

Basic studies on the solvent extraction with Uranium, Neptunium-239, and Strontium-85

Tae Won Cho^{a*}, Kwang Heon Park^b, Jaeyeong Park^a, Sunwoo Park^b, Jongmin Lee^c, Jueun Kim^b

^aUlsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea

^bKyungHee University, 1732, Deogyong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 17104, Republic of Korea

^cSejong University, 209, Neungong-ro, Gwangjin-gu, Seoul 143-747, Republic of Korea

*Corresponding author: xodnjs6270@gmail.com

1. Introduction

Solvent extraction technology has been widely adopted in nuclear industry. First, it is used to produce medical isotopes. Many studies on the extraction of Mo-99 from irradiated uranium has been carried out to obtain Tc-99m for diagnostic imaging. Second, it is utilized for the management of spent nuclear fuel. Some reprocessing technologies have been developed to extract uranium and plutonium. For example, PUREX (Plutonium Uranium Refining by Extraction) process was suggested and widely used for the reprocessing. This is a wet reprocessing technology, which is based on the solvent extraction by ion-exchange. In this process, it is important to remove long-lived actinides or high-level radioactive waste such as Am, Cm, Np, and Tc. Especially, ²³⁷Np is known as a highly radiotoxicity nuclide having a half-life of 2.14×10^{16} years. In the reprocessing process, it is required to obtain a high separation efficiency. Therefore, it is important to understand the behavior of nuclides and find an optimum condition for the extraction.

Under the "2018 Nuclear Global Research & Education Program for Advanced Nuclear Fuel Cycle" supported by KoniCof, a solvent extraction experiment was conducted at IMRAM (Institute of Multidisciplinary Research for Advanced Materials) in Tohoku university to understand the PUREX process. Two kinds of experiment were carried out: (1) milking of ²³⁹Np from ²⁴³Am and (2) solvent extraction of U from ²³⁹Np and ⁸⁵Sr. In this experiment, a simulated solution composed of U, ⁸⁵Sr, and ²³⁹Np was used instead of spent nuclear fuel due to the restriction for the usage of high radiotoxicity materials. Note that ²³⁹Np was used instead of ²³⁷Np. It is known that the extraction characteristics are similar for the isotopes. ²³⁷Np has a very long half-life and it is very expensive while ²³⁹Np is a short-lived beta-emitter with $T_{1/2}=2.355$ days and good gamma-ray emission. It is a daughter nuclide of ²⁴³Am, which is a long-lived alpha-emitter with $T_{1/2}=7370$ years. From the experiment, the behavior of nuclides was observed, and the mechanism of solvent extraction was investigated. In addition, an optimum condition for the uranium extraction was explored from the measured data.

2. Experimental

The experiment consists of three stages: (1) milking of ²³⁹Np from ²⁴³Am, (2) Solvent extraction from simulated

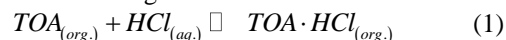
spent nuclear fuel, and (3) activity measurement. All detailed steps and procedures are described as below.

2.1 Milking of ²³⁹Np from ²⁴³Am

Milking process is an extraction of a daughter nuclide from a parent nuclide. In this experiment, ²³⁹Np was extracted from the ²⁴³Am stock solution. The procedure of milking process is conventionally divided into pre-equilibrium, solvent extraction, stripping (or back-extraction), and fuming.

(1) Pre-equilibrium:

In general, it has been highly recommended to prepare a pre-equilibrated organic phase before the solvent extraction. Although it seems that organic phase and aqueous phase are immiscible, they could make a weak bonding each other so that a part of HCl can be extracted by the organic phase [1, 2]. The extraction reaction of HCl with TOA can be given as follows:

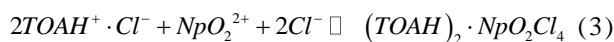
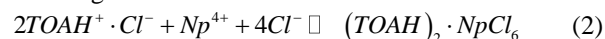


Without the pre-equilibrium stage, the reaction could occur during the solvent extraction simultaneously, which lead a volume change.

In this experiment, 25ml of 5% Tri-n-Octylamine (0.114 M TOA) in xylene was mixed with 10 ml of concentrated hydrochloric acid (12.0 M HCl) in a separation funnel, which was mixed for 15 second. The organic phase was kept in separation funnel while the aqueous phase was discarded.

