

## **A Study on Enhancement of Np Extraction by TBP Through the Electrochemical Adjustment of Np Oxidation State by Using a Glassy Carbon Fiber Column Electrode**

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### **Abstract**

The changes of Np oxidation state in nitric acid and the effect of nitrous acid on the oxidation state were analyzed by spectrophotometry, solvent extraction, and electrochemical methods. An enhancement of Np extraction to 30 vol.% TBP was carried out through adjustment of Np oxidation state by using a glassy carbon fiber column electrode system. The information of electrolytic behavior of nitric acid was important because the nitrous acid affecting the Np redox reaction was generated during the electrolytic adjustment of the Np oxidation state. The Np solution used in this work consisted of Np(V) and Np(VI) without Np(IV). The composition of Np(V) in the range of 0.5M ~ 5.5 M nitric acid was 32% ~ 19%. The electrolytic oxidation of Np(V) to Np(VI) in the solution enhanced Np extraction efficiency about five times higher than the case without the electrolytic oxidation. It was confirmed that the nitrous acid of less than about 10<sup>-5</sup> M acted as a catalyst to accelerate the chemical oxidation reaction of Np(V) to Np(VI).

**Key Words** : neptunium, oxidation state, TBP, extraction, electrochemical, glassy carbon fiber

### **1. Introduction**

The concept of partitioning-transmutation to treat HLLW (high-level radioactive liquid waste) has been studied in several countries during the last decade, because it could diminish the potential toxicity of long-lived minor actinides (Am, Cm,

Np, etc.), meet the public's acceptance, and encourage further development of nuclear power for peaceful uses[1-3]. Np, among the long-lived minor actinides, is liable to spread over the different streams in the partitioning process due to the complicated chemical behavior of Np in nitric acid, where it can exist simultaneously in three

stable oxidation states: Np(IV) ( $\text{Np}^{4+}$ ), Np(V) ( $\text{NpO}_2^+$ ), Np(VI) ( $\text{NpO}_2^{2+}$ ). [4-5] The Np ions of different oxidation states exhibit different extraction behaviors to TBP (tri-butyl phosphate). In nitric acid, Np(VI) is easily extractable, Np(IV) is less extractable, and Np(V) is nearly unextractable. [5] These oxidation states are readily interconvertible depending on the nitric acid and nitrous acid concentrations. The nitrous acid severely affecting Np oxidation states could be produced through the reduction of the nitric acid during electrolysis for controlling the oxidation state of Np in nitric acid or through the radiolysis of nitric acid. Moreover, the nitric acid concentration has an effect on the Np valences through a disproportionation reaction as well. The ratio of the Np oxidation states in HLLW from several countries' reprocessing plants has been known to be different. [4] For example, at CEA in France, Np(V) and Np(VI) exist. At ORNL in U.S.A, the ratio of Np(IV):Np(V):Np(VI) is 10:80:10. At Windscale in England, Np(IV) exists in significant quantity. This discrepancy in the Np oxidation states is considered to be due to the differences of nitrous acid and nitric acid concentrations at each facility.

Accordingly, the estimation of the ratio of the Np ions of different oxidation states and the change of the oxidation states to a desired state are necessary to improve the partitioning process. Controlling the Np oxidation states electrochemically is promising. The electrochemical method does not require, in principle, the reactive reagents, which minimizes generation of secondary wastes and change of the stoichiometric concentrations of the other components. Also the chemical reagents can bring out the corrosion problem in the process. As mentioned above, because the nitrous acid, which could be generated during the process of controlling Np oxidation states in nitric acid, affects the Np oxidation state,

it is necessary to know the electrochemical redox behaviors of nitric acid and Np simultaneously. However, there are only a few publications about quantitative data of Np oxidation states in a wide range of nitric acid concentration, taking into consideration the effect of nitrous acid on Np oxidation states. Moreover, the electrochemical redox mechanism of nitric acid is complicated such that there are a few papers on the electrochemical behaviors of Np in nitric acid, which mostly deal with low nitric acid concentration of less than 3 M.

