

## Training Course of Experimental Chemistry in the Nuclear Fuel Cycle: Solid State and Solution Chemistry

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### 1. Introduction

In this experimental study program in Tohoku University, basic experiments were done by the participants. First one is the hydrogen reduction experiment of the mixture of  $\text{UO}_2$  and  $\text{ZrO}_2$ . Second one is to observe microscopic structure of solid solution of  $\text{UO}_2$  and  $\text{ZrO}_2$  using SEM/EDX and XRD system, simulated fuel debris. Third one is milking process of  $^{239}\text{Np}$  from  $^{243}\text{Am}$  by solvent extraction using Tri-n-Octylamine (TOA). Last one is solvent extraction in PUREX by the simulated mixed aqueous solution of U,  $^{85}\text{Sr}$  and  $^{239}\text{Np}$  which is represented minor actinide elements included in the spent nuclear fuel.

### 2. Materials and Methods

In this section, experimental methods and procedures are described about each experiments.

#### 2.1. Solid State Experiment; Solid Solution Experiment of $\text{UO}_2$ and $\text{ZrO}_2$ Mixture.

##### 2.1.1. Materials

$\text{UO}_2$  and  $\text{ZrO}_2$  powders of different composition are needed. First of all, prepare 5 mol % and 10 mol % of  $\text{ZrO}_2$  comparing with 200g  $\text{UO}_2$ . To make the former one, we used 0.1940 g of  $\text{UO}_2$  and 0.0043 g of  $\text{ZrO}_2$ . To make the latter one, we used 0.1960 g of  $\text{UO}_2$  and 0.0104 g of  $\text{ZrO}_2$ . Then, mixed each of oxides put into mortar respectively. And grind each of samples about 20 min to get very fine powder with homogeneous mixture.

##### 2.1.2. Heat Treatment

Heat each samples up to 1400 °C using a high temperature furnace in  $\text{Ar-10\%H}_2$  atmosphere which flow rate is 20 mL/min.

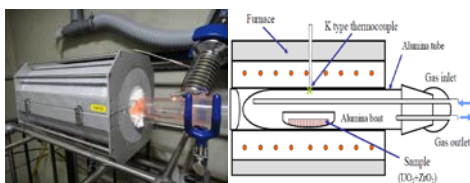


Fig 1. High temperature tube furnace and schematic figure of this furnace cross section.

In this experiment, we designed the heating regions as

following figure. Actual heated furnace temperature is not exactly same with figure 2. It is slightly different so we need buffer region which is 1000 °C to 1400 °C to be able to very close to 1400 °C.

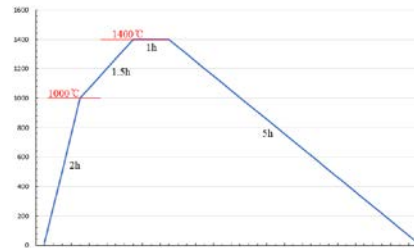


Fig 2. Designed heating region. The region 1000 °C to 1400 °C is a buffer region which make actual heated temperature follows closely to 1400 °C.

#### 2.1.3. SEM/EDX and XRD Analysis

We analyzed the crystal structure of  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$  compound and calculated lattice parameter using XRD to evaluate  $\text{UO}_2$  solid solution formation. Also, we analyzed the surfaces which are formed solid solution of  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$  compound using SEM/EDX to check the elements ratio of Zr, U and O.

#### 2.2. Solution Chemistry Experiment (1); Milking of $^{239}\text{Np}$ from $^{243}\text{Am}$ by Solvent Extraction

##### 2.2.1. Materials

At first,  $^{243}\text{Am}$  is needed which is in secular equilibrium state. Next, 25 ml of 5% Tri-n-octylamine (TOA) and xylene mixture and concentrated HCl (12M) are needed for extraction. And concentrated  $\text{HNO}_3$  is needed to eliminate organic solution for purification.

##### 2.2.2. Experimental Methods

In this section the procedures of milking process are described.

