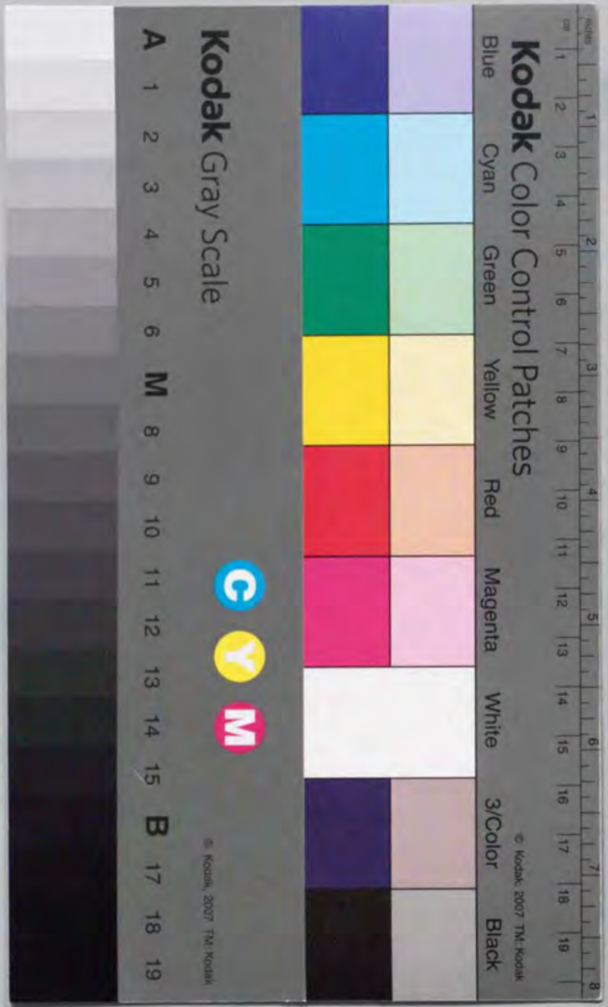

SEPARATION OF NEPTUNIUM
FROM HIGH-LEVEL RADIOACTIVE WASTE
BY EXTRACTION
WITH DIISODECYLPHOSPHORIC ACID

ジイソデシルリン酸抽出法による
高レベル放射性廃液からの
ネプツニウムの分離

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CONTENTS

CHAPTER I

INTRODUCTION

The primary aim of the nuclear activity is to produce energy which is indispensable to human being by burning a nuclear fuel in a nuclear reactor. The nuclear reactors include fusion reactors in a broad sense, but naturally mean fission reactors. Among the fission reactors, only the light water reactor (LWR) is operated on a commercial scale over the world. In LWR, low-enriched uranium is burned up and then spent fuel is discharged. The spent fuel still contains fissile and fertile U and Pu. Therefore, it should be reprocessed to recover these two elements. In other words, nuclear fuel cycle should be closed even in the LWR system. It is a matter of course that reprocessing is a requisite in the fast breeder reactor system, where U resource can be utilized more effectively.

After U and Pu are recovered from the spent fuel in the reprocessing, most of the other elements, fission products and the other actinides, are transferred to the high-level liquid waste (HLW). The present strategy of the HLW management in various countries is to immobilize elements in HLW into glass without additional separation of the elements and to dispose of the glass waste into a deep underground. Intense studies are being performed from various viewpoints to demonstrate the safety of this disposal. It is not impossible but difficult to do so because the period to be considered reaches 10^6 years or more and the environmental parameters and their values are inevitably uncertain.

Partitioning has been studied as an alternative method to the HLW management(1-11), where noted elements in HLW are separated into some groups according to their radiological and chemical properties. If extremely long-lived actinides are separated from HLW, they can be transmuted to fission products, of which half-lives are generally less than 10^2 years, or can be disposed of in more secure way because the volume of the separated actinides is much smaller than that of the HLW glass. If Sr and Cs, which are the main contributors to heat generation in HLW, are separated, the other elements can be immobilized into a smaller volume of waste.

Separated Sr and Cs can be solidified into a thermally stable material, and then the total volume of wastes after partitioning would be reduced compared with the volume of the HLW glass waste without partitioning(8).

As mentioned above, partitioning gives a more reasonable solution to the problem in the HLW management. From a different point of view, HLW can be considered as resources which still contains valuable elements(12-18). Partitioning opens the way for utilization of these elements. Actinides can be used as nuclear fuel or as valuable radioisotopes. Separated and immobilized Sr and Cs can be used as heat or radiation sources(14-16). Platinum group elements are the scarce metals reserved underground in the world(17,18).

At Japan Atomic Energy Research Institute (JAERI), partitioning of HLW have been studied since 1973(8,19). The author has been engaged in the study since 1982. Until that time, JAERI had developed a partitioning process, of which main step was the solvent extraction with diisodecylphosphoric acid (DIDPA) for the recovery of Am and Cm(8,20). The developed process was in the stage of being tested with an actual HLW.

In this partitioning process, Np was not the objective element to be separated because ^{237}Np was considered as a less hazardous element from the evaluation of potential hazard of HLW using Maximum Permissible Concentration (MPC) in ICRP (International Commission on Radiological Protection) Publication 2 as a measure of radiological toxicity of an individual nuclide. In 1979 to 1981, ICRP showed a new measure of radiological toxicity, Annual Limit on Intake (ALI), in Publication 30(21), which was derived by a new method(22) of calculating man's exposure using new metabolic data. In the hazard evaluation based on ALI, ^{237}Np became one of the most important nuclides to be partitioned(23,24).

From this reason, the author and his colleagues started the study on the separation of Np from HLW. The present thesis describes the results of the studies on the Np separation process as a part of a partitioning process for HLW.

In foreign countries, particularly in USA, many studies were carried out on the Np separation: the recovery of Np in the Purex process and the separation from HLW. However, the purpose of these studies was to separate ^{237}Np to be used as a target isotope for producing ^{238}Pu. Accordingly, investigation for a high recovery was of little importance.

At JAERI, 99.95 % removal of Np from HLW was set as a goal of the study on the separation process from the evaluation of the potential hazard based on ALI(9,25). The present study aims at the same goal. In JAERI's evaluation the value of 3×10^3 Bq was used as ALI of ^{237}Np, which was the original value published in 1980(21). After the first publication, ALIs of transuranium elements were revised according to their new metabolic data, and ALI of ^{237}Np increased to 2×10^4 Bq(26). Recently, ICRP showed further new data of ALI in Publication 61(27), based on the new recommendation(28), where ALI of ^{237}Np is 3×10^4 Bq. Using this new value, 99.5 % removal of Np became sufficient in the same evaluation.

Thus, the revision of the evaluated radiological toxicity of an individual nuclide causes the change of the objective removal ratio of the element in partitioning. The above method of determining the removal ratio itself was not a definitive method and needs further discussion. It is not easy to determine to what degree the objective element should be separated in partitioning. In the present study, 99.95 % removal of Np from HLW, which is the highest value, is a target of the development of a separation process.

The following is a brief review of the past studies on the Np separation in foreign countries. As mentioned above, most of the studies were performed for the purpose of obtaining a target isotope for producing ^{238}Pu, which can be used as a excellent heat source(29). The studies are classified into two groups according to the point where Np was separated from the irradiated fuel. One group of the studies dealt with the separation in the Purex process. First, Np was extracted together with U and Pu at the co-extraction step where fission products (FP) were separated. At the later step, Np was separated from U and Pu. The other group of the studies dealt with the separation from HLW. In these studies, first effort was directed to the transfer of Np to the raffinate of the co-extraction step. Then Np was recovered from HLW by ion exchange or solvent extraction.

In the former scheme, Np recovery in Purex process, Np was extracted with tributylphosphate (TBP) at the co-extraction step, as it was oxidized from Np(V) to Np(VI) with HNO_3 catalyzed by HNO_2(30). The equation of the oxidation reaction is shown below(31).

$$NpO_2^+ + n\,H^+ \overset{slow}{\leftrightarrow} Np(V)^* \text{ (Activated state)} \cdots\cdots\cdots\cdots \text{(I-1)}$$

$$Np(V)^* + HNO_2 \overset{fast}{\leftrightarrow} NpO_2^{2+} + NO + (n-1)\,H^+ + H_2O \cdots\cdots \text{(I-2)}$$

$$2\,NO + NO_3^- + H^+ + H_2O \overset{fast}{\leftrightarrow} 3\,HNO_2 \cdots\cdots\cdots\cdots \text{(I-3)}$$

The above three equations give the following as a whole.

$$2\,NpO_2^+ + NO_3^- + 3\,H^+ \leftrightarrow 2\,NpO_2^{2+} + HNO_2 + H_2O \cdots\cdots \text{(I-4)}$$

Nitrous acid acts as a catalyst in the oxidation of Np(V) with HNO_3 and acts as a reductant for Np(VI) at the same time. The reaction reaches equilibrium finally.

As shown in Equation (I-4), higher concentration of HNO_3 and lower concentration of HNO_2 make the ratio of Np(VI) higher in this reaction(32-37). The reaction rate is faster at higher concentration of HNO_2(38-39).

The feed solution to the co-extraction step in the Purex process always contains HNO_2 because of the radiolysis of HNO_3 and the addition of NO_x gas or formerly $NaNO_2$ for the adjustment of Pu oxidation state(40) and recently for the removal of iodine as I_2 gas(41). Therefore, Np(V) is oxidized to Np(VI) so that the reaction shown in Equation (I-4) reaches equilibrium. At the co-extraction step, Np(VI) is removed from the aqueous solution by extraction with TBP, and then remaining Np(V) is oxidized to Np(VI) to re-establish the equilibrium of the reaction (I-4)(42). Consequently Np was extracted together with U and Pu in the high percentage. Table I-1 summarizes the Np behavior in the Purex plants of various countries (including test plants). In all plants, Np was extracted at the co-extraction step, although Np was mostly in the pentavalent state after dissolution and the Np extraction was not intended. Behavior of Np after the co-extraction step varied with plant conditions such as the flow rate ratio of organic to aqueous solutions and the reagent used for Pu reduction(45,46,53).

When the Np extraction was intended in Purex process, this oxidation reaction was used and the HNO_2 concentration was controlled to obtain a higher recovery.

At the Hanford Purex Plant(54-57) in the USA, Np extracted in this way was transferred to the raffinate at the U purification step. Recovery as a Np product was more than 80 %. The similar study(54,58) was carried out at Oak Ridge National Laboratory (ORNL).

At the Marcoule Plant(54,59) in France, Np was transferred to the Pu fraction at the U-Pu separation step, and the Np was recovered from the raffinate of the Pu purification step by extraction with trilaurylamine (TLA).

At the WAK (Wiederaufarbeitungsanlage Karlsruhe)(44-46) in Germany, studies were carried out to recover Np that was transferred to the purification steps for U and Pu without control of the Np behavior at the preceding steps.

At the Savannah River Plant(33,54,60), 97 % of Np was recovered from highly enriched U spent fuel that contained little Pu by a different method. In this plant, Np was reduced to Np(IV) by Fe(II) and was extracted together with U at the first extraction step, and then it was separated from U by preferential back–extraction.

On the other hand, the following methods were studied to recover Np from HLW. Burns et al.(61) studied the separation of Np(IV), reduced with hydrazine, from HLW by extraction with di(2–ethylhexyl)phosphoric acid (DEHPA). The Np recovery in this method was more than 99 %. Schulz et al.(62) applied the above method to the Purex Acid Sludge solution and recovered 95 % of Np. He and his colleagues also tested the extractions with dibutylbutylphosphonate (DBBP)(63) and with TLA(64). In both extractions, Np was first reduced to Np(IV). The recovery was 90 ~ 95 %.

Extractions of actinides with bidentate neutral organophosphorous compounds, dihexyl–N,N–diethylcarbamoylmethylphosphonate (DHDECMP, CMP)(65,66) or octylphenyl–N,N–diisobutylcarbamoylmethylphosphine oxide (OFD[iB]CMPO, CMPO)(67,68), have been studied from a viewpoint of the HLW partitioning. The TRUEX process where CMPO was used as an extractant was developed to treat many kinds of the defense waste(69,70).

The Np separation by an ion exchange method was developed at the Savannah River Plant(33,60). After reduction to Np(IV), it was recovered from HLW together with Pu by the anion exchange method. Average recovery of Np for 10 years operation was 98 %(54).

In all separation methods for Np recovery from HLW, mentioned above, Np has to be reduced to Np(IV) or oxidized to Np(VI) prior to its separation, because Np(V), which is the most stable in solutions of low acid concentration, is hardly extracted with any extractants and hardly adsorbed with any ion exchangers. In this case, Np recovery is determined by the initial fraction of the reduced or oxidized form. The very high recovery such as 99.95 % requires exhaustive reduction or oxidation of Np(V), which is

difficult particularly in HLW which contains many kinds of elements. Therefore, to obtain the high recovery of Np, it is necessary to develop a method which does not need the adjustment of the Np oxidation state before separation or a method where the redox reaction of Np proceeds fast as the separation proceeds and the reverse reaction does not take place. The present study was carried out on the basis of this consideration.