In this work, Np oxidation states in nitric acid of 0.5 M to 5.5M were analyzed by spectrophotometry, solvent extraction, and electrochemical methods, and then the effect of nitrous acid on the Np extraction to TBP was investigated. An enhancement of Np extraction by controlling the Np oxidation states using a glassy carbon (GC) fiber column electrode system was carried out.

## 2. Experimental

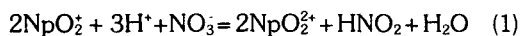
All reagents used in this work were chemical reagent grade and used as received. Np obtained from AEA Technology in England as Np-237 in 2.0 M nitric acid (total alpha percent : 99.82%) was used without further purification. A set of two GC fiber column electrode systems was used for controlling Np oxidation state. Details of the GC column electrode system were described in other work. [6] The Np extraction was carried out by mixing vigorously the aqueous solution of Np with 30 Vol.% TBP/dodecane in a batch at a phase ratio of 1 for 30 minutes. Np concentrations in aqueous and organic phases were measured by a  $\gamma$ -spectrometer with a HP-Ge detector (Oxford Inc., Model 5000 Radiation analyzer). Nitric acid concentrations in the solution before and after the electrolysis were measured by an auto-titrator (Kyoto Electronics, Model AT-400). The concentration of nitrous acid in the nitric acid

solution after the electrolysis was determined by a colorimetric method proposed by B.E. Saltzman.[8] In this method, the nitrous acid reacts with sulfanilic acid to form a diazonium salt which is coupled with  $\alpha$ -naphthylamine to form a red dye. The absorbance at 547nm was measured by a UV-VIS spectrometer (Shimadzu, Model UV-160A). The standard solution was prepared from the sodium nitrite reagent. Np absorption spectrum in the range of 350-1,300 nm was measured by a UV-IR spectrophotometer (Varian, Model Cary 5E UV-VIS-NIR). All experiments were done at  $23 \pm 0.5^\circ\text{C}$ .

### 3. Results and Discussion

Neptunium ions of different oxidation states give absorption peaks at specific wavelengths. For example, Np(IV) is representatively detected at 960 nm and 723 nm, Np(V) at 618nm and 980 nm, and Np(VI) at 1,223 nm. Figure 1 shows an absorption spectrum of  $8.0 \times 10^{-4}$  M Np in 2.0 M nitric acid obtained from AEA Technology. Three peaks are observed at 981 nm, 616 nm, and 1,223 nm. They are for Np(VI) and Np(V). Np(IV) is concluded not to exist in the solution because there are no peaks at 723 nm and 960 nm.

When the Np oxidation state in nitric acid is electrochemically controlled, nitrous acid can be generated, depending on the nitric acid concentration. The generated nitrous acid affects the redox of Np in two ways as follows. When the concentration of nitrous acid is below *ca.*  $10^{-5}$  M, the nitrous acid acts as a catalyst to accelerate oxidation of Np(V) to Np(VI) as Eq. (1)



When the nitrous acid is more than *ca.*  $10^{-4}$  M, the nitrous acid in nitric acid acts as a reductant so that it reduces Np(VI) to Np(V) rapidly. The reason