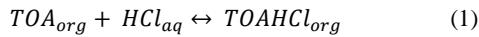


Fig 3. Flow diagram for milking of  $^{239}\text{Np}$  from  $^{243}\text{Am}$  by solvent extraction using Tri-n-octylamine

##### 2.2.2.1. Pre-equilibrium

Before solvent extraction, the pre-equilibrium is

necessary between the organic phase (TOA in xylene) and the aqueous phase (HCl). The extraction reaction of HCl by TOA can be written as follows:



Prepare 25 ml of 5 % TOA in xylene (0.114 M) for organic phase and 10ml of concentrated HCl (12.0 M) for aqueous phase. Mix these solutions in the funnel for 15 seconds. When these solutions are stabilized, discard the aqueous phase.

### 2.2.2.2. Extraction and Washing

Mix stock solution of  $^{243}\text{Am}$  and prepared solution (xylene with TOA) of previous procedure for 1 min. In this process,  $^{239}\text{Np}$  is extracted from aqueous phase to organic phase. In this step, 12 M of HCl is used.

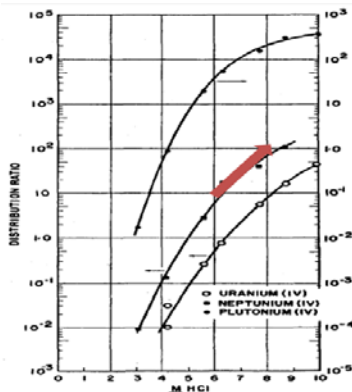


Fig 4. Extraction mechanism of Np(IV) by TOA from HCl solution. Distribution ratio increases rapidly, when HCl concentration goes high [1]

Figure 4, trend of Np(IV) distribution ratio rapidly goes high according to the mole numbers of HCl increase. It means that almost Np (IV, VI) are extracted in organic phase. On the other hand,  $^{243}\text{Am}$  remains in aqueous phase.

However, not all of  $^{239}\text{Np}$  atoms are extracted only this procedure. Therefore, washing process is needed. The process is exactly same with extraction process except the volume of HCl, 10 ml for washing.

### 2.2.2.3. Np Stripping

In this process,  $^{239}\text{Np}$  is back extracted into aqueous phase because the concentration of chloride ion decreases. In this step, 25 ml of  $\text{H}_2\text{O}$  is injected to  $^{239}\text{Np}$  solution which is organic phase. Thus, concentration of chloride ion goes down. As a result,  $^{239}\text{Np}$  is back extracted from organic phase to aqueous phase.

### 2.2.2.4. Fuming

Little amount of organic solution may remain in the act of back extraction process due to human handling. Therefore, fuming process is needed. First, put 5M

$\text{HNO}_3$  into the beaker which contains  $^{239}\text{Np}$  solution. Next, heat approximately 190 ~ 200 °C. And do these steps 2 or 3 times. In this process, 5 M  $\text{HNO}_3$  causes chemical decomposition of TOA & Xylene mixture. It makes nitride, involving  $\text{NO}_x(\text{g})$  and little  $\text{CO}_2(\text{g})$  emission comes from organic structure.

## 2.3. Solution Chemistry Experiment (2); Solvent Extraction of PUREX simulated

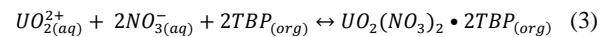
### 2.3.1. Materials

Table 1: The composition of sample solutions

Sample no.	S1	S2	S3
$\text{HNO}_3$	0.1 M	1 M	5 M
$\text{UO}_2^{2+}$		$5.0 \times 10^{-2} \text{ M}$	
$^{85}\text{Sr}^{2+}$		$1.0 \times 10^{-3} \text{ M}$	
TBP		30% in dodecane	

### 2.3.2. Experimental Methods

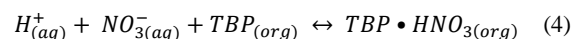
In the solvent extraction of PUREX, TBP is usually used as an extractant. The extraction chemical reaction of uranium ion can be represented by the equation (3). The oxidation state of uranium is hexa-valent in the nitric acid.