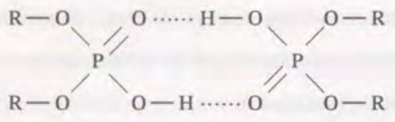
The aim of the present study is to develop a separation process for Np by extraction with DIDPA. The process should give a very high recovery, 99.95 % as mentioned before, and should not require the Np oxidation state adjustment before extraction not to increase the waste volume and not to give rise to operational difficulties.

The author found that Np which is initially in the pentavalent state could be extracted with DIDPA. In this extraction, the redox reaction proceeds as the extraction proceeds and, therefore, there was a possibility that it gave a high recovery of Np. Therefore, he performed a fundamental study on the Np extraction with DIDPA and examined its applicability to an actual separation plant.

As mentioned before, DIDPA has been used as an extractant to separate trivalent actinides, Am and Cm, from HLW in the partitioning process developed at JAERI. Like the well–known extractant DEHPA, DIDPA belongs to the acidic phosphoric esters, narrowly the dialkylphosphoric acids. The extraction with a dialkylphosphoric acid is generally expressed by the following equation(71):

$$M^{3+} + 3\,(HA)_2 \leftrightarrow M(HA_2)_3 + 3\,H^+ \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (I\text{–}5)$$

where M^{3+} is a trivalent metal ion and $(HA)_2$ is a dimerized dialkylphosphoric acid. It exists as a dimer in non–polar solvents such as aliphatic hydrocarbon, combining each other through hydrogen bond as shown below(72).



The extraction with DIDPA does not quite follow the Equation (I-5). The coefficients differs from 3 in the DIDPA extraction(73). However, there is no difference in extraction mechanism, which is the cation exchange between a metal ion and hydrogen ions. The lower concentration of hydrogen ion makes the distribution ratio of a metal ion higher. Since the acid concentration in HLW is usually 2 M or higher, it should be lowered before the extraction with a dialkylphosphoric acid. One of the most important factors which measure the applicability of this kind of extractants to the HLW partitioning is the highest acid concentration which gives sufficient distribution ratios of trivalent actinides for their extraction.

In the extraction with DEHPA, the acid concentration should be lowered to about 0.1 M in order to extract Am and Cm effectively(74). When DIDPA is used, 0.5 M of the acid concentration is enough for their separation(20,73). This is one of the important advantages of DIDPA because coprecipitation of Am and Cm (and Np as well) with a precipitate formed by the decrease of the acid concentration of HLW can be minimized(75,76). When the acid concentration is lowered to about 0.1 M or less than that, the coprecipitation of actinides can not be neglected.

It is preferable to separate Np together with Am and Cm simultaneously. Therefore, the Np extraction process with DIDPA the present study aims at should keep the conditions for the Am-Cm extraction. This is one of the important viewpoints in the development of the Np separation.

At JAERI, the partitioning process, which was developed by applying the DIDPA extraction as a main step, was tested with an actual HLW in 1983(8). The present study began with the examination of the Np behavior in this partitioning test. The examination and additional tracer experiments revealed that Np initially in the pentavalent state could be extracted with DIDPA. Further studies were given to the mechanism and the rate of the extraction. Chapter II of the present thesis describes the results of these studies.

The rate of the Np extraction with DIDPA was a little slow under the condition which could be applied to the separation from HLW, such as the acid concentration, DIDPA concentration and temperature. Long extraction time is required for high recovery of Np. Contacting time of the organic and aqueous phases should be as short as possible in order to minimize the radiolysis of the solvent. Accordingly, studies in the next phase were directed at the acceleration of the Np extraction. These are described in Chapter III.

Even if the contacting time is made the shortest, the solvent will be more or less degraded radiolytically and chemically. By radiolysis, DIDPA is degraded to its monoester, monoisodecylphosphoric acid (MIDPA). The radiolysis also generates another miscellaneous materials such as alcohol, H_3PO_4, nitrocompounds when HNO_3 coexists with the solvent, etc. Among these degradation products, MIDPA would be the most influential.

Like DIDPA, MIDPA is a acidic phosphoric ester and can extract metal ions. Generally, the monoester forms a stronger complex with ions than the diester and therefore the generation of the monoester makes the distribution ratio of the metal ions higher. This effect will become a problem in back-extraction process. However, there is no difference in basic nature between the mono- and di- esters. They differ only in degrees concerning extracting powers and do not show reverse effects.

Irradiation of neutral organophosphorous compounds such as CMPO forms acidic extractants, which has a very different character. For example, the reverse dependence of distribution ratio on the acid concentration is found in the extraction with the acidic extractant compared with the extraction with the neutral extractant. Therefore, radiolysis of neutral extractants produces much worse effect on the back-extraction. In the extraction with originally acidic compounds, less effect of their radiolysis will be observed, which is one of the advantages of the acidic extractants such as DIDPA.

Nevertheless, the effect of the DIDPA radiolysis, particularly the effect of MIDPA formation should be examined from various points of view. Besides, MIDPA unavoidably accompanies with DIDPA as an impurity formed during the synthesis of DIDPA. Attention should be paid to the effect of MIDPA also in this aspect.

Effects of the DIDPA radiolysis and of the presence of MIDPA have been already examined on the extraction of Am by Tachimori et al.(77), but the results of these studies can not be directly applied to the extraction of Np because the mechanism of the Np extraction is different from that of the Am extraction. Chapter IV describes the effects of MIDPA and of degradation of the DIDPA solvents on the extraction and back-extraction of Np.

Those chapters mentioned above deal with the results and discussion on batchwise experiments. In the usual extraction that is governed by distribution ratio at equilibrium, we can predict the behavior of an individual element in an actual separation process, that is the counter-current continuous extraction process, using the data of distribution ratios obtained through batchwise experiments under various conditions. However, the 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 to examine the ratio of Np extracted that is actually obtainable in the continuous process. Chapter V describes these studies. The operating condition of a continuous extractor for Np separation is also discussed from a viewpoint of the application to a large scale plant.

These studies mentioned above showed that quantitative separation of Np initially in the pentavalent state could be achieved by some modifications of the process developed for the separation of trivalent actinides at JAERI, such as addition of H_2O_2 and an increase in temperature. Behaviors of fission and corrosion products in the

DIDPA extraction process have been already examined at JAERI(78) but the modification of the process may have some influence on them. Therefore, the counter-current extraction was performed to examine the behaviors of the other elements in the modified DIDPA extraction process. The results are described in Chapter VI.

Among the corrosion products, Fe is the most important elements in the extraction with DIDPA because it forms the third phase (emulsion) when its concentration is high(78,79). The condition and the prevention of the third phase formation had not been fully examined yet. The Fe extraction with DIDPA is determined by the rate like the Np extraction. Extraction of Fe is an interesting subject in these aspects. Chapter VI also describes the extraction behavior of Fe and its third phase formation.

The present study offers a promising prospect of separating Np from HLW with a very high recovery by the DIDPA extraction process. The process works also for the separation of other actinides. Conclusion of the present study is described in Chapter VII.

Table I–1 Neptunium Behavior in Purex Plants of Various Countries

Plant	After dissolution	Co–extraction step	U–Pu separation step			U purification step	Ref.
	Np oxidation state	Np extracted	Reductant	Np in U fraction	Np in Pu fraction	Np in raffinate	
Trombay, India	mainly (V), 30–35 % in (IV) at higher acidity	80–90 %	Fe(II)	~60 %	~40 %	~10 %	(43)
MILLI, Germany	(V), but oxidized to (VI) with prolonged boiling	~90 %	U(IV)	50–85 %	50–15 %	99–99.5 % (dilute flow sheet)	(44)
WAK, Germany	ditto	~50 %	U(IV)	30–93 %	70–7 %	–	(45,46)
ORNL, USA	(IV):(V):(VI) = 10:80:10	~80 %	Fe(II)	~0 %	~100 %	–	(47)
Windscale, UK	(V)	~70 %	Fe(II)	~85 %	~15 %	~100 %	(48,49)
Dounreay, UK	–	1st cycle ~90 % 2nd cycle ~50 %	U(IV)	~0 % (~20% of total Np was found in Pu product.)	~100 %	–	(42,50)
Marcoule, France	(V) and (VI)	1st cycle ~90 % 2nd cycle 35–80 %	U(IV) HAN, hydrazine	~0 %	~100 %	0.1 % of the Np in feed solution	(51)
Tokai, Japan	–	1st cycle ~100 % 2nd cycle 40–60 %	U(IV)	30–40 %	70–60 %	–	(52)

CHAPTER II

EXTRACTION OF NEPTUNIUM INITIALLY IN THE PENTAVALENT STATE WITH DIISODECYLPHOSPHORIC ACID

II-1 INTRODUCTION

Japan Atomic Energy Research Institute (JAERI) had developed a partitioning process, of which main step was the solvent extraction with DIDPA(19). In 1980 a partitioning test facility(80) was constructed to use up to 3,000 Ci (1.11×10^{14} Bq) of an actual HLW. After an operational test with a simulated HLW and a semi-hot test with radioactive tracers(78), the partitioning process was tested using an actual HLW(81,82) generated at the Purex test plant of Power Reactor and Nuclear Fuel Development Corporation (PNC).

As the first step of the present study on the development of a Np separation process, the behavior of Np in the hot test of the developed partitioning process with an actual HLW was examined by means of the analysis of ^{237}Np which was originally contained in the HLW.

Then, some tracer experiments were carried out in order to explain the behavior of Np. The following subjects regarding the Np extraction with DIDPA were studied: extraction behavior of Np in various oxidation states, valence of Np after denitration, influence of La which represents elements extractable into DIDPA, influence of nitrite which plays an important role in the Np extraction with TBP(30), and back-extraction behavior of Np. These studies are described in Section II-2.

The tracer experiments showed that Np which was initially in the pentavalent state could be extracted with DIDPA. The Np extraction proceeds slowly, and the extracted Np cannot be back-extracted with HNO_3, which indicates that a redox reaction of Np took place during the extraction. In Section II-3, the oxidation state of Np in the DIDPA solution was identified by spectrophotometric analysis in order to verify the occurrence of the redox reaction.

The extraction rate of Np initially in the pentavalent state, which is influenced by this redox reaction, was examined under various conditions. This is one of the most important subjects to determine whether the extraction can be applied to an actual separation process for partitioning. The dependence of the extraction rate on the concentrations of Np, DIDPA and HNO_3 and on the temperature was examined in order to clarify the basic factors for the effective separation.

II-2 BEHAVIOR OF NEPTUNIUM IN THE PARTITIONING PROCESS DEVELOPED AT JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

PARTITIONING PROCESS DEVELOPED AT JAERI

Figure II-1 shows a flow sheet of the partitioning process tested with an actual HLW. The process conditions are as follows:

(1) Residual U and Pu are extracted with TBP from HLW after adjustment of the acidity to 2 M HNO_3. [TBP extraction step]

(2) Raffinate of the TBP extraction step (TBP raffinate) is denitrated with formic acid to about 0.5 M HNO_3 solution (pH 0.5–0.8), and here most of Zr and Mo are removed as a precipitate. [Denitration step]

(3) Transplutonium elements (Am and Cm) and rare earths (RE) are extracted with 0.5 M DIDPA - 0.1 M TBP - n-dodecane and are back-extracted with 4 M HNO_3. [DIDPA extraction step]

(4) The transplutonium elements are separated from RE with pressurized cation exchanger columns.

(5) From the raffinate of the DIDPA extraction step, Sr and Cs are adsorbed with inorganic ion exchangers: titanic acid and zeolite. [Adsorption step]

In the DIDPA extraction step, TBP is added to the DIDPA solvent to make the phase separation faster.

Figures II-2 (a) and (b) show operating conditions of the mixer-settler for the extraction steps with TBP and DIDPA, respectively. Both steps make three fractions: elements which are not extracted (raffinate fraction), elements which are extracted and back-extracted (U, Pu fraction and Am, RE fraction) and used solvent (TBP fraction and DIDPA fraction).

EXPERIMENTAL

Analysis of Np in Samples of Partitioning Test

Neptunium-237 in samples obtained through the partitioning test with an actual HLW was separated from the other α-emitters by the thenoyltrifluoroacetone (TTA) extraction method(83,84). The aqueous sample was adjusted to 1 M HNO_3 solution, and hydroxylamine and ferrous sulfamate were added to reduce Np to the tetravalent state. The reduced Np was extracted with 0.5 M TTA - xylene solution and then back-extracted with 10 M HNO_3. An aliquot of the back-extracted aqueous sample was pipetted to a stainless steel disk. After drying and heating the disk, α-activity of ^{237}Np was measured with 2π-gas-flow proportional counter for total-α and with silicon solid state detector for α-spectrometric analysis.

Neptunium in the organic samples (TBP) was first back-extracted with ammonium carbaminate(85), and then treated and analyzed by the same method.

Experiments for Behavior of Np

Neptunium-237 was obtained from Amersham International plc. in United Kingdom as a nitrate in a HNO_3 solution and used without further purification. The solution of Np(V) was prepared by the method of Srinivasan et al.(30) Ferrous sulfamate and hydroxylamine were used for the reduction of Np to the tetravalent state, and potassium dichromate was used for the oxidation to the hexavalent state.

