations in aqueous phases at the extraction section (stage No. 7 to 1) decreased with the stage numbers. This decrease depends on the extraction rate of Np. The plots of the aqueous concentrations gave a straight line since the extraction of Np in the presence of H₂O₂ is the first-order reaction with respect to the Np concentration. The first-order rate constant (K) in the continuous extraction can be calculated from the slope of the line and residence time of the aqueous phase in the mixer.

The slope of the line can be transformed to the reduction factor "r" of Np concentration per one stage of the mixer-settler, defined in the equation:

$$C_n = r \cdot C_{n+1} \dots\dots\dots (V-1)$$

where C_n represents the Np concentration at the stage No. n (n = 7-1). On the other hand, using K and contacting time "t_c" at the mixer (extraction time per one stage of the mixer) the following equation can be derived.

$$C_n = C_{n+1} \exp(-K \cdot t_c) \dots\dots\dots (V-2)$$

Therefore,

$$r = \exp(-K \cdot t_c) \dots\dots\dots (V-3)$$

$$K = -\frac{\ln(r)}{t_c} \dots\dots\dots (V-4)$$

The value of K in the Run No. 4 (45 °C) was found to be $9.0 \times 10^{-3} \text{ s}^{-1}$, and in the Run No. 3 at 25 °C, K was $5.4 \times 10^{-3} \text{ s}^{-1}$. The Rate Constant obtained in batchwise extraction from 0.5 M DIDPA - 0.1 M TBP solution was $3.13 \times 10^{-3} \text{ s}^{-1}$ at 25 °C in the presence of 0.5 M H_2O_2 , which was plotted in Fig. IV-1. When the H_2O_2 concentration decreases to 0.25 M (the same concentration in the present continuous experiment), the Constant becomes $2.21 \times 10^{-3} \text{ s}^{-1}$, which was calculated using the 1/2-power dependence on the H_2O_2 concentration. The above K , $5.4 \times 10^{-3} \text{ s}^{-1}$, does not agree with this value and is 2.44 times larger. This is due to the difference in the ratio of the organic to aqueous phase (O/A). In the present continuous extraction, $O/A = 2$, while in the batchwise extraction, $O/A = 1$. An additional experiment showed that the extraction rate became 2.39 times larger when O/A increased from 1 to 2. Thus, there is no difference in the extraction between continuous and batchwise experiment.

In the present study, it is important to investigate the concentration profile of Np in the aqueous phase at the extraction section. Figure V-3 shows the profiles in the Runs at 25 °C and Fig. V-4 does at 45 °C.

In the Runs No. 5 and No. 6 with Nd, the ratio of Np extracted was smaller than that in the Runs No. 3 and No. 4, respectively. This is due to the decrease of the concentration of free DIDPA. The Nd concentrations in the organic phases are higher at the stages closer to the feed point (stage No. 7). The extraction of Np, therefore, proceeded slowly in the first two or three stages (from No. 7 to No. 6 or No. 5). In the latter half of the extraction stages, Np was extracted at almost the same rate as in the run without Nd. As shown in Fig. V-4, the line from stage No. 4 to No. 1 in the Run No. 6 was parallel to that in the Run No. 4.

When Pd and Fe were added to the feed solution, the extraction of Np was accelerated by their catalytic effect, in particular at the stages closer to the feed point. As described in Chapter III, the combination of Fe and Pd accelerates the Np extraction. The deleterious effect of Nd disappeared or was hidden by the great acceleration by Fe and Pd. The rate constant, K , at the first stage in the Run No. 8 was found to be $2.7 \times 10^{-2} \text{ s}^{-1}$, which was 3.0 times as large as in the Run No. 4 without the catalysts.

On the contrary, the extraction of Np became slow at the latter stages (stage No. 3 to No. 1). The plot for the Run No. 8 in Fig. V-4 gave not a straight line but a curve. This deceleration was due to the decomposition of H_2O_2 . The formation of gas bubbles was observed at the stages of No. 7 to No. 5. The presence of Pd and Fe accelerated not only the extraction of Np but also the decomposition of H_2O_2 . The concentration of H_2O_2 at the latter stages of the extraction section was so low that the effect of H_2O_2 on the Np extraction disappeared. The additional feed of H_2O_2 to compensate its decomposition will, therefore, increase the extraction ratio of Np.

The behavior of Np in the extraction from the simulated HLW (Runs No. 9 and No. 10) was very similar to that in the runs with Pd and Fe, since the catalysts were included also in the simulated HLW. The ratio of Np extracted was, however, a little decreased. Its reason was not clear, but it is supposed that some of the other elements in HLW still influence the Np extraction. The rate constant in the beginning of the extraction in the Run No. 10 was $1.75 \times 10^{-2} \text{ s}^{-1}$, which is 1.9 times as large as in the Run No. 4, but 0.65 times of K in the Run No. 8.

Figure V-5 shows the concentration profiles of Np in the Runs No. 13 and No. 14 which have the additional feed of H_2O_2 to the stage No. 3. As shown by the plot for the Run No. 13, the rate of Np extraction increased again at the stage No. 3. When the concentration of H_2O_2 was increased (the Run No. 14), the Np extraction was further accelerated and 99.0 % of Np was extracted.

In the Run No. 15, the number of extraction stages was doubled and H_2O_2

solutions were poured into two of the stages, as shown in Fig. V-1 (b). Then more than 99.96 % of Np was extracted from the simulated HLW. The concentration profile of Np is shown in Fig. V-6. This result confirms that this extraction is a promising method for the Np separation from HLW. The reason why such a high recovery of Np was achieved is that the reduction and extraction of Np take place simultaneously in the presence of DIDPA and H_2O_2 . However, more quantitative discussion is required for the application of this method to an actual plant, and will be given in the next section.

V-3 CONSIDERATION ON APPLICATION OF THE NEPTUNIUM EXTRACTION TO AN ACTUAL PLANT

EXPERIMENTAL

Procedure

Experiments on batchwise extraction to be compared with the continuous extraction were carried out using a 1-stage mixer which was modified to prevent the liquid flow. Extraction from the simulated HLW which was not denitrated was performed to examine the effect of the chemical forms of elements in HLW. The other experimental conditions are the same as in the experiments of the preceding section.

RESULTS AND DISCUSSION

Comparison between continuous and batchwise extractions

As the first step, an experiment on batchwise extraction of Np was carried out using a 1-stage mixer, keeping the initial condition the same as at the first extraction stage in the Runs No. 14 and No. 15, which were shown in the preceding section. Figure V-7 shows the comparison of the results between the batchwise and continuous extractions. Plots for the batchwise extraction (\bullet) lay well on the curve representing the results of the continuous extraction (\circ and \square , which were plotted against the total residence time in the mixer). This agreement indicates that the progress of the Np extraction was determined by the contacting time of the aqueous and the organic phases regardless of contacting manner, with or without the liquid flow, and with or without settling of the two phases. In the continuous extraction, the aqueous phase stays in the

settler for a longer time (around 500 s) than in the mixer (42–43 s). However, the settling does not affect the Np extraction. The result of another batchwise extraction which had the settling time showed that the Np extraction was independent of the length of the settling time (Table V-3). It can be considered that both the change of the Np oxidation state (reduction) and the decomposition of H_2O_2 in the settler is negligible for the Np extraction. These findings show that it is possible to make a quantitative estimate for the Np extraction in a counter-current extractor from the experiment on batchwise extraction. The batchwise extraction shown in Fig. V-3 leads to the overall evaluation of the Np extraction including the effect of the H_2O_2 decomposition.

As mentioned before, some elements catalyze the Np extraction and the H_2O_2 decomposition. These catalytic effects may depend on the chemical form of the elements. To examine such phenomena, the aqueous solution was changed to the simulated HLW which was directly prepared as a 0.5 M HNO_3 solution without denitration, where the chemical form of the elements may be different. The result was also plotted by \blacktriangle in Fig. V-7. The Np extraction was very fast in the beginning but soon became slow, which means that H_2O_2 decomposed faster. As was expected, the chemical form of the elements influenced the extraction behavior of Np. However, even when H_2O_2 decomposes faster, further addition of H_2O_2 must keep the high recovery of Np because the Np extraction is very fast at the beginning and at the point where a new H_2O_2 solution is poured. In other words, the influence by the difference in chemical forms of the catalyzing elements can be reduced by designing the best way to add H_2O_2 .

The denitration of HLW might make each element in a particular chemical form. If that is the case, only the chemical form after denitration should be examined for the Np extraction and the H_2O_2 decomposition.

Application of the Np Extraction to other extractors

Figure V-8 shows concentration profiles of Np in aqueous phase at extraction section in the Runs No. 14 and No. 15. In this figure, stages are numbered from the feed point to make it easy to compare the results. The rate of Np extraction was faster just after the contact with added H_2O_2 (the stage of No. 0 and the stages pointed by downward arrows), but became slow stage by stage. Such decrease of the rate was due to the decomposition of H_2O_2 , which had been discussed already.

In order to explain the Np behavior, it is necessary to know the extraction rate at each stage precisely, but is very complicated. That is because the concentration of H_2O_2 at each stage can hardly be evaluated. However, this discussion is still very important to find the optimum condition for Np separation such as the required number of stages and to know how to maintain the high recovery of Np in other extractors including a plant scale one.

As the first trial, the reduction of Np concentration after a certain number of stages was evaluated. This is the overall evaluation which was mentioned in the preceding sub-section. Table V-4 shows the reduction factor, which is the ratio of Np concentration after the 3 stages to the concentration before 3 stages. The two experiments showed almost the same results. Average reduction factors were 0.078 at the first 3 stages from the feed point and 0.173 after the addition of the H_2O_2 solution. Concentrations of H_2O_2 were 0.5 and $0.35+\alpha$ M, respectively (α means the concentration of the residual H_2O_2 from the previous stage.).

The following can be estimated using these reduction factors. When the same type of mixer-settler is used and H_2O_2 is added to the scrub solution and to every 3-stages at the same concentrations, as shown in Fig. V-9, the Np concentration in the raffinate would become $0.078 \times (0.173)^3 = 4.0 \times 10^{-4}$ times of the initial concentration, which means 99.96 % recovery can be achieved. The number of the extraction stages can be reduced from 14 to 12 by increasing the addition of H_2O_2 from twice to three

times.

When other type of mixer-settler is used, the above estimation can not be applied directly. However, the applicability can be improved by considering the residence time of the aqueous solution in the mixer. The batchwise experiments described in the preceding sub-section showed that both the Np extraction and the decomposition of H_2O_2 were determined by the length of mixing and were independent of settling. Only the mixing time should be considered to evaluate the Np extraction behavior in other type of mixer-settler or to design a new extractor and its operation.

Since the residence time in the mixer was 42–43 s in the present experiment, H_2O_2 should be added every 126–129 ((42–43)×3) s of the contacting time of the two phases in the extraction section to make its concentration higher than 0.35 M and also to the scrub solution (1.0 M), and the total contacting time should be more than 516 (43×12) s. Then more than 99.95 % recovery can be achieved even with other types of extractors.

V-4 CONTINUOUS BACK-EXTRACTION OF NEPTUNIUM WITH A OXALIC ACID SOLUTION

EXPERIMENTAL

Reagents

The DIDPA solvent containing Np(IV) was obtained in the continuous extraction described in Section V-2. The Np concentration in the solvent was 2×10^{-6} M. The solvent also included some of the elements in the simulated HLW which were extracted and not back-extracted with 4 M HNO_3 . The elements in the solvent used in the present experiment were not analyzed but would be Fe, Ru and Rh. In cold experiments without Np, which is described in the next chapter, the solvent after back-extraction with 4 M HNO_3 contained 5×10^{-3} M Fe, 2×10^{-4} M Ru and 1×10^{-4} M Rh.