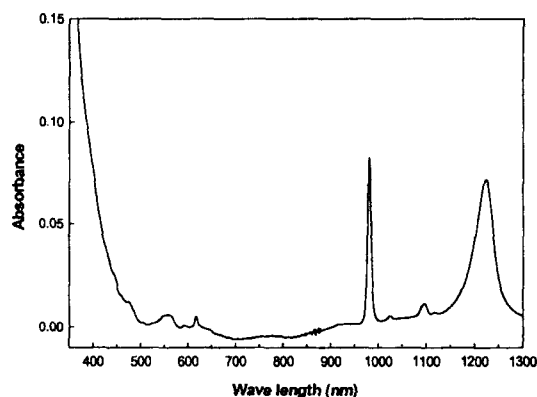
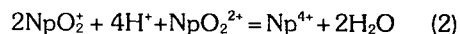
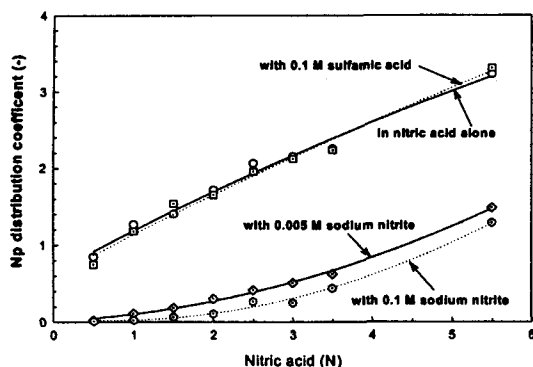


Fig. 1. Absorbance Spectrum of  $8.0 \times 10^{-4}$  M Np in 2.0 M Nitric Acid

can be explained by the fact that the backward reaction rate of Eq. (1) increases according to the Le Chatelier's principle when the concentration of the nitrous acid is higher. And Np(V) can change to Np(VI) or Np(IV) spontaneously through a disproportionation reaction as Eq. (2), depending on the nitric acid concentration.



The interconversion of  $\text{NpO}_2^{2+}$  to  $\text{Np}^{4+}$  requires an extensive rearrangement of the primary coordination sphere of  $\text{NpO}_2^+$  (*i.e.* a change in the linear dioxo structure) before electron transfer. This results in a relatively high activation barrier such that the rate of the disproportionation is slow and can be considered to be negligible in reprocessing process from which HLLW comes. This can be a reason why Np(IV) doesn't exist in the nitric solution as shown in Fig.1. Because the nitrous acid, which could be generated during controlling Np in nitric acid, severely affects the Np oxidation state, it is required to understand the electrochemical redox behaviors of nitric acid and Np at the same time. Some experimental results on the electrolytic reaction of nitric acid were reported in our previous paper [7] where sulfamic

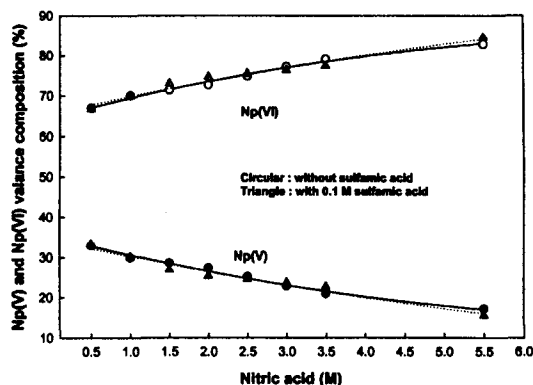


**Fig. 2. Np Distribution Coefficient in Nitric Acid with and Without Sulfamic Acid and Sodium Nitrite**  
Initial Aqueous Np : 0.0011M, Organic Phase : 30Vol.% TBP

acid of 0.1 M was confirmed to be enough to decompose the nitrous acid generated during the electrolytic reaction of nitric acid of less than 3.5 M.

Figure 2 shows the effect of nitric acid concentration on an apparent distribution coefficient of Np from the aqueous solution of Np(VI) and Np(V) mixture into 30 Vol.% TBP without controlling the oxidation state. The apparent distribution coefficients increase with an increase of nitric acid concentration and they are between those of pure Np(V) and those of Np(VI). Figure 2 shows that there is no effect of the sulfamic acid on the Np extraction. However, in the presence of more than  $10^{-3}$ M nitrite ion, the distribution coefficient drops a lot. This can be explained by considering that the nitrous acid resulted from nitrite ion and proton of nitric acid acts as a reductant toward Np(VI) as Eq. (1) so that the portion of Np(V) in the system increases.

The distribution coefficients of pure Np(VI) and Np(V) are well known and the compositions of Np(VI) and Np(V) can be estimated from the apparent distribution coefficient of Np in Fig.2 by using the following Eqs. (3) and (4). The results of the estimation are shown in Fig.3.



