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Separation of Uranyl Nitrate Hexahydrate Crystal from Dissolver Solution of Irradiated Fast Neutron Reactor Fuel

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1. Introduction

Batch crystallization is widely used for the separation and high purification of organic and inorganic materials in the fine chemical, food, pharmaceutical and biochemical industries. In the atomic power industry, application of crystallization to U purification of the Plutonium Uranium Reduction Extraction (PUREX) first cycle product was attempted in Kernforschungszentrum Karlsruhe (KfK), Germany (Ebert et al., 1989). The feed solution had 240−480 g/dm^3 U concentration and 0.1 g/dm^3 fission products (FPs) concentration in 5−6 mol/dm^3 HNO$_3$ solution. Reducing conditions were achieved with 2.4 g/dm^3 of U(IV) which was added to change the Pu valence to Pu(IV) which was required for good separation of Pu from U. In a six-stage cascade crystallizer, the feed solution was cooled down in steps from 30 to −30°C in the course of about 30 min. More than 90% of U was recovered in form of uranyl nitrate hexahydrate (UNH) crystals with an average diameter of 0.2 mm, while a much greater proportion of the transuranium (TRU) elements and FPs remained in the mother liquor. The decontamination factors (DFs) of several of the FPs were determined for one crystal step plus several crystal washing operations. The measured DFs of Pu and Cs were 10^2 and 10^3, respectively.

An advanced aqueous reprocessing for a fast neutron reactor fuel cycle named "New Extraction System for TRU Recovery (NEXT)" has been proposed as one fast neutron reactor fuel reprocessing method (Koyama et al., 2009) and is being developed in Japan Atomic Energy Agency (JAEA). On the advanced aqueous reprocessing for fast neutron reactor fuel cycle, it is supposed to recover not only U and Pu but also minor actinides (MAs; Np, Am and Cm) for the efficient utilization of resources. It will be also effective in decreasing the environmental impact because of their long half-life and high radiotoxicity. These elements are loaded in a fast neutron reactor and are burned as core fuel. Figure 1 shows schematic diagram of NEXT process for fast neutron fuel reprocessing. The NEXT consists of highly efficient dissolution of fuel with HNO$_3$ solution (Katsurai et al., 2009), U crystallization for partial U recovery (Shibata et al., 2009), simplified solvent extraction for U, Pu and Np co-recovery using tri-*n*-butyl phosphate (TBP) as an extractant (Sano et al., 2009), and extraction chromatography for mutual separation of actinide elements and lanthanide elements from a raffinate (Koma et al., 2009). The powdered fuel was dissolved

by the highly efficient dissolution process and the dissolver solution was adjusted to high heavy metal concentration. Then, U is recovered as UNH crystals from dissolver solution derived from fast neutron reactor fuel. Since the amount throughput will be reduced in the simplified solvent extraction process, the adoption of the crystallization process is expected to reduce the radioactive waste, equipment, and hot cell volume. In addition, U/Pu ratio in the dissolver solution is adjusted in the crystallization process to be a suitable Pu content for core fuel fabrication. In the NEXT, Np is changed to Np(VI) in the high HNO_3 concentration feed solution and is co-extracted with U and Pu in the simplified solvent extraction system. The FPs in the raffinate obtained from the simplified solvent extraction process is removed using *N,N,N',N'*-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) absorbent in the extraction chromatography I. The actinide elements such as Am and Cm is recovered from the solution containing actinide and lanthanide elements by chromatography with 2,6-bis-(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine (R-BTP) absorbent in the extraction chromatography II.
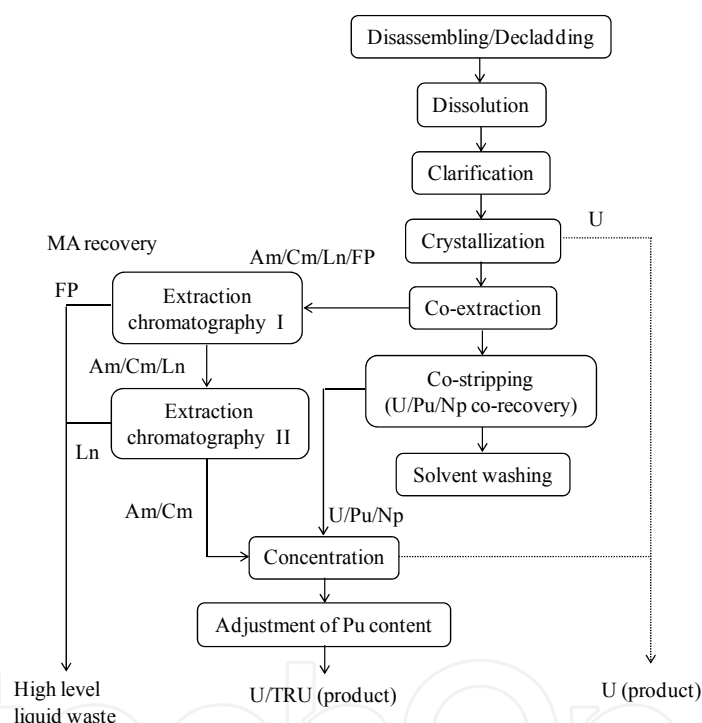