The $H_2C_2O_4$ concentration was 0.8 M, which is less than 80 % of the solubility limit at room temperature.

Procedure

The same mixer-settler was used for continuous back-extraction with $H_2C_2O_4$ at 25 °C. The whole 16 stages are used and the flow rates of both phases were 300 ml/h.

RESULTS AND DISCUSSION

Figure V-10 shows the result of counter-current continuous back-extraction of Np with $H_2C_2O_4$ solution. Concentration of Np in the organic phase at No. 12 stage was less than 2×10^{-9} M, which was the detection limit for this solution. It was

confirmed that more than 99.9 % of Np was recovered with the 0.8 M $\text{H}_2\text{C}_2\text{O}_4$ solution. Concentration profile shown in Fig. V-10 could be explained with distribution ratio at equilibrium (D) obtained through the experiment on batchwise back-extraction. Under the present condition, D of Np is 0.52. In the initial stages (from No. 1 stage) the presence of Fe, which is back-extracted with $\text{H}_2\text{C}_2\text{O}_4$, influenced the Np back-extraction. In batchwise back-extraction from the present organic feed solution, D of Np was found to be 0.84. The concentration profiles of Np calculated by using the two values of D, 0.84 for No. 1 stage and 0.52 for other stages, agreed closely with the profiles shown in Fig. V-10.

Since Np in the organic phase, extracted in the presence of H_2O_2 , was in the tetravalent state and the Np distributed itself between the DIDPA solvent and the $\text{H}_2\text{C}_2\text{O}_4$ solution without the change of its oxidation state, it is much easier to understand the Np behavior in the continuous back-extraction. For 99.9 % recovery, it is not necessary to use 16 stages.

V-5 CONCLUSION

In counter-current continuous extraction with DIDPA using a mixer-settler, 95.6 % of Np was separated from the simulated HLW by 7-stages extraction at 45 °C with the addition of H_2O_2 to scrub solution. Some elements in the simulated HLW accelerated not only the Np extraction but also the H_2O_2 decomposition. Therefore, further addition of H_2O_2 to the extraction section was required to increase the ratio of Np extracted. The 14-stage extraction and twice addition of H_2O_2 increased the Np recovery to more than 99.96 %. This result showed that the Np extraction with DIDPA in the presence of H_2O_2 was a promising method for the separation of Np from HLW with a very high recovery.

The results of the continuous extraction agreed with the results of batchwise extraction using 1-stage mixer without the liquid flow. This gave a good prospect of designing a large scale extractor.

At the extraction step, temperature should be raised and H_2O_2 should be added several times. The contacting time of the aqueous and organic phases is the most important parameter for Np extraction. If the total contacting time is more than 512 s and H_2O_2 is properly added, 99.95 % recovery of Np would be able to be achieved even with other types of extractors.

The back-extraction of Np with $\text{H}_2\text{C}_2\text{O}_4$ is a simple process which is independent of the change of Np oxidation state. In 12-stage continuous back-extraction, more than 99.9 % of Np was recovered from the DIDPA solvent.

A separation process for Np by extraction with DIDPA from HLW can be established from the present study. First, Np is extracted from 0.5 M HNO_3 HLW with the 0.5 M DIDPA - 0.1 M TBP solvent in a very high recovery by adding H_2O_2 . Here, Pu, Am and Cm (and rare earths) are extracted simultaneously. After back-extraction of trivalent actinides, Am and Cm, with 4 M HNO_3 , Np (and Pu) is back-extracted

with $H_2C_2O_4$. The process gives a very high yield of Np as a product.

Table V-1 Composition of Simulated HLW
Used in Continuous Extraction.

Element	Conc.(M)	Reagent used
Na	0.038	NaNO ₃
Cr	0.0046	Cr(NO ₃) ₃ ·9H ₂ O
Fe	0.019	Fe(NO ₃) ₃ ·9H ₂ O
Ni	0.0030	Ni(NO ₃) ₂ ·6H ₂ O
Rb	0.0037	RbNO ₃
Sr	0.0083	Sr(NO ₃) ₂
Ru	0.017	RuNO(NO ₃) ₃
Rh	0.0040	Rh(NO ₃) ₃
Pd	0.0090	Pd(NO ₃) ₂
Cs	0.019	CsNO ₃
Ba	0.010	Ba(NO ₃) ₂
Nd	0.063	Nd(NO ₃) ₃ ·6H ₂ O
Np	6.8×10 ⁻⁶	NpO ₂ ⁺

Table V-2 Experimental Condition of the Continuous Counter-Current Extraction and the Ratio of Np Extracted.

Run No.	Temp. (°C)	Feed solution	Extracting stages	[H ₂ O ₂] in scrub (M)	Addition of H ₂ O ₂ Stage No.	Conc.(M)	Extracted (%)
1	25	Np alone	7	0	-	-	24.6
2	45	Np alone	7	0	-	-	45.4
3	25	Np alone	7	0.5	-	-	78.8
4	45	Np alone	7	0.5	-	-	92.7
5	25	Np, Nd	7	0.5	-	-	70.6
6	45	Np, Nd	7	0.5	-	-	83.2
7	25	Np, Nd, Pd, Fe	7	0.5	-	-	98.4
8	45	Np, Nd, Pd, Fe	7	0.5	-	-	98.5
9	25	Simulated HLW	7	0.5	-	-	92.1
10	45	Simulated HLW	7	0.5	-	-	95.6
12	25	Simulated HLW	7	0.5	3	5.0	95.5
13	45	Simulated HLW	7	0.5	3	5.0	98.2
14	45	Simulated HLW	7	1.0	3	8.0	99.0
15	45	Simulated HLW	14	1.0	3 & 7	8.0	>99.96

Table V-3 Dependence of the Np Extraction on the Length of Settling Time in the Batchwise Extraction.

Initial condition was the same as in Fig. V-7

Mixing : 40 s × 3 times = 2 min.

Settling : variable length, twice.

Settling time (min)	Ratio of Np remaining in aqueous phase
2 × 2 = 4	0.0794
5 × 2 = 10	0.0757
10 × 2 = 20	0.0767

Table V-4 Reduction Factors of Np Concentration after 3- Stages

Extraction at Runs No. 14 and No. 15.

" α " means the concentration of the residual hydrogen peroxide from the previous stages.

Run No.	[H ₂ O ₂] (M)	Reduction Factor	Stage No. in Fig.V-8
14	0.488	0.0819	0 to 3
	0.353 + α	0.180	4 to 7
15	0.502	0.0738	0 to 3
	0.372 + α	0.164	7 to 10
	0.322 + α	0.175	11 to 14

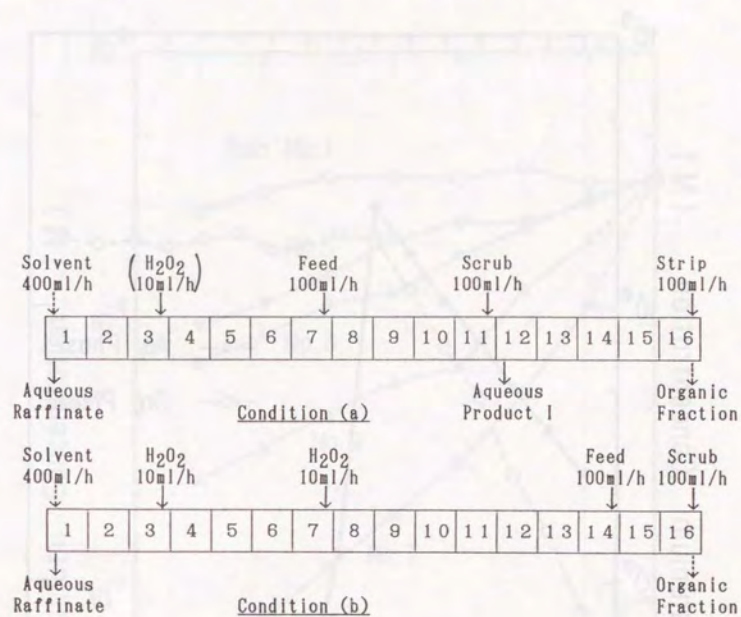


Fig. V-1 Operating Condition of the Mixer-Settler.

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 or 1.0 M

Strip : 4.0 M HNO₃

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

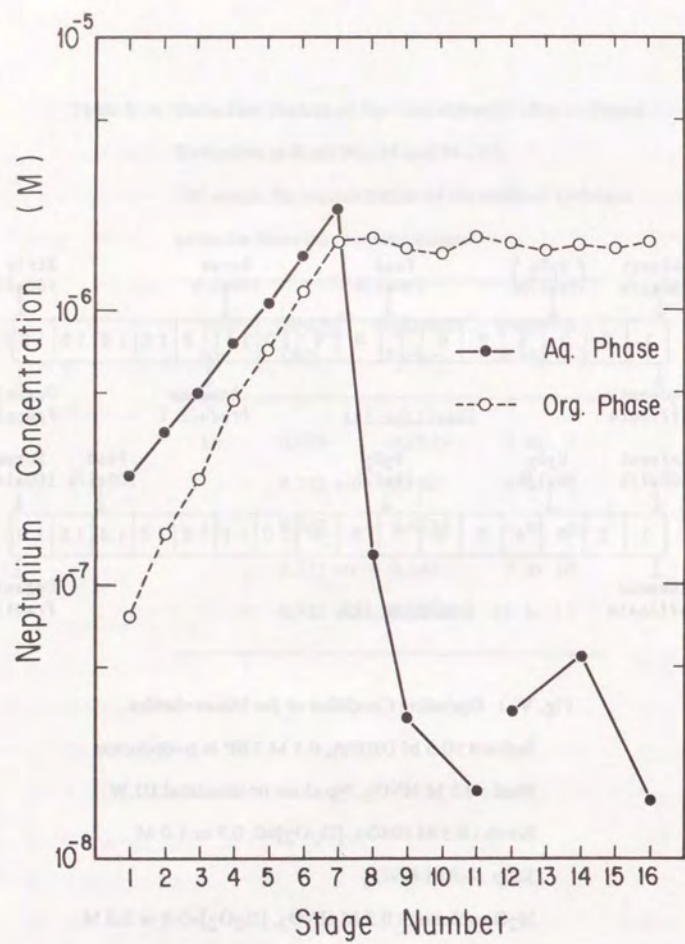


Fig. V-2 Concentration Profile of Np in the Mixer-Settler. -Run No.4-

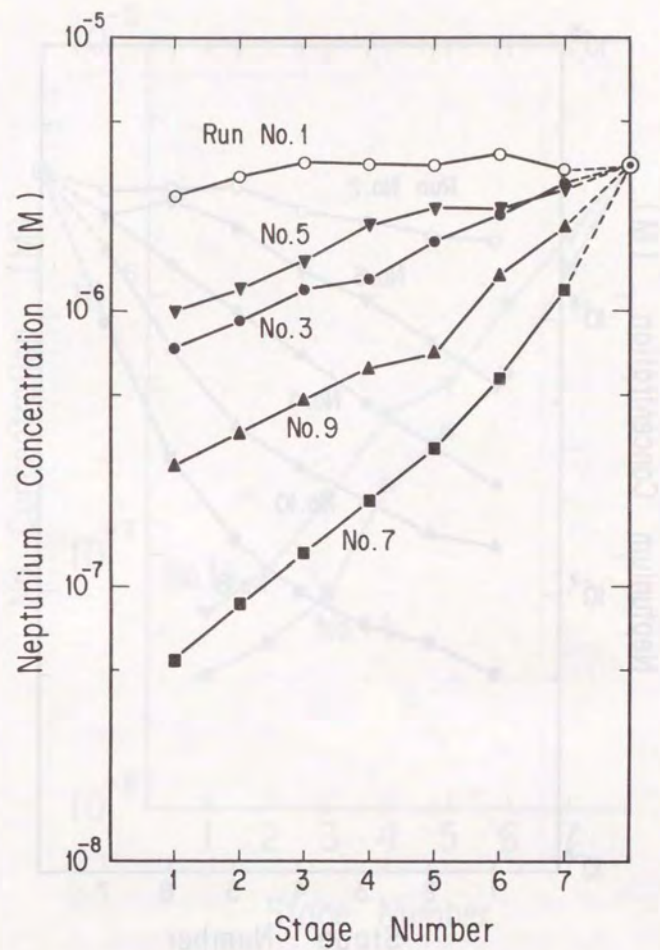


Fig. V-3 Concentration Profile of Np in Aqueous Phase at the Extraction Section.

