An experimental study of the purification of uranium by using simulated spent fuel

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1. Introduction

All irradiated nuclear fuels contain many nuclides including the fissile and fertile isotopes, which can undergo fission and be converted to fissile nuclide by neutron capture respectively. The spent fuels contained fissile and fertile isotopes can be reused by some processes [1].

The solvent extraction method is conventionally used for reuse of irradiated nuclear fuel. The solvent extraction is an aqueous method for the recovery of uranium. The extracted uranium can be converted into new fuel for nuclear power plant [2].

Solvent extraction is a method to separate compounds based on difference of density and their relative solubilities in two different immiscible liquids.

To extract the uranium in the irradiated nuclear fuel, as shown in the fig.1, spent fuel should be dissolved in nitric acid as the first step. After the first step, an organic solvent which contains 30% (by volume) of tri-n-butyl phosphate (TBP) in dodecane is used to extract the uranium in the spent fuel [3]. Finally, U(VI) as UO_2^{2+} can move into the organic phase because the actinides which have the +4 and +6 oxidation state have a good affinity with TBP. Other fission products (FPs) and minor actinides (MAs) are remained in the aqueous phase by following chemical equilibria [2].

$$UO_2^{2+} + 2NO_3^- + 2TBP \rightleftarrows [UO_2(NO_3)_2 \cdot 2TBP] \qquad (1)$$

During the extraction, U(VI) is extracted from the organic phase. However, in some conditions FPs and MAs can be extracted with uranium unwillingly. The solubility of actinides which have the oxidation state of +3 or lower, is very low in organic phase [2]. Furthermore, Np(V) as NpO_2^+ which has +5 oxidation state has very lower solubility in the organic phase. Therefore, we need to understand the behaviors of nuclides during the solvent extraction to improve the efficiency of extraction of uranium for new fuels for nuclear power plant.

In this study, we are focusing on the understanding the solvent extraction and the behaviors of MAs and FPs during the solvent extraction by using uranium, ^{239}Np and ^{85}Sr. ^{239}Np and ^{85}Sr were added to understand the behaviors of MAs and FPs respectively. This study attempted to find the best condition for the extraction of uranium only from simulated solution. To achieve the objectives of this study, 3 different simulated solutions which have various nitric acid concentration as 0.1M, 1.0M and 5.0M are prepared. To investigate the behavior of nuclides, radioactivity measuring is conducted by using Liquid Scintillation Counter (LSD) and High Purity Germanium (HPGe) detector.

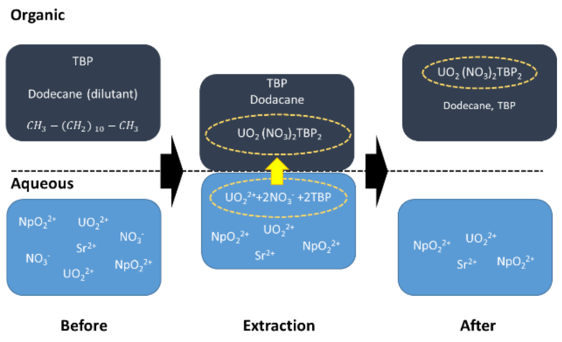

Fig. 1. Schematic of uranium extraction during solvent extraction.

2. Experimental procedures

The processes of experiment can be divided into two parts roughly: solvent extraction and radioactivity measurement.

2.1 Solvent extraction: separation of uranium from simulated solution

The 3 types of samples are prepared to investigate the behavior of nuclides during the solvent extraction. Each sample has equal UO_2^{2+} and Sr^{2+} concentration and various nitric acid concentration, 0.1M, 1.0M, 5.0M respectively as listed in Table I.

To make simulated solution, put 15 ml of HNO_3 into funnel first, then put organic solvent into funnel, which contains 30% of TBP in dodecane. Pre-equilibrium is conducted to prevent volumetric changes in the organic phase prior to solvent extraction. The organic phase and aqueous phase are mixed for 2 minutes by shaking and the aqueous phase was discarded to keep the organic phase in a funnel only.

Table I: Contents of samples.