Fig. 1. Schematic diagram of the NEXT process

A dissolver solution of irradiated fast neutron reactor mixed oxide (MOX) fuel in JAEA contains a number of TRU elements and FPs than in KfK. Since U is used as blanket fuel and TRU elements are supposed to recover by other chemical process, it is need to remove TRU elements and FPs from UNH crystals in the U crystallization process. It would be also bring about reduction in the cost for the recovered U storage and the blanket fuel fabrication due to decreased radiation shielding. Therefore, the behavior of TRU elements and FPs in the U crystallization process must be confirmed experimentally.

Since U is recovered as UNH crystal for a blanket fuel fabrication in the U crystallization process, the crystal ratio of U should be evaluated with a dissolver solution of irradiated fast neutron reactor. The crystal ratio of UNH affects HNO_3 concentration in the feed

solution. In this study, the feed solution was changed in HNO_3 concentration and the influence on the UNH crystal ratio was examined in the cooling batch crystallization. Two experiments, crystal ratio and the co-existing element behavior, were carried out with a dissolver solution derived from irradiated fast neutron reactor "JOYO" core fuel in a hot cell of the Chemical Processing Facility (CPF), JAEA. Additionally, current status of crystallization apparatus and crystal purification method for the NEXT is described in this paper.

2. Principal of uranium crystallization

In a HNO_3 solution, U ions are crystallized as UNH by the following reaction.

$$UO_2^{2+} + 2NO_3^- + 6H_2O \leftrightarrow UO_2(NO_3)_2 \cdot 6H_2O \tag{1}$$
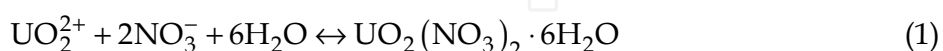
Figure 2 shows the solubility curves of U in HNO_3 solution (Hart & Morris, 1958). The results represent the mean of two temperatures observed for the first formation and final disappearance of crystal on, respectively, slowly cooling and warming solutions with vigorous agitation. The U ions concentration decreases with decreasing temperature in the solution before reaching the eutectic point, where H_2O and HNO_3 start to crystallize. Thus, U crystallization process should be performed in the right region of the minimum point in this figure. A high HNO_3 solution is desirable for achieving a low U concentration in the solution, therefore yielding more UNH crystals because the eutectic point shifts from right to left as the HNO_3 concentration increases.

