

Simulated PUREX Solvent Extraction Experiments Using ^{238}U , ^{239}Np and ^{85}Sr Solution

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1. Introduction

PUREX (plutonium uranium redox extraction) is an aqueous reprocessing method that separates U from spent nuclear fuel using a solvent extraction process. In solvent extraction process, predicting the behavior of U, MA (minor actinides) and TRU (transuranic elements) is important, because efficiency of

U recovery is determined by their combined behavior. In this study, PUREX-simulated aqueous solution was prepared by varying $[\text{HNO}_3]$ as 0.1 M, 1 M, and 5 M, to measure U extraction behavior. ^{85}Sr and ^{239}Np , which are a good tracer, were selected as representative nuclides of MA and TRU. ^{239}Np was prepared from ^{243}Am by milking extraction. Respectively TOA (tri-n-octylamine) and TBP (tri-n-butyl phosphate) in organic solvent, were used as extractant in ^{239}Np preparation and U separation experiments. After separation of U, alpha and gamma radioactivity of samples in each phase was measured.

2. Materials and Methods

In the scope of this study, two experiments are covered. Milking of ^{239}Np from ^{243}Am and solvent extraction of U from PUREX simulated solution.

2.1. Milking of ^{239}Np from ^{243}Am by Solvent Extraction

^{239}Np is a useful RI tracer of Np having short lifetime ($T_{1/2} = 2.2$ days) and good gamma ray emission (106 keV, $I_\gamma = 27\%$). This tracer is daughter nuclide of ^{243}Am ($T_{1/2} = 7370$ years), therefore, can be extracted from ^{243}Am in its radioactive equilibrium by solvent extraction using Tri-n-octylamine (TOA) [1].

2.1.1. Pre-equilibrium

Pre-equilibrium aims to saturate Cl⁻ ion in organic phase and to avoid volume change during experiment. Prepare 25 ml of 5% TOA in xylene (0.114 M) for organic phase and 10 ml of concentrated HCl (12.0 M) for aqueous phase. Put organic and aqueous solution in the same funnel. To mix these two solutions, shake this funnel horizontally by hand for 15 seconds.

2.1.2. Extraction and Washing

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

Almost Np(IV,VI) atoms are extracted to the organic phase. On the other hand, ^{243}Am remains in aqueous phase.

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

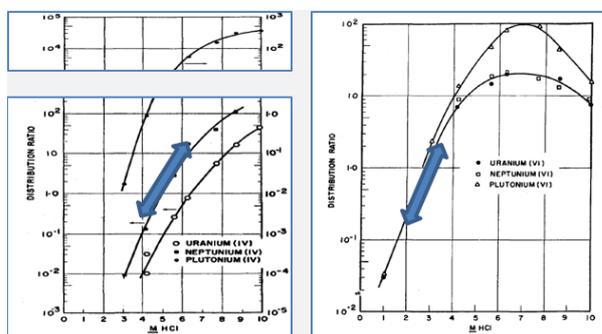


Fig 1. Distribution ratio of Np(IV,VI) from Xylene solution with TOA. According to the HCl concentration [2]

2.1.3. Np Stripping

^{239}Np is back extracted into aqueous phase because the concentration of chloride ion decreases. Its theoretical principle is same with the extraction process. In this step, 25 ml of H₂O is injected to ^{239}Np solution which is organic phase. Thus, concentration of chloride ion goes down. As a result, ^{239}Np is back extracted from organic phase to aqueous phase.

2.1.4. Fuming and Np stock

Fuming aims to make higher purification. Little amount of organic solution may remain in the act of back extraction process due to human handling. First, put 5 M HNO₃ into the beaker which contains ^{239}Np solution. Next, heat approximately 190 ~ 200 °C. And do these steps 2 or 3 times. In this process, 5 M HNO₃ causes chemical decomposition of TOA & Xylene mixture. It makes nitride, involving NO_x(g) and little CO₂(g) emission comes from organic structure

Np stock solution process is necessary for another experiment which is PUREX simulation. Therefore, pH should be changed. In this step, 5 ml of 0.1 M HNO₃ solvent is used on behalf of HCl.