-Runs at 25 °C-

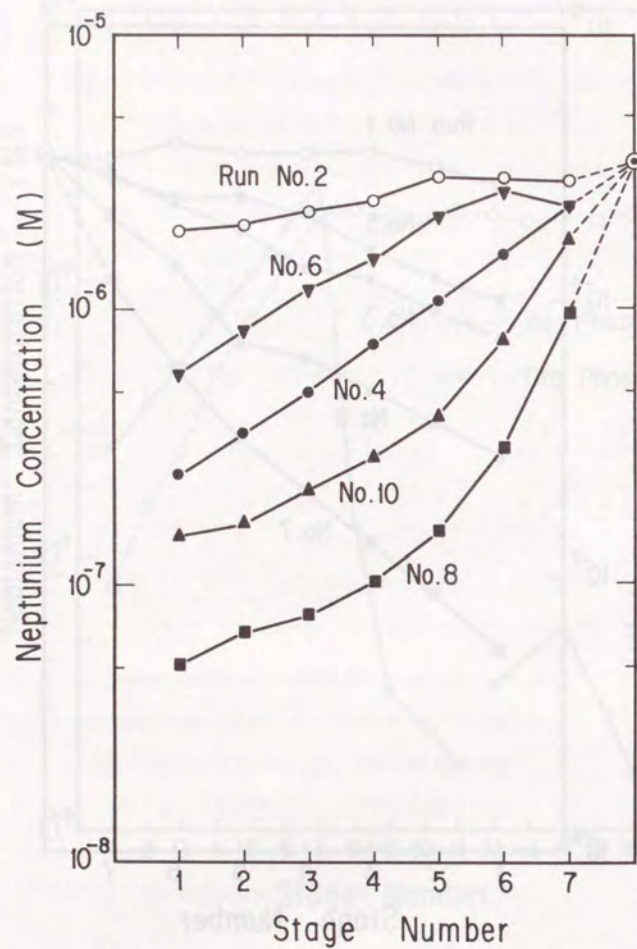


Fig. V-4 Concentration Profile of Np in Aqueous Phase at the Extraction Section.

-Runs at 45 °C-

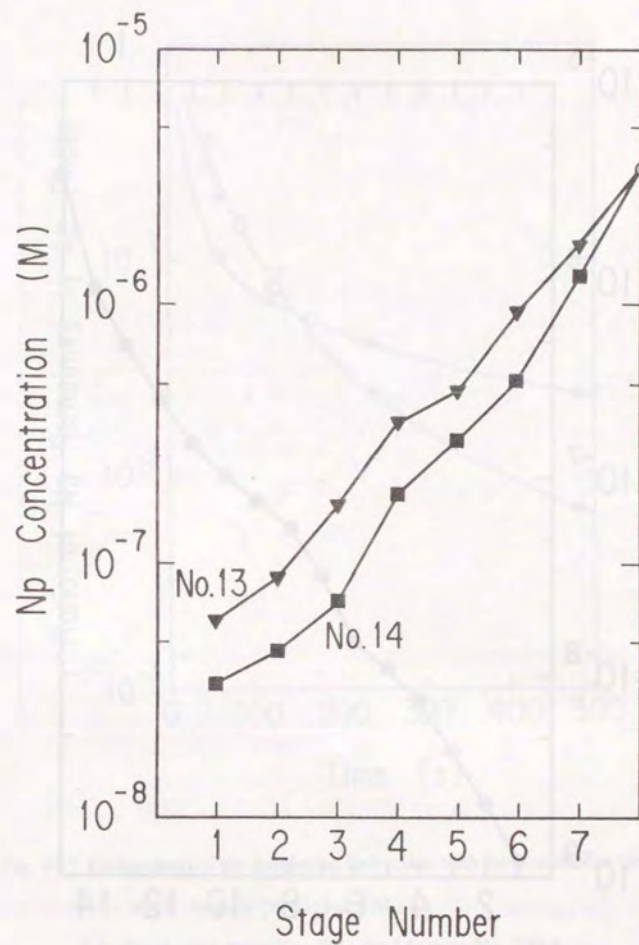


Fig. V-5 Concentration Profile of Np in Aqueous Phase at the Extraction Section.

-Runs No. 13 and No. 14 at 45 °C-

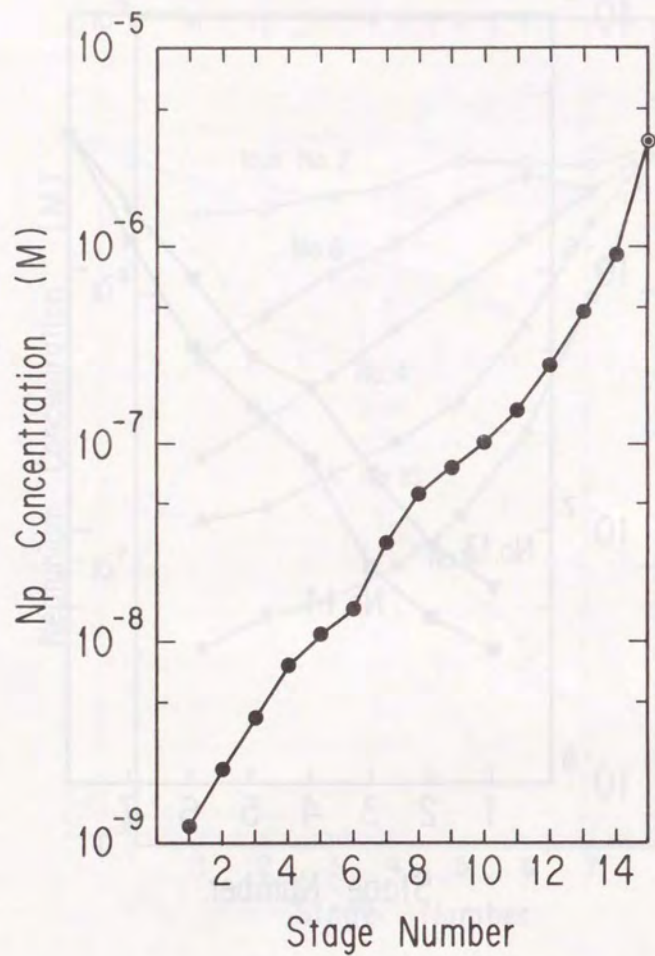


Fig. V-6 Concentration Profile of Np in Aqueous Phase at the Extraction Section.
-Run No. 15-

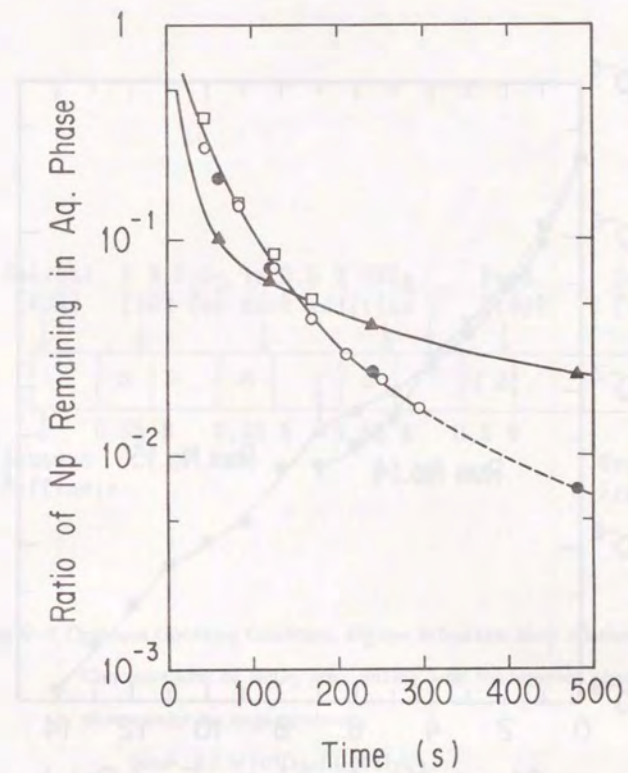


Fig. V-7 Comparison of the Batchwise Extraction with the Continuous One.
45 °C. Initially [H₂O₂]=0.5 M.

- : Continuous extraction, Run No.14, stage No. 7 to 4.
- : Continuous extraction, Run No.15, stage No. 14 to 8.
- : Batchwise extraction, Denitrated simulated HLW.
- ▲ : Batchwise extraction, Not denitrated simulated HLW.

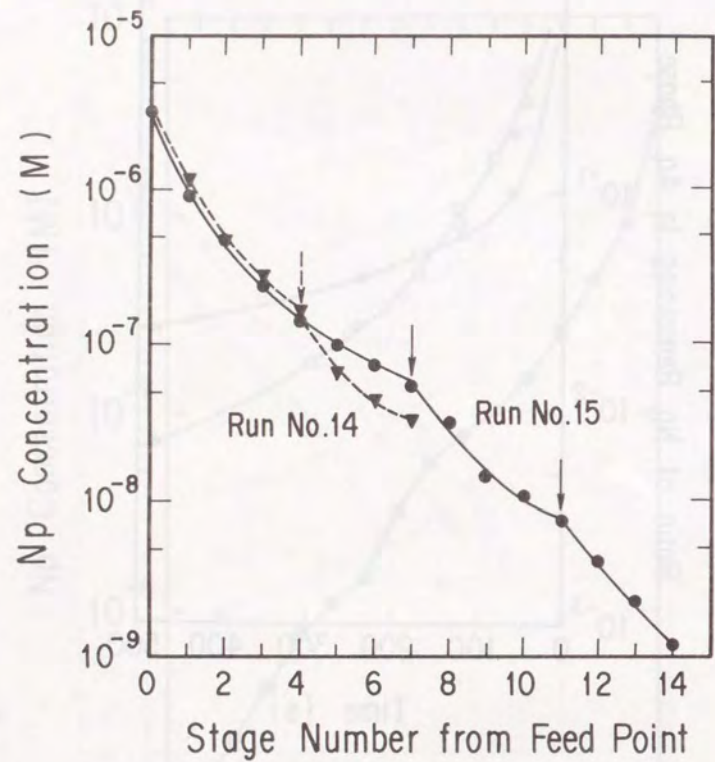


Fig. V-8 Concentration Profile of Np in Aqueous Phase at the Extraction Section in Runs No. 14 and No. 15.
Downward arrows show the points where H_2O_2 solutions are added.