In $Pu(NO_3)_4$-HNO_3-H_2O system, the crystallization behavior of plutonyl nitrate hexahydrate (PuNH) was examined. Figure 3 shows the solubility curves of Pu in HNO_3 solution (Yano et al., 2004). The Pu solution was prepared by dissolving PuO_2 powder with 4 mol/dm³ HNO_3 solution containing 0.05 mol/dm³ $AgNO_3$ electrochemically. In the experiments, the Pu valence was adjusted as following methods. The valence of Pu was changed to Pu(IV) with a few drops of 100% H_2O_2. On the other hand, the Pu solution was oxidized to Pu(VI) by Ag^{2+} ion and Ag in the solution was separated by ion exchange. The Pu solution was cooled quickly to −20°C and then cooled at −1 °C/min to −55°C. In the Pu(IV) solution appeared to be a green quasi-liquid (crystals in liquid). In all runs, PuNH was not crystallized in the experimental conditions but crystals of H_2O and $HNO_3 \cdot 3H_2O$ were observed. In the NEXT, PuNH would not precipitate solely in the U crystallization process.

The influence of Pu valence in the feed solution was examined in the U crystallization process (Yano et al., 2004). When Pu(IV) existed in the feed solution, the yellow crystal was observed. On the other hand, the appearance of the crystal was orange in the feed solution adjusted so that Pu valence was Pu(VI), this color likely resulting from the mixture of the yellow crystal of UNH and the red crystal of PuNH. Plutonium(VI) in the feed solution was co-crystallized with U(VI) in the course of U crystallization. The crystal yields of Pu were smaller than those of U (Ohyama et al., 2005). The fact that the crystal ratio of Pu is smaller than that of U suggests a mechanism of U-Pu co-crystallization in which U begins to crystallize when the saturation point of U is reached by cooling the feed solution, and then Pu is crystallized on the UNH crystal.
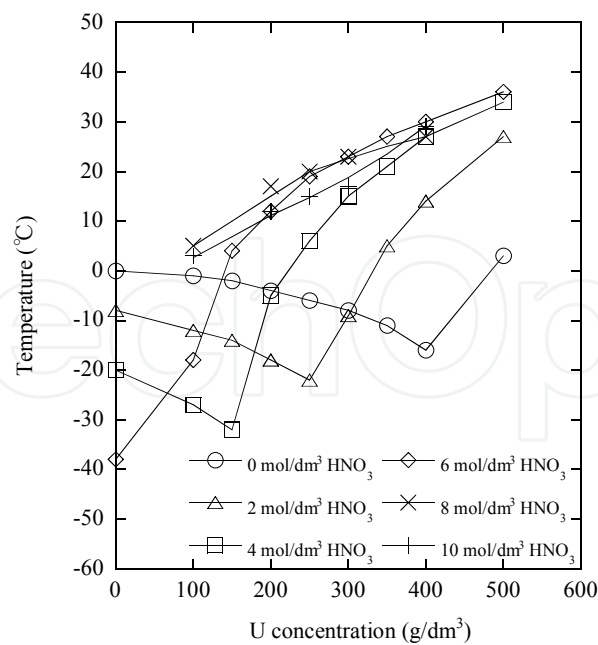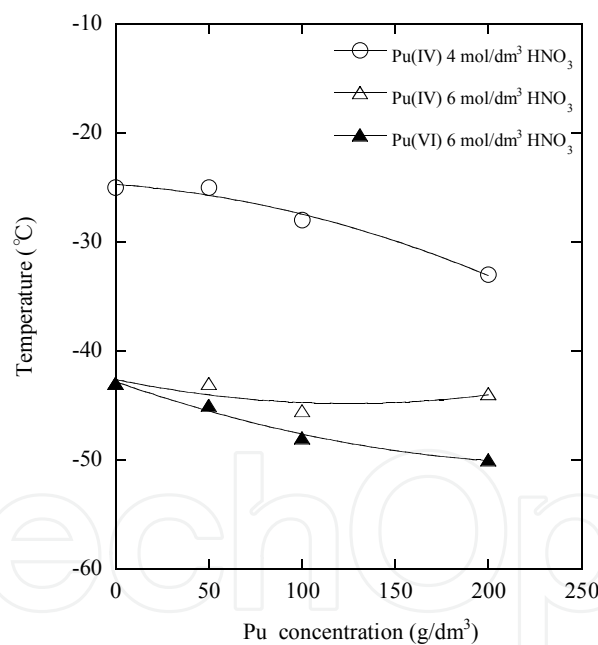
Fig. 2. Solubility of U in HNO$_3$ solution

