

Simulation of PUREX Solvent Extraction Experiments Using ^{238}U , ^{152}Eu and ^{85}Sr Solution

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1. Introduction

Recently, in Korea, nuclear-spent fuel problem come to be an important social problem. The reprocessing is widely known method to solve this problem. In reprocessing technology, there are two methods existed. One is dry reprocessing, which is represented by pyro-processing. And the other one is the aqueous reprocessing, what is represented by the PUREX (Plutonium Uranium Redox Extraction).

PUREX is an aqueous reprocessing technology that separates U and Pu from nuclear spent fuel using the solvent extraction process. In the solvent extraction process, predicting the behavior of U, minor actinides (MA) and transuranic elements (TRU) are important. Because the efficiency of U separation is determined by their behavior.

In this study, experiments were conducted on the laboratory scale to understand the PUREX process and its mechanism.

2. Materials and Methods

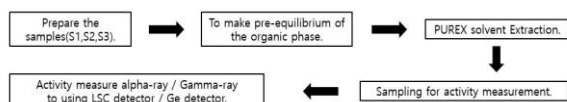


Fig. 1. Flow chart for experiment

Figure 1 is describing the simulation process of PUREX. Three types of HNO_3 concentration aqueous solutions used in the PUREX simulation were prepared for comparing U extraction behavior. The concentration of each solutions are 0.1 M, 1.0 M, and 5.0 M. ^{85}Sr and ^{152}Eu were selected and injected to describe MA and TRU in nuclide waste. Tri-n-butyl phosphate (TBP) in an organic solvent was used as an extractant in U separation experiments. After separation of U, samples was separated by 2 types for detecting alpha and gamma radioactivity.

2.1. Sample preparation

First of all, 3 types of samples were prepared. U separation efficiency by the concentration of HNO_3 could be compared because of the different concentration of each samples.

The composition of each sample is described in Table 1.

Table 1: The composition of stock sample solutions

Sample no.	S1	S2	S3
HNO_3	0.1 M	1.0 M	5.0 M
UO_2^{2+}		5.0×10^{-2} M	
$^{85}\text{Sr}^{2+}$		1.0×10^{-3} M	

In Fig 2, stock samples have a yellow color because of the yellow color of HNO_3 and UO_2 compounds.



Fig. 2. Stock samples (left), injected samples (right)

^{85}Sr and ^{152}Eu were selected as representative materials of MA and TRU in nuclear-spent fuel. The composition of samples after injecting described in Table 2.

Table 2: The composition of sample solutions

Sample no.	S1	S2	S3
HNO_3	0.96 $\times 10^{-7}$ M	0.96 $\times 10^{-6}$ M	4.8 $\times 10^{-6}$ M
UO_2^{2+}		4.8×10^{-2} M	
$^{85}\text{Sr}^{2+}$		0.96×10^{-3} M	
$^{152}\text{Eu}^{3+}$		2.0×10^{-7} M	

2.2. Pre-equilibrium



Fig. 3. Organic solution (left, 30% TBP+70% dodecane), 0.1M HNO_3 (right, 0.1M)

In this procedure, an organic acid solution was used containing 30% TBP + 70% dodecane and the aqueous acid solution was used 0.1 M HNO_3 . 10ml of an aqueous solution was put into the funnel, and 15ml of the organic solution was put into a funnel. Then, separation funnel was shaken for 2 minutes to reach equilibrium. And left the funnel at rest until two-phase re-separation completed. Then discarded the aqueous phase and kept the organic phase in a glass bottle.



Fig 4. Before pre-equilibrium process (left), after pre-equilibrium process (right)

Pre-equilibrium step is important procedure to an experiment. HNO_3 that presents in aqueous solution can move to organic phase by forming complexes with the TBP. Without Pre-equilibrium, reaction between HNO_3 and $\text{UO}_2(\text{NO}_3)_2$ can interrupt uranium extraction. Therefore, have to conduct a pre-equilibrium step as a pre-combination of TBP & HNO_3 .

