

Plutonium Behavior under the Condition of Uranium Crystallization from Dissolver Solution

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Abstract – Uranium crystallization process has been developed as a part of advanced aqueous reprocessing system. In the process the great part of uranium is separated from dissolver solution by crystallization as uranyl nitrate hexahydrate (UNH). Two types of experiments were carried out to clarify the plutonium behavior under the condition of the uranium crystallization. Hexavalent plutonium is co-crystallized with uranium and tetravalent plutonium is not, although plutonium concentration is lower than that expected by its solubility. Therefore, the adjustment of plutonium valence at tetravalent is needed in order to avoid co-crystallization of plutonium with uranium.

INTRODUCTION

Japan Nuclear Cycle Development Institute (JNC) has been developing uranium crystallization process as a part of “New Extraction System for TRU Recovery (NEXT)” [1] to separate the great part of uranium from dissolver solution of FBR spent fuel. Crystallization process for the NEXT is expected to have some advantages over the current PUREX process as follows;

- the relative simplicity for remote operation
- volume reduction of organic solvent in the extraction process
- reduction in cost for equipments and the hot cell volume
- reduction of waste volumes

The crystallization process as a part of reprocessing had been developed in Germany [2]. Although their work gives useful information on the uranium crystallization behavior, there are limited data on plutonium behaviour under the condition of high concentration of heavy metals and high acidity because the process was developed for purification of uranium product from LWR reprocessing. For the application of the crystallization technology to the NEXT process, it is important to know the behavior of plutonium under the operating condition of uranium crystallization from highly concentrated dissolver solution to prevent plutonium from accompanying uranium. Two types of beaker scale tests as follows were conducted;

- (i) cooling Pu solutions
- (ii) crystallizing from U/Pu mixed solutions.

The purpose of these tests is to provide the crystallization temperature of plutonium in nitric acid solution. The purpose of the test (ii) is also to know plutonium behavior under the operating

condition of uranium crystallization from uranium and plutonium mixed solution. This report gives the results of test (i) and (ii).

EXPERIMENTAL AND RESULTS

Test (i): Cooling Pu Solutions

Preparation of Solutions

Feed solution was prepared by electrochemical dissolution of plutonium dioxide with 4M nitric acid solution containing 0.05M silver nitrate. Tetravalent plutonium was then adjusted with a few drops of hydrogen peroxide. Hexavalent plutonium was obtained with divalent silver ion. Silver was separated from the solution by ion exchange after the plutonium oxidation. Plutonium valence was confirmed by UV/vis. spectrometry.

Table1 shows the composition of the feed solutions prepared for the test (i).

Table1 Composition of Feed Solutions for the Test (i)

No.	Conc. of Pu (g/L)	Acidity (M)	Pu valence
i-1	200		
i-2	100	4	
i-3	50		
i-4	200		IV
i-5	100	6	
i-6	50		
i-7	200		
i-8	100	6	VI
i-9	50		

Equipment

The reaction vessel shown in Fig.1 was installed in a glovebox. The vessel had a cooling jacket in which coolant flowed, overhead stirring unit and thermocouple probe.

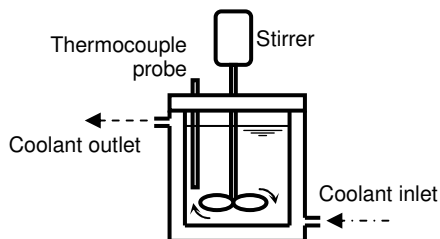


Fig.1 Reaction Vessel

Experimental Procedure

The feed solution was put in the reaction vessel and stirred gently while the temperature was reduced at approximately -1°C per minute from -5°C . The cooling operation was continued until approximately -60°C regardless of any phase change. Then, the solution was heated up. Temperature of the solution was recorded to observe phase transition with thermal reaction. Samples for gamma spectroscopy were taken before the cooling operation, and also during warming operation at the temperature of approximately -40 , -30 , -20 , and -10°C to determine plutonium concentration.