Fig. 3. Solubility of Pu in HNO$_3$ solution

3. Batch crystallization with dissolver solution of irradiated fast neutron reactor fuel

3.1 Experimental procedure

In the experiments, HNO$_3$ from Wako Pure Chemical Industries, Ltd., was used without further purification. Irradiated core fuel of the fast neutron reactor "JOYO" Mk-III with an averaged burnup 53 GWd/t and cooling time of 2 y was used for the U crystallization

experiments. The sheared pieces of core fuel comprising 166 g of heavy metal were dissolved with 325 cm³ of 8 mol/dm³ HNO_3 solution at 95°C. The valence of Pu in the dissolver solution was changed to Pu(IV) by NO_x gas bubbling. In the crystal ratio experiments, the U and Pu concentrations in the feed solution were approximately 450 and 50 g/dm³, respectively. In co-existing element behavior experiment, the HNO_3 concentration in the feed solution was 4.5 mol/dm³ in the U crystallization process. The $CsNO_3$ solution was prepared by dissolving $CsNO_3$ (Wako Pure Chemical Industries, Ltd.) powder in 2 mol/dm³ HNO_3 solution, and added to the dissolver solution. The Cs concentration was 4.0 g/dm³ in the feed solution.

A schematic diagram of the batch cooling crystallizer is shown in Figure 4. The crystallizer made from Pyrex glass was used for cooling the solution volume capacity was 200 cm³, and it had a cooling jacket for cooling and heating media whose temperature was controlled by a thermostat. The feed solution was placed in the crystal vessel and was initially maintained at about 50°C. The feed solution was cooled from 50 to 4°C while being stirred. The spontaneously nucleated and grown crystalline particles were quickly centrifuged from the mother liquor at 3000 rpm for 20 min. After solid-liquid separation, the UNH crystals were washed using 8 mol/dm³ HNO_3 solution at 4°C and then centrifuged at 3000 rpm for 20 min.

The acidity of the solution was determined by acid-base titration (COM-2500, Hiranuma Sangyo Co., Ltd.) and the Pu valence in the feed solution was confirmed as Pu(IV) by optical spectrometry (V-570DS, JASCO Corporation) of the ultraviolet (UV)-visible region. The U and Pu concentrations were measured by colorimetry. The concentrations of Np, Am and Cm were measured by α-ray spectrometry (CU017-450-100: detector and NS920-8MCA: pulse height analyzer, ORTEC). The FPs concentrations were analyzed by γ-ray spectrometry (GEN10: detector and 92XMCA: pulse height analyzer, ORTEC) and inductively coupled plasma atomic emission spectrometry (ICP-AES; ICPS-7500, Shimadzu Corporation).
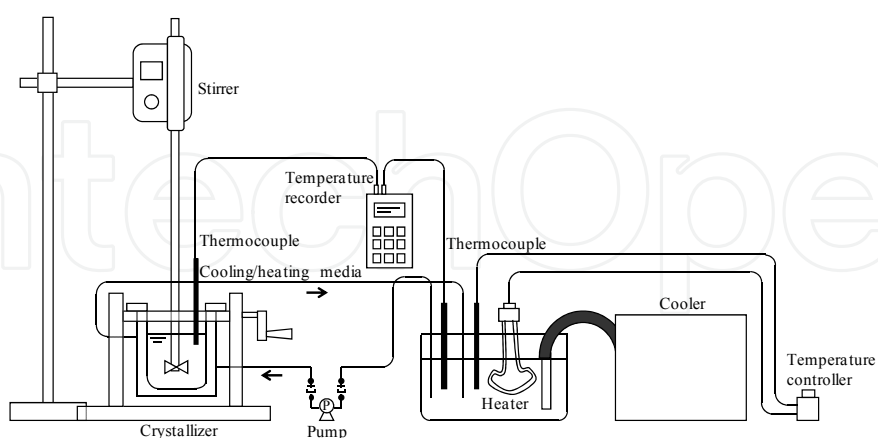