2.3. Solvent extraction

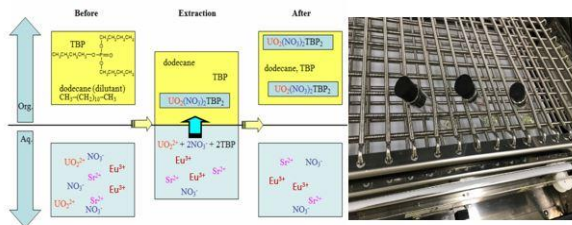
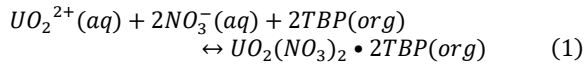


Fig. 5. Solvent extraction process (left), samples tilted by 45 degrees during they are stirred (right)



In this process, U separation was started. In interface area that made between organic acid and aqueous acid, U behavior has occurred like the chemical formula (1). The product of this chemical reaction, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, was solved into the organic phase. The reaction has happened at the interface, so to increase reactivity, samples was tilted by 45 degrees during samples was stirred.

2.4. Radioactivity

After samples were stirred, the radioactive detector was used to confirm radioactive materials behavior.

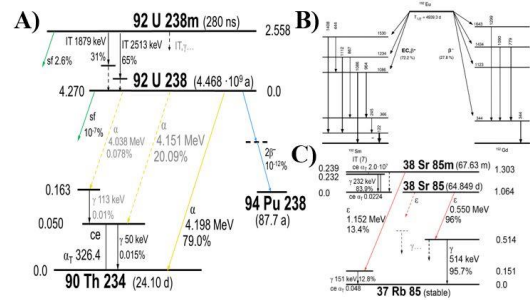


Fig. 6. Decay scheme of radioactive materials in samples (A: ^{238}U , B: ^{152}Eu , C: ^{85}Sr)

Radioactive materials in samples are ^{238}U , ^{85}Sr , and ^{152}Eu . As can see in Fig. 6, ^{152}Eu and ^{85}Sr emit gamma-ray, ^{238}U emit alpha-ray. Therefore, LSC detector was used when confirming the behavior of ^{152}Eu and ^{85}Sr . And the HPGe detector was used when confirming the behavior of ^{238}U . Hence, 4 samples for detecting were made in each sample, totally 12 samples made.

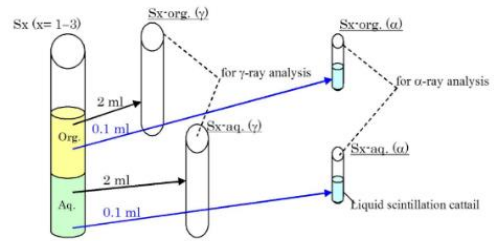


Fig. 7. Sampling procedure for radioactive detect



Fig. 8. LSC detector



Fig. 9. HPGe detector

3. Results and Discussion

3.1. Separation of U from PUREX Simulated Solution

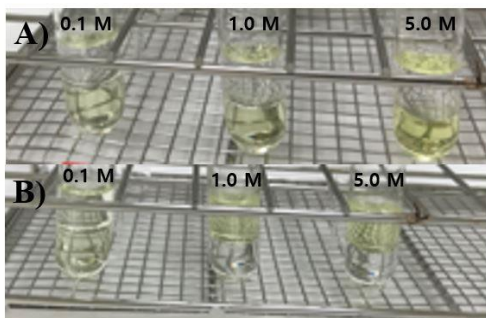


Fig. 10. The color change of samples (A: before stirred, B: after stirred)

Fig. 10 shows the change of the sample color after this procedure. There's no change in the 0.1M HNO₃ inserted sample compare to the before process state. However, 1.0M and 5.0M HNO₃ inserted samples have significant change compared to the before process state. In the last two cases, the yellow color exists in the aqueous phase was moved to the organic phase. These phenomena were decided from the product of HNO₃ and UO₂. With the color change, the behavior of U was confirmed. [1]

3.2. Pulse Analysis

3.2.1 LSC Pulse Analysis

The energy of alpha rays is much higher than energy of beta rays and gamma rays. Therefore, the energy gained by the phosphor due to the alpha rays is much higher than the other two radiations. Due to the high energy, the phosphor emits light longer. And it makes a longer signal.