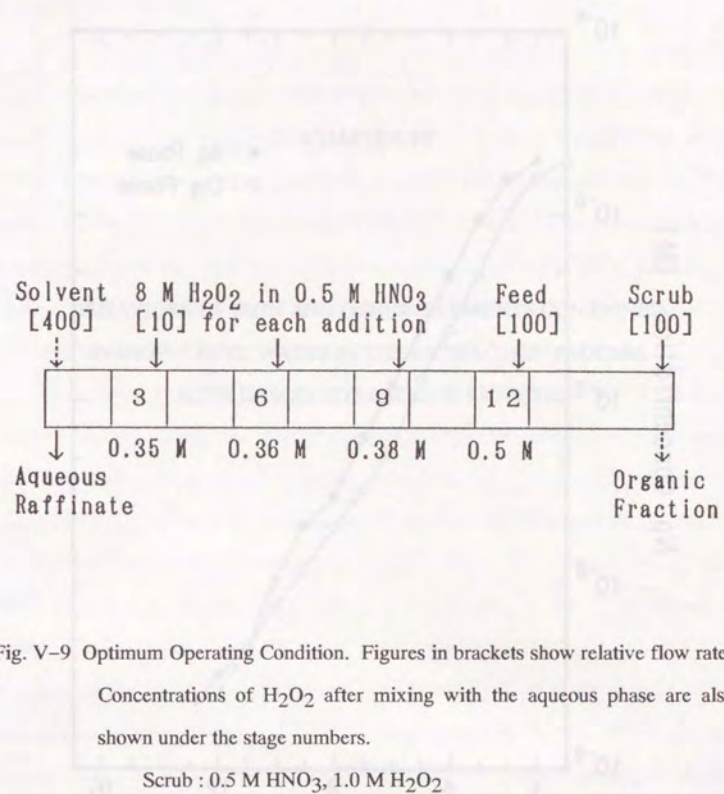


Fig. V-9 Optimum Operating Condition. Figures in brackets show relative flow rates.
Concentrations of H_2O_2 after mixing with the aqueous phase are also shown under the stage numbers.

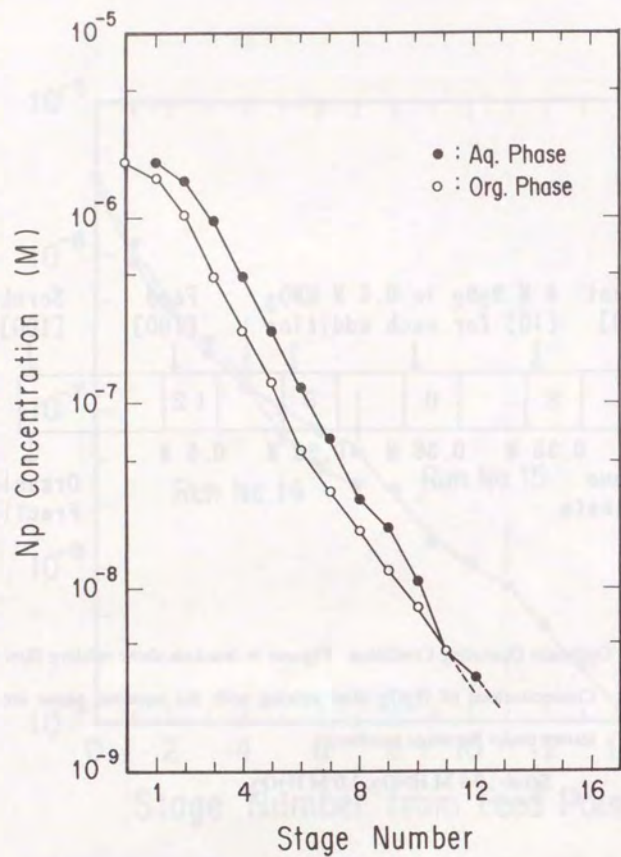


Fig. V-10 Concentration Profile of Np in the 16-Stage Back-Extraction with $H_2C_2O_4$ at 25 °C

Feed : the DIDPA solvent containing $2 \times 10^{-6} M$ Np.

Strip: 0.8 M $H_2C_2O_4$.

CHAPTER VI

BEHAVIORS OF IRON AND OTHER ELEMENTS CONTAINED
IN HIGH-LEVEL WASTE IN THE EXTRACTION PROCESS
WITH DIISODECYLPHOSPHORIC ACID

VI-1 INTRODUCTION

Studies described in the previous chapters showed that quantitative separation of Np initially in the pentavalent state could be achieved by some modifications of the DIDPA extraction process developed for the separation of trivalent actinides at JAERI. For the high recovery of Np, H_2O_2 should be added and temperature should be raised. Experiments on counter-current continuous extraction of Np with DIDPA showed that more than 99.96 % of Np was separated from the simulated HLW. The extracted Np could be back-extracted with $\text{H}_2\text{C}_2\text{O}_4$.

Behaviors of fission and corrosion products (FP and CP) in the DIDPA extraction process have been already examined at JAERI(78,79,81,82), but the examination was performed at room temperature without the addition of H_2O_2 . The modification of the process for Np recovery may have some influence on the behaviors of FP and CP. Therefore, the counter-current continuous extraction with DIDPA and back-extraction with 4 M HNO_3 carried out under the same condition as in the Np extraction to examine the behavior of FP and CP.

The solvent after back-extraction with 4 M HNO_3 will go to the next step of the back-extraction with $\text{H}_2\text{C}_2\text{O}_4$, which is newly added for the Np recovery. The resulting solvent from the above experiments still contained some elements, Fe, Ru and Rh. Behaviors of these elements in the continuous back-extraction with $\text{H}_2\text{C}_2\text{O}_4$ were also examined.

Among the corrosion products, Fe is the most important elements in the DIDPA extraction process because it forms the third phase (emulsion) when its concentration is high(78,79) and because it is extracted at a little slow rate and is not back-extracted with 4 M HNO_3 . The condition and the prevention of the third phase formation, the extraction rate and the back-extraction behavior of Fe with $\text{H}_2\text{C}_2\text{O}_4$ were examined in batchwise experiment. The present chapter also describes their results.

VI-2 BEHAVIOR OF IRON IN EXTRACTION WITH DIISODECYLPHOSPHORIC ACID

EXPERIMENTAL

Reagents

The extractant, DIDPA, was used without further purification, after it was diluted with *n*-dodecane. Unless otherwise specified, the DIDPA concentration was 0.5 M.

In experiments on the extraction rate and the third phase formation, the DIDPA solvent was pre-equilibrated with HNO_3 of which concentration was the same as that of Fe solution to be examined.

Ferric nitrate ($\text{Fe}(\text{NO}_3)_3$) was used as a reagent of Fe.

Procedure

(1) Experiments on Extraction Rates

Two cubic centimeters of the DIDPA solvent and a HNO_3 solution of Fe were taken in a test tube and mixed vigorously for an appropriate period of time with a shaker in a thermostatted air bath. After separation of two phases by centrifugation, 1 cm^3 of the aqueous phase was taken, and its Fe concentration was analyzed by atomic absorption spectrophotometry after dilution. The Fe concentration in the organic phase was determined by subtracting the concentration in the aqueous phase after extraction from the initial concentration.

(2) Experiments on the Third Phase Formation.

Whether the third phase was formed or not was determined by observation. The third phase caused by Fe appeared as a white creamy substance at the high Fe

concentration, but at lower Fe concentration only a slight white precipitate was observed in the organic phase. This white precipitate was considered as the third phase in the present study. However such a precipitate will not necessarily disturb the extraction process.

By changing temperature and concentrations of DIDPA and Fe, the condition where the third phase was formed was investigated keeping the HNO_3 concentration 0.5 M. The extraction was continued for 15 min. More than 99 % of Fe is transferred to the organic phase in this extraction.

(3) Experiments on Back-extraction

The behavior of Fe in the back-extraction with $\text{H}_2\text{C}_2\text{O}_4$ was examined in batchwise procedure. An organic DIDPA solution containing Fe was prepared by the following procedure: first Fe was extracted from 0.01 M Fe^{3+} - 0.5 M HNO_3 solution with the DIDPA solvent, and the solvent was washed with 4 M HNO_3 . Procedure of the back-extraction was the same as that of extraction experiments.

RESULTS AND DISCUSSION

Extraction Rate

It has been already confirmed that Fe was extracted with DIDPA at a slow rate and the extraction was the first-order reaction with respect to the Fe concentration⁽⁷⁹⁾. Figure VI-1 shows the dependence of the first-order rate constant of the extraction on the HNO_3 concentration. The extraction rate decreased with the increase of HNO_3 concentration and reached the minimum at 1-2 M HNO_3 and increased again with the HNO_3 concentration. The slope of the straight line in the region of HNO_3 concentration lower than 0.5 M was -1.5. Such a dependence was similar to that of the

Np extraction rate shown in Fig. II-9 in Chapter II.

On the other hand, the rate of Fe extraction did not depend on the DIDPA concentration as shown in Table VI-1 (directly found by comparing A and B). In this respect, the Fe extraction is different from the Np extraction where the rate is proportional to the square of the DIDPA concentration. The reason why the Fe extraction proceeds independently of the DIDPA concentration would be that the change of the chemical form of Fe in the aqueous phase determines the extraction rate.

Almost constant extraction rates were found in other experiments in Table VI-1. In experiments B, C and D, both Fe and DIDPA concentrations were changed while the concentration ratio of DIDPA to Fe was kept constant. When the $[DIDPA]/[Fe]$ ratio decreased to less than 50, the rate of Fe extraction decreased as shown in Fig. VI-2. In experiments with 0.005 M and 0.01 M Fe solutions (the ratios were 10 and 5 respectively), the third phase was formed as the extraction proceeded. Therefore, in experiments shown in Table VI-1 the $[DIDPA]/[Fe]$ ratio was kept larger than 50.

Distribution ratio of Fe at equilibrium was very large, more than 10^2 when $[DIDPA] = 0.05$ M and more than 10^3 when $[DIDPA] = 0.5$ M.

Figure VI-3 shows the dependence of the extraction rate on temperature. The rate at 45°C was $2.4 \times 10^{-2} \text{ s}^{-1}$, which is 4.5 times as large as the rate at 25°C .

In the Np extraction process, the total contacting time should be more than 512 s. When the rate constant of the Fe extraction is $2.4 \times 10^{-2} \text{ s}^{-1}$ (45°C), only 0.0005 % of Fe remains in the raffinate of the Np extraction process. The value of $2.4 \times 10^{-2} \text{ s}^{-1}$ was obtained in the absence of H_2O_2 , but the extraction rate of Fe in the presence of H_2O_2 was no slower than in the absence of H_2O_2 as described in the next section. Consequently, Fe is extracted almost quantitatively in the extraction process with DIDPA where Np is recovered quantitatively.

The Third Phase Formation

Table VI-2 shows the results of experiments on the third phase formation where concentrations of Fe and DIDPA and temperature were experimental parameters. When the $[DIDPA]/[Fe]$ ratio became small ($[Fe]$ became large), the white precipitate was formed as the third phase. At the same $[DIDPA]/[Fe]$ ratio, higher concentration of DIDPA (higher concentration of Fe in the organic phase) and lower temperature caused the third phase formation. Moreover, in the organic phase which did not have the third phase at higher temperature, the white precipitate appeared after the organic solution was cooled. The above results indicate that the solubility of the complex of Fe with the extractant concerns the third phase formation and that the solubility depends on the DIDPA concentration.

The $[DIDPA]/[Fe]$ ratio will serve to some extent as a measure of the third phase formation. Even when $[DIDPA]$ becomes half, the highest ratio of $[DIDPA]/[Fe]$ where the third phase was formed changed only a little (about 10–15 %).