Sample No.	S1	S2	S3
$[HNO_3]$	0.1M	1M	5M
$[UO_2^{2+}]$		5.0×10^{-2}M	
$[Sr^{2+}]$		1.0×10^{-3}M	

Put the 2ml of pre-equilibrated organic solvent and aqueous solution, which contains 1.86 ml of uranium sample (S1, S2 and S3), 40 µl of ^{85}Sr stock solution and 100 µl of ^{239}Np stock solution, in the new glass tube. Centrifuge is conducted for 5 minutes with 1000 rpm to separate the organic and aqueous phase.

2.2 Radioactivity measuring

Because uranium is the alpha ray emitter and both ^{239}Np and ^{85}Sr are the gamma ray emitter, radioactivity of nuclides in simulated solution was measured by radioactivity detectors to investigate the behavior of radioactive nuclides. ^{239}Np and ^{85}Sr can be characterized by their gamma ray energy spectrum which has the energy of 228 keV and 278 keV for ^{239}Np, 514 keV for ^{85}Sr. Therefore, we can infer the behaviors of radioactive nuclides by detecting their radioactivity.

After the centrifuging, the phases in the glass tube are separated into the organic and aqueous phase due to their density difference.

To prepare the gamma measurement samples, 1.0 ml of the organic phase and aqueous phase were pipetted into new glass tubes. And for the alpha measurement samples, 0.1 ml of the organic phase and aqueous phase were pipetted into new glass tubes too. Furthermore, 1 ml of liquid scintillation cocktail was added into alpha measurement sample. And mixing by using vibrating mixer to make solutions homogeneous until the solutions become clear. Radioactive measurement samples of different nitric acid concentrations which have concentration of 0.1M, 1.0M, 5.0M were prepared in the same manner.

The alpha measurement is conducted by LSC detector for 1000 seconds for each alpha measurement samples. The gamma measurement is conducted by HPGe detector which can detect finely due to its high energy resolution for 800 seconds.

3. Results and discussion

3.1 Analysis of radioactivity peaks

From the results of alpha measurement by LSC as shown in the figure 2, we can get the counts per second ratio. At lower nitric acid concentration, we can see the alpha ray is detected in both of organic and aqueous phase also, however, as the concentration of nitric acid is increasing, alpha signal decreases in the aqueous phase. In the organic phase we can see the alpha signal is increasing. In the figure 2, the offset of y axis is not calibrated, however, in the numeric data indicate the increasing of signals. On the other hand, the alpha signals from the aqueous phase is decreasing as the concentration of nitric acid of solution increases.

The peaks marked with red color in figure 3 indicate the existence of the gamma ray emitting nuclides. 228 keV and 278 keV peaks indicate ^{239}Np and 514 keV peak indicates ^{85}Sr.

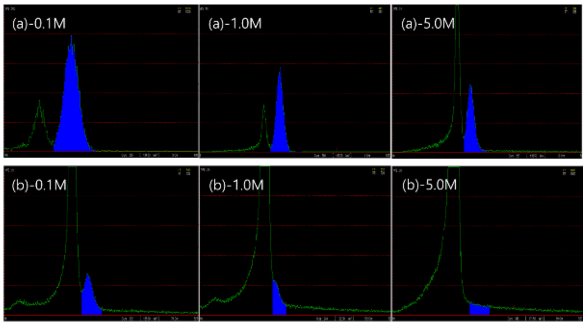

Fig. 2. The alpha ray energy spectrum detected by LSC: (a) from the organic phase, (b) from the aqueous phase.

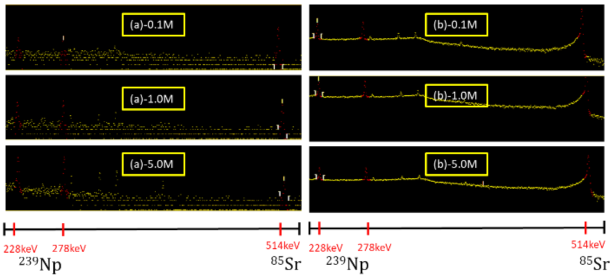

Fig. 3. The gamma ray energy spectrum detected by HPGe: (a) from the organic phase, (b) from the aqueous phase. .