2.2. Separation of U from PUREX Simulated Solution

2.2.1. Experimental Methods

By varying concentrations of HNO₃ as 0.1 M, 1 M, and 5 M, three sample solutions are prepared.

Table 1: The composition of sample solutions

| Sample no. | S1 | S2 | S3 |
|--------------------------------|-------|--------------------------|-----|
| HNO ₃ | 0.1 M | 1 M | 5 M |
| UO ₂ ²⁺ | | 5.0 X 10 ⁻² M | |
| ⁸⁵ Sr ²⁺ | | 1.0 X 10 ⁻³ M | |
| TBP | | 30% in dodecane | |

2.2.2. Pre-equilibrium

The pre-equilibrium is also necessary for TBP solvent extraction like TOA solvent extraction to avoid volume change. A 15 ml of 30 % TOA in dodecane was mixed with 15 ml of 0.1 M nitric acid in a separation funnel and shaken for 2 minutes.

2.2.3. Solvent Extraction of U(VI)

The organic phase being in pre-equilibrium was moved to the 3 glass tubes as 2 ml for each tube. Likewise, 1.86 ml of each sample solutions, 40 μl of ⁸⁵Sr stock solution and 100 μl of ²³⁹Np stock solution were put into each glass tube.

The glass tubes are shaken for 30 minutes by automatic shaker. And centrifuge for 5 minutes to separate organic and aqueous phases.

2.2.4. Activity Measurement

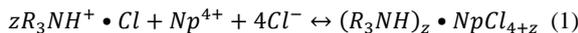
Radioactivity of six separated samples are measured by LSC (liquid scintillation counter) and HPGe (high purity germanium detector), to check how well uranium is extracted to the organic phase and to calculate separation efficiency. LSC is for gamma ray of ⁸⁵Sr and ²³⁹Np. HPGe detector is for alpha ray of U.

3. Results and Discussion

3.1. Milking of ²³⁹Np from ²⁴³Am by Solvent Extraction

3.1.1. Np Extraction Mechanisms by TOA

During the Np extraction, we assumed behavior of Np(IV,VI) with TOA. The reaction of Np(IV) and TOA (denoted as R) is as below [2].



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

$$K = \frac{[(R_3NH)_z \cdot NpCl_{4+z}]}{[Np^{4+}][Cl^-]^4[R_3NH^+ \cdot Cl]^z} \quad (2)$$

$$D = \frac{[(R_3NH)_z \cdot NpCl_{4+z}]_{org}}{[Np^{4+}]} \quad (3)$$

In our case, only unknown value is z. Apply log function to equation (3) both sides:

$$\log(D) = z \log([R_3NH \cdot Cl]) + const. \quad (4)$$

Ignoring the constant equation (4) reduces to:

$$z = \frac{\log(D)}{\log([TOA])} \quad (5)$$

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

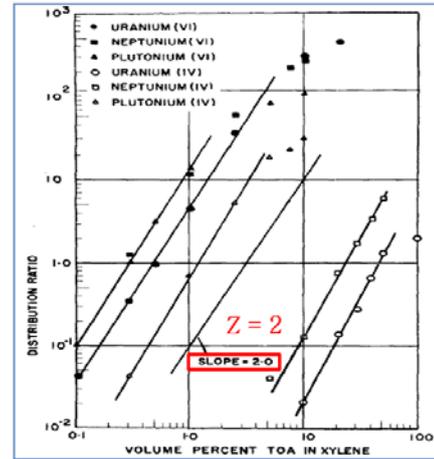


Fig 2. Distribution ratio of Np according to the volume percent of TOA in xylene [2]

We can guess the chemical structures of NpCl₆²⁻ and NpO₂Cl₄²⁻ are an octahedral crystal in the organic phase by analogy of similarity of Np and U behaviors.