The extractant, DIDPA, obtained from Daihachi Chemical Industry Co., Ltd., was used without further purification. Purity of DIDPA was about 91 %, and main impurities were its monoester, MIDPA, (about 4 %), its triester (about 3 %) and isodecyl alcohol (about 2 %). (These were obtained through a private communication with Daihachi Chemical Industry and were also confirmed by titration described in Chapter IV.) The DIDPA solution was prepared in the same composition as that used

in the partitioning process, 0.5 M DIDPA - 0.1 M TBP in n-dodecane.

In batchwise extraction, 2 or 3 ml of the DIDPA solution and the same volume of aqueous solution were taken in a test tube, and were shaken vigorously. After separation of the two phases by centrifugation, samples of 1 ml of each phase were pipetted into polyethylene tubes and their γ-activities were counted with a well-type NaI(Tl) scintillation detector or Ge detector(86). Distribution ratio (D) was determined by the equation:

$$D = \frac{\text{Concentration of Np in organic phase (cps/ml)}}{\text{Concentration of Np in aqueous phase (cps/ml)}}$$

A shaker with an air bath was used in the extraction experiment for the temperature dependence. Other experiments were carried out at room temperature.

A simulated HLW used at a denitration experiment was prepared according to the calculated composition which was estimated on the assumption that LWR fuel burned up to 28,000 MWd/tU was reprocessed by the Purex process(87). Table II-1 shows the composition of the simulated HLW. All the chemicals were of the reagent grade.

RESULTS AND DISCUSSION

Behavior of Np in the Partitioning Process

Table II-2 shows the material balance of ^{237}Np at the TBP extraction step. About 86 % of Np was not extracted and was transferred to the next step of denitration. This behavior means that most of Np in the feed solution was in the pentavalent state.

At the denitration step, co-precipitation of Np should be discussed. It was impossible to measure the Np quantities accurately before and after the denitration because the change of the solution volume could not be determined accurately. Therefore, the concentration change of Np was compared with that of ^{137}Cs which did not precipitate at all. As shown in Table II-3, it is clear that Np did not co-precipitate at the denitration step. The tracer experiment(75) also indicated that only 0.8 % of Np was precipitated at the denitration to 0.5 M HNO_3 solution.

The material balance at the DIDPA extraction step is shown in Table II-4. Concentrations of ^{237}Np both in the raffinate fraction and in the Am, RE fraction were under a detection limit. It means that more than 90 % of Np was still loaded on the DIDPA fraction. Neptunium was extracted with DIDPA and was not back-extracted with 4 M HNO_3. This behavior will be discussed at the next sub-section.

Discussion for Behavior of Np at the DIDPA Extraction Step

First of all, the behaviors of Np in the extraction with DIDPA were examined for the various oxidation states. Table II-5 shows Distribution ratios (D) of Np(IV), Np(V) and Np(VI). Distribution ratios of Np(IV) and Np(VI) are very large in a wide acidity range. Neptunium initially in the pentavalent state has a rather large D at a low acidity. (The reason why this expression, "initially pentavalent", is used is that Np is not in the pentavalent in the organic phase after extraction, which will be described at the next section.) These data were obtained after 15 min shaking. With further shaking, D of Np(V) became larger, as shown in Fig. II-3. Additionally, it was found that the extraction rate was sensitive to temperature (Fig. II-4). Although Np(V) is generally known to be unextractable in any extractants at the acidity examined, it can be extracted with DIDPA. Later, some consideration will be given on the extraction mechanism.

Now the attention should be paid to the oxidation state of Np before the DIDPA extraction step in the partitioning process, that is, after denitration. From this point of view, a denitration experiment was carried out using a simulated HLW, and distribution ratio of Np for the DIDPA solution was determined with the denitrated solution including Np. Distribution ratio of Np was 0.27 at 15 min shaking for the simulated HLW which was denitrated to 0.5 M HNO_3. Consequently, most of Np in the denitrated solution was in the pentavalent state. Table II-6 shows D of Np extracted from the solution caontaining La, which represents extractable elements for DIDPA. The value of 0.27 in distribution ratio suggests that all the Np were not pentavalent, because D of Np(V) decreased to less than 0.1 with 0.1 M La (total concentration of extractable elements in the simulated HLW was about 0.13 M). A few of Np may have been tetravalent and/or hexavalent after dentration.

It has been already proved that Np could be extracted with DIDPA even in the pentavalent state initially, but it seems difficult to get a sufficient value of D at the DIDPA extraction step because of the slow rate of the extraction. Only from the results shown above, it can not be explained that more than 90 % of Np was extracted with the DIDPA solution in the partitioning process.

Table II-7 (a) and (b) show the effects of formic acid (HCOOH) and nitrite, both of which may remain after denitration, on the extraction of Np(V). The presence of HCOOH does not have a great influence on D of Np. Distribution ratio shows only less than 5 % increase with 0.1 M of HCOOH for 15 min shaking. Nitrite at a high concentration such as 0.1 M makes D a little larger, but it is impossible for nitrite to remain at such a high concentration after denitration. It can be concluded that nitrite has no effects on the behavior of Np at the DIDPA extraction step, either.

On the other hand, in order to understand the back-extraction behavior, Np which was extracted with the DIDPA solution from the pentavalent state was back-extracted with 4 M HNO_3. Only 1.2 % of Np was back-extracted by 15 min shaking. Even with 0.2 M $La(NO_3)_3$ - 0.5 M HNO_3 solution (La is extracted with DIDPA), only 3.7 % were back-extracted by 30 min shaking. The extraction of Np initially in the pentavalent state is an irreversible process. Therefore, it could be understood that Np was extracted even with a small distribution ratio in a short shaking time and was not back-extracted with 4 M HNO_3 at the DIDPA extraction step in the partitioning test with actual HLW.

The extraction of Np initially in the pentavalent state with DIDPA and its mechanism will be discussed in the following section.

II-3 EXTRACTION OF NEPTUNIUM INITIALLY IN THE PENTAVALENT STATE WITH DIISODECYLPHOSPHORIC ACID

EXPERIMENTAL

Reagents

Neptunium-237 was obtained from Amersham International plc. (United Kingdom) as a nitrate in HNO_3 solution and used without further purification. To prepare the solution of Np(V) for spectrophotometric analysis, Np(VI) was removed by the DIDPA extraction from the Np stock solution, which contained Np(V) and Np(VI) with ratio of 3 : 7. Since distribution ratio of Np(VI) is higher than 10^3 for 0.5 M DIDPA as described in the previous section, Np(VI) can be easily removed. Tetravalent Np was prepared by the reduction with ferrous sulfamate and hydroxylamine.

For experiments on the extraction rate, the oxidation state of Np was adjusted to pentavalent by the method of Srinivasan et al.(30) The Np concentration was about 10^{-4} M.

The extractant, DIDPA, obtained from Daihachi Chemical Industry Co., Ltd. was used without further purification. In experiments in the present section, TBP was not added to the solvent in order to examine the extraction with DIDPA itself. n-Dodecane was used as a diluent.

Before extraction, DIDPA - n-dodecane solution (DIDPA solution) was pre-equilibrated with HNO_3 of which concentration was the same as that of the Np solution to be examined.

Procedure

For spectrophotometric measurement, organic or aqueous solution of Np was taken in a glass cell of 1 cm optical path, and analyzed with a spectrophotometer in the regions of 650 - 780 nm for Np(IV) and 900 - 1,000 nm for Np(V)(88,89). Hexavalent Np has no absorption peaks in the region of 400 - 1,000 nm.

In the experiments for the extraction rate, both HNO_3 solution of Np and the DIDPA solution were adjusted in advance to a temperature to be maintained during extraction, normally 25 °C, with a water bath. Two cubic centimeters of each solution were taken together in a test tube and mixed vigorously with a shaker in a thermostatted air bath. After separation of two phases by centrifugation, 1 ml of each phase was pipetted into a polyethylene tube and its γ-activity was measured with Ge-detector(86). Absolute quantity of Np was determined by the measurement of α-activity with 2π-gas-flow proportional counter.

RESULTS AND DISCUSSION

Redox Reaction in Extraction

Figure II-5 shows absorption spectra of Np(IV) in the aqueous HNO_3 solution and in the organic DIDPA solution. Concentration of Np(IV) in the DIDPA solution can be determined by the absorbance at 734 nm. In practice, net absorption shown in Fig. II-5 was used for better quantitative accuracy. When the absorbance is low, it is advantageous to relate the height of the peak to neighboring zone of minimum adsorption instead of relating to the electrical base line(88). Then the net absorbance was determined by the subtraction of the absorbance at 760 nm from the absorbance at 734 nm. The relation between the concentration of Np(IV) and the net absorbance obeys Beer's law and the molar extinction coefficient for the net absorbance was found

to be $74.8 \pm 1.3\ M^{-1} \cdot cm^{-1}$.

The solution of DIDPA that was shaken with 0.5 M HNO_3 solution of Np(V) was observed to have the absorption peak at 734 nm. The net absorbance was 0.0295 ± 0.0010, which corresponds to $(3.94 \pm 0.15) \times 10^{-4}$ M of Np(IV). Total Np concentration, which was determined by the radioactivity measurement, was $(8.56 \pm 0.19) \times 10^{-4}$ M, and hence the concentration ratio of Np(IV) to total Np was found to be 46.0 ± 2.0 %. Furthermore the solution did not contain Np(V) since there was no adsorption for Np(V). Therefore, the other half of Np was hexavalent. Pentavalent Np in the aqueous phase converted to Np(IV) and Np(VI) with ratio of 1:1 in the organic phase after extraction. This result means that disproportionation reaction took place in the extraction of Np(V) with DIDPA.

Extraction Rate

(1) Progress of Extraction

Figure II-6 shows the progress of the extraction of Np(V) with DIDPA. The ordinate in this figure is a logarithmic scale of the concentration ratio of the residual Np to the initial Np in the aqueous phase. The curve shown in Fig. II-6 indicates that the order of the reaction with respect to the Np concentration is larger than unity, which is due to the concern of the disproportionation reaction of which reaction order is second. In the present study the extraction rate was evaluated by an initial rate, which was obtained from the slope of the straight line shown in Fig. II-6. Since this slope corresponds to the first-order rate constant, it is named Initial Rate Constant.

As shown in Fig. II-6, Np(V) was extracted slowly, while Np(IV) and Np(VI) were nearly quantitatively extracted within 300 s in the same conditions. Therefore, it can be considered that the extraction rate of Np(V) is controlled by the disproportionation reaction.

(2) Dependence on Np Concentration

Figure II–7 shows the dependence of the Initial Rate Constant on the initial concentration of Np in the aqueous phase. As mentioned above, the reaction order with respect to the Np concentration is larger than unity. Therefore, the Initial Rate Constant increased with the Np concentration. It was proportional to the 0.22–power of the Np concentration. This fact causes the difficulty in obtaining a high recovery because the extraction rate becomes slow as the Np concentration reduces.

(3) Dependence on DIDPA Concentration

The Initial Rate Constant was proportional to the square of the DIDPA concentration, as shown in Fig. II–8. Since the extraction rate of Np(V) is sensitive to the DIDPA concentration, it may be influenced by the presence of rare earths (RE) in the organic phase. The extracted RE consumes DIDPA molecules and reduces the concentration of free DIDPA. Concentration of RE in HLW is higher by a factor of about 30 than that of Np.

In order to know the influence of RE exactly, 1×10^{-4} M Np(V) – 0.066 M $La(NO_3)_3$ – 0.5 M HNO_3 solution was mixed with 0.5 M DIDPA solution containing 0.039 M La. These La concentrations were in extraction equilibrium. Under these conditions the Initial Rate Constant was found to be 4.8×10^{-5} s^{-1}, which is about 1/7 of the value for 0.5 M DIDPA solution without RE and corresponds to the value for 0.19 M DIDPA solution. A saturated concentration of RE in 0.5 M DIDPA solution is about 0.06 M(73), which means that one ion of RE is complexed with 8 molecules of DIDPA. Therefore, 0.312 M DIDPA is consumed by complexing 0.039 M La, and the concentration of free DIDPA, which does not combine with metal ion, is estimated to be 0.188 M. Thus, the decrease of the extraction rate of Np(V) is explained by the decrease in the concentration of free DIDPA.

On the other hand, extracted Np is hardly back–extracted even with the RE solution because Np in the organic phase has disproportionated to Np(IV) and Np(VI) and their distribution coefficients are very large. For example, only less than 1 % of Np was back–extracted with 0.2 M La – 0.5 M HNO_3 solution.

In the separation process of Np from HLW, at the stage close to HLW feed point in the counter–current extractor the concentration of free DIDPA is much reduced by the presence of RE at high concentration. In these stages the extraction rate of Np is very slow. However, as the aqueous phase approaches to the exit, RE concentration is getting lower and Np begins to be extracted. The Np extracted into the counter flowing organic phase is not back–extracted even when it goes back to the stage close to the feed point for the reason described above.