Iron exists in the trivalent state, as well as rare earths which are extractable elements also. Nevertheless, the high concentration of Fe causes the third phase formation. This would be due to the difference in ionic radius. The radius of Fe^{3+} is 0.064 nm, while that of rare earths is around 0.1 nm (La^{3+} : 0.106 nm, Gd^{3+} : 0.094 nm)⁽¹¹⁵⁾. It seems natural to consider that a smaller ion of Fe makes a different kind of complexes from ions of rare earths.

To prevent the third phase formation, temperature should be raised and the Fe concentration should be lowered. If Fe at high concentration is extracted at raised temperature, it should be soon back-extracted without cooling the organic phase. If we limit the Fe concentration, we have to know the Fe concentration in HLW exactly. However, it cannot be obtained by calculation where concentration of fission product can be determined. The Fe concentration depends on the type of spent fuel and the condition of reprocessing (the dissolution of the spent fuel and the concentration step

for the first cycle raffinate). When the Fe concentration is 0.016 M, the third phase is not formed in the extraction with the same volume of 0.5 M DIDPA solution at 25 °C as shown in Table VI-2. Then 0.064 M of Fe in HLW is acceptable in the extraction process tested for the Np extraction because the flow ratio of the organic phase to the HLW feed is four. However, we have to consider the consumption of DIDPA by extracted elements such as rare earths. As one ion of rare earths consumes 8 molecules of DIDPA, 0.063 M of rare earths in the HLW feed decreases the free DIDPA concentration from 0.5 M to 0.374 M. Then 0.047 M of Fe would be acceptable.

The DIDPA used in the present study contains MIDPA as an impurity as described before. The MIDPA may have concern with the third phase formation by Fe. However, as shown in Table VI-3, higher concentration of MIDPA prevents the third phase formation. Complexes of Fe with MIDPA would be more soluble in the organic phase. There is only a small difference in the lowest concentration of Fe which forms the third phase between 0.017 M of MIDPA and 0.1 M. Therefore, as far as MIDPA is contained as an impurity or produced by radiolysis, it has little effect on the third phase formation.

Back-Extraction of Fe

Iron can be back-extracted with a $\text{H}_2\text{C}_2\text{O}_4$ solution, but the rate of the back-extraction was not so fast, shown in Fig. VI-4. Higher temperature is favorable for the Fe back-extraction, but even at lower temperature Fe would be able to be back-extracted (D for 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ solution decreased less than 1 within 12 min.). Consequently, Fe will accompany Np both in the extraction and in the back-extraction.

Figure VI-5 shows the dependence of D on the $\text{H}_2\text{C}_2\text{O}_4$ concentration. At equilibrium, D of Fe is smaller than that of Np(IV). This does not necessarily mean that Fe is back-extracted quantitatively in the process for Np back-extraction because the rate of the Fe back-extraction is rather slow. The behavior of Fe in continuous

back-extraction with $\text{H}_2\text{C}_2\text{O}_4$ will be discussed in the next section.

VI-3 BEHAVIORS OF FISSION AND CORROSION PRODUCTS IN COUNTER-CURRENT EXTRACTION WITH DIISODECYLPHOSPHORIC ACID

EXPERIMENTAL

Reagent

Simulated HLW used in the present experiments is the same as in the experiments of the Np extraction described in Chapter V except that it does not contain Np. The solvent, DIDPA - TBP - n-dodecane, is also the same.

Procedure

The same mixer-settler was used in the same procedure. Figure VI-6 shows the operating condition. In the present experiments, H₂O₂ was added only to the scrub solution. The experiments were carried out twice, at 25 °C and 45 °C.

The solvent obtained in the above experiment at 45 °C was used in the continuous back-extraction with H₂C₂O₄, which was carried out in the same procedure as in the Np experiment.

Concentrations of the elements were analyzed by inductively coupled plasma atomic emission spectroscopy, flame photometry or atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Continuous Extraction with DIDPA and Back-extraction with 4 M Nitric Acid

Figure VI-7 and VI-8 show concentration profiles of Nd and Fe in the mixer-

settler in the experiments at 25 °C and 45 °C respectively. In both experiments, Nd, a representative of rare earths and trivalent actinides, was extracted with a yield of more than 99.99 %, but there was a small difference in the profiles. At higher temperature, Nd was extracted less effectively, but back-extracted with 4 M HNO₃ more effectively. This is because its distribution ratio decreases with the increase of temperature. Raising temperature acts as disadvantage in the extraction step but as advantage in the back-extraction step. The former disadvantage makes no influence on Nd separation actually because the number of extraction stage should be larger to extract Np than the number that the Nd extraction requires. Even 7 stages were enough for Nd extraction and, the ratio of Nd in raffinate was less than 0.003 % in both experiments. On the other hand, the latter advantage made a little difference in ratios of Nd in the organic fraction after back-extraction with 4 M HNO₃, which were 0.57 % at 25 °C and 0.006 % at 45 °C. Totally raising temperature have a good effect also on the Nd separation. At 45 °C, more than 99.99 % of Nd was recovered as a product. Since distribution ratio of Am is almost equal to that of Nd, the above result shows that also Am can be separated with a satisfactory yield.

From the concentration profiles of Fe in Figs. VI-7 and VI-8, the rate constants in the present experiments were obtained as $7.4 \times 10^{-3} \text{ s}^{-1}$ at 25 °C and $2.9 \times 10^{-2} \text{ s}^{-1}$ at 45 °C. Those in the batchwise extraction at the same temperatures without addition of H₂O₂ were $5.3 \times 10^{-3} \text{ s}^{-1}$ and $2.4 \times 10^{-2} \text{ s}^{-1}$, as shown in Fig. VI-3. The addition of H₂O₂ may increase the rate of the Fe extraction slightly. Anyhow, Fe is extracted with DIDPA together with Np and trivalent actinides. Since Fe was not back-extracted with 4 M HNO₃, it can be separated from Nd with a high decontamination factor (about 10³).

Concentration profiles of other elements in the run at 45 °C are shown in Figs. VI-9 (Ru and Rh), VI-10 (Sr, Cs, Ba and Rb) and VI-11 (Na, Cr, Ni and Pd). Table VI-4 shows ratios (%) of the elements in the three fractions in the experiment at

45 °C. Two of these elements, Ru and Rh, were partly extracted and not fully back-extracted with 4 M HNO₃. About 5 % of Ru and about 10 % of Rh were remained in the organic phase after the back-extraction. Such behavior of Ru has been observed also in the test of the DIDPA extraction process with an actual HLW at JAERI^(81,82). It seems their chemical forms determine their extraction behaviors. Difference in concentration profile of Rh between the two experiments (at 25 and 45 °C) could not be simply explained by the change of distribution ratio at the different temperature. If the chemical forms determine the extraction behaviors, the result depends on the method of preparing the simulated HLW, and Ru and Rh in the actual HLW might show the different result from the present one. However, HLW is to be denitrated before DIDPA extraction and the present simulated HLW was denitrated in its preparation. Denitration would cause the change of chemical forms of the two elements and after denitration each of the elements would be in a certain chemical form or a mixture of some chemical species in a certain ratio, peculiar to the denitrated solution. Therefore, the present result can be considered as a general one for the denitrated HLW.

The other elements were not extracted and were transferred to the raffinate with more than 99.5 % yield. Concentration profiles of these elements indicated that a little more number of scrubbing stages would improve the decontamination factors of these elements from Nd.

Continuous Back-Extraction with Oxalic Acid

Figure VI-12 shows the concentration profiles of Fe, Ru and Rh in the continuous back-extraction with 0.8 M H₂C₂O₄ solution at 25 °C. No other elements can be detected in this experiment.

The extracted Fe was back-extracted with H₂C₂O₄ with a yield of 97 %. The back-extraction of Fe is a rather slow process, though its distribution ratio is small enough, as described in the preceding section. Complete back-extraction can be

achieved by raising temperature and/or increasing the contact time.

As for the other two extracted elements, Rh was back-extracted up to 98 %, but ratio of Ru back-extracted was only 20 %. However, Ru concentration in used solvent was not so high (2×10^{-4} M) that the solvent could be recycled several times without clean-up.

VI-4 CONCLUSION

The rate of the Fe extraction with DIDPA was examined by batchwise procedure. The dependence of the rate on the HNO_3 concentration was similar to that of the Np extraction. However, the mechanism of the Fe extraction is quite different from that of the Np extraction because the extraction rate of Fe is independent of the DIDPA concentration.

The first-order rate constant of the Fe extraction was large enough, compared with that of the Np extraction. Therefore, Fe is extracted almost quantitatively in the extraction process where Np is extracted quantitatively, which was also confirmed in continuous extraction using a mixer-settler.

When Fe is extracted with DIDPA at high concentration, the third phase (precipitate or emulsion) appears in the organic phase. The concentration ratio between DIDPA and Fe in the organic phase will serve to some extent as a measure of the third phase formation. To prevent the third phase formation, temperature should be raised and the Fe concentration should be lowered.

The extracted Fe was back-extracted with $\text{H}_2\text{C}_2\text{O}_4$ at a little slow rate. In continuous back-extraction with 0.8 M $\text{H}_2\text{C}_2\text{O}_4$ using 16-stages mixer-settler, 97 % of Fe was recovered from the DIDPA solvent. Complete back-extraction can be achieved by raising temperature and/or lengthening the contacting time. Thus, Fe accompanies Np both in the extraction and in the back-extraction.

Experiments of continuous extraction with DIDPA and back-extraction with 4 M HNO_3 using a simulated HLW was carried out to examine the effect of H_2O_2 addition and raising temperature on the behaviors of fission and corrosion products. The addition of H_2O_2 had almost no influence on the behaviors. Raising temperature has a good effect on the separation of Nd, which is a representative of trivalent actinides and rare earths.

Among the other elements, Ru and Rh were the only two elements which were partly extracted and not fully back-extracted with 4 M HNO_3 . About 10 % of Rh was remained in the organic phase after the back-extraction with 4 M HNO_3 , but was back-extracted with $\text{H}_2\text{C}_2\text{O}_4$. A small part of Ru remains in the used solvent (after the back-extraction with $\text{H}_2\text{C}_2\text{O}_4$). However, its concentration was not so high that its remaining in the solvent would have no influence on the several times recycling the solvent.

Consequently, modification of the DIDPA extraction process for the Np separation, H_2O_2 addition and raising temperature, does not alter the behaviors of the other elements. The function of the DIDPA extraction for the Am-Cm separation from HLW, from fission products, is maintained.

Table VI-1 Dependence of the Fe Extraction Rate on the Concentration of DIDPA and Fe.

Organic phase : DIDPA in n-Dodecane

Aqueous phase : Fe in 0.5 M HNO₃

Temperature : 25 °C

Symbol	[Fe] (M)	[DIDPA] (M)	[DIDPA] /[Fe]	Rate constant (s ⁻¹)
A	0.001	0.5	500	5.08×10 ⁻³
B	0.001	0.05	50	4.88×10 ⁻³
C	0.004	0.2	50	5.33×10 ⁻³
D	0.01	0.5	50	5.40×10 ⁻³

Table VI-2 Effects of DIDPA and Fe Concentrations and Temperature on the Third Phase Formation.