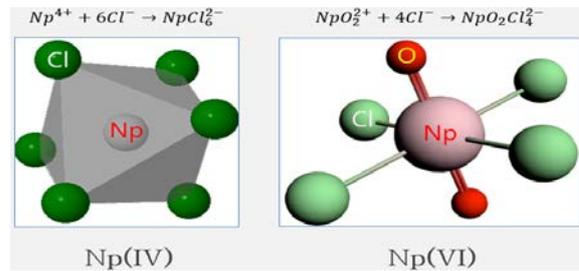


Fig 3. Chemical structure of Np(IV, VI) in organic phase. It is called octahedral crystal

3.1.2. Oxidation state of Np

As you can see in the following figure 4, the highest existence possibility of Np in normal water pH is NpO₂⁺ (which is Np(V)). Therefore, we should decrease pH in order to minimize NpO₂⁺ region and increase that of Np⁴⁺ (which is Np(IV)) and NpO₂²⁺ (which is Np(VI)).

For back extraction process, Np(V) is advantageous for dissolving into aqueous phase. That is why H₂O should be injected into Np solution. Its mechanism is just opposite by extraction process.

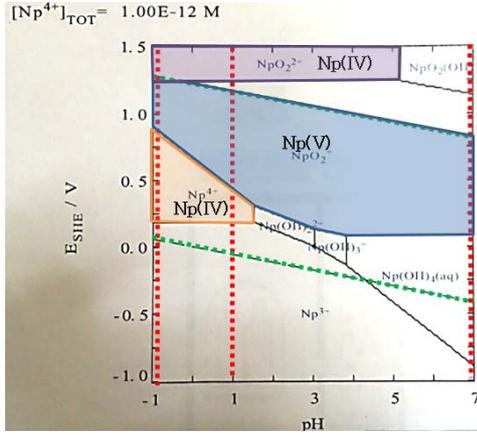


Fig 4. Oxidation states of Neptunium by pH difference. Within green line Np compounds can exist in aqueous phase [1].

3.1.3. Disproportionation of Np

In HNO₃ condition, Np can exist simultaneously in tetra-, penta- and hexavalent and its mechanism is complex. Np(V) is dominantly in the normal water pH and it has interconvertible oxidation state called disproportionation.

Np(V) changes into Np(IV) and Np(VI) in nitric acid condition according to following chemical formula:

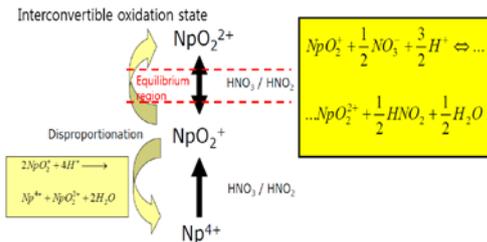
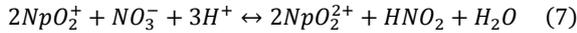
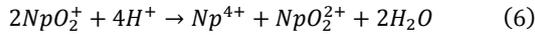


Fig 5. Interconvertible oxidation state of Np in nitric acid condition caused by disproportionation [3]

In this experiment, 5 M HNO₃ is used and its pH is 1.0, and therefore we can expect the abundance of oxidation state of Np according to the figure 4. And the rank is Np(V) >> Np(IV), and Np(VI) cannot exist as a solute in aqueous phase which pH is 1.