Results

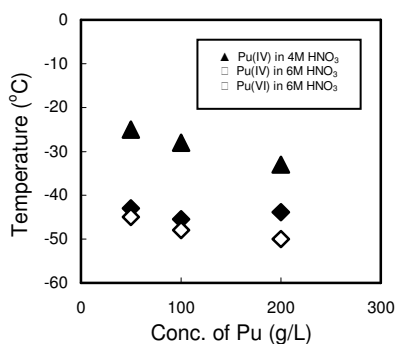


Fig.2 Solidification Temperature of Plutonium-Nitric Acid Solution

Solidification temperature of plutonium-nitric acid solution measured in test (i) is plotted in Fig.2.

In every case, solidification in sample solution occurred under -20°C . The solid

obtained was considered as eutectic crystal of nitric acid and water ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) from the change in plutonium concentration of liquid phase.

Since plutonium was not solely crystallized in test (i), it is concluded that plutonium would remain in the liquid phase under the condition of uranium crystallization process; for example, operation temperature is higher than 0°C and initial acidity of feed solution is about 5N.

Test (ii): Crystallizing U/Pu Mixed Solution

Preparation of Solutions

Uranium and tetravalent or hexavalent plutonium mixed solution were prepared. Hexavalent plutonium was adjusted by aforementioned method.

The dissolver solution of irradiated LWR fuel was given for the uranium and tetravalent plutonium solution. Reduction of plutonium from hexavalence to tetravalence was carried out by careful addition of hydrogen peroxide.

Table2 shows the composition of feed solutions prepared for the test (ii).

Table2 Composition of Feed Solutions for the Test (ii)

No.	Conc.(g/L)		Acidity (M)	Pu Valence	Final Temp.(°C)
	U	Pu			
ii-1	446	60.8	4.6	VI	10
ii-2					0
ii-3	456	47.4	4.6	IV	10
ii-4					0

6M nitric acid solutions saturated with uranyl nitrate were prepared as scrub solutions for each case of 0-10%.

Equipment

A diagram of crystallization equipment used for the test (ii) is shown in Fig.3. The equipment consisted of three vessels; a scrub feed vessel, a crystallization vessel, and a scrub/filtration vessel. Each of these vessels had a jacket of a recirculated thermoregulation fluid.

The crystallization vessel had a mechanical stirrer and thermocouple. The scrub/filtration vessel was fitted with a glass filter. A collecting flask was connected to the glass outlet tube of the scrub/filtration vessel. A plastic tube was

connected to a vacuum pump for the suction filtration by decompression. The scrub solution was cooled up to the desired temperature in the scrub feed vessel.

The equipment was sited in a glovebox (in the test of uranium and hexavalent plutonium solution) or in a hot cell (in the test of uranium and tetravalent plutonium solution).

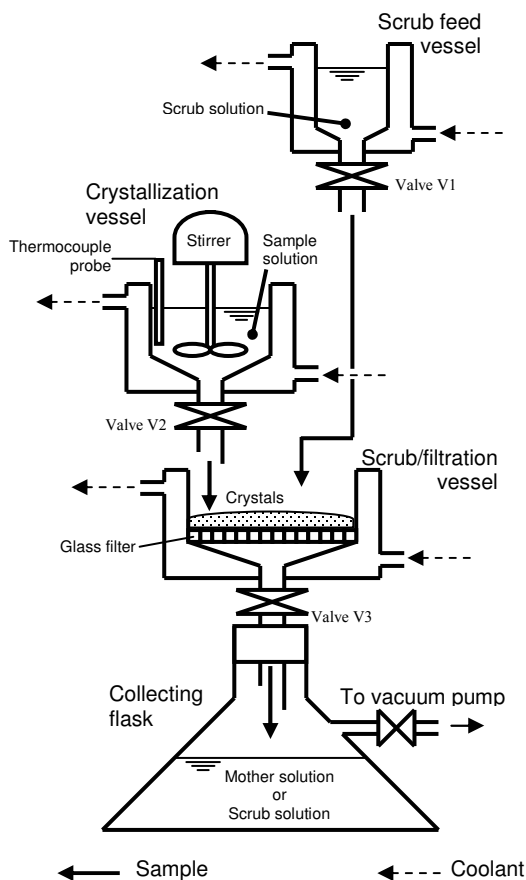


Fig.3 Crystallization Equipment

Experimental Procedure

The feed solution was initially kept at over 40°C or higher. The solution was transferred to the crystallization vessel and stirred. At the same time, the scrub solution was placed in the scrub feed vessel.