Fig. 4. Schematic diagram of the batch cooling crystallizer

3.2 Crystal ratio of uranyl nitrate hexahydrate

The cooling curve in the U crystallization is shown in Figure 5. The feed solution was placed in the crystallizer and cooled 45.0 to 3.3°C over 150 min. When the temperature of the feed

solution reached 23.8°C at 74 min, a small increase in temperature was observed in the feed solution. This indicates the start of crystallization, where heat is released by nucleation.

Figure 6 shows the appearance of UNH crystal recovered the dissolver solution of irradiated fast reactor "JOYO" Mk-III core fuel. After crystal washing, lemon yellow crystals were obtained on a filter.
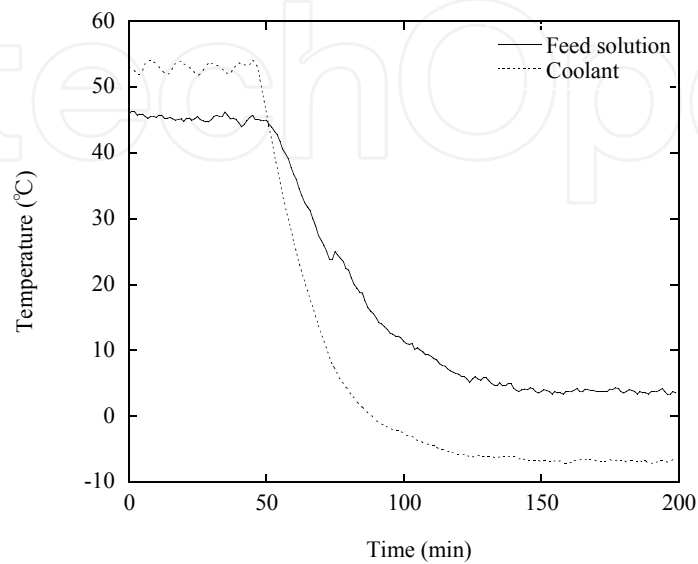

Fig. 5. Cooling curve of feed solution during U crystallization

Fig. 6. Appearance of UNH crystal after crystal washing

The crystal ratio of UNH in the dissolver solution of irradiated fast neutron reactor fuel was examined by changing in HNO_3 solution in the feed solution. The crystal ratio, $R_{c,j}$, is calculated by the following equation.

$$R_{c,j} = 1 - \frac{C_{F,H^+} C_{M,j}}{C_{M,H^+} C_{F,j}} \qquad (2)$$

where C_{F,H^+} and C_{M,H^+} are H^+ concentration in the feed solution and mother liquor, respectively, and $C_{F,j}$ and $C_{M,j}$ are metal j concentration in the feed solution and mother liquor, respectively. Figure 7 shows the relationship between HNO_3 concentration in the