(4) Dependence on HNO_3 Concentration

Figure II–9 shows the dependence of the extraction rate on the HNO_3 concentration in the aqueous phase. Up to 2 M in HNO_3 concentration, Np(V) was extracted more rapidly at the lower concentration of HNO_3.

It is preferable to reduce acid concentration for the extraction of Np(V), but moreover it is important to avoid coprecipitation of actinides with the precipitate which is generated in HLW by reducing acid concentration. In studies at JAERI(75,87) it was concluded that acid concentration of 0.5 M was the best choice for the prevention of the actinide coprecipitation and for the secure operation of denitration process.

(5) Dependence on Temperature

As shown in Fig. II–10, higher temperature made the extraction rate faster. For example, the rate was twice faster at 40 °C than at 25 °C. There are no significant difficulties in operating the extractor with controlling the temperature of the solution to about 40 °C. Temperature should be raised in an actual plant to obtain a high recovery of Np.

Discussion for Extraction Mechanism

The disproportionation reaction of Np(V) in an aqueous acid solution is expressed in the following equation and the rate of the forward reaction is known to be proportional to the square of the hydrogen ion concentration(90,91).

$$2\,NpO_2^{+} + 4\,H^{+} \leftrightarrow Np^{4+} + NpO_2^{2+} + 2\,H_2O \cdots\cdots\cdots\cdots\cdots\cdots (\text{II}-1)$$

In practice, however, Np(V) was extracted more rapidly at lower acid concentration as shown in Fig. II–9. Therefore, it can be considered that the disproportionation of Np(V) during the DIDPA extraction does not take place in the aqueous phase.

Aslanishivili et al.(92,93) pointed out that Np(V) disproportionated much more rapidly in the organic solution of DEHPA than in an aqueous acid solution. Since DIDPA is a similar extractant to DEHPA, it is reasonable to consider that the rapid disproportionation reaction takes place also in the DIDPA solution. It is supposed, therefore, that Np(V) interacts with DIDPA and then disproportionates to Np(IV) and Np(VI). The probability of the interaction is considered to increase with the decrease of hydrogen ion concentration in the aqueous phase because DIDPA is a cation exchange type extractor. This would be the reason why the extraction rate is faster at lower acid concentration.

When the interaction of DIDPA is taken into account, there is no need for the direct participation of hydrogen ion, because DIDPA release some hydrogen ions when it complexes Np(IV) and Np(VI). The following equation can be derived:

$$2\,NpO_2^{+} + (6+m+n)/2\,(HA)_2$$
$$\rightarrow NpA_4(HA)_m + NpO_2A_2(HA)_n + 2\,H_2O + 2\,H^{+} \cdots\cdots (\text{II}-2)$$

or

$$2\,NpO_2^{+} + (5+m+n)/2\,(HA)_2 + NO_3^{-}$$
$$\rightarrow NpNO_3A_3(HA)_m + NpO_2A_2(HA)_n + 2\,H_2O + H^{+} \cdots\cdots (\text{II}-3)$$

where $(HA)_2$ is the dimer of DIDPA in the organic phase. Before disproportionation, Np(V) would interact with DIDPA.

$$NpO_2^{+} + (1+x)/2\,(HA)_2 \rightarrow NpO_2A(HA)_x + H^{+} \cdots\cdots\cdots\cdots\cdots\cdots (\text{II}-4)$$

Then it disproportionates.

$$2\,NpO_2A(HA)_x + (4+m+n-2x)/2\,(HA)_2$$
$$\rightarrow NpA_4(HA)_m + NpO_2A_2(HA)_n + 2\,H_2O \cdots\cdots\cdots\cdots\cdots (\text{II}-5)$$

or

$$2\,NpO_2A(HA)_x + (3+m+n-2x)/2\,(HA)_2 + NO_3^{-} + H^{+}$$
$$\rightarrow NpNO_3A_3(HA)_m + NpO_2A_2(HA)_n + 2\,H_2O \cdots\cdots\cdots (\text{II}-6)$$

At higher concentration of HNO_3 than 2 M, extraction rate increased slightly with the acid concentration, as shown in Fig. II–9. The reason for it would be that the disproportionation reaction in the aqueous phase shown in equation (II–1) became influential.

II-4 CONCLUSION

The behavior of Np in the partitioning process developed at JAERI was examined and found to be as follows. At the TBP extraction step, most of Np was not extracted and was transferred to the next denitration step. At the denitration step, coprecipitation of Np was not observed. At the DIDPA extraction step, Np was extracted and was not back-extracted with 4 M HNO_3.

In tracer experiments, it was found that Np initially in the pentavalent state could be extracted with DIDPA. This extraction proceeds through disproportionation reaction of Np(V), which was confirmed by the oxidation state analysis of Np in the organic phase. This disproportionation reaction did not take place in the aqueous phase because the extraction rate was faster at lower acid concentration. The disproportionation reaction can be considered to be initiated by the interaction of Np(V) with DIDPA. The extractant supplies the hydrogen ions necessary for the disproportionation.

The extraction rate of Np(V) was proportional to the square of DIDPA concentration. When the DIDPA solution contains metal ions such as RE, the extraction rate of Np(V) is determined by the concentration of free DIDPA which does not combine with metal ions. Raising temperature is important for the effective separation.

The extractant of DIDPA has an excellent character, because Np initially in the pentavalent state can be extracted without a troublesome oxidation state adjustment, but the extraction rate is a little slow. Therefore, an improvement on the extraction rate should be achieved in order to apply the DIDPA extraction to an actual process for the Np separation from HLW.

Table II-1 Composition of the simulated HLW Used in Denitration Experiment.

Element	Conc.(M)	Reagent used
H^+	2.0	HNO_3
Na	0.076	$NaNO_3$
Cr	0.0091	$Cr(NO_3)_3 \cdot 9H_2O$
Fe	0.038	$Fe(NO_3)_3 \cdot 9H_2O$
Ni	0.0060	$Ni(NO_3)_2 \cdot 6H_2O$
Rb	0.0074	$RbNO_3$
Sr	0.0165	$Sr(NO_3)_2$
Zr	0.069	$ZrO(NO_3)_2 \cdot 2H_2O$
Mo	0.069	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
Ru	0.034	$Ru(NO_3)_3$
Rh	0.0080	$Rh(NO_3)_3$
Pd	0.018	$Pd(NO_3)_2$
Ag	0.00085	$AgNO_3$
Cd	0.00085	$Cd(NO_3)_2 \cdot 4H_2O$
Te	0.0068	$H_2TeO_4 \cdot 2H_2O$
Cs	0.037	$CsNO_3$
Ba	0.0207	$Ba(NO_3)_2$
La	0.127	$La(NO_3)_3 \cdot 6H_2O$
Np	8×10^{-6}	NpO_2^+

Table II-2 Material Balance of ^{237}Np at the TBP Extraction Step in the Partitioning Process Developed at JAERI.

Fraction	^{237}Np concentration (nCi/ml)	Solution flow rate (ml/h)	^{237}Np flow rate (μCi/h)	Fractional distribution (%)
Feed	8.16	290	2.37	
Raffinate	5.61	395	2.22	85.9
U, Pu	3.19	103	0.329	12.7
TBP	0.176	205	0.036	1.4

Table II-3 Concentration Profile of ^{237}Np and ^{137}Cs Before and After Denitration Step in the Partitioning Process Developed at JAERI.

	^{237}Np	^{137}Cs
(1) TBP Raffinate (Ci/ml)	5.61×10^{-9}	3.71×10^{-2}
(2) DIDPA Feed (Ci/ml)	1.30×10^{-9}	7.66×10^{-3}
Ratio [(2)/(1)]	0.232	0.206

Table II-4 Material Balance of ^{237}Np at the DIDPA Extraction Step in the Partitioning Process Developed at JAERI.

Fraction	^{237}Np concentration (nCi/ml)	Solution flow rate (ml/h)	^{237}Np flow rate (μCi/h)	Fractional distribution (%)
Feed	1.30	106	0.138	100
Raffinate	<0.047	210	<0.0103	<7.5
Am, RE	<0.077	102	<0.0078	<5.7
DIDPA		399		>90

Table II–5 Distribution Ratio of Np for Extraction with DIDPA Solution.

Shaking time : 15 min

HNO$_3$	Valence of Np		
(M)	IV	V	VI
0.02	–	3.6×10^{2}	–
0.04	–	7.95×10^{1}	–
0.09	$>3\times10^{3}$	6.19×10^{0}	$>10^{3}$
0.24	$>3\times10^{3}$	8.06×10^{-1}	$>10^{3}$
0.5	$>3\times10^{3}$	2.53×10^{-1}	$>10^{3}$
1.0	$>3\times10^{3}$	9.35×10^{-2}	$>10^{3}$
2.0	$>3\times10^{3}$	7.96×10^{-2}	9.5×10^{2}
4.0	$>3\times10^{3}$	2.01×10^{-1}	7.4×10^{2}

Table II–6 Distribution Ratio of Np for Extraction with DIDPA Solution. Effect of rare earths.

Shaking time : 15 min, [HNO$_3$] = 0.5 M

Concentration of	Valence of Np		
La(NO$_3$)$_3$ (M)	IV	V	VI
0	$>10^{3}$	0.322	$>10^{3}$
0.05	–	0.120	–
0.1	–	0.0935	–
0.2	>500	0.0903	>500

Table II–7 Distribution Ratio of Np for Extraction with DIDPA Solution.

Shaking time : 15 min, [HNO$_3$] = 0.5 M

(a) Effect of formic acid

Concentration of HCOOH (M)	Distribution ratio
0	0.176
0.1	0.181
0.3	0.195
0.5	0.210

(b) Effect of nitrite

Concentration of NaNO$_2$ (M)	Distribution ratio
0	0.227
10^{-4}	0.244
10^{-3}	0.265
10^{-2}	0.308
10^{-1}	0.589

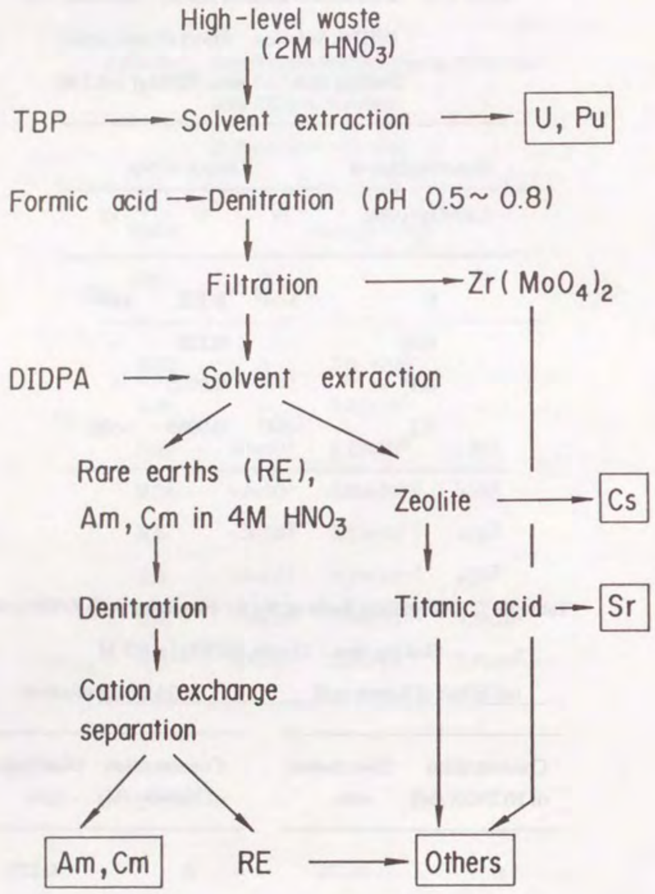
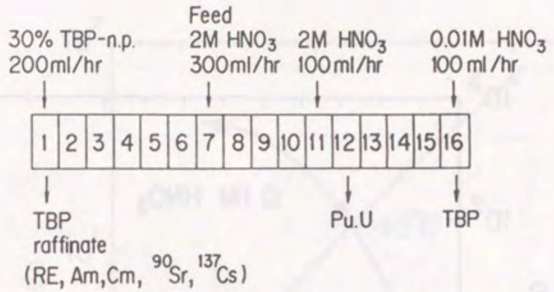
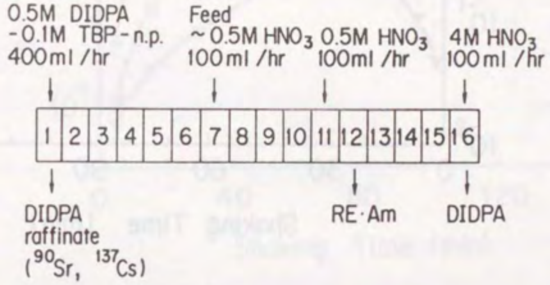


Fig. II-1 Flow Sheet of the Partitioning Process Developed at JAERI.



(a) TBP extraction step



(b) DIDPA extraction step

Fig. II-2 Operating Conditions of Mixer-Settlers at Extraction Steps of the Partitioning Process Developed at JAERI.