(2) Extraction:

²⁴³Am stock solution was dissolved in 25ml of concentrated HCl, which was sequentially mixed with the equilibrated organic solution for 1 minute. In this step, ²³⁹Np was separated from the aqueous phase to the organic phase while ²⁴³Am remained in the aqueous phase [2]. The extraction could occur through the following two reactions:



The organic phase was separated using a separation funnel and the aqueous phase was discarded.

(3) Stripping (Back-extraction):

The stripping means re-extraction of targeted nuclide from organic phase to aqueous phase. The intimacy to the organic phase is dependent on the concentration of

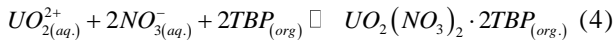
hydrochloric acid. As the concentration is high, it tends to be extracted to the organic phase. Adding 25 ml of water decreased the HCl concentration, thus Np could be back-extracted to the aqueous phase. After 1 minute of mixing, they were kept for 30 minutes to achieve equilibrium state. Finally, the aqueous phase was removed from separation funnel and stored in a glass for further treatments.

(4) Fuming (or Purification):

To decompose the remaining organic phases in aqueous phase due to the reaction between TOA and HCl, it was mixed with a high-concentrated nitric acid (5M HNO₃) and dried. Since the TOA and xylene consists of carbon, hydrogen, oxygen, and nitrogen, the nitric acid can decompose them into CO₂, H₂O, O₂, and NO_x. This process was repeated two times for complete removal of the organic phase. After the reaction, pale yellow color appeared due to the nitrides. After fuming was over, 5 ml of 0.1M HNO₃ was added to the Np salt in order to prepare ²³⁹Np stock solution for solvent extraction.

2.2 Solvent extraction from simulated spent nuclear fuel

In solvent extraction from spent nuclear fuel, Tributyl Phosphate (TBP) is usually adopted as an organic phase. In the nitric acid, it is known that the oxidation state of uranium is mostly hexavalent. The extraction of uranium occurs through following reaction:



In this experiment, the procedure of solvent extraction consists of pre-equilibrium, solvent extraction, and sampling. To investigate the effects of concentration of nitric acid, three different sample solutions were prepared, and their compositions are described in Table 1.

Table 1. Compositions of sample solutions.

Sample No.	S1	S2	S3
[HNO ₃]	0.1 M	1 M	5 M
[UO ₂ ²⁺]	5.0 × 10 ⁻² M		
[⁸⁵ Sr ²⁺]	1.0 × 10 ⁻³ M		

(1) Pre-equilibrium:

TBP can make a weak bonding with HNO₃, which is similar to TOA and HCl. There is an extraction reaction of HNO₃ by TBP as follows:



This reaction can also lead a volume change. Therefore, the pre-equilibrium is required to avoid the reaction. In this experiment, 15 ml of 30% TBP in dodecane was mixed with 15 ml of 0.1 M nitric acid in a separation funnel for 2 minutes. After the stabilization, the aqueous phase was distinguished and discarded.

(2) Solvent extraction:

Three glass tubes were prepared and filled with 2ml of pre-equilibrated organic phase. First, 1.86 ml of each sample solutions were added to each glass tube. Next, 40 µl of ⁸⁵Sr stock solution and 100 µl of ²³⁹Np stock solution were poured into the glass tubes. The total volume was 2 ml. The glass tubes were mixed for 30 minutes by automatic shaker. Last, the mixture was centrifuged for 5 minutes to separate organic and aqueous phases. The mixed solutions are shown in Fig. 1.

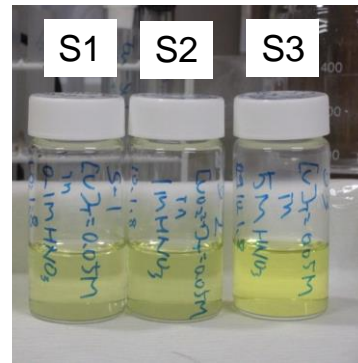


Fig. 1. Three sample solutions of uranyl dioxocation

(3) Sampling:

After the solvent extraction, all sample solutions were composed of organic phase (upper side) and aqueous phase (lower side). First, 1.0 ml of organic phases were pipetted from S1, S2, and S3 solutions, respectively and they were moved into new glass tubes for the measurements of gamma-ray. Next, 0.1 ml of organic phases were pipetted and moved into the small glass cuvettes filled with 1 ml of liquid scintillation cocktail for the measurement of alpha-ray. The mixed solutions were shaken by automatic vibrator until the solutions became transparent for homogeneous phase. In a same method, sampling for the aqueous phases were conducted.