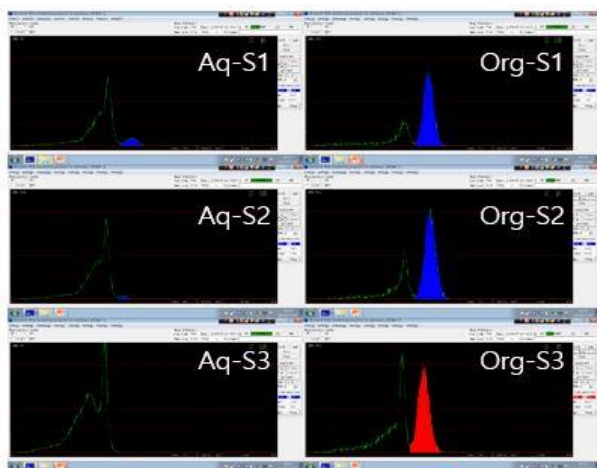


Fig. 11. Radioactivity pulse data from LSC (left: aqueous phase, right: organic phase)

Samples were measured at 10000 counts per each sample. Comparing the data shows that the alpha line peaks of the organic phase are clearly large. As a result, it can be seen that uranium which is an alpha particle emitter, was reliably transferred to the organic phase. In addition, it can be seen that uranium migration is large in samples with a high concentration of nitric acid.

3.2.1 HPGe Pulse Analysis

Gamma-ray peaks of nuclides vary widely. Therefore, some of these gamma-ray peaks should be selected. In this experiment, the peaks at 122.0 keV for ¹⁵²Eu and 514.8 keV for ⁸⁵Sr were selected as detection targets. These peaks were selected because they show the highest rate of release for each nuclide. HPGe was measured by 800 sec for each sample.

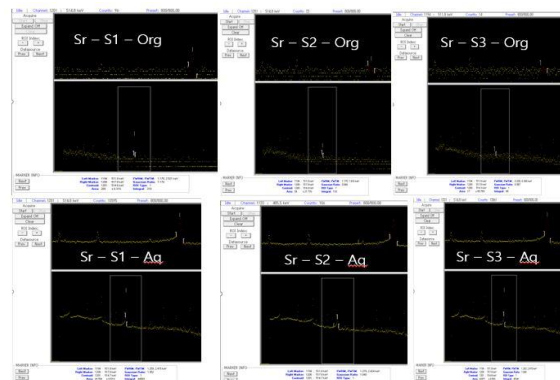


Fig. 12. Result of gamma detecting (⁸⁵Sr)

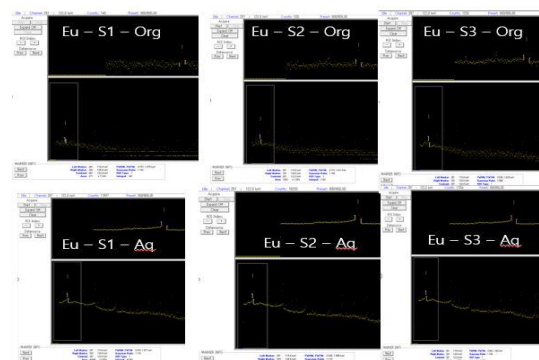


Fig. 13. Result of gamma detecting (¹⁵²Eu)

In both nuclides, the radiation intensity of the aqueous phase was higher than the radiation intensity of the organic phase.

3.3 Distribution coefficients of ²³⁸U, ¹⁵²Eu, and ⁸⁵Sr depends on nitric acid concentration

Distribution coefficients (D) of the elements were determined by Eq. (2)

$$D_{element} = \frac{[element]_{org}}{[element]_{aqueous}} = \frac{cps_{org}}{cps_{aqueous}} \quad (2)$$

Calculated distribution coefficients are compared with the concentrations of HNO₃.