Organic phase : DIDPA in n-Dodecane

Aqueous phase : Fe in 0.5 M HNO₃

[DIDPA] (M)	[Fe] in Org. ¹⁾ (M)	[DIDPA] /[Fe]	Temp. (°C)	Third phase formation ²⁾
0.5	0.016	31	25	-
0.5	0.018	28	25	○
0.5	0.020	25	25	○
0.5	0.020	25	45	-
0.5	0.022	23	45	-
0.5	0.024	22	45	○
0.25	0.0089	28	25	-
0.25	0.010	25	25	○
0.25	0.014	18	25	○
0.25	0.0092	27	45	-
0.25	0.012	21	45	-
0.25	0.014	18	45	○

1) This is the same as the initial concentration in aqueous phase before extraction.

2) "○" means that the third phase was formed.

Table VI-3 Effects of MIDPA on the Third Phase Formation.

Organic phase : DIDPA, MIDPA and 0.1 M TBP in n-Dodecane

Aqueous phase : Fe in 0.5 M HNO₃

Room Temperature (-15°C)

"O" means that the third phase was formed.

Extractant (M)		[Fe] in Org. ¹⁾ (M)					
[DIDPA]	[MIDPA]	0.008	0.010	0.011	0.012	0.020	0.030
0.483	0.017	-	○	○	○	○	○
0.40	0.10	-	-	-	○	○	○
0.30	0.20	-	-	-	-	-	○

1) This is the same as the initial concentration in aqueous phase before extraction.

Table VI-4 Behaviors of Fission and Corrosion Products in the Continuous Counter-Current Extraction, Carried out at 45 °C under the Condition Shown in Fig. VI-6.

- Ratios (%) of each element in the three fractions.

Element	Raffinate	4 M HNO ₃ (Product I)	Organic Fraction
Na	>99.6	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

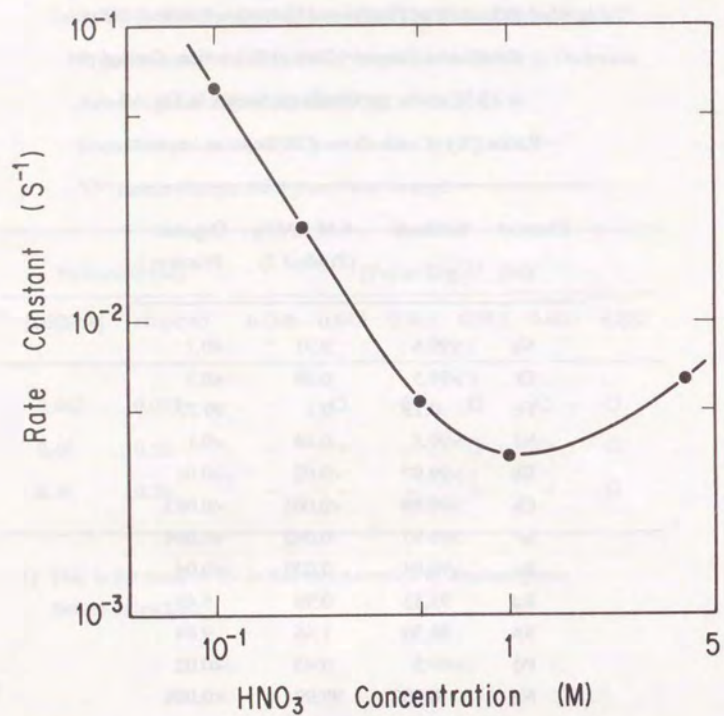


Fig. VI-1 Dependence of the First-Order Rate Constant for Fe Extraction on HNO₃ Concentration.
 Organic phase : 0.5 M DIDPA in n-dodecane
 Temperature : 25 °C

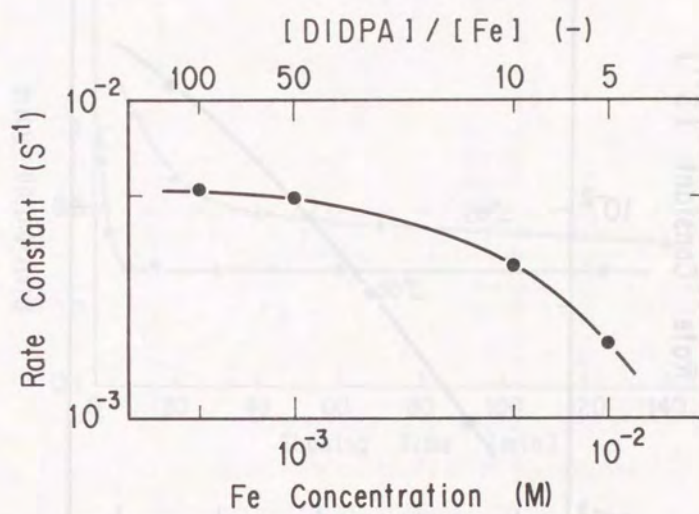


Fig. VI-2 Dependence of the Rate Constant on Fe Concentration at Low [DIDPA]/[Fe] Ratio.

Organic phase : 0.5 M DIDPA in n-dodecane

Aqueous phase : Fe(III) in 0.5 M HNO₃

Temperature : 25 °C

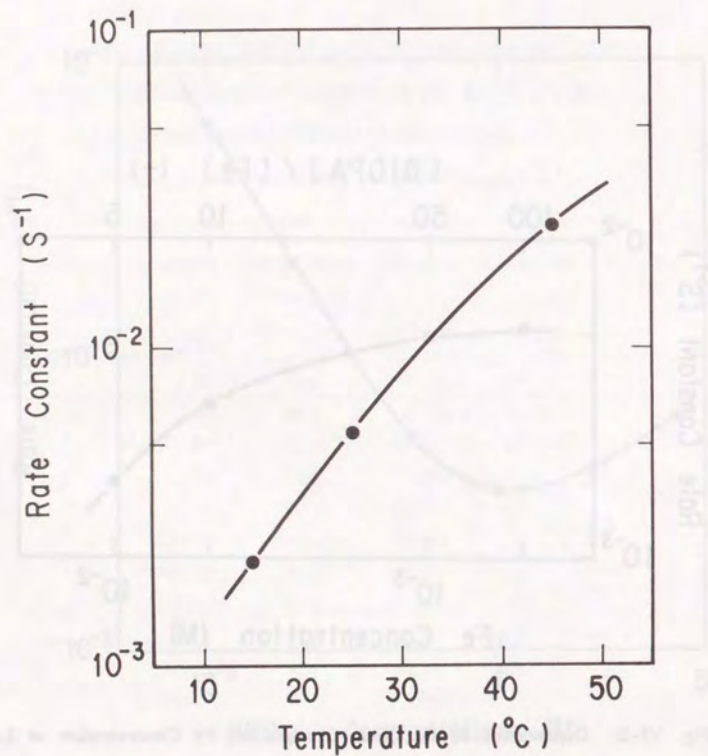


Fig. VI-3 Dependence of the Rate Constant on Temperature.

Organic phase : 0.5 M DIDPA in n-dodecane

Aqueous phase : Fe(III) in 0.5 M HNO₃

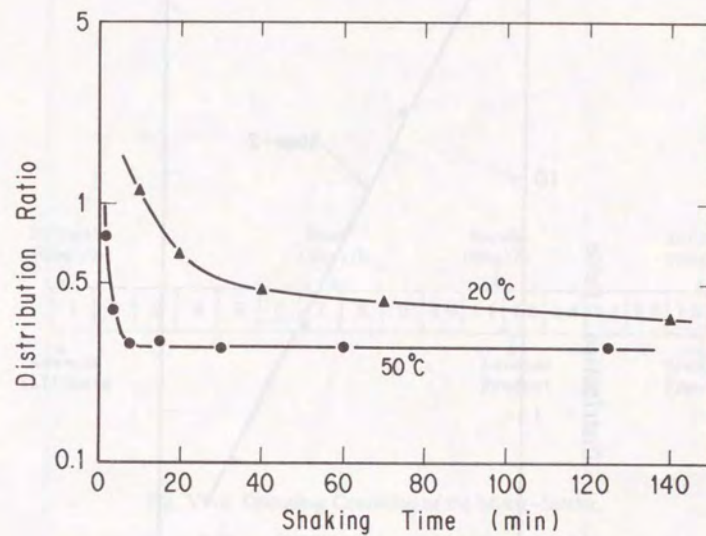


Fig. VI-4 Dependence of Distribution Ratio on Shaking Time.

Organic phase : 0.5 M DIDPA - 0.1 M TBP n-dodecane solution containing Fe

Aqueous phase : 0.5 M H₂C₂O₄

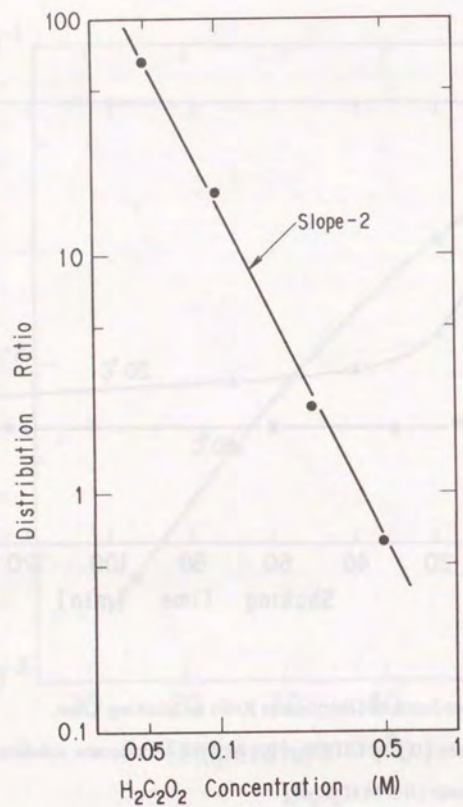


Fig. VI-5 Dependence of Distribution Ratio on $H_2C_2O_4$ Concentration.

Organic phase : 0.5 M DIDPA - 0.1 M TBP n-dodecane solution containing Fe

Shaking time : 30 min Room temperature

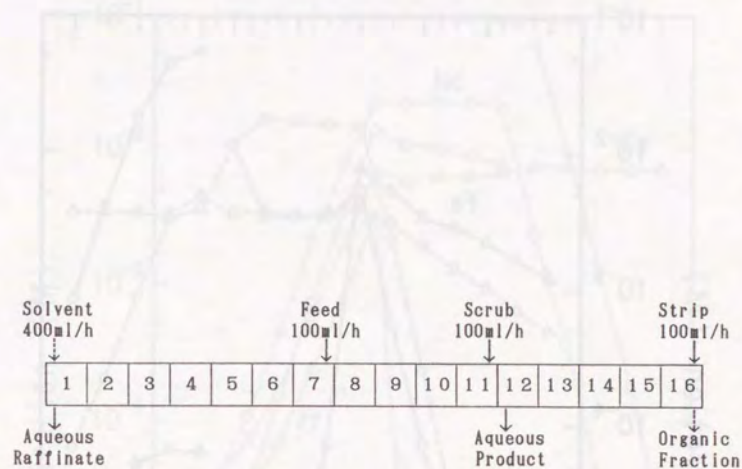


Fig. VI-6 Operating Condition of the Mixer-Settler.