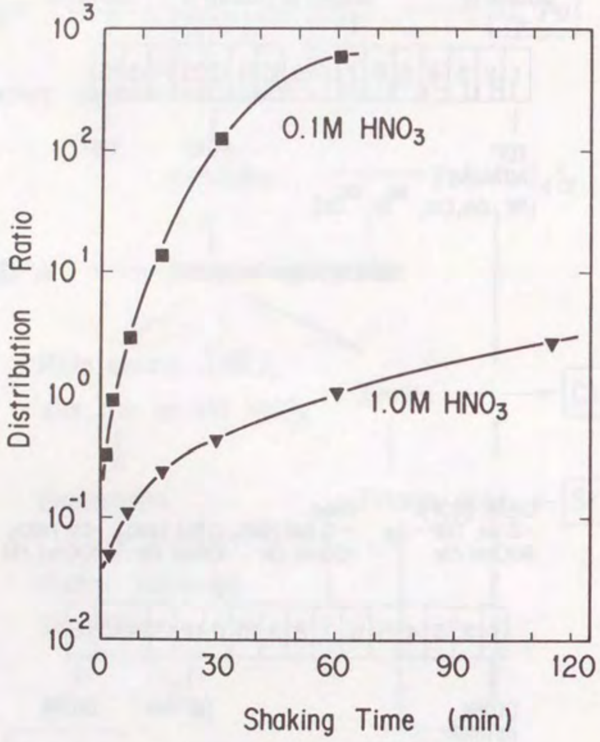


Fig. II-3 Increase of Distribution Ratio with Shaking Time for Extraction of Np(V) with DIDPA solution.

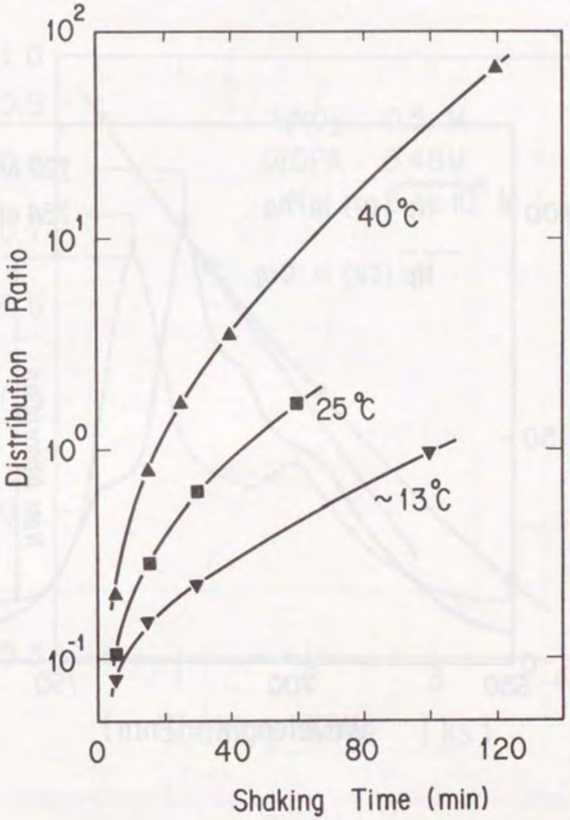


Fig. II-4 Effect of Temperature on Distribution Ratio for Extraction of Np(V) with DIDPA Solution.

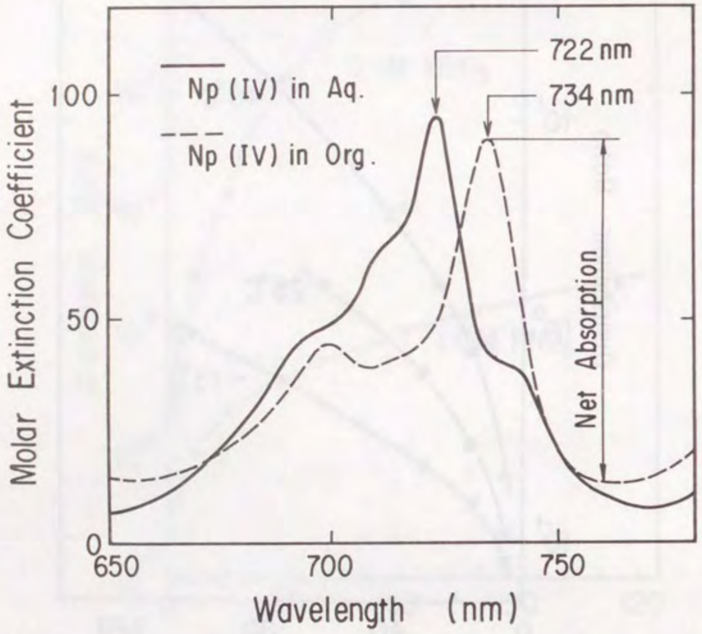


Fig. II-5 Absorption Spectra of Np(IV).

Aqueous phase : 1.94×10^{-3} M Np(IV) in 0.5 M HNO_3 solution

Organic phase : 2.02×10^{-3} M Np(IV) in 0.5 M DIDPA solution

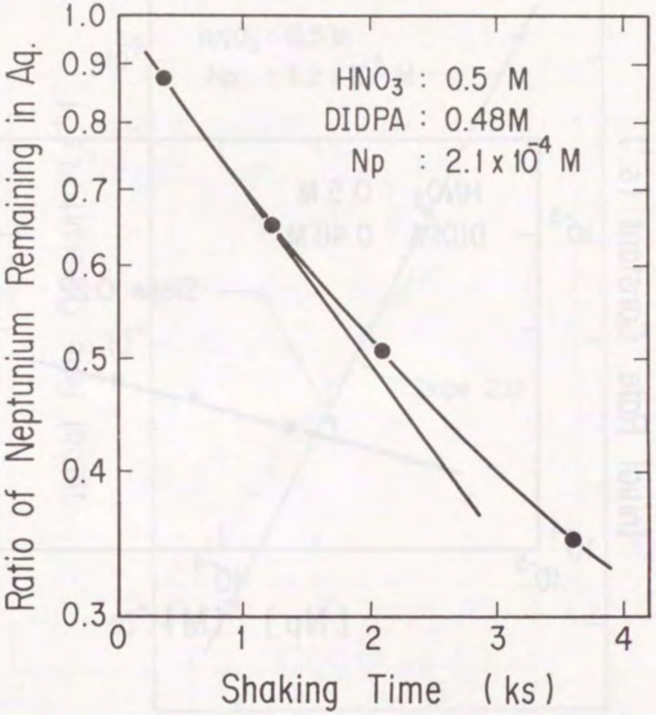


Fig. II-6 Progress of Extraction of Np(V) with DIDPA; Concentration ratio of residual Np to initial Np in aqueous phase vs. shaking time.

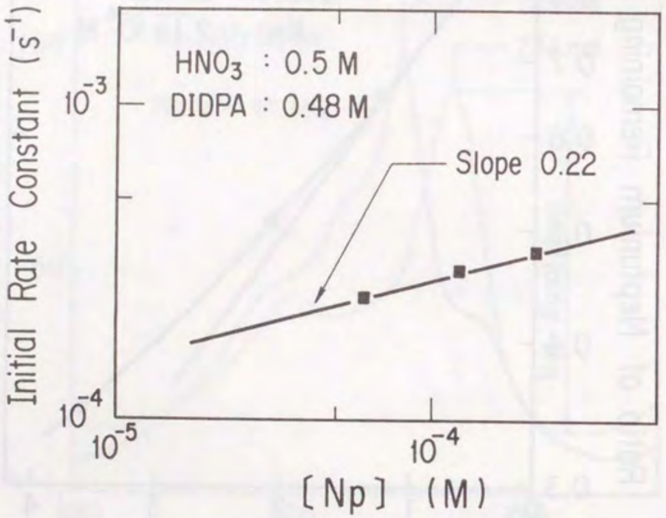


Fig. II–7 Dependence of Initial Rate Constant on Initial Concentration of Np.

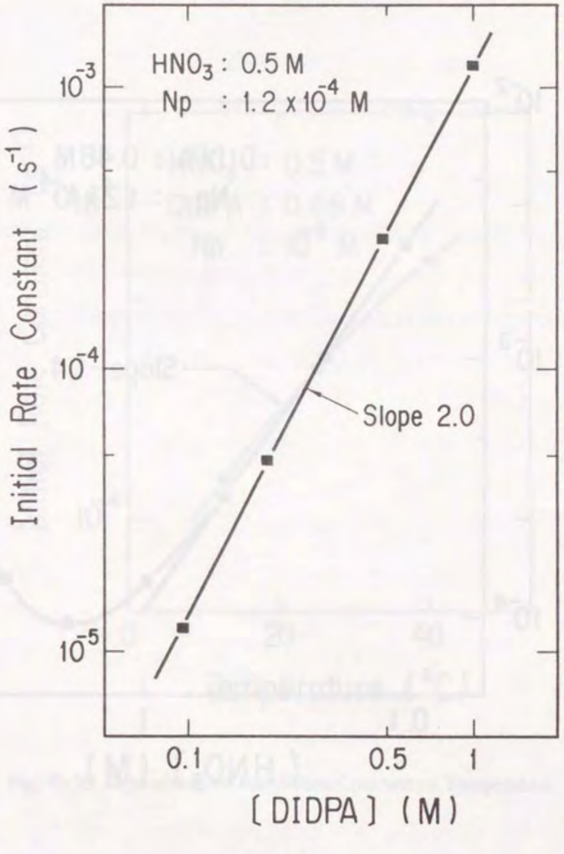


Fig. II–8 Dependence of Initial Rate Constant on DIDPA Concentration in Organic Phase.

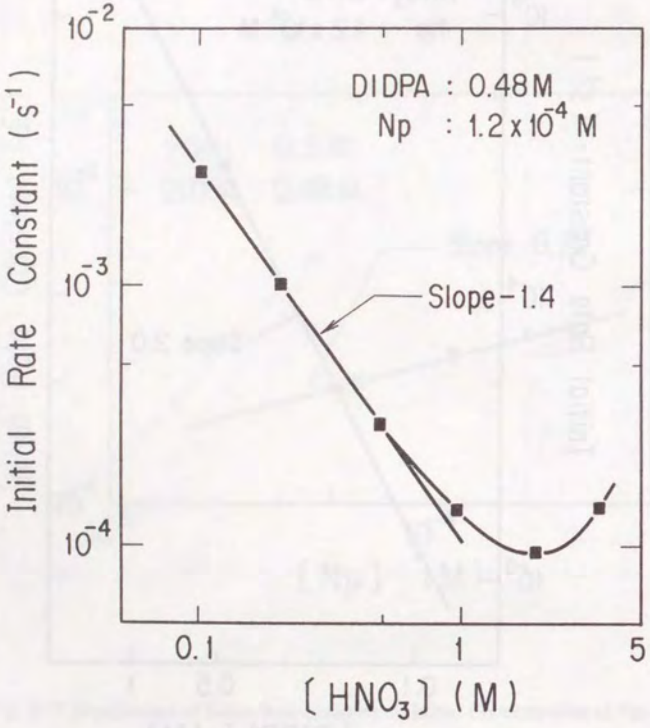


Fig. II–9 Dependence of Initial Rate Constant on HNO_3 Concentration in Aqueous Phase.

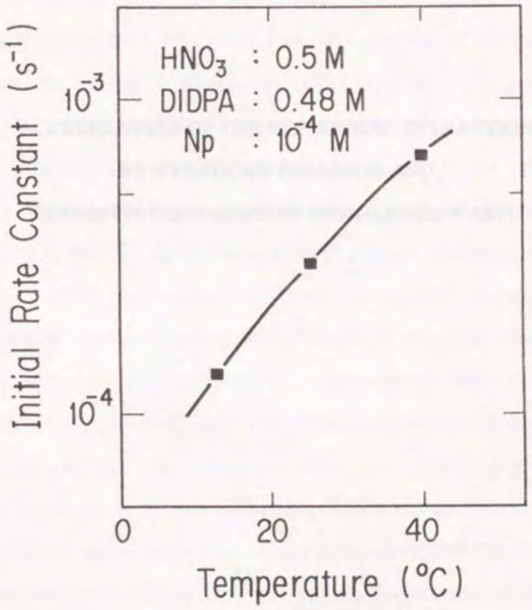


Fig. II–10 Dependence of Initial Rate Constant on Temperature.

CHAPTER III

ACCELERATION OF THE NEPTUNIUM EXTRACTION BY HYDROGEN PEROXIDE AND ELEMENTS CONTAINED IN HIGH–LEVEL WASTE

III-1 INTRODUCTION

The extraction of Np(V) with DIDPA is a rather slow process. The study described in the preceding chapter on the extraction rate showed that in order to improve the rate, the acidity should be lowered, the concentration of DIDPA should be increased and the temperature should be raised. The first two of these modifications; i.e., lowering the acidity and increasing the extractant concentration, have disadvantages. If the concentration of HNO_3 is decreased lower than 0.1 M, actinides coprecipitate with Mo and Zr to a significant extent(75,76). If the concentration of DIDPA is increased, the viscosity and the density of organic phase are increased, and consequently, separation of organic and aqueous phases becomes difficult. Prolonged extraction, for example two-hours contact of the aqueous and organic phases, will make it possible to separate Np quantitatively. However, it cannot be applied to the HLW partitioning because solvent degradation by radiolysis becomes a serious problem.