feed solution and UNH crystal ratio in the batch cooling crystallization process. These experimental results show high HNO_3 concentration in the feed solution increased with increasing the UNH crystal ratio in the batch cooling crystallization process. These results were in agreement with the reported experimental data (Hart & Morris, 1958).
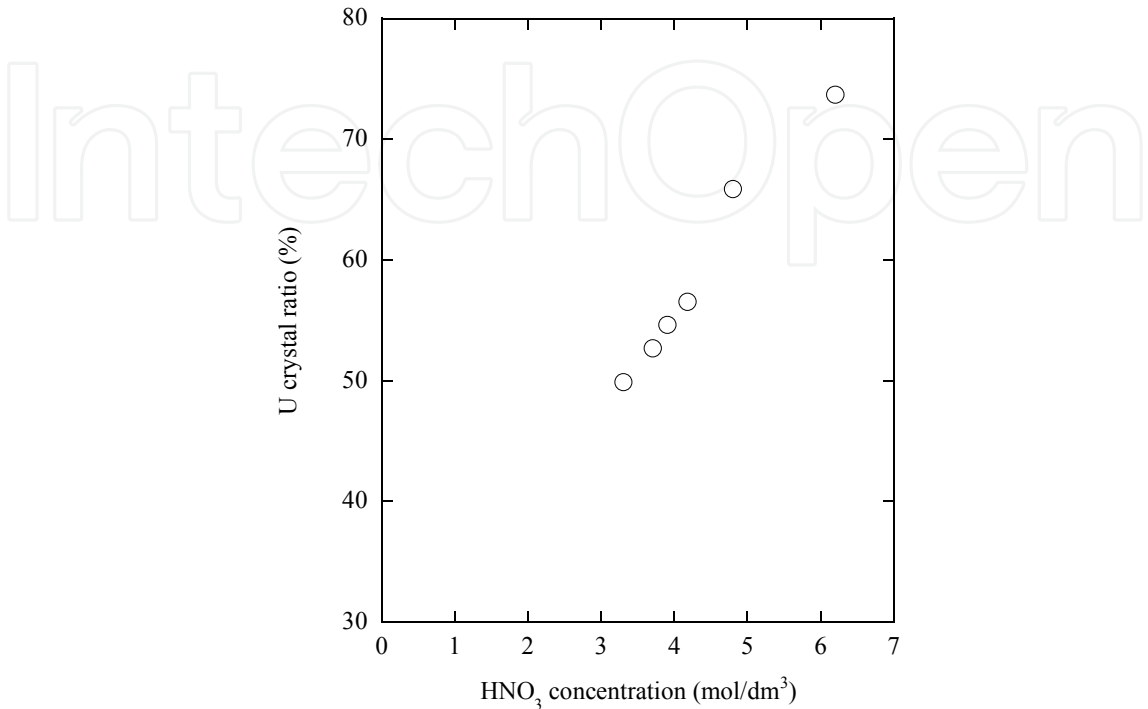

Fig. 7. Relationship between HNO_3 concentration in the feed solution and U crystal ratio

Element	Feed solution (g/dm^3)	Decontamination factor (−)	
		Before washing	After washing
U	4.18×10^2	−	−
Pu	4.00×10^1	8.5	24
Ba	3.70×10^{-2}	3.9	4.7
Nuclide	Feed solution (Bq/cm^3)	Decontamination factor (−)	
		Before washing	After washing
^{95}Zr	1.84×10^7	7.5	46
^{95}Nb	3.32×10^7	8.2	55
^{106}Ru	3.18×10^8	13	79
^{125}Sb	6.56×10^7	12	129
^{137}Cs	1.04×10^9	2.2	3.4
^{144}Ce	2.42×10^9	15	164
^{144}Pr	2.42×10^9	15	164
^{155}Eu	7.72×10^7	14	118
^{237}Np	2.38×10^4	3.3	6.7
^{241}Am	9.02×10^8	9.8	109
^{242}Cm	2.20×10^7	8.2	115

Table 1. Composition of the feed solution and DFs of metals for UNH crystal

3.3 Behavior of transuranium elements and fission products in uranium crystallization process

Table 1 summarizes the composition of feed solution and the DFs of metals in the U crystallization process. The DFs of metals, $\beta_{c,j}$, are calculated by the following equation.

$$\beta_{c,j} = \frac{\dfrac{C_{F,j}}{C_{F,U}}}{\dfrac{C_{P,j}}{C_{P,U}}} \tag{3}$$

where $C_{F,U}$ is U concentration in the feed solution, and $C_{P,U}$ and $C_{P,j}$ are U and metal j concentrations in the UNH crystal, respectively.

Plutonium behavior in the U crystallization process depends on the Pu valence in the feed solution. In this study, the Pu valence in the feed solution was changed to Pu(IV) by NO_x gas bubbling. After the crystallization, almost all the Pu remained in the mother liquor and attached to the surface of the UNH crystal. The mother liquor on the surface of crystal was efficiently removed after the UNH crystal was washed.