**Fig. 3. Np(VI) and Np(V) in Nitric Acid with and Without**

$$X_{Np(V),i} D_{Np(V),i} + X_{Np(VI),i} D_{Np(VI),i} = D_{App.Np(VI),Np(V),i} \quad (3)$$

i : nitric acid

$$X_{Np(V),i} + X_{Np(VI),i} = 1, i : \text{nitric acid} \quad (4)$$

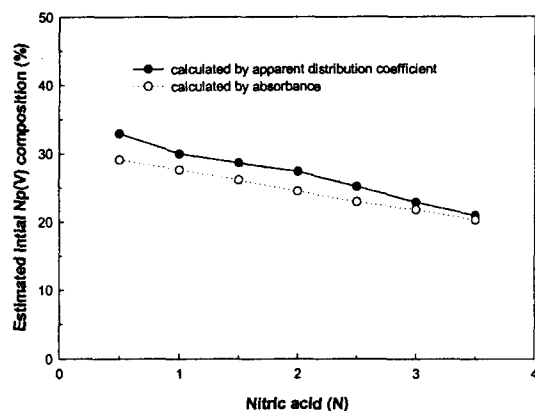
where

$X_{Np(V)}$ ,  $X_{Np(VI)}$  : mole fractions of Np(V) and Np(VI), respectively.

$D_{Np(V)}$ ,  $D_{Np(VI)}$  : distribution coefficients of pure Np(V) and Np(VI), respectively.

$D_{App.Np(VI),Np(V)}$  : apparent distribution coefficient of Np in the solution of Np(VI) and Np(V) coexisting

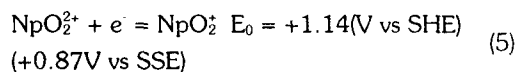
Because the disproportionation rate increases with an increase of the concentration of nitric acid as Eq. (2), the composition of Np(VI) in Fig.3 increases and consequently that of Np(V) decreases with an increase of nitric acid concentration. From this result, it is confirmed that the composition of Np(V) in the initial Np solution is less than 30% for the nitric acid concentration from 0.5 M to 5.5 M. Figure 4 shows a comparison of mole fractions of Np(V) estimated by solvent extraction method(cf. Fig.3) with those estimated by spectrophotometry (cf. Fig.1) using an extinction coefficient of Np(V) of  $390 \text{ M}^{-1}\text{cm}^{-1}$ .



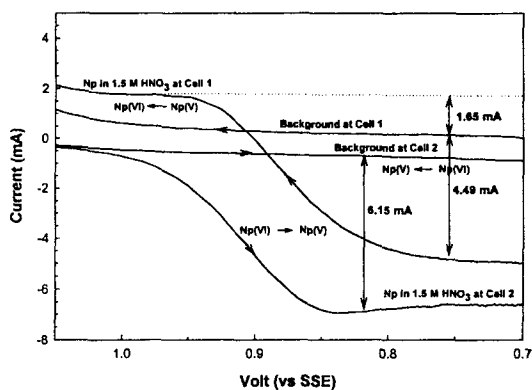
**Fig. 4. Speciation of Np(V) Estimated by Absorbance and Apparent Distribution Coefficient**

They agree relatively well with a maximum error of 4%.

Figure 5 shows a voltammogram observed in the positive potential scanning with  $5.1 \times 10^{-3}$  M Np in 1.5 M nitric acid being fed into cell 1, a voltammogram in the negative scanning direction for the Np solution coming out of cell 1 where a constant potential of +1.05 V was supplied, and their respective background voltammograms. The redox reaction of Np(VI) and Np(V) are expressed as follows.