2.3 Activity measurements

Since the activities of nuclides are proportional to the concentration of them, a concentration of U, Np, and Sr can be estimated by measuring the activity of solution. It is known that ²³⁹Np has peaks at 228 keV and 278 keV, and ⁸⁵Sr has a peak at 514 keV.

In this experiment, two types of detector were used as seen in Fig. 2. Since ²³⁹Np and ⁸⁵Sr are nuclides emitting gamma-ray, a high purity germanium (HPGe) detector were used to measure gamma-ray. For U, it emits alpha-ray, thus liquid scintillation counting (LSC) detector was adopted to measure alpha-ray.

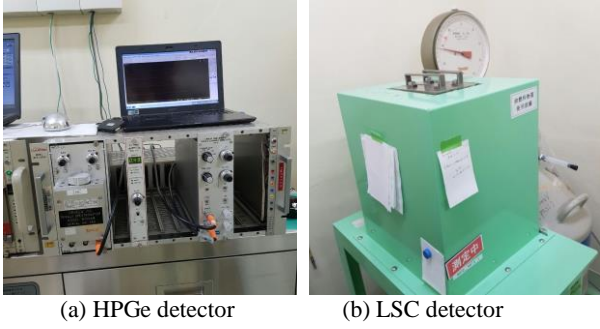


Fig. 2 Detectors used for the measurements of alpha- and gamma-ray.

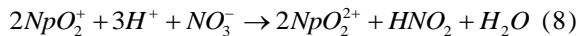
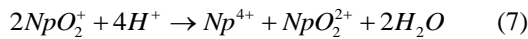
3. Results and Discussion

From the measured activity data, distribution coefficients of ^{85}Sr , ^{239}Np , and U were quantitatively evaluated. The distribution coefficient is defined as a concentration ratio of nuclide between organic solution and aqueous solution. It is proportional to the activity and is given by:

$$D_{\text{nuclide}} = \frac{[\text{nuclide}]_{(\text{org.})}}{[\text{nuclide}]_{(\text{aq.})}} = \frac{(\text{count/sec})_{(\text{org.})}}{(\text{count/sec})_{(\text{aq.})}} \quad (6)$$

Fig. 3 shows distribution coefficients of ^{85}Sr , ^{239}Np , and U as a function of HNO_3 concentration. It is remarkable that the distribution coefficients of U and ^{239}Np exponentially increases while ^{85}Sr decreases as the concentration of HNO_3 increases. It indicates that more U and Np can be extracted to organic phase as the concentration of HNO_3 increases by leaving ^{85}Sr in aqueous phase.

The behavior of Np in nitric acid is dependent on the oxidation state. Fig. 4 shows the extractabilities of Np ions in 30% TBP/nitric acid: $\text{Np(IV)} > \text{Np(VI)} \gg \text{Np(V)}$. The comparison with sample solutions shows that Np in S1 solution is possibly composed of Np(V), but the Np(V) changed to Np(IV) or Np(VI) as the nitric acid increases. Fig. 5 shows a pourbaix diagram for Np in nitric acid. There are two possible mechanisms for Np(VI) to be converted to Np(IV) or Np(VI): (1) disproportionation, and (2) oxidation by nitrates. The chemical reaction can be described as follows:



To investigate the efficiency of separation, a concept of separation factor was introduced, which indicates the ratio of compositions of two components. The separation factor for the extraction of Np(IV) or Np(VI) and U(VI) with is given by:

$$\gamma_{\text{U/Np}} = \frac{[\text{U}]_{\text{org}} / [\text{U}]_{\text{org}}}{[\text{Np}]_{\text{org}} / [\text{Np}]_{\text{org}}} = \frac{D_{\text{U}}}{D_{\text{Np}}} \quad (9)$$

$$\gamma_{\text{U/Sr}} = \frac{[\text{U}]_{\text{org}} / [\text{U}]_{\text{org}}}{[\text{Sr}]_{\text{org}} / [\text{Sr}]_{\text{org}}} = \frac{D_{\text{U}}}{D_{\text{Sr}}} \quad (10)$$