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

Feed : 0.5 M HNO_3 , simulated HLW

Scrub : 0.5 M HNO_3 , $[H_2O_2]=0.5$ M

Strip : 4.0 M HNO_3

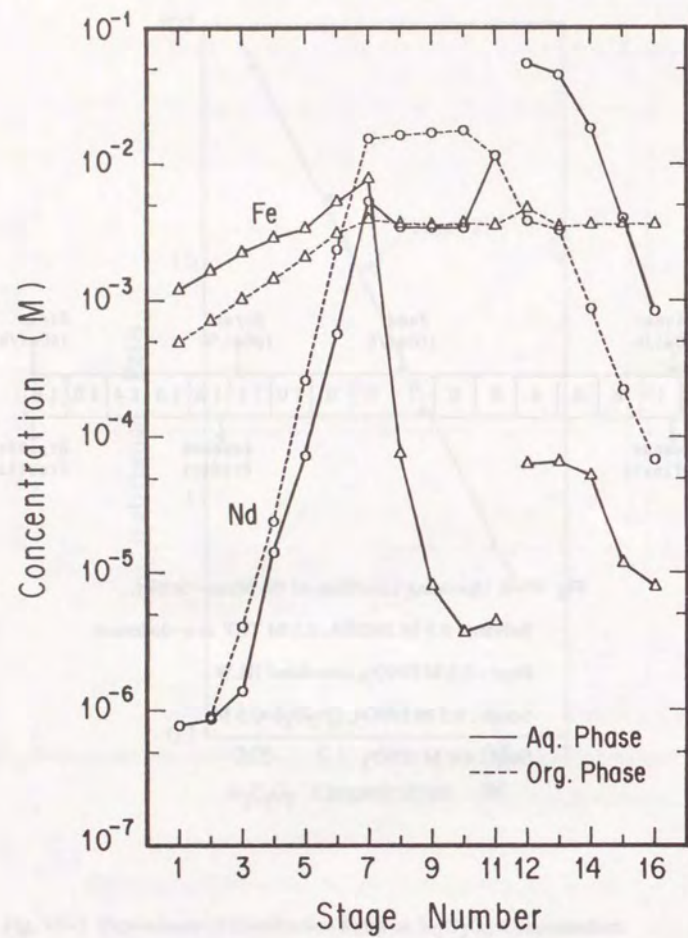


Fig. VI-7 Concentration Profiles of Nd and Fe in the Mixer-Settler.

Temperature : 25 °C, ○ : Nd, △ : Fe

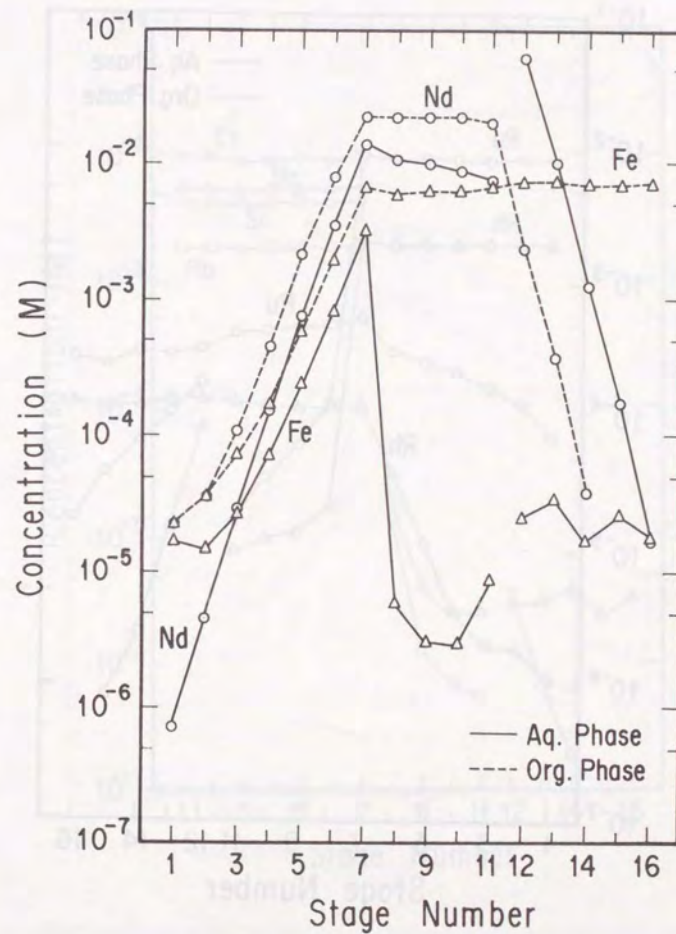


Fig. VI-8 Concentration Profiles of Nd and Fe in the Mixer-Settler.

Temperature : 45 °C, ○ : Nd, △ : Fe

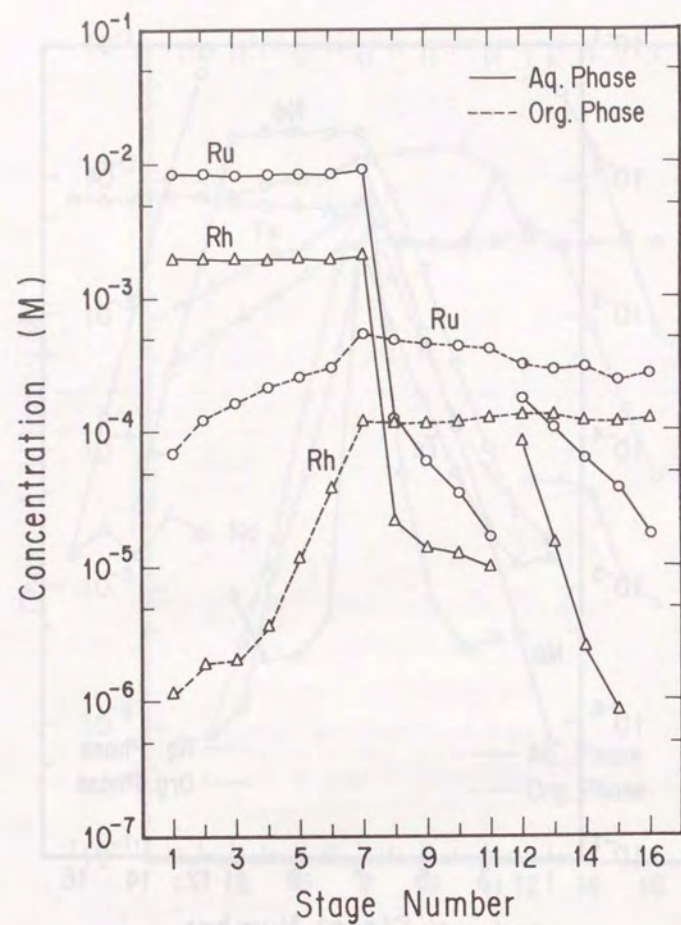


Fig. VI-9 Concentration Profiles of Ru and Rh in the Mixer-Settler.

Temperature : 45 °C, ○ : Ru, △ : Rh

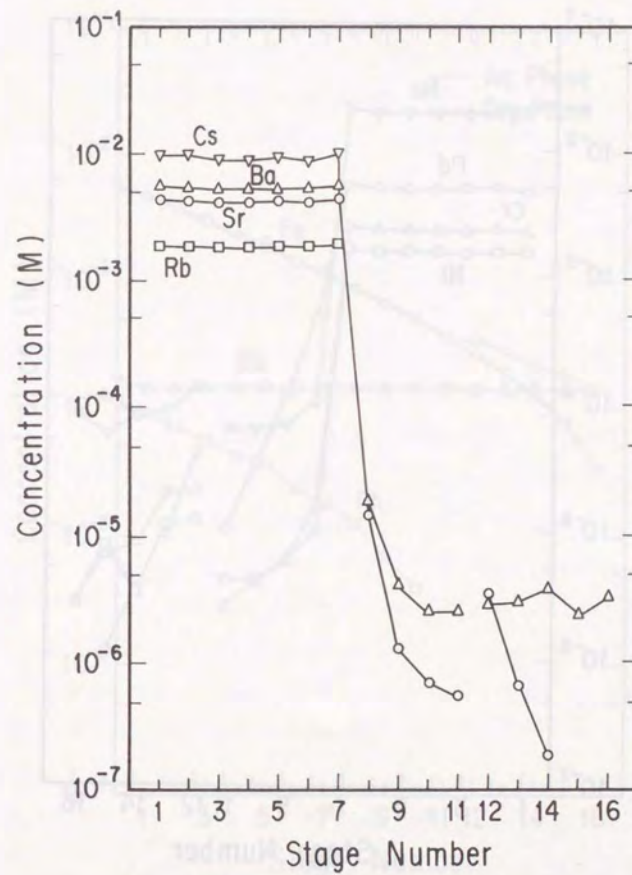


Fig. VI-10 Concentration Profiles of Sr, Cs, Ba and Rb in the Mixer-Settler.

Temperature : 45 °C, ○ : Sr, ▽ : Cs, △ : Ba, □ : Rb

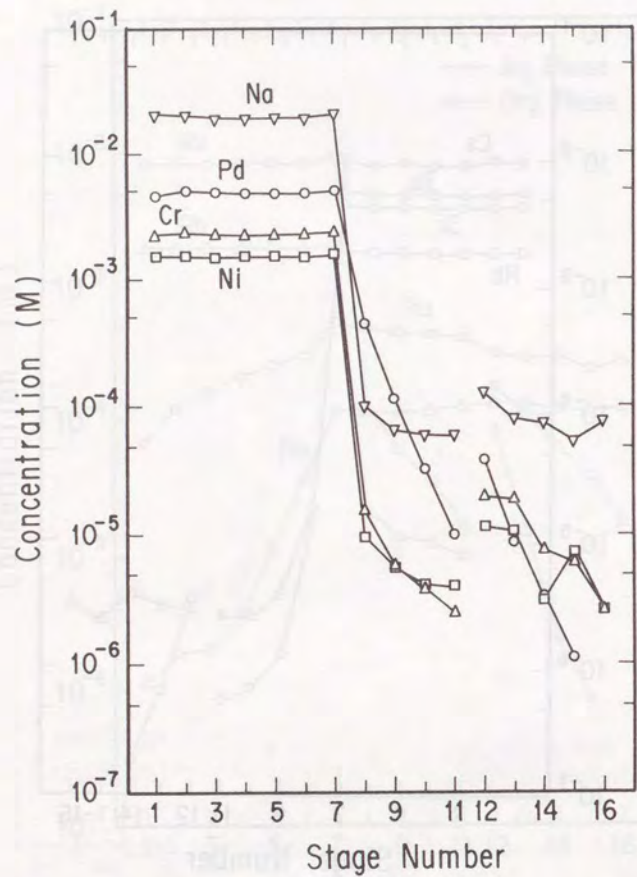


Fig. VI-11 Concentration Profiles of Na, Cr, Ni and Pd in the Mixer-Settler.

Temperature : 45 °C, ∇ : Na, \triangle : Cr, \square : Ni, \circ : Pd

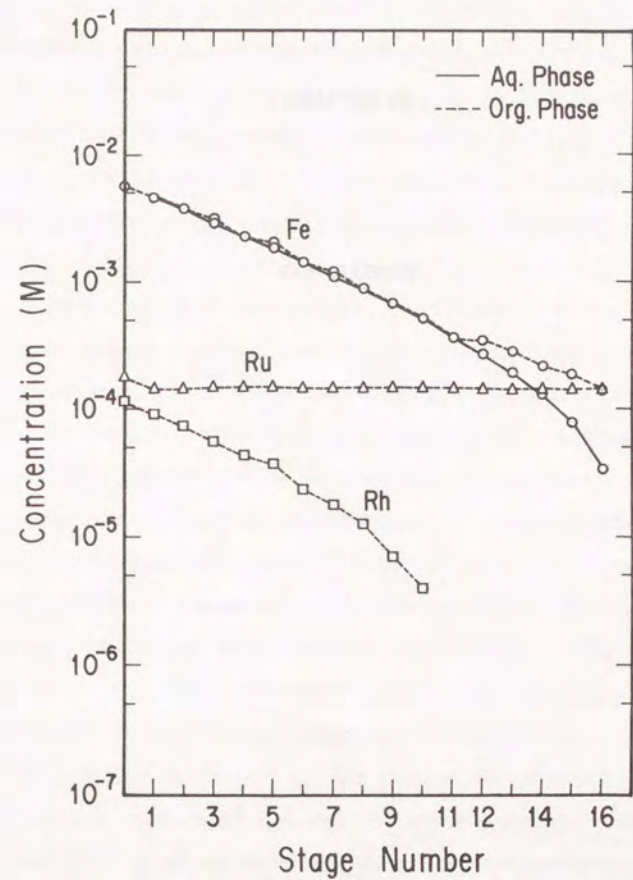


Fig. VI-12 Concentration Profiles of Fe, Ru and Rh in the Mixer-Settler in the continuous back-extraction with $H_2C_2O_4$.