Because of these problems, additional studies were directed to accelerating the extraction of Np, initially in the pentavalent state. As a result, H_2O_2 was found to improve the extraction rate. If Np is oxidized to hexavalent or reduced to tetravalent oxidation states by a strong redox agent, it can be extracted with DIDPA from HLW. However, by addition of such agents, operational difficulty would be increased because the other elements in HLW may be influenced and the waste volume would be increased. The adjustment of the Np oxidation state before extraction is not the method the present study aims at in the beginning. On the other hand, H_2O_2 does not show any redox reaction against Np(V) in the aqueous solution at a low acid concentration, and its addition does not mean the oxidation state adjustment before extraction. From the aspects of the influence on other elements and of the increase of the waste volume, H_2O_2 is very convenient because it is a mild and salt free reagent and is easily decomposed to H_2O and O_2.

Section III-2 describes the effect of H_2O_2 on the extraction of initially Np(V) with DIDPA. Parameters examined are concentrations of H_2O_2 and HNO_3. Extraction mechanism is also studied by examining the redox reaction of Np(V).

The above examination showed that reduction of Np(V) took place during the extraction in the presence of H_2O_2. Some of the elements that HLW contains may work as catalysts in the reduction and accelerate the extraction. Such an effect was described in Section III-3.

Since the extracted Np is in the tetravalent state when H_2O_2 is present (or in the mixture of tetra- and hexavalent states in the absence of H_2O_2), it cannot be back-extracted with HNO_3 solution of concentration as high as 4 M, where Am, Cm and rare earths can be back-extracted. In separation process with other extractants, $H_2C_2O_4$ is widely used for the back-extraction of tetravalent actinides(10,70,94) since it makes strong complexes with tetravalent actinides(95). Like H_2O_2, $H_2C_2O_4$ is a salt free reagent and it can be easily decomposed to CO_2 and H_2O(96). Also the Np extracted with DIDPA was found to be back-extracted with $H_2C_2O_4$, which is shown in Section III-4.

III-2 ACCELERATION OF THE NEPTUNIUM EXTRACTION BY HYDROGEN PEROXIDE

EXPERIMENTAL

Reagents

Solutions of Np(V) were prepared by the method of Srinivasan et al.(30) The concentration of Np in extraction rate experiments was 1.3×10^{-4} M.

The extractant, DIDPA, was used without further purification. n-Dodecane was used as a diluent.

Before extraction, DIDPA - n-dodecane solution (DIDPA solution) was pre-equilibrated with HNO_3 of which concentration was the same as that of the Np solution to be examined.

Procedure

Experimental procedure for the Np extraction and the method for evaluating the extraction rate were the same as in the experiments described in Chapter II, Section II-3. Temperature was kept at 30 °C during the extraction.

Oxidation state of Np was determined by spectrophotometric measurements, as described before.

RESULTS AND DISCUSSION

Extraction rate

Figure III-1 shows the increase of distribution ratio with shaking time in the extraction of Np, initially in the pentavalent state, in the presence of H_2O_2. The extraction of Np(V) was accelerated by H_2O_2 effectively. To evaluate the acceleration, the rate constant should be derived like the Initial Rate Constant in the absence of H_2O_2 described in Chapter II. Figure III–2 is the same plot as Fig. II–6 where the Initial Rate Constant was defined. In the present figure the plot gave a straight line, which means that the reaction order of the extraction in the presence of H_2O_2 is first with respect to the Np concentration. This is another advantage of the H_2O_2 addition because the extraction rate is independent of the Np concentration. In the absence of H_2O_2, the rate decreased with the Np concentration as shown in Fig. II–7. The word "Initial" is not required in the extraction in the presence of H_2O_2, but was added to keep consistency with the extraction in the absence of H_2O_2.

From the data plotted in Fig. III–1, the Initial Rate Constant was obtained and its dependence on the concentration of H_2O_2 is illustrated in Fig. III–3. Higher concentration of H_2O_2 gives faster extraction. For example, the Initial Rate Constant in the presence of 0.2 M H_2O_2 was about four times larger than without H_2O_2.

However, when the concentration of H_2O_2 was very low (4×10^{-3} M), extraction of Np(V) became slower than without H_2O_2 (plotted by ○ in Fig. III–3). The point at 4×10^{-3} M H_2O_2 is believed to be continuous with the other points for higher concentrations of H_2O_2 (plotted by ● in Fig. III–3). Figure III–4 is a logarithmic plot of the same data shown in Fig. III–3. The point for 4×10^{-3} M H_2O_2 is on the line drawn from points obtained at higher H_2O_2 concentrations, which proves the continuity of this point. The extraction without H_2O_2 is rather specific because there is a difference in mechanism of the extraction which takes place in the presence and in the absence of H_2O_2. The extraction mechanism will be discussed later.

Figure III–4 also shows that the extraction rate was almost proportional to the 1/2–power of the H_2O_2 concentration.

Dependence of the extraction rate on the HNO_3 concentration is shown in Fig. III–5. It seems that there is also a difference between the extractions from high and low concentrations of HNO_3. When the HNO_3 concentration was below 1 M, the extraction rate for 4×10^{-4} M H_2O_2 was lower than without H_2O_2. However, the extraction from HNO_3 solution of higher than 1 M was faster even with 4×10^{-4} M H_2O_2. On the other hand, when H_2O_2 concentration was 0.2 M, the extraction rate was higher for all the range of HNO_3 concentration examined, but the extent of acceleration of the extraction changed at 1 M HNO_3. Figure III–6 shows the ratio of the Initial Rate Constant for 0.2 M H_2O_2 to the Constant without H_2O_2. The straight line changes its slope at 1 M HNO_3.

Extraction mechanism

From these studies, it seems necessary to investigate the extraction mechanism separately, with and without H_2O_2, at both low and high concentrations of HNO_3. To elucidate the extraction mechanism, the oxidation state of Np in the organic phase was determined by spectrophotometric measurement.

Figure III–7 shows absorption spectra of Np(IV) in the DIDPA solution. In this measurement, Np was reduced to Np(IV) with ferrous sulfamate and hydroxylamine before extraction. The spectrum of Np(IV) extracted from 4 M HNO_3 solution has a larger absorption peak than from 0.5 M HNO_3. This change may be due to a difference in the extracted form, which contains some NO_3^- ions. The concentration of Np(IV) in the DIDPA solution was determined by this absorption peak at 734 nm as was done in Section II–3.

The phenomenon which should be examined is how the oxidation state of Np (initially Np(V) in the aqueous phase) is changed after the extraction. Table III–1 shows the ratio of Np(IV) in the DIDPA solution to the total Np extracted.

The mechanism of the extraction from 0.5 M HNO_3 solutions without H_2O_2 was discussed in the previous chapter. It was found that the extraction of Np(V) proceeded by a disproportionation reaction, which was different from the well-known reaction in aqueous strong acid solutions. The disproportionation which took place during the extraction was considered to be influenced by DIDPA and to be initiated by the interaction of Np(V) with DIDPA.

When Np(V) was extracted from 4 M HNO_3 solution, half of the Np in the organic phase also changed into Np(IV) after extraction, as shown in Table III–1. The other half of the Np was in the hexavalent state because Np(V) could not be found by spectrophotometry. Thus, it is clear that the disproportionation reaction also takes place in the extraction from 4 M HNO_3 solution. This reaction includes the disproportionation reaction in the aqueous strong acid solution.

In the presence of H_2O_2, all the extracted Np was tetravalent in the DIDPA solution, either in the extraction from 0.5 M HNO_3 or from 4 M HNO_3. Krot et al.(97) reported that Np(V) is reduced to Np(IV) with H_2O_2 in the solution of higher than 6 M HNO_3. Therefore, in the extraction from 4 M HNO_3, Np(V) would be able to be reduced in the aqueous phase, and then Np(IV) is extracted with DIDPA. To check this hypothesis, reduction of Np(V) with H_2O_2 in 4 M HNO_3 solution was examined by spectrophotometric analysis. Figure III–8 shows the increase in the ratio of Np(IV) to total Np by the reduction with H_2O_2 in 3.8 M HNO_3 solution. Thus, it was confirmed that Np(V) was reduced also in 3.8 M HNO_3 solution.

Figure III–8 also shows the reduction of Np(V) during the extraction with DIDPA. Here the ratio of Np(IV) means the ratio of Np in the organic phase. The data in Fig. III–8 show that reduction during the extraction was faster than in aqueous solution alone. Krot et al.(97) pointed out that Np(VI), which can be extracted with DIDPA, was also produced temporarily with H_2O_2. However, only Np(IV) was observed in the organic phase in the present experiments. If the reaction of Np with H_2O_2 is reversible, i.e., if the oxidation of Np(IV) also takes places, it was natural that increase of Np(IV) in aqueous solution was less than that during the extraction because the reverse

oxidation reaction cannot take place during the extraction. [Np(IV) is extracted and complexed with DIDPA immediately.] However, Krot et al. also claims that the reduction of Np(V) with H_2O_2 was an irreversible reaction in >6 M HNO_3 solution. If this fact is applicable also to 4 M HNO_3 solution, then the reduction of Np(V) with H_2O_2 may be accelerated by the interaction with DIDPA similarly to the disproportionation reaction in the extraction without H_2O_2.

When the HNO_3 concentration is 0.5 M, the acceleration of Np(V) reduction with H_2O_2 by the presence of DIDPA is much more conspicuous. Reduction of Np(V) with H_2O_2 in 0.5 M HNO_3 could not be observed. However, Np was extracted with DIDPA in the tetravalent state.

In the extraction with thenoyltrifluoroacetone (TTA), which has a very large value of distribution ratio of Np(IV) in solutions of low acid concentration, distribution ratio was still about 10^{-3} after 30 min extraction even in the presence of 0.2 M H_2O_2. Moreover, Koltunov et al.(98) show that Np(IV) is oxidized to Np(V) with H_2O_2 in 0.02–0.1 M HNO_3. Therefore, reduction of Np(V) with H_2O_2 during the extraction from 0.5 M HNO_3 cannot be explained without involving the interaction of DIDPA.

Consequently, it can be considered as follows; Np(V) becomes easy to be reduced with H_2O_2 in the presence of DIDPA, and after reduction, Np(IV) is strongly complexed by DIDPA, which prevents reoxidation to Np(V).

Reduction of Np(V) with H_2O_2 in an aqueous acid solution is represented by the following equation:

$$NpO_2^+ + 1/2\,H_2O_2 + 3\,H^+ \rightarrow Np^{4+} + 1/2\,O_2 + 2\,H_2O \cdots\cdots\cdots\cdots \text{(III–1)}$$

Since the reduction of Np(V) needs hydrogen ions, it takes place more readily at higher HNO_3 concentrations. On the other hand, when the interaction of DIDPA is taken into account, there is no need for the direct participation of hydrogen ions, because DIDPA release some hydrogen ions when it forms a complex with Np(IV). The following equation can be derived:

$$\begin{aligned}&NpO_2^+ + (4+m)/2\,(HA)_2 + 1/2\,H_2O_2\\ &\quad \rightarrow NpA_4(HA)_m + 1/2\,O_2 + 2\,H_2O + H^+ \cdots\cdots\cdots\cdots \text{(III-2)}\end{aligned}$$

or

$$\begin{aligned}&NpO_2^+ + (3+m)/2\,(HA)_2 + 1/2\,H_2O_2 + NO_3^-\\ &\quad \rightarrow NpNO_3A_3(HA)_m + 1/2\,O_2 + 2\,H_2O \cdots\cdots\cdots\cdots \text{(III-3)}\end{aligned}$$

where $(HA)_2$ is the dimer of DIDPA in the organic phase. The 1/2–power dependence of the extraction rate on H_2O_2 concentration (Fig. III–4) would correspond to the coefficient of 1/2 for H_2O_2 in the above equations. Before reduction, Np(V) may interact with DIDPA.

$$NpO_2^+ + (1+x)/2\,(HA)_2 \rightarrow NpO_2A(HA)_x + H^+ \cdots\cdots\cdots\cdots \text{(III-4)}$$

Then it is reduced with H_2O_2.

$$\begin{aligned}&NpO_2A(HA)_x + (3+m-x)/2\,(HA)_2 + 1/2\,H_2O_2\\ &\quad \rightarrow NpA_4(HA)_m + 1/2\,O_2 + 2\,H_2O \cdots\cdots\cdots\cdots \text{(III-5)}\end{aligned}$$

or

$$\begin{aligned}&NpO_2A(HA)_x + (2+m-x)/2\,(HA)_2 + 1/2\,H_2O_2 + NO_3^- + H^+\\ &\quad \rightarrow NpNO_3A_3(HA)_m + 1/2\,O_2 + 2\,H_2O \cdots\cdots\cdots\cdots \text{(III-6)}\end{aligned}$$

As mentioned before, there is a difference between the extractions from high and low concentrations of HNO_3, and as shown above, the extraction may proceed through two steps: interaction of Np(V) with DIDPA and reduction with H_2O_2. The rate determining step may change depending on the HNO_3 concentration, which may be the reason of the phenomena shown in Figs. III–5 and III–6.