3.2 Distribution coefficient

For quantitative analysis of radionuclides behavior, the concept of distribution coefficient is used. The distribution coefficient is expressed by the following equation.

$$D = \frac{nuclides\ in\ organic\ phase}{nuclides\ in\ aqueous\ phase} \qquad (2)$$

The distribution coefficient is the ratio between solubility of element in organic phase and solubility of element in aqueous phase, as shown in equation (2). Therefore higher coefficient means higher solubility in organic phase. The distribution coefficient can be calculated with counts per second ratio from the detecting information in the each phases by the following equation.

$$D = \frac{cps\ of\ nuclide\ in\ organic\ phase}{cps\ of\ nuclide\ in\ aqeuous\ phase} \qquad (3)$$

The calculated distribution coefficients by equation (3) are listed on the table II.

As shown in the figure 4. The distribution coefficients of uranium and ^{239}Np have increasing tendency. The distribution coefficient of ^{85}Sr has a tendency of decreasing by increasing molar concentration of nitric acid.

Table II: The calculated distribution coefficient, Np1 indicates 228 keV peak and Np2 indicates 278 keV peak.

Sample No.	**S1** $[HNO_3]$=0.1 M	**S2** $[HNO_3]$=1.0 M	**S3** $[HNO_3]$=5.0 M
D_Sr	0.0056	0.0018	0.0007
D_Np1	0.0181	0.0722	0.7871
D_Np2	0.0190	0.0755	0.8104
D_U	0.2408	2.0019	3.1749

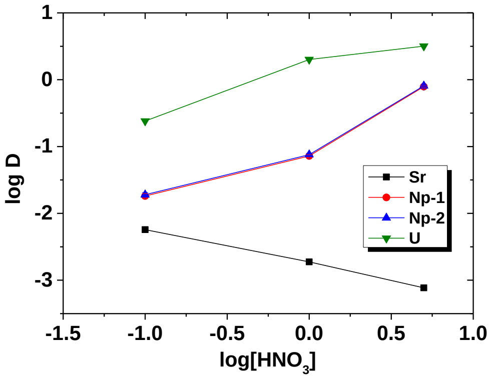

Fig. 4. The distribution coefficient of radioactive nuclides.

^{239}Np has only one beta decay mode that means the distribution coefficients from 228 keV (Np1) and 278 keV (Np2) should be same. However, the distribution coefficients from Np1 and Np2 have very little difference. The reason of this difference might be come from the statistical error of gamma ray yields. As shown on the table III, The yields between Np1 and Np2 have about 4% yields difference. Because the higher yields, Np2 has smaller statistical error. Therefore, the distribution coefficient of Np2 is more reliable as a result of our experiments.

Table III: Yields of gamma rays of ^{239}Np.

Energy [keV]	Yields
106	27.2%
228	10.8%
278	14.4%
316	1.6%
334	2.1%

3.3 behavior of radioactive nuclides

The distribution coefficient of ^{239}Np behaves differently depending on the oxidation state of neptunium as Np(IV), Np(V) and Np(VI). Figure 5 shows the variation of the distribution coefficients of Neptunium by increasing the concentration of nitric acid. Np(IV), Np(VI) have high distribution coefficient, whereas Np(V) does not. Therefore, Np(IV) and Np(VI) can be extracted to the organic phase but Np(V) cannot be well extracted to the organic phase.

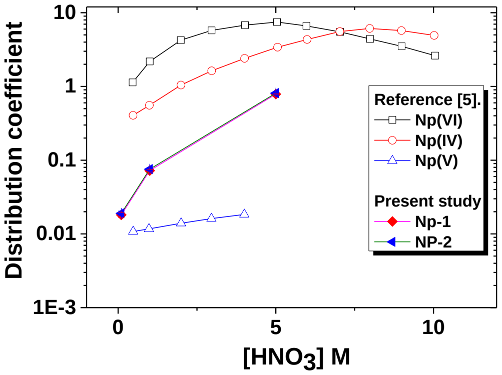

Fig. 5. Extractability of neptunium ions in 30% TBP and nitric acid solution compared with results of present study [4].

From our results shown in the figure 5, the oxidation state Np(V) was dominant at first. As the concentration of nitric acid increases, the distribution coefficients of present study increase steeply more than Np(V) distribution coefficient of reference. Therefore, Np(V) of early state which has 0.1M concentration of nitric acid is converted into Np(VI) and Np(IV).