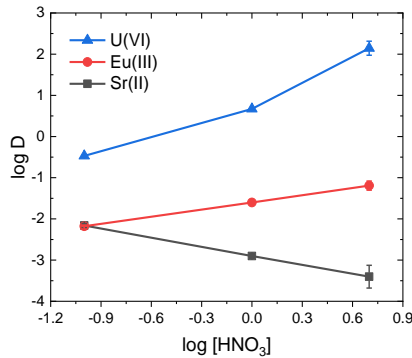


Fig. 14. Distribution coefficients (D) of Sr (II), Eu (III), and U (VI) depending on Nitric acid concentration ($[HNO_3]$)

From Fig. 14, the distribution coefficients of Eu (III) and U (VI) increased with the increasing of the concentration of HNO_3 . This result means the concentration of HNO_3 can increase the efficiency of solvent extraction. This trends also can be confirmed in Dawn et al's study [2]. However, in the case of Sr (II) that has poor selectivity, the distribution coefficient was decreased. Therefore, the equilibrium constant of Sr (II) is less than that of hydrogen. Thus the expected equilibrium constant value should follow in order of ($K_U > K_{Eu} > K_H > K_{Sr}$). K is calculated through Eq. (3) form.

$$K_U = \frac{[UO_2(NO_3)_2 \cdot 2TBP]}{[UO_2^{2+}][NO_3^-]^2[TBP]^2} \quad (3)$$

Selection of proper HNO_3 concentration was also done from the experiment result. Normally, the distribution coefficient of uranium improves with the increasing of HNO_3 concentration. The maximum distribution coefficient of uranium was observed when using 5 M of HNO_3 sample. However, in Jamel et al's study [3], the decrement of the distribution coefficient of uranium was observed, above 5 M of HNO_3 condition, due to the competition of HNO_3 with TBP.

In short, 5 M of the nitric acid condition is a proper condition for U and Eu purification, whereas Sr purification could be efficient in a lower nitric acid condition.

3.4 Chemical reaction of U, Eu, and Sr

In this experiment system, 4 chemical reaction can possible.

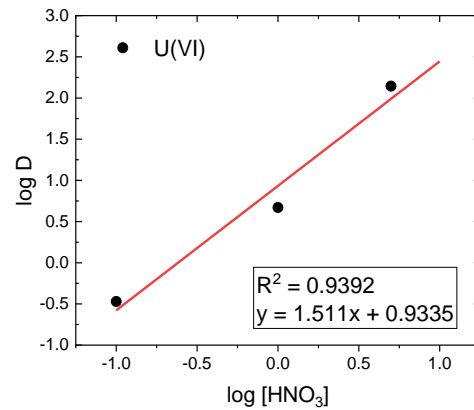
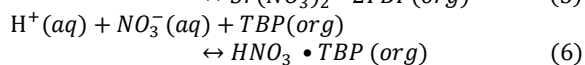
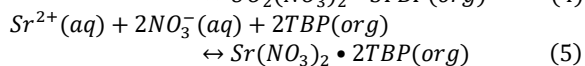
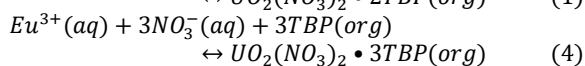
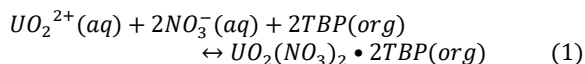


Fig. 15. Linear fitting result ($\log [HNO_3]$ vs $\log D$) from experimental result of Uranium

Fig. 15 shows the experimental result with the slope value of 1.511. But the ideal slope value is 2. The reasons can be possible are the reaction of Eu^{3+} and Sr^{2+} with nitrate, which can interrupt to form $UO_2(NO_3)_2$. Besides, the decomposition of nitrate from HNO_3 was not sufficient under experimental pH condition, which can result in different concentration of nitrate from ideal nitrate concentration. As a result, the result indicates that four chemical reactions are in competition.

4. Conclusion

In this study, PUREX was simulated using uranium, strontium and europium. Uranium is separated from aqueous phase to organic phase during solvent extraction procedure using TBP and dodecane. Concentrations of U (VI), Eu (III), and Sr (II) samples were analyzed by LSC and germanium detector. The distribution coefficients get from counts ratio of radioactive detector. Distribution coefficients of Eu (III), and U (VI) increased with the increasing nitric acid concentration. On the other hand, decrements of Sr (II) distribution coefficients were observed. 5 M of nitric acid concentration can be a proper condition for U extraction.

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