III-3 ACCELERATION OF THE NEPTUNIUM EXTRACTION BY ELEMENTS CONTAINED IN HIGH-LEVEL WASTE

EXPERIMENTAL

Reagents

Table III-2 shows elements examined on the acceleration of the Np extraction and their concentration. To the solution containing some or all of these elements, Np(V) prepared by the method of Srinivasan et al.(30) and H_2O_2 were added just before extraction.

The organic solvent used in the present experiment is a 0.5 M DIDPA - 0.1 M TBP - n-dodecane solution.

Procedure

The extraction rates in the presence of some elements were compared by the distribution ratio of Np after 5 min shaking. The rate constant was not obtained because of experimental difficulty. Coexistence of H_2O_2 and the elements shown in Table III-2 caused a bubble formation, which inhibited long time extraction using a test tube.

RESULTS AND DISCUSSION

Table III-3 shows the change of the distribution ratio of Np by the presence of some elements. Some of the elements accelerated the extraction of Np(V) in the presence of H_2O_2. The group of Mo, Zr and Te gives much effect on the extraction.

However, this effect is not important because they have been removed before the extraction as a precipitate formed by denitration of HLW to about 0.5 M HNO_3(75). The presence of Nd decreases the extraction rate. This is due to the decrease of the concentration of free DIDPA which does not combine with metal ions. This reverse effect of rare earths has been already mentioned in Chapter II.

Presence of Pd, one of the platinum group elements, accelerated the Np extraction. Distribution ratio after 5 min shaking was increased to 12.1 from 1.84 by the addition of Pd. This acceleration was not produced by Pd alone. The combination of Pd and Fe gives a much effect, as shown in Table III-4. This would be due to the catalytic effect of Pd and Fe on the reduction of Np(V) with H_2O_2. Without Pd, Fe does not work as a catalyst, which is found from the comparison between the results shown in the bottom two lines in Table III-3. Thus, the influence of the elements in HLW was desirable one for the Np extraction, but it makes it difficult to predict the Np behavior.

In these experiments using a kind of simulated HLW, the formation of gas bubbles was observed, which is due to the decomposition of H_2O_2. The nascent hydrogen would be produced by Pd catalysis during the decomposition of H_2O_2 and may reduce Fe(III) to Fe(II), and the resultant Fe(II) reduces Np(V). These may be the reason why the combination of Pd and Fe accelerates the Np Extraction.

Other two of the platinum group elements, Ru and Rh, were not added in the above experiments, but their effects were examined separately. Solution of Ru^{3+} was prepared by precipitating $Ru(OH)_3$ from a $RuCl_3$ solution through neutralization and by dissolving it into a HNO_3 solution, and used in the Np extraction. However, Ru^{3+} thus prepared showed very different effect on the Np extraction. Even in the absence of H_2O_2, Np was extracted very fast with high distribution ratio. Two kinds of mechanism are considered: one is the reduction of Np(V) to Np(IV) with Ru(IV) which is considered to exist in Ru(III) solution(99), the other is the extraction of a cation-cation complex of Np(V) with Ru(III)(100). This phenomenon is very interesting but beyond the scope of the present study. It is not important to examine the influence of Ru(III) as far as HLW concerns, because in the actual HLW, Ru is in its nitrosyl form complexing with NO_3^- and/or NO_2^-, $RuNO(NO_3)_x(NO_2)_y(H_2O)_z^{3-x-y}$(101−104). Nitrosyl Ru did not cause such extraction, which was found in other experiments. Nitrosyl Ru was used in the continuous extraction of Np from simulated HLW, described in Chapter V.

Like Pd, Rh may accelerate the Np extraction. Divalent Rh prepared by dissolving $Rh(NO_3)_2$ caused the third phase formation in extraction with DIDPA, but Rh in denitrated solution did not. The third phase formation would be due to incomplete dissolution of $Rh(NO_3)_2$. Simulated HLW used in experiments in Chapter V was denitrated before extraction.

III−4 BACK−EXTRACTION OF NEPTUNIUM

EXPERIMENTAL

Procedure

First, Np(V) prepared by the method of Srinivasan et al.(30) was extracted with 0.5 M DIDPA − 0.1 M TBP − n−dodecane solution in the presence or absence of H_2O_2. The organic solution containing Np(IV) or mixture of Np(IV) and Np(VI) was used in back−extraction of Np with $H_2C_2O_4$. The two phases were shaken for 15 min at 25 °C, which was confirmed to be long enough to reach equilibrium. Distribution ratio was defined as the ratio of Np concentration in the organic phase to that in the aqueous phase, regardless of the direction of the extraction.

RESULTS AND DISCUSSION

Oxalic acid is widely used for the back−extraction of tetravalent actinides from various extractants(10,70,94). Similarly, $H_2C_2O_4$ was found to be an effective reagent for the back−extraction of Np(IV) from the DIDPA solvent. Figure III−9 shows the dependence of distribution ratio (D) at equilibrium on the $H_2C_2O_4$ concentration. The D of Np(IV) decreased with the increase of the $H_2C_2O_4$ concentration and became less than 1 at 0.6 M $H_2C_2O_4$. The slope of the line was −2.5 in the $H_2C_2O_4$ concentration region of 0.5 to 1 M.

On the other hand, Np extracted in the absence of H_2O_2 is in the 1 : 1 mixture of Np(IV) and Np(VI) in the organic DIDPA solution. Distribution ratio of such Np at equilibrium in the back−extraction with $H_2C_2O_4$ was found higher than that of Np(IV).

With 0.8 M $H_2C_2O_4$, D of the Np which was extracted in the absence H_2O_2 was 1.46, while D of Np(IV) was 0.422. Such difference in D is due to the higher D of Np(VI). Assuming that the oxidation state of Np, particularly Np(VI), does not change in the back-extraction (which was confirmed in other experiments described in Chapter IV, Section IV-2), the following equations can be derived:

$$\frac{O_4 + O_6}{A_4 + A_6} = D_t = 1.46$$

$$O_4 + A_4 = O_6 + A_6 \qquad (\text{ Np(IV) : Np(VI) = 1 : 1 })$$

$$\frac{O_4}{A_4} = D_4 = 0.422$$

where O and A are the concentrations of Np in the organic and aqueous phases respectively, and subscripts 4 and 6 are used for Np(IV) and Np(VI) respectively. By solving the above equations, D of Np(VI) (D_6) can be calculated.

$$D_6 = \frac{D_t (2 + D_4) - D_4}{1 + 2\,D_4 - D_t} = 8.1$$

Thus, D of Np(VI) was 19 times larger than D of Np(IV).

Presence of H_2O_2 in the extraction of Np with DIDPA is favorable not only for accelerating the extraction but also for decreasing D of Np in the back-extraction with $H_2C_2O_4$ because H_2O_2 makes the oxidation state of Np in the solvent tetravalent.

III-5 CONCLUSION

The extraction of Np initially in the pentavalent oxidation state with DIDPA was found to be accelerated by the addition of H_2O_2. The extraction rate was closely proportional to the 1/2-power of the H_2O_2 concentration. The reaction order of the extraction in the presence of H_2O_2 is first with respect to the Np concentration. This is another advantage of the H_2O_2 addition because the extraction rate is independent of the Np concentration.

When H_2O_2 was added, reduction of Np(V) took place during the extraction and the Np in the organic phase was tetravalent. At low HNO_3 concentrations, the reduction of Np(V) with H_2O_2 does not proceed in the aqueous phase, but the extraction proceeded. Therefore, the reduction during the extraction is considered to be initiated by the interaction of Np(V) with DIDPA. The extractant supplies the hydrogen ions necessary for the reduction. However, when HNO_3 concentration is high (e.g., 4 M), reduction of Np(V) in the aqueous solution proceeded and would contribute to the Np extraction.

The combination of Pd and Fe was found to make the Np extraction faster by the catalytic effect.

These batchwise experiments on the acceleration of the Np extraction showed that DIDPA was a promising reagent for Np separation from HLW. In order to demonstrate the separation, however, it is still 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 with the H_2O_2 decomposition.

Tetravalent Np can be easily back-extracted from the DIDPA with $H_2C_2O_4$. Distribution ratio of Np(VI) was higher than that of Np(IV). Presence of H_2O_2 in the extraction of Np with DIDPA is favorable not only for accelerating the extraction but also for decreasing D of Np in the back-extraction with $H_2C_2O_4$ because H_2O_2 makes the oxidation state of Np in the solvent tetravalent.

Table III-1 Ratio of Np(IV) to Total Np in Organic Phase after Extraction.

Organic phase : 0.5 M DIDPA in n-dodecane

	$[H_2O_2]$ = 0 M	$[H_2O_2]$ = 0.2 M
$[HNO_3]$ = 0.5 M	46.6 ± 2.1 %	100.8 ± 2.8 %
$[HNO_3]$ = 4.0 M	48.1 ± 2.0 %	101.8 ± 2.8 %

Table III–2 Elements Examined on the acceleration of the Np Extraction.

Element	Conc.(M)	Reagent used
Na	0.038	$NaNO_3$
Cr	0.0046	$Cr(NO_3)_3{\cdot}9H_2O$
Fe	0.019	$Fe(NO_3)_3{\cdot}9H_2O$
Ni	0.0030	$Ni(NO_3)_2{\cdot}6H_2O$
Rb	0.0037	$RbNO_3$
Sr	0.0083	$Sr(NO_3)_2$
Zr	0.0345	$ZrO(NO_3)_2{\cdot}2H_2O$
Mo	0.0345	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$
Pd	0.0090	$Pd(NO_3)_2$
Te	0.0034	$H_2TeO_4{\cdot}2H_2O$
Cs	0.0186	$CsNO_3$
Ba	0.0104	$Ba(NO_3)_2$
Nd	0.0635	$Nd(NO_3)_3{\cdot}6H_2O$
Np	$1.3{\times}10^{-4}$	NpO_2^+

Table III–3 Effect of the elements in HLW on Distribution Ratio (D) of Np after 5 min Shaking.

Organic phase : 0.5 M DIDPA, 0.1 M TBP in n–dodecane

Aqueous phase : 0.55 M HNO_3, 0.5 M H_2O_2

Element added	D
Na, Rb, Cs, Sr, Ba, Fe, Cr, Ni, Pd, Nd, Mo, Zr, Te	47.3
Na, Rb, Cs, Sr, Ba, Fe, Cr, Ni, Pd, Mo, Zr, Te	53.0
Na, Rb, Cs, Sr, Ba, Fe, Cr, Ni, Pd, Nd	7.32
Na, Rb, Cs, Sr, Ba, Fe, Cr, Ni, Pd	12.1
Na, Rb, Cs, Sr, Ba, Fe, Cr, Ni	1.84
No Elements Added	1.64

Table III–4 Identification of the Elements Which Show Catalytic Effect on Distribution Ratio (D) of Np after 5 min Shaking.