After the temperature of the solution reached 10 or 0°C, it was maintained as it was for at least 5 minutes. The temperature inside the scrub/filtration vessel was checked with the thermocouple system. The valve V2 was opened

to allow the crystal to move to the scrub/filtration vessel with stirring. The valve V3 was opened to allow the liquid being drained to the collecting flask underneath and vacuum was applied. The suction was maintained for at least 3 minutes. After the filtration, vacuum filtration was stopped, the valve V3 was closed and the collecting flask was replaced with another for the first scrub liquid.

The temperature of scrub solution was confirmed as 10°C and the valve V1 was opened. When all the scrub solution had drained into the scrub/filtration vessel, the scrub solution gently mixed using a stirrer for at least 1 minute. After stirring, the valve V3 was opened, and vacuum was applied to suck the solution into the second collecting flask. Vacuum aspiration again lasted for at least 3 minutes.

The above scrubbing process was repeated for three times.

Results

The photographs of crystals obtained in the test (ii) are shown in Fig.4.



Fig.4. Crystals Obtained in Test (ii)
left: U+Pu(VI)
right: U+Pu(IV), through lead glass

In the case of uranium and tetravalent plutonium solution test, the color of crystal was always lemon yellow. The produced crystal looked uranium nitrate hexahydrate without significant amount of impurity including plutonium. In the case of uranium and hexavalent plutonium solution test, however, the color of crystals was orange. It implies that the orange crystal was a mixture of uranyl nitrate hexahydrate and plutonyl nitrate hexahydrate (deep red).

The values of decontamination factors (DFs) for plutonium of uranium recovered as crystals were calculated from concentrations of uranium and plutonium by equation (1) as follow and were shown in table3.

$$DF = \text{Erreur !} \quad (1)$$

X: element

Table3 DFs for plutonium of uranium recovered as crystals

No.	The Number of Scrub			
	0	1	2	3
ii-1	1.3	1.3	1.2	1.1
ii-2	1.4	1.4	1.4	1.5
ii-3	14	130	260	680
ii-4	7	66	370	680

These results indicated that hexavalent plutonium accompanies uranium to the crystal and that tetravalent plutonium does not.

In the case of uranium and tetravalent plutonium, the feed solution contained miner actinide (MA) and fission product (FP) elements. Then, DFs for some MAs and FPs were calculated by equation (1) and were shown in table4.

Table4 DFs for MAs and FPs of uranium recovered as crystals

		The Number of Scrub			
		0	1	2	3
ii-3	Am-241	12	100	250	3000
	Cs-137	13	100	170	740
	Eu-155	11	100	240	860
ii-4	Am-241	6	58	550	1700
	Cs-137	6	57	420	1300
	Eu-155	6	56	530	1400

The values in table4 indicated that MAs and FPs don't accompany with uranium under the condition of uranium crystallization.

DISCUSSION

According to the test (i), the concentration of plutonium in the feed solution used in the test (ii) was lower than the solubility of plutonium in this medium. Hexavalent plutonium accompanied with uranium at approximately same proportion of the feed solution. It suggests that hexavalent plutonium co-crystallizes with uranium under the crystallization condition of uranyl nitrate hexahydrate from dissolver solution.

One of the possible reasons for the co-crystallization is the similarity of structure of plutonyl nitrate hexahydrate and uranyl nitrate

hexahydrate. Both nitrate hexahydrate crystals have the same type of structure and approximately the same lattice constant [3].

One presumable theory is that the behavior of hexavalent plutonium is same as that of uranium under the co-crystallization condition. If this hypothesis is true, it is considered that the crystallizing elements are not only uranium but also other hexavalent actinides, especially neptunium, when dissolver solution is cooled. Therefore, crystallization process, aiming rough separation of uranium from dissolver solution, needs to adjust plutonium valence to tetravalent in advance to avoid plutonium co-crystallization with uranium.

CONCLUSION

From the results of cooling test of plutonium solution, the solubility of plutonium is over 200g/L in 4 and 6M nitric acid solutions. Under the condition that plutonium exists with uranium, however, hexavalent plutonium co-crystallized with uranium, where the plutonium concentration is lower than that expected by its solubility.

Therefore the adjustment of plutonium valence at tetravalent is needed in advance to avoid co-crystallization of plutonium with uranium.

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