In this experiment, the procedure of solvent extraction for uranium is divided into pre-equilibrium, solvent extraction.

#### 2.3.2.1. Pre-equilibrium

The pre-equilibrium is also necessary for TBP solvent extraction for avoiding a volume change like Milking process. There is an extraction reaction of  $\text{HNO}_3$  by TBP. This can be written as follows:



A 15 ml of 30% tributyl phosphate in dodecane was mixed with 15 ml of 0.1 M  $\text{HNO}_3$  in a separation funnel for 2 minutes.

#### 2.3.2.2. Solvent extraction of hexa-valent uranium

The organic phase being in pre-equilibrium was filled into the 3 glass tubes as 2 ml respectively. Then, 1.86 ml of each sample solutions were put into each glass tube. Likewise, 40  $\mu\text{l}$  of  $^{85}\text{Sr}$  stock solution and 100  $\mu\text{l}$  of  $^{239}\text{Np}$  stock solution were put into each glass tube.

The glass tubes should be mixed for 30 minutes by automatic shaker for extraction. After mixing, centrifuge for 5 minutes to separate organic and aqueous phases.

#### 2.4.2.3. Activity measurement

First, 1.0 ml of organic phases were pipetted from S1, S2, and S3. And they are moved into new glass tubes (Sx-org. ( $\gamma$ )). 0.1 ml of organic phases were pipetted and moved into the small glass cuvettes filled with 1 ml of liquid scintillation cocktail (Sx-org. ( $\alpha$ )). For homogeneous phase, the cuvettes should be shaken by automatic vibrator until the solutions became transparent.

After that, it could be possible to do sampling of aqueous phase. Each sample (Sx-aq. ( $\gamma$ ), Sx-aq. ( $\alpha$ )) were taken in the same way with organic phase sampling.

### 3. Results and Discussion

#### 3.1. XRD and SEM/EDX analysis of $Zr_yU_{1-y}O_2$

After heating them up to make compound, the net weight of  $UO_2$  and  $ZrO_2$  mixture (95:5) is changed to 0.1751 g and the net weight of  $UO_2$  and  $ZrO_2$  mixture (90:10) is changed to 0.1883 g.

The sizes of  $UO_2$ ,  $ZrO_2$  and  $Zr_yU_{1-y}O$  are 0.73  $\mu m$ , 1.02  $\mu m$  and 1.89  $\mu m$ .

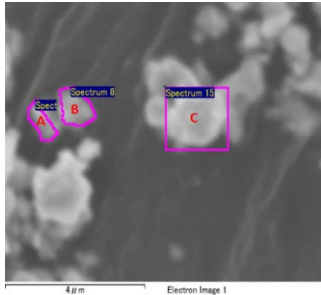


Fig 5. Microscopic view of  $UO_2$ ,  $ZrO_2$  and  $Zr_yU_{1-y}O$  using SEM/EDX

By using XRD, we are able to measure the lattice parameter according to the ratio of compound. Using Bragg's law, we can get the lattice parameter.

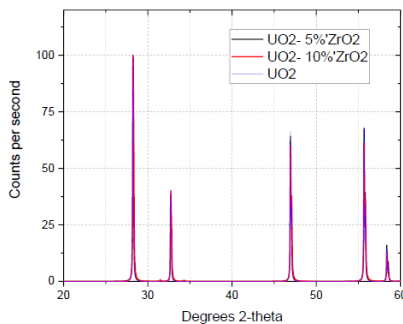


Fig 6. XRD patterns of  $UO_2$ ,  $ZrO_2$  and  $Zr_yU_{1-y}O_2$  compounds

When we see Fig 6, there are no big differences between compounds and  $UO_2$ . However 2theta of  $UO_2$  and  $ZrO_2$  mixture (95:5) is bigger than others.