Organic phase : 0.5 M DIDPA, 0.1 M TBP in n–dodecane

Aqueous phase : 0.485 M HNO_3, 0.5 M H_2O_2

Element added	D
No Elements Added	2.13
Pd	2.83
Pd + Fe	6.47
Pd + Cr	2.81
Pd + Ni	3.03
Pd + Na, Rb, Cs, Sr, Ba	3.07

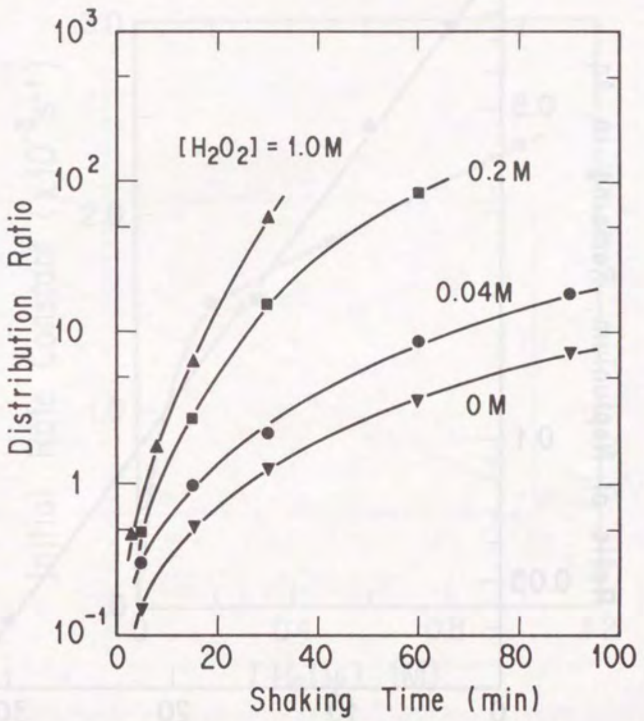


Fig. III–1 Effect of H_2O_2 Addition on Extraction of Initially Np(V) with DIDPA.
[DIDPA] = 0.5 M, [HNO_3] = 0.5 M, 30 °C

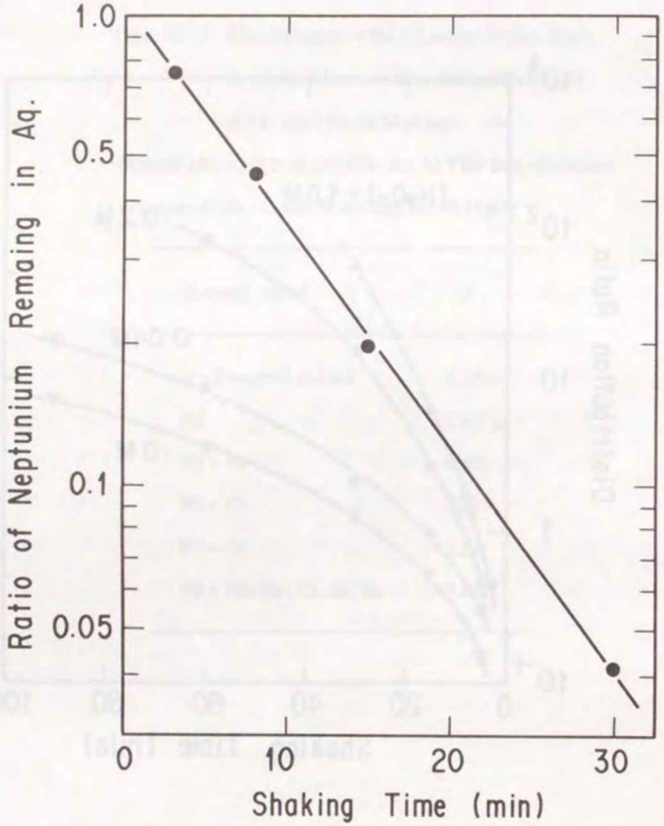


Fig. III–2 Progress of Extraction of Initially Np(V) with DIDPA in the Presence of H_2O_2. [DIDPA] = 0.48 M, $[HNO_3]$ = 0.5 M, $[H_2O_2]$ = 0.5 M, 30 °C

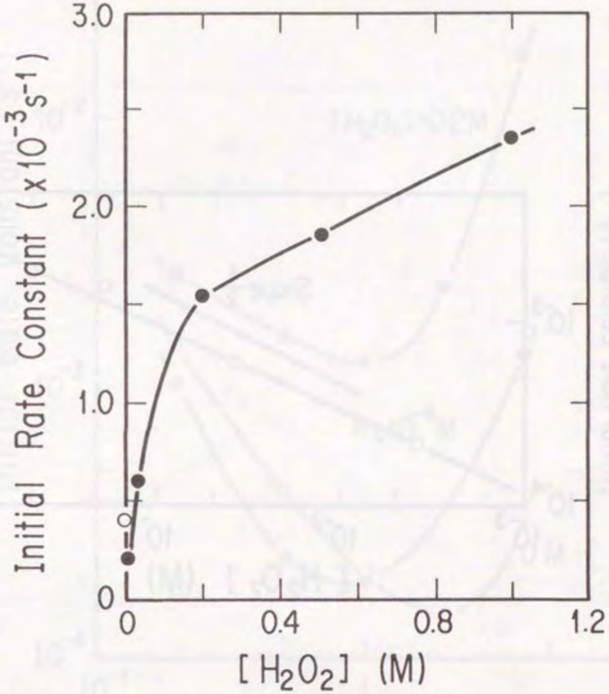


Fig. III–3 Dependence of Initial Rate Constant on H_2O_2 Concentration for Extraction of Initially Np(V) with DIDPA.

[DIDPA] = 0.5 M, $[HNO_3]$ = 0.5 M, 30 °C

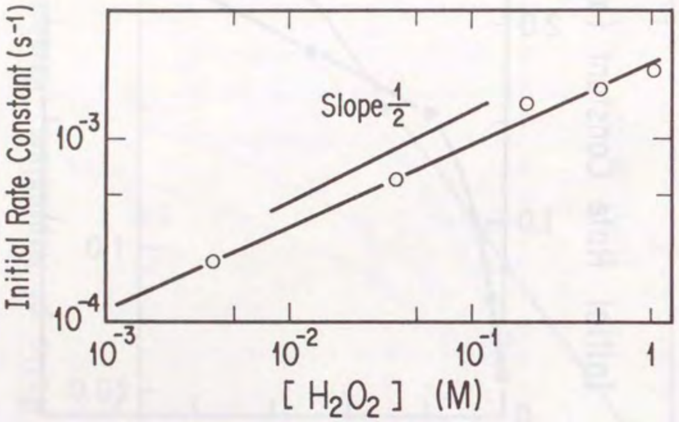


Fig. III–4 Dependence of Initial Rate Constant on H_2O_2 Concentration for Extraction of Initially Np(V) with DIDPA.

[DIDPA] = 0.5 M, [HNO_3] = 0.5 M, 30 °C

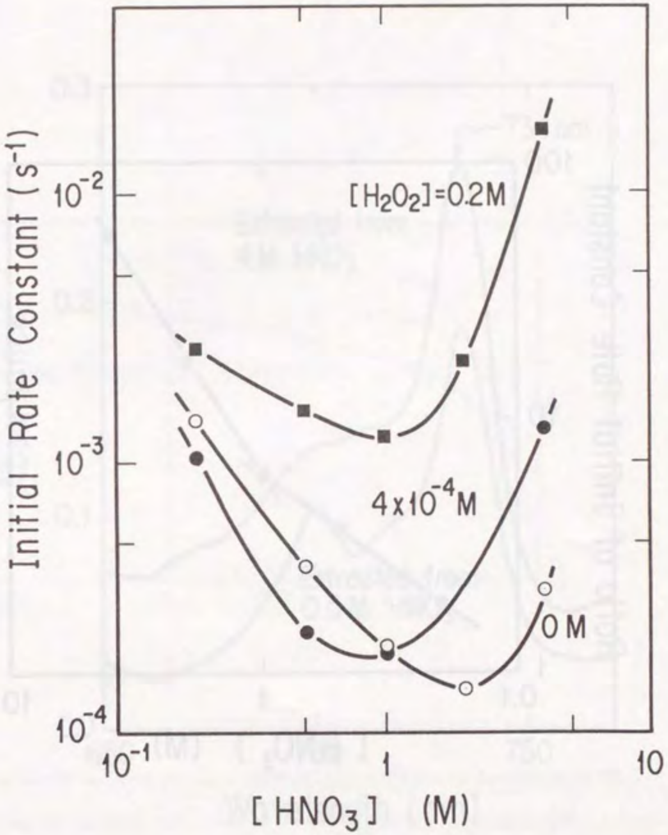


Fig. III–5 Dependence of Initial Rate Constant on HNO_3 Concentration for Extraction of Initially Np(V) with DIDPA.

[DIDPA] = 0.5 M, [HNO_3] = 0.5 M, 30 °C

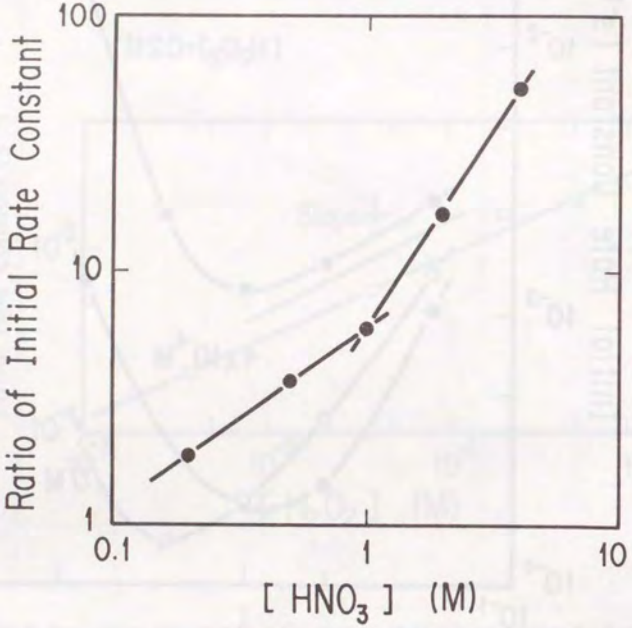


Fig. III–6 Ratio of Initial Rate Constant for 0.2 M H_2O_2 to That without H_2O_2; Dependence on HNO_3 Concentration.

[DIDPA] = 0.5 M, 30 °C

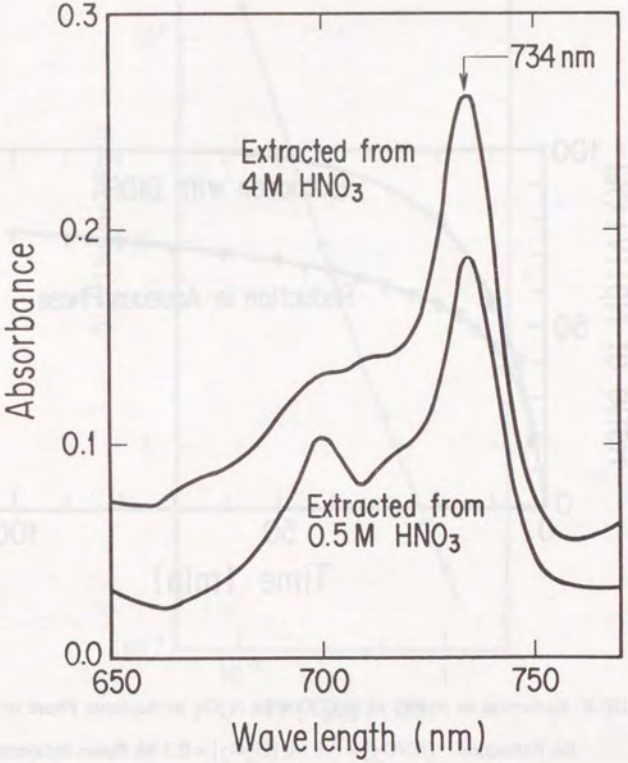


Fig. III–7 Absorption Spectra of Np(IV) in 0.5 M DIDPA – n–Dodecane.

[Np(IV)] = 2.26×10^{-3} M.

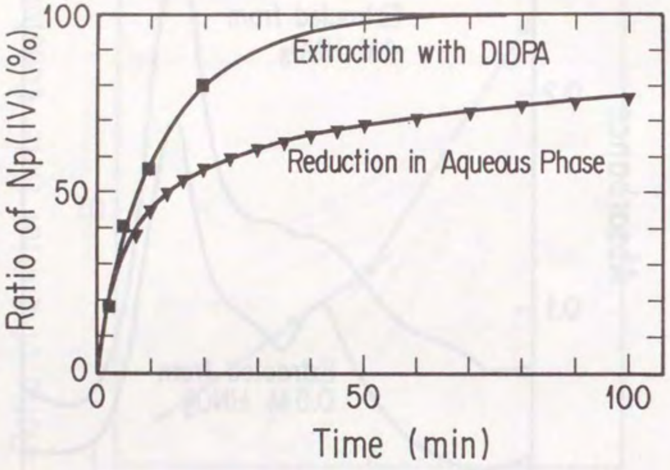


Fig. III-8 Reduction of Np(V) to Np(IV) with H_2O_2 in Aqueous Phase or during the Extraction. $[HNO_3] = 3.8$ M, $[H_2O_2] = 0.2$ M, Room temperature.

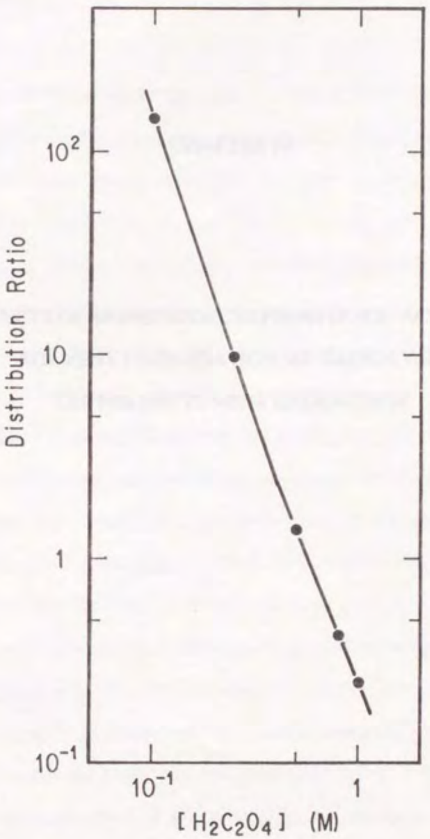


Fig. III-9 Dependence of Distribution Ratio for Back-Extraction on $H_2C_2O_4$ Concentration.

Extraction condition: $[DIDPA] = 0.5$ M, $[TBP] = 0.1$ M,
$[HNO_3] = 0.5$ M, $[H_2O_2] = 0.5$ M