3.2. Separation of U from PUREX Simulated Solution

The final results of this experiment are on Table 2. D means the distribution ratio of a nuclide subscript and it is calculated by the equation (8)

$$D_{nuclide} = \frac{[nuclide]_{org}}{[nuclide]_{aq}} = \frac{[counts/second]_{org}}{[counts/second]_{aq}} \quad (8)$$

Table 2: The measurement data of exp. A and B. All unit of data, except for D, are count/second. Np1 is for 228 keV and Np2 is for 278 keV.

| Phase/ Ratio | Experiment A | | | Experiment B | | |
|-----------------|--------------|----------|----------|--------------|----------|----------|
| | S1 0.1M | S2 1M | S3 5M | S1 0.1M | S2 1M | S3 5M |
| Org. | 7.164 | 23.825 | 30.793 | 7.351 | 27.111 | 31.966 |
| Aq. | 29.082 | 12.175 | 2.361 | 27.036 | 9.668 | 3.013 |
| D_U | 0.246 | 1.957 | 13.042 | 0.272 | 2.804 | 10.610 |
| Org. | 0.063 | 0.015 | 0.001 | 0.083 | 0.040 | 0.145 |
| Aq. | 11.824 | 12.076 | 11.368 | 11.988 | 12.145 | 12.895 |
| D_Sr | 0.005 | 0.001 | 0.000 | 0.007 | 0.003 | 0.011 |
| Org. | 0.311 | 0.995 | 9.994 | 0.199 | 0.674 | 7.588 |
| Aq. | 14.095 | 15.480 | 5.388 | 9.213 | 8.958 | 2.904 |
| D_Np1 | 0.022 | 0.064 | 1.855 | 0.022 | 0.075 | 2.613 |
| Org. | 0.293 | 1.071 | 10.706 | 0.236 | 0.686 | 8.035 |
| Aq. | 16.483 | 16.236 | 5.538 | 9.933 | 9.254 | 3.318 |
| D_Np2 | 0.018 | 0.066 | 1.933 | 0.024 | 0.074 | 2.422 |

3.2.1. Pulse Analysis

There are all results of alpha-ray measurement for exp. A on the Figure 6. The orange area is representing total-alpha counts. These are verifying where the uranium exists. In the graph almost uranium is in the organic phase. Generally, in the aqueous phase, the orange peaks are not observed, but a small total-alpha peak in the aqueous phase of sample 1 represents that uranium still remain.

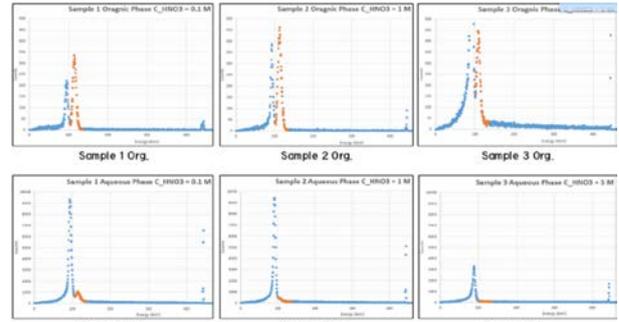


Fig 6. Pulse spectra for all samples. Energy (linear-scale) vs. count (log-scale)

3.2.2. The Behavior of Neptunium in Solvent Extraction

In nitric acid, neptunium can exist simultaneously in three stable oxidation states; Np(IV), Np(V), Np(VI) by disproportionation. Figure 7 shows the extractabilities of Np(IV, V, VI) in 30% TBP / nitric acid [4]. The extraction of Np(IV, VI) can be represented as follows:

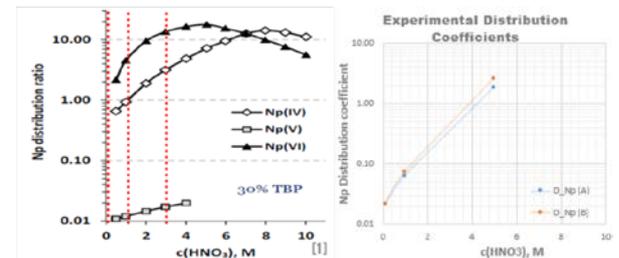
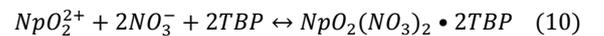
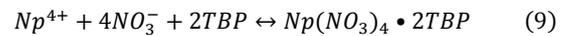


Fig 7. Comparison between reference of extractability of Np ions in 30% TBP / nitric acid and experimental data

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 neptunium ion. And, as the concentration is increased, Np(VI) is generated by oxidation.