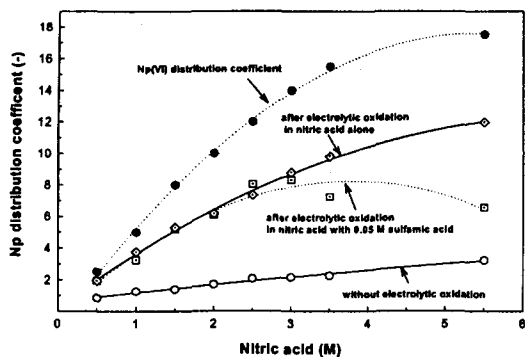


In the voltammogram at cell 1, a reduction limiting current observed at more negative potential than +0.8V is considered to be due to the reduction of Np(VI) in the feeding solution to Np(V) and an oxidation limiting current at more positive than +0.95V is considered to be due to the oxidation of Np(V) to Np(VI). On the basis of the background current at cell 1, the current difference between the oxidation limiting current and the background current is 1.65mA, and the one between the reduction limiting current and the background



**Fig. 5. Voltammograms for Reduction and Oxidation of Np(VI) and Np(V) in 1.5M Nitric Acid at Cell 1 and Cell 2**  
Feeding Flow Rate : 0.7ml/min, Np Concentration :  $5.1 \times 10^{-3}$ M

current is 4.49mA. The current ratio is the ratio of the compositions of Np(VI) and Np(V) in the nitric acid which is fed into cell 1. The compositions of Np(V) and Np(VI) in 1.5 M nitric acid calculated from the ratio are 27% and 73%, respectively, which are very close to those calculated by spectrometry as given Fig.4. The net current between the limiting oxidation and reduction currents at cell 1 is 6.14mA. From this voltammogram of Np oxidation, the potential over +0.95 is enough to oxidize Np(V) to Np(VI). Accordingly, when +1.05 V is applied constantly to cell 1 into which  $5.1 \times 10^{-3}$  M Np in 1.5 M nitric acid is fed, the solution coming out from cell 1 contains only Np(VI) so that the voltammogram in the negative scanning direction at cell 2 represents the reduction of pure Np(VI) to Np(V). The net current between the voltammogram and its background at cell 2 is 6.15mA which is very close to the net current between the limiting oxidation and reduction currents at cell 1. From the results of Fig.1 to Fig. 5, it can be said that the Np(V) composition in 0.5M to 5.5M nitric acid solution is 32% to 19% and Np(VI) is



**Fig. 6. Np Distribution Coefficient with Electrolytic Oxidation**

**Np Concentration :  $1.1 \times 10^{-3}$  M, Organic Phase : 30Vol.% TBP, Applied Potential at Cell 1 : 1.02V vs. SSE**

dominant in the solution and increases with an increase of the concentration of nitric acid. The other papers dealing with Np oxidation in nitric acid of more than 5.5M mentioned that the degree of disproportionation of Np(V) was 76.2%, in other words, the composition of Np(V) is 23.8%, which was close to 19% as shown in Fig.4 even though there are a few errors among both values.

Figure 6 shows the distribution coefficient of Np in the solution eluting from cell 1 of +1.05 V, after mixing with 30 Vol.% TBP. The distribution coefficients obtained with the electrolytic oxidation of Np(V) to Np(VI) are about 5 times higher than those without the electrolytic oxidation. However, they are lower than those of pure Np(VI) shown in the previous papers[5] where Np(VI) were prepared by chemical oxidants in excess. Np(VI) generated in cell 1 is assumed to be partially re-reduced to Np(V) during the extraction. Np(VI) is known to be reduced to Np(V) easily. Figure 6 also shows the effect of sulfamic acid on the Np distribution coefficient after the electrolytic oxidation. In nitric acid containing 0.05 M sulfamic acid, the distribution