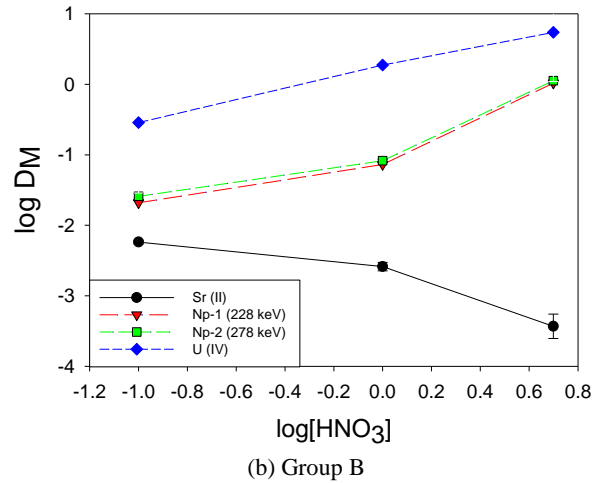
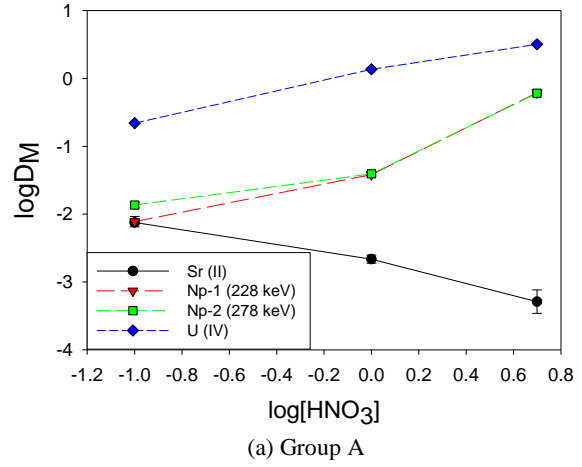


Fig. 3. Distribution coefficients of ^{85}Sr , ^{239}Np , and U as a function of HNO_3 concentration.

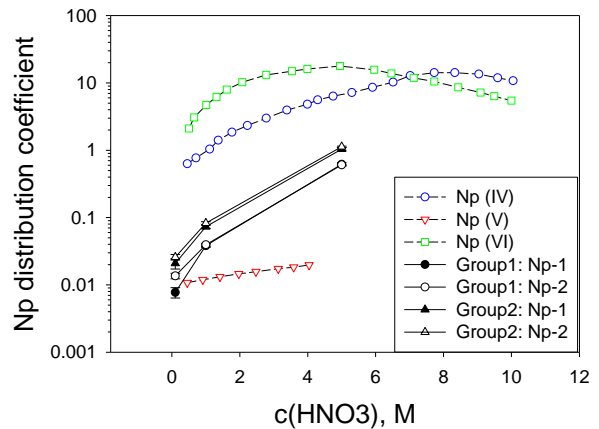


Fig. 4. Comparison of distribution coefficients of Np in 30% TBP/nitric acid [3].

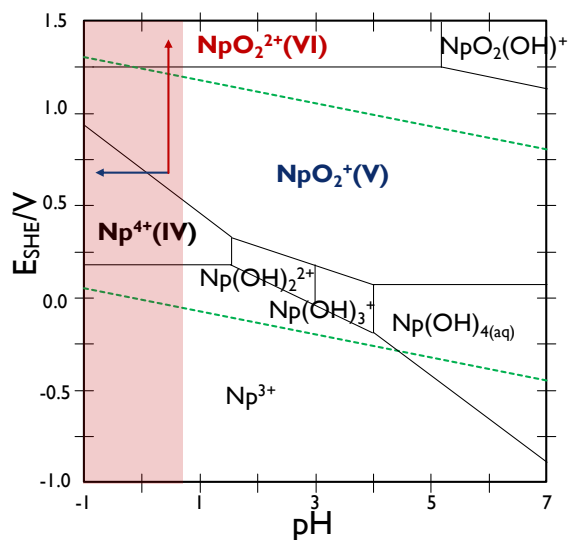


Fig. 5. Pourbaix diagram for Np in nitric acid. [4]