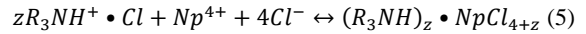
By calculating the lattice parameter,  $UO_2$  and  $ZrO_2$  mixture (95:5) has 5.4728 Å and  $UO_2$  and  $ZrO_2$  mixture (90:10) has 5.4699 Å. The crystal radius of U and Zr are 0.87 Å and 0.86 Å each.

This reaction is related about diffusion coefficient. In literature, the diffusion coefficient of O in  $UO_2$  at 1400 °C is  $10^{-7}$  cm<sup>2</sup>/s and the diffusion coefficient of U in  $UO_2$  at

1400 °C is  $10^{-13}$  cm<sup>2</sup>/s [2]. It is well known that values of cation diffusion coefficients are much lower than those associated with anion diffusion coefficient. For in this process it is the cation transport that is the rate-limiting step.

#### 3.2. Mechanisms of Np extraction

During the Np extraction, we assumed behavior of Np(IV) and Np(VI) with TOA. The reaction of Np(IV) and TOA (denoted as R) is as below [1].



To identify the mechanism of Np extraction, we used the relation of equilibrium constant (K) and distribution ratio (D).

$$K = \frac{[(R_3NH)_z \cdot NpCl_{4+z}]}{[Np^{4+}][Cl^-]^4[R_3NH^+ \cdot Cl^-]^z} \quad (6)$$

$$D = \frac{[(R_3NH)_z \cdot NpCl_{4+z}]_{org}}{[Np^{4+}]} \quad (7)$$

In our case, only unknown value is z. Apply log function to equation (7) both sides:

$$\log(D) = z \log([R_3NH \cdot Cl]) + const. \quad (8)$$

Ignoring the constant equation (8) reduces to:

$$z = \frac{\log(D)}{\log([TOA])} \quad (9)$$

For the identification of z value, we referred distribution ratio (D) graph according to vol. % of TOA in xylene, as shown in Figure 7 [3]. In case of Np, the slope is about 2. It means that one Np(IV) ion forms neutralized compound with 2 TOA ion.

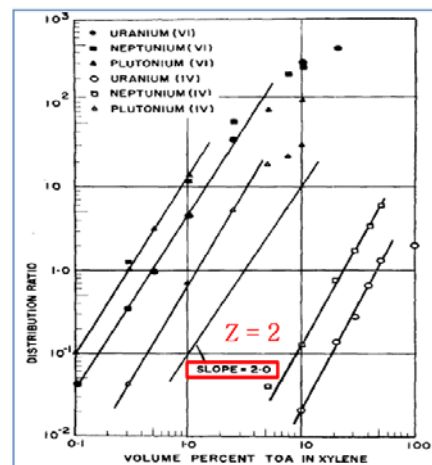


Fig 7. Distribution ratio of Np according to the volume percent of TOA in xylene [1]

We can guess the chemical structures of  $NpCl_6^{2-}$  and  $NpO_2Cl_4^{2-}$  are an octahedral crystal in the organic phase by analogy of similarity of Np and U behaviors.

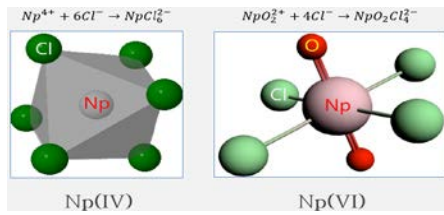
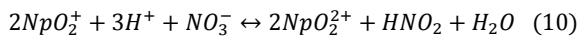


Fig 8. Chemical structure of Np(IV, VI) in organic phase. It is called octahedral crystal

### 3.3.2 The behavior of neptunium in solvent extraction.

In nitric acid, Np can exist simultaneously in three stable oxidation states; Np(IV, V, VI) by disproportionation. Also, oxidation states of Np in nitric acid is electrochemically controlled, nitrous acid can be generated, depending on the nitric acid concentration [4]. The generated nitrous acid affects the redox of neptunium as the equation (10).