coefficients deviate from those measured in nitric acid when the concentration is higher than 2 M. This could be explained as follows. The existence of a small amount of nitrous acid allow Np(V) to be oxidized to Np(VI) at a high nitric acid concentration, cf. Eq. (1). Without sulfamic acid as a nitrous acid scavenger, nitrous acid, which could be generated during the oxidation of Np(V) at cell 1, is considered to help Np(V) partially converted from Np(VI) during the extraction to re-oxidize to Np(VI). However, with sulfamic acid, there is no chance for the oxidation of Np(V) to Np(VI) during the extraction. In order to confirm the existence of nitrous acid in the eluents from cell 1 at +1.02 V and from cell 2 at +0.72 V, nitrite ion concentrations from the eluents were analyzed by a colorimetric method and the results are plotted in Fig.7. The nitrous acid in the effluent from cell 1 is less than  $10^{-5}$  M, which implies that nitrous acid acts as a catalyst shown by Eq. (1). However, in the solution from cell 2, the nitrous acid concentration is  $\sim 10^{-3}$  M, which indicates the auto-catalytic reactions of the nitrous acid generated at the cell 1.[7] From the results of Fig.6 and Fig.7, a small amount of nitrous acid may accelerate the oxidation of Np(V) to Np(VI) and the sulfamic acid is considered not to be necessary in the feeding nitric acid solution only for the preparation of Np(VI) by the electrolytic oxidation. Figure 8 shows the distribution coefficient of Np in the eluents from cell 2 at +0.72 V with cell 1 at +1.02 V after mixing with 30 Vol.% TBP. The nitric acid solution from cell 2 is considered to contain only Np(V). The distribution coefficient increases exponentially with an increase of nitric acid concentration up to 5.5 M. This is attributable to the re-oxidation of Np(V) through the disproportionation reaction of Eq. (4) during the extraction step. The equilibrium constant of Eq. (2) is known to be  $4 \times 10^{-7}$  in 1.0 M nitric acid and 0.13 in 5.3 M nitric acid.

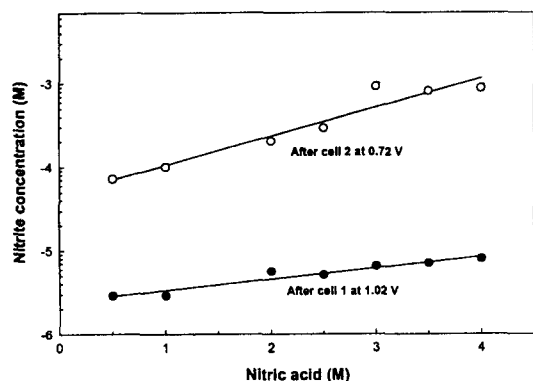


Fig. 7. Nitrite Concentrations After Cell 1 of + 1.02V and Cell 2 of +0.72V  
Flow Rate : 0.6ml/min

#### 4. Conclusions

An enhancement of Np extraction efficiency into 30Vol.% TBP was carried out through the adjustment of Np oxidation state by using GC fiber column electrode system. The Np solution used in this work consisted of Np(V) and Np(VI). The composition of Np(V) in 0.5M ~ 5.5 M nitric acid solution was 32% ~ 19%. The electrolytic oxidation of Np(V) in the solution enhanced the TBP extraction efficiency of Np about five times higher than that without the electrolytic oxidation.

#### Acknowledgement

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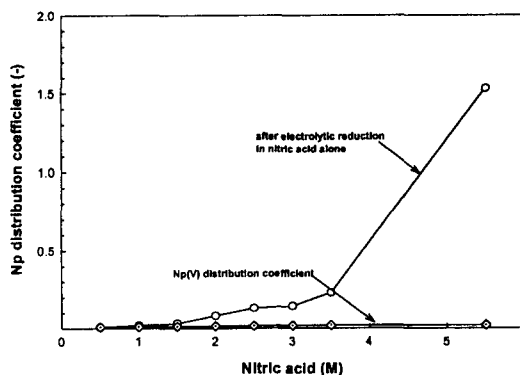


Fig. 8. Np Distribution Coefficient with Electrolytic Reduction at Cell 2  
Np Concentration :  $1.1 \times 10^{-3}$ M, Organic Phase : 30Vol.% TBP, Applied Potential at Cell 2 : 0.72 vs. SSE

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