Temperature : 25 °C, \circ : Fe, \triangle : Ru, \square : Rh



Figure 1. Concentration of various components in the reaction mixture as a function of stage number.

CHAPTER VII

CONCLUSION

The synthesis of poly(2-vinylpyridine) (P2VP) has been studied in detail. A preliminary study was carried out to determine the effect of various factors on the polymerization process. The results showed that the reaction rate and the molecular weight of the polymer depend on the concentration of the monomer, the concentration of the initiator, and the temperature. The effect of the concentration of the monomer and the initiator was studied in detail. The results showed that the reaction rate increases with the concentration of the monomer and the initiator. The effect of the temperature was also studied. The results showed that the reaction rate increases with the temperature. The effect of the concentration of the monomer and the initiator was studied in detail. The results showed that the reaction rate increases with the concentration of the monomer and the initiator.

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The extraction of Np with diisodecylphosphoric acid (DIDPA) was studied to develop a process for Np separation from high-level radioactive waste (HLW) as a part of a partitioning process. The process should give a very high recovery, 99.95 %, should not require the troublesome oxidation state adjustment of Np before extraction, and should keep the conditions for Am-Cm separation in the DIDPA extraction process, which was developed at Japan Atomic Energy Research Institute. The aim of the present study is to develop a process that meets the above requirement.

Neptunium initially in the pentavalent state could be extracted with DIDPA. During the extraction, a disproportionation reaction of Np(V) took place, which was confirmed by the analysis of the oxidation state of Np in the organic phase. The well-known disproportionation reaction of Np(V) in an aqueous solution proceeds faster at a higher acid concentration. However, the Np extraction proceeds faster at a lower acid concentration. Therefore, the disproportionation reaction during the extraction does not take place in the aqueous phase and can be considered to be initiated by the interaction of Np(V) with DIDPA. The probability of the interaction increases with the decrease of the acid concentration because DIDPA is a cation exchange type extractant. Even at a lower acid concentration, the disproportionation reaction can take place because DIDPA supplies the hydrogen ions necessary for the reaction.

Thus, Np initially in the pentavalent state can be extracted with DIDPA. Resultant Np(IV) and Np(VI) have very high distribution ratios in the DIDPA extraction. This suggests the possibility of establishing the separation process for Np without the troublesome oxidation state adjustment. However, the extraction rate is a little slow for the application to an actual process. Lowering the acidity and increasing the DIDPA concentration improve the extraction rate, but both have disadvantages.

The addition of H_2O_2 accelerated the extraction of Np initially in the pentavalent state. When H_2O_2 was added, reduction of Np(V) took place during the extraction and

the Np in the organic phase was tetravalent. The reduction in an aqueous solution does not proceed when the HNO_3 concentration is relatively low such as 0.5 M. However, the extraction and the reduction of Np(V) in the presence of H_2O_2 proceeded even at that acidity. The reduction during the extraction can be considered to be initiated by the interaction of Np(V) with DIDPA. The extractant supplies the hydrogen ions necessary for the reduction.

The combination of Pd and Fe was found to make the Np extraction faster by the catalytic effect. They accelerated also the decomposition of H_2O_2 .

The improvement of the Np extraction rate by H_2O_2 and the elements contained in HLW gives a promising prospect of separating Np from HLW by the DIDPA extraction.

Tetravalent Np could be easily back-extracted from the DIDPA solvent with $\text{H}_2\text{C}_2\text{O}_4$. Distribution ratio of Np(VI) was higher than that of Np(IV). Presence of H_2O_2 in the extraction of Np is favorable not only for accelerating the extraction but also for reducing the distribution ratio of Np in the back-extraction with $\text{H}_2\text{C}_2\text{O}_4$.

Radiolysis of DIDPA should be considered to apply to an actual process for HLW. One of the degradation products, monoisodecylphosphoric acid (MIDPA), accelerated the Np extraction. Even if MIDPA is produced by the radiolysis of DIDPA, it would give no deleterious influence on the forward-extraction of Np. On the other hand, the increase of the MIDPA concentration makes the back-extraction of Np with $\text{H}_2\text{C}_2\text{O}_4$ difficult. The tolerable concentration, however, was found to be as high as 0.066 M.

Radiolysis of 0.5 M DIDPA in *n*-dodecane with and without addition of 0.1 M Tributylphosphate (TBP) was studied by irradiating the solvents with ^{60}Co γ -rays in the presence or absence of HNO_3 . The results showed that DIDPA is not less stable than TBP. The increase of the MIDPA concentration to 0.066 M required the absorption dose of 0.5 MGy. The dose of 0.5 MGy corresponds to the more than 25

times recycle use of the solvent in an actual partitioning plant. Therefore, the effect of the solvent degradation would be within an acceptable region from the aspect of the Np back-extraction.

In the experiment on the Np extraction with the irradiated solvents, it was found that both the presence of TBP in the solvent and the addition of H_2O_2 to the aqueous solution reduced the change of the extraction rate caused by the solvent degradation. The rate of the Np extraction with the irradiated solvents did not change until the absorbed dose increased to more than 0.5 MGy. The radiolysis of the DIDPA solvent gives practically no influence also on the forward-extraction of Np.

In order to demonstrate the high recovery of Np by the DIDPA extraction, it is necessary to carry out experiments on continuous extraction using a counter-current extractor. The Np behavior in an extractor is not simply predictable because the extraction rate determines the Np behavior and it changes stage by stage as H_2O_2 is decomposed.

In counter-current continuous extraction with DIDPA using a mixer-settler, 95.6 % of Np was separated from the simulated HLW by 7-stage extraction at 45 °C with the addition of H_2O_2 to the scrub solution. Because of the H_2O_2 decomposition, the extraction rate of Np decreased gradually. Therefore, further addition of H_2O_2 to the extraction section was required to increase the ratio of Np extracted. In the experiment with this modification, 99 % of Np was extracted in 7 stages. The 14-stage extraction and twice addition of H_2O_2 increased the Np recovery to more than 99.96 %. A high recovery of Np, the most important requirement in the separation process the present study aims at, was demonstrated in a continuous method.

The mixing time of the aqueous and organic phases is the most important parameter for Np extraction. Effect of settling was negligible. Optimization and generalization of the process conditions showed that a recovery of 99.95 % would be achieved even in other types of extractors when the total time of mixing the aqueous

and organic phases leaches 9 minutes and H_2O_2 is added three times with about 2 minutes interval in the mixing time.

In continuous back-extraction with 0.8 M $H_2C_2O_4$ solution, more than 99.9 % of Np was recovered from the DIDPA solvent in 12 stages.

Behaviors of fission and corrosion products in the DIDPA extraction was examined under the conditions modified for the effective recovery of Np, which are conditions of raised temperature and the presence of H_2O_2 . The addition of H_2O_2 had almost no influence on the behaviors. Raising temperature had a good effect on the separation of Nd, which was used as a representative of trivalent actinides and rare earths. The modification for the Np separation had no serious effects on the behaviors of the other elements.

A separation process for Np by extraction with DIDPA from HLW can be established from the present study. The process works also for the separation of the other actinides. Figure VII-1 shows the flow sheet of the DIDPA extraction process. First, Np is extracted from 0.5 M HNO_3 HLW with the 0.5 M DIDPA - 0.1 M TBP solvent in a very high recovery by adding H_2O_2 and raising temperature. Here, Pu, Am and Cm (and rare earths) are extracted simultaneously. In the second step, trivalent actinides, Am and Cm, (and rare earths) are back-extracted with 4 M HNO_3 . Raising temperature is advantageous also in this step. In the third step, Np and Pu are back-extracted with $H_2C_2O_4$. Since Pu is in the tetravalent state in HLW and also in the organic phase after extracted, it accompanies Np. Only Fe and a small amount of Ph are included in the back-extracted Np-Pu fraction. Finally, U should be back-extracted. In this process, Np can be separated with a very high yield from HLW and recovered in the $H_2C_2O_4$ solution as a product.

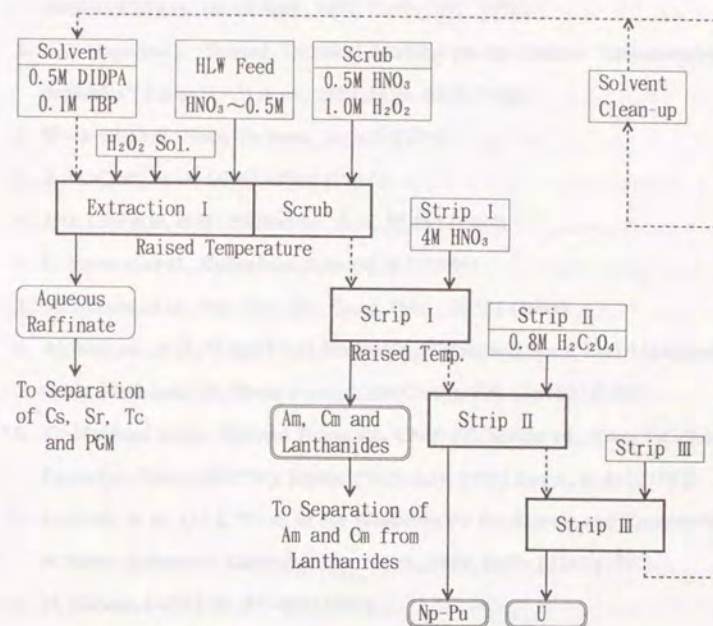


Figure VII-1 Flow Sheet of the DIDPA Extraction Process for the Actinide Separation from High-Level Waste Developed in the Present Study.

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ACKNOWLEDGMENT

The author wishes to express his deeply gratitude to Professor Atsuyuki Suzuki, Professor Satoru Tanaka and Assistant Professor Takayuki Terai of the University of Tokyo for their kind advice and encouragement in preparing this thesis. He is indebted to Dr. Masumitsu Kubota of Japan Atomic Energy Research Institute for his continuing guidance and valuable discussions in the course of this work.

The author is also grateful to Professor Yasushi Inoue and Assistant Professor Osamu Tochiyama for their kind suggestions. He was favored to have the helpful assistance of Dr. Shinya Nagasaki of the University of Tokyo, Dr. Young-joon Shin of Korea Atomic Energy Research Institute, Mr. Masahiro Yoneya of Toyo Engineering Corporation and Mr. Shunji Tani of Japan Nuclear Fuel Conversion Co., Ltd., who had worked with the author in Japan Atomic Energy Research Institute

Finally, the author cordially thanks his wife for her supports during the preparation of this thesis.

The content of this thesis was published as the following papers and report.

1. Behavior of Neptunium in Chemical Process of Partitioning Long-Lived Radionuclides from High-Level Waste
Y. Morita, M. Kubota,
J. Nucl. Sci. Technol., 22, (8) 658 (1985) (Chapter II)
2. Extraction of Pentavalent Neptunium with Di-Isodecyl Phosphoric Acid
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