Each behavior of neptunium ion in the solvent extraction is definitely different as their oxidation state. Figure 9 shows the extractabilities of Np(IV, V, VI) in 30% TBP / nitric acid [5]. In nitric acid, Np(VI) is easily extractable, Np(IV) is less extractable, and Np(V) is nearly unextractable. The extraction of Np(VI) and Np(IV) can be represented as follows:

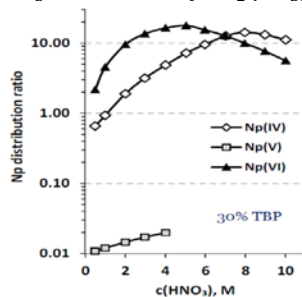
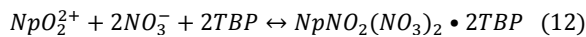
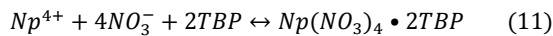


Fig 9. Extractability of Np ions in 30% TBP / nitric acid [5]

In nitric acid, there are three kinds of Np ions, the extraction behavior of Np measured by activity is the combined form of all Np ions. As we compare the combined behavior with each behavior, we can guess which oxidation state is dominant in each solution. The distribution coefficient of  $^{239}\text{Np}$  in this experiment can be plotted, as the scale of axis being made same with Figure 10.

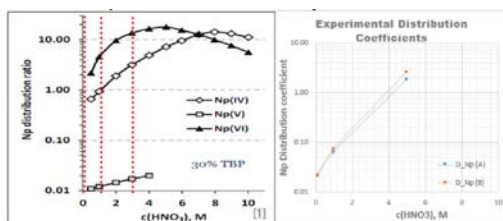


Fig 10. Comparison between reference and experimental of distribution coefficient of neptunium ion

The red lines on the left-side graph of Figure 10 are representing the samples used in this experiment (0.1, 1.0, and 5.0 M of  $\text{HNO}_3$ ). At 0.1 M, the experimental distribution coefficient is similar with referred distribution coefficient of Np(V). At 1.0 M, it is slightly increased. At 5.0 M, it is a little bit more than referred distribution coefficient of Np(IV). In conclusion, at low concentration of nitric acid, Np(V) is the most common oxidation state. And, as the concentration is increased, Np(VI) is generated by oxidation.

It is hard to determine the optimum nitric acid concentration for extraction using only U ion because the mechanism is very complicated. It can't be calculated by mathematics, but, in this experiment, we just use only 3 points of nitric acid concentration. There for in our case, the optimum concentration is 0.5 M of nitric acid. If more accurate estimation should be needed, more experiments are needed.

## 4. Conclusion

We used XRD, SEM to get information of  $\text{Zr}_y\text{U}_{1-y}\text{O}$ . It is not adequate to get high ratio of  $\text{Zr}_y\text{U}_{1-y}\text{O}$  just heating up at  $1400^\circ\text{C}$  for 1h of 5 or 10 % mole numbers of Zr, By using XRD, we are able to guess the effect of cation to the lattice parameter. The smaller the size of cations is, the smaller the lattice parameter is. And we know the diffusion coefficient of U and O in  $\text{UO}_2$ . The diffusion coefficient of U is much smaller than O in  $\text{UO}_2$ . So U is the rate limiting step in  $\text{UO}_2$  compound. Namely, U governs the interaction in  $\text{UO}_2$ .

Uranium is separated from aqueous phase to organic phase during solvent extraction procedure using TBP and dodecane. Also, neptunium can be extracted to organic phase as nitric acid concentration change. The extraction behavior of neptunium is different by oxidation state in aqueous phase. The behavior of neptunium is represented as a combined form of these oxidation states in experiment. Therefore, because the oxidation states of neptunium can be controlled by controlling the concentration of nitric acid, the extractability of neptunium can be controlled.

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