The nitric acid has very strong oxidizing property, for this reason, Np(V) at early state must be converted into Np(VI). The equation (4) indicates the oxidation process of Np(V) as NpO_2^+ to Np(VI) as NpO_2^{2+}.

$$2NpO_2^+ + 3H^+ + NO_3^- \leftrightarrow 2NpO_2^{2+} + HNO_2 + H_2O \qquad (4)$$

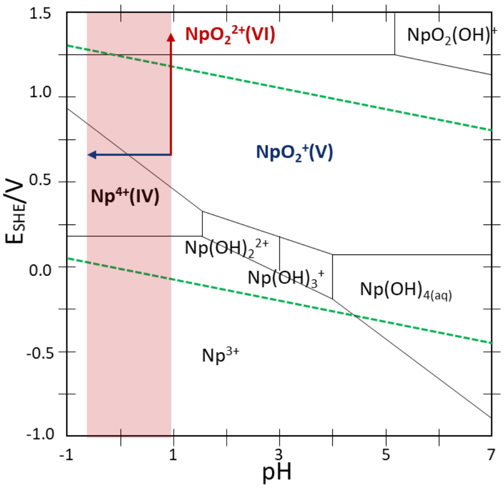

Fig. 6. Pourbaix diagram for neptunium [5].

The behavior of Np(V) is shown in the figure 6. Np(V) in the early state is converted into Np(VI) by oxidation process dominantly along the red arrow on the figure 6. In addition, as the concentration of nitric acid increases, pH of solution is decreased. Therefore, some Np(V) might be converted into Np(IV) also along the blue arrow on the figure 6. Consequently, the distribution coefficient of Np is increased as the concentration of nitric acid increases, due to being converted into Np(VI) and

Np(IV). From the point of view of oxidation state, the lower the concentration of nitric acid, the neptunium has the smaller distribution factor so that we can get the purified uranium from the organic phase.

3.4 Separation factor

To determine the optimized concentration of nitric acid for purification, we consider the other concept called separation factor (SF). The separation factor is expressed by the following equation.

$$\gamma = \frac{[U]_{organic} \,/\, [U]_{aqeous}}{[Np]_{orgarnic} \,/\, [Np]_{aqeous}} = D_U/D_{Np} \qquad (5)$$

In other words, the higher value of separation factor means that we can get much more purified uranium during the solvent extraction process. Figure 7 shows the calculated separation factor.

According to the distribution factor as shown in the figure 5 and separation factor as shown in the figure 7 both, near the 1.0M of nitric acid concentration is the optimized concentration for purification of uranium. However, for the exact result for purification of uranium, more experiments at more nitric acid concentrations are needed.

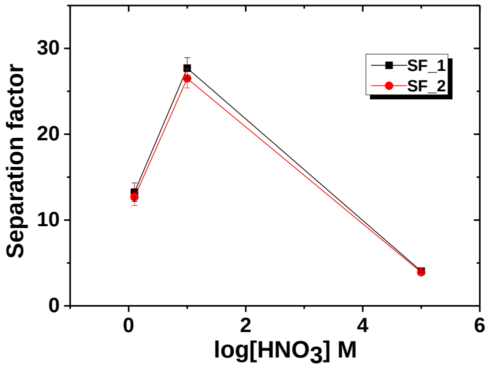

Fig. 7. The separation factors of neptunium.

4. Conclusions

The behaviors of uranium and other radioactive nuclides during simulated experiment are investigated. Uranium and radioactive nuclides are extracted by solvent extraction method. To investigate the behavior of nuclides in organic phase and aqueous phase, distribution coefficient and separation factor are considered. The key findings are summarized as follow.

(1) To reuse the uranium in the spent fuels, the solvent extraction is conventionally used.
(2) During the extraction, the behaviors of MAs and FPs are affected by a lot of variables sensitively.
(3) Neptunium can be existed in aqueous phase as 3 oxidation state: Np(IV), Np(V) and Np(VI). 3 oxidation states have different distribution coefficient so that we can control the extraction efficiency by understanding the behavior of neptunium.
(4) The distribution coefficients are increasing by the concentration of nitric acid increases. The lower nitric acid concentration is more favorable in aspect of distribution coefficient analysis.
(5) 1.0M concentration of nitric acid as an optimized nitric acid concentration is attained by calculating the separation efficiency and distribution coefficient.
(6) To get more optimized value for better uranium purification, need more experiments at the broad concentration range of nitric acid.

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