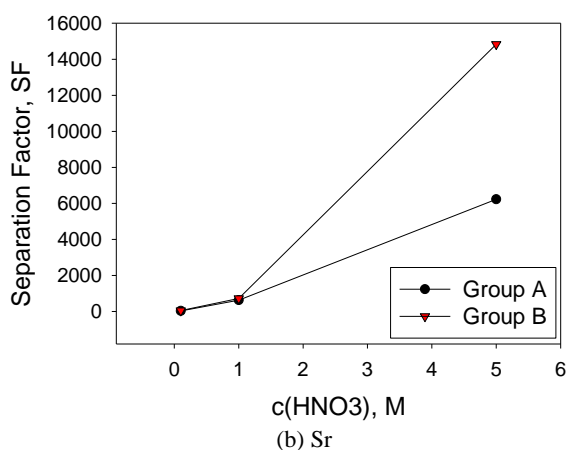
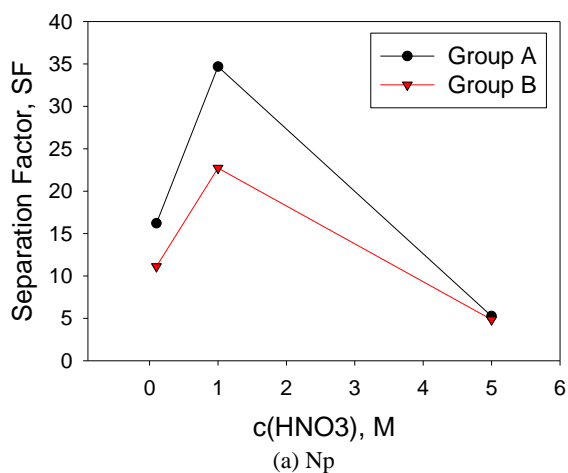


Fig. 6. Separation factor of U from Np and Sr as a function of HNO₃ concentration.

Fig. 6 shows the separation factors of U against Np and Sr. The separation factor of U/Sr increases with HNO₃ concentration while the separation factor of U/Np shows a peak when the HNO₃ concentration is 1.0 M.

Therefore, it seems that at least two solvent extraction processes are required to obtain pure U.

3. Conclusions

Solvent extraction experiments were carried out in Tohoku university to investigate the behavior of nuclides. It showed that the extraction behavior of nuclides is closely related to the extraction conditions. U and Np were extracted more as the concentration of HNO₃ increases while Sr was less extracted. Especially, the behavior of Np was more complicated since it is dependent on the oxidation state in aqueous phase. In nitric acid, neptunium ion can exist simultaneously in tetra-, penta-, and hexavalent. Np exists mostly in Np(V) in low nitric concentration, which is nearly unextractable. However, Np(V) changes to Np(IV) or Np(VI) by disproportionation and oxidation, which increases the extractability. Therefore, Np extraction can be controlled by adjusting the concentration of nitric acid.

The optimum nitric acid concentration for the pure uranium was evaluated. Although high nitric acid is advantageous for the extraction of uranium, it also extracts another nuclide. The separation factors showed that U was separated from Sr as the nitric concentration increases, but U was most-well separated from Np when nitric concentration was 1.0M. In PUREX process, it is important to increase the separation efficiency of uranium and plutonium. However, there are many nuclides in real spent nuclear fuel. The mechanism of solvent extraction gets more complicated, as the number of elements is increased. Therefore, it is more important to understand the behaviors of FPs and MAs during the solvent extraction.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (No. 2016M2B2A8A08945). We also appreciate the supports from Korea Nuclear International Cooperation Foundation (KoniCof).

REFERENCES

- [1] Stas, J., Alsawaf, H. Liquid-Liquid Extraction of Hydrochloric Acid from Aqueous Solutions by Tri-n-dodecylamine and Tri-n-octylamine/diluents. *Periodica Polytechnica. Chemical Engineering*, 60, 130, (2016)
- [2] Keder, W. E., Extraction of tetra- and hexavalent actinides from hydrochloric acid by tri-n-octylamine in xylene. *Journal of Inorganic and Nuclear Chemistry*, 24, 561-570, (1962).
- [3] Paulenova, A. (n.d.). Radiochemistry Webinars Actinide Chemistry Series Meeting
- [4] Taylor, P., Nakahara, M., Sano, Y., Koma, Y., Kamiya, M. Separation of Actinide Elements by Solvent Extraction Using Centrifugal Contactors in the NEXT Process Separation of Actinide Elements by Solvent Extraction Using Centrifugal Contactors in the NEXT Process. *Journal of Nuclear Science and Technology*, 44(3), 373-381, (2012).