3.2.3. Separation Efficiency

It is hard to determine the optimum nitric acid concentration. Now, the separation factor is introduced. It indicates the ratio of compositions of two components. The separation factor for uranium is written as follow:

$$\gamma = \frac{[U]_{org}/[U]_{aq}}{[Np]_{org}/[Np]_{aq}} = \frac{D_U}{D_{Np}} \quad (11)$$

Using equation (11), it is possible to find an optimum nitric acid concentration for the extraction of only uranium from the experimental results. For analysis, we introduced trend lines of experimental values, and the optimum nitric acid was analyzed between 0.1 M and 5.0 M. We used the data of only 228 keV for Np. By substituting estimated value calculated from trend line for separation factor, the biggest value of separation factor could be found.

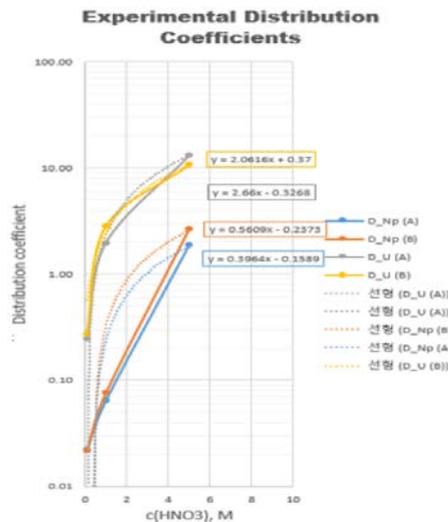


Fig 8. Experimental distribution coefficient values and their trend lines

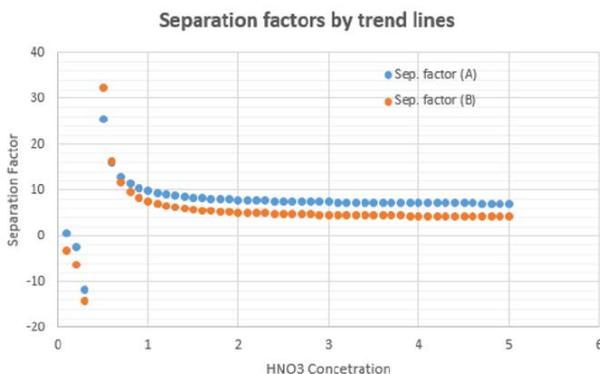


Fig 9. Separation factors by trend lines

Figure 9 shows the biggest values of separation factor are 25.527 at 0.5 M of HNO₃ for exp. A, 32.463 at 0.5 M of HNO₃ for exp. B. At range of lower than 0.5 M, even though it is unreasonable, there are negative separation factors because of using trend lines.

4. Conclusion

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. In nitric acid, neptunium ion can exist simultaneously in tetra-, penta-, and hexavalent. Np(VI) is easily extractable, Np(IV) is less extractable, and Np(V) is nearly unextractable. 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 the concentration of nitric acid, the extractability of neptunium can be controlled.

It is hard to determine the optimum nitric acid concentration for extraction of only uranium because the mechanism is very complicated. It can't be calculated by mathematics, but, in this experiment, only 3 points of nitric acid concentration exist. Anyway, the optimum point is at 0.5 M of nitric acid. Therefore, estimation of the optimum point is not correct. If more accurate estimation should be needed, more experiments are needed.

How to increase the separation efficiency of uranium and plutonium is very important for PUREX process. However, in real spent nuclear fuel, there are many nuclides, about 50 elements of FPs and MAs. The mechanism of solvent extraction is more complicated, as elements participated in reaction are increased. Therefore, understanding the behaviors of FPs and MAs during the solvent extraction is very important. The highest separation efficiency can be obtained and designed, when we make the appropriate modeling of the solvent extraction process in the view of engineering.

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