The DF of Np was 3.3 and 6.7 before and after washing, respectively. These experimental results implied Np was present in the form of solid impurities in the mother liquor because its DF was not improved by the crystal washing. Generally, Np can exist simultaneously in three stable oxidation state; Np(IV), Np(V) and Np(VI), in a HNO_3 solution. The oxidation states of Np are interconvertible in HNO_3 medium and exhibit different behavior in the reprocessing. Its valence is strongly affected by oxidation and reduction reactions with agents used in the reprocessing and other co-existing ions. All the kinetics of the oxidation and reduction reactions is not elucidated. One of these reactions is the oxidation of Np(V) by HNO_3, which is the principal influential reaction as follows.

$$2NpO_2^+ + 3H^+ + NO_3^- \leftrightarrow 2NpO_2^{2+} + HNO_2 + H_2O \tag{4}$$
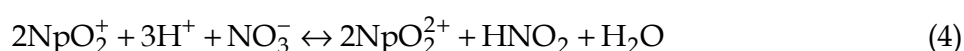
In this reaction, HNO_2 plays the important role of oxidation and reduction between Np(V) and Np(VI). This reaction shows that higher HNO_3 and lower HNO_2 concentrations bring about more oxidation of Np(V) to Np(VI). When the U ions crystallize as UNH in HNO_3 solution, it requires a certain amount of H_2O. As a result, the HNO_3 concentration of the mother liquor is higher than that of the feed solution. It brings about more oxidation of Np(V) to Np(VI) in the mother liquor. When the Pu valence is changed to Pu(VI), Pu(VI) is co-crystallize with U(VI). The chemical behavior of Np(VI) is similar to that of Pu(VI), and it is likely to co-crystallize with U(VI) in the course of U crystallization. Since the Np was incorporated into the UNH crystal, it is difficult to remove from the UNH by the crystal washing operation. If the Np valence is adjusted to Np(IV) or Np(V), the behavior of Np would be different from that of Np(VI). The addition of reductant agent, e.g., U(IV), is effective for preventing from the Np oxidation to Np(VI). Thereby, the Np might remain in the mother liquor after cooling the feed solution.

Americium and Cm are supposed to recover by an extraction chromatography process in the NEXT, and are desired to remain in the mother liquor in the U crystallization process.

The experimental results indicated the DFs of Am and Cm for the UNH crystal were 9.8 and 8.2 before washing, respectively. These elements remained in the mother liquor and attached on the surface of the UNH crystal. The adhesion of liquid impurities was washed away with HNO_3 solution. After washing, the DFs of Am and Cm for the UNH crystal increased by a factor of 109 and 115, respectively.

In the experiments, the behavior of Cs was evaluated in the U crystallization process. The DF of Cs showed 2.2 and 3.4 before and after washing. It is reported that alkali metals react with tetravalent actinide elements and form a double salt in a HNO_3 solution (Staritzky & Truitt, 1949). The reaction of Cs and Pu(IV) is expressed by the following equation.

$$2Cs^+ + Pu(NO_3)_6^{2-} \leftrightarrow Cs_2Pu(NO_3)_6 \tag{5}$$

This reaction indicates that an abundance of $Pu(NO_3)_6^{2-}$ is advantageous for forming of $Cs_2Pu(NO_3)_6$. Figure 8 show the abundance ratio of $Pu(NO_3)_6^{2-}$ in HNO_3 solution (Ryan, 1960). The abundance ratio of $Pu(NO_3)_6^{2-}$ increases with an increase in HNO_3 concentration. In the crystal growth of UNH, a certain amount of H_2O molecules is needed in the feed solution. The mother liquor of HNO_3 concentration is higher than that of feed solution after the U crystallization. Therefore, the formation of $Cs_2Pu(NO_3)_6$ is easy in the course of U crystallization. Anderson reported that double salt of Pu nitrate, $(C_9H_7NH)_2Pu(NO_3)_6$, $Rb_2Pu(NO_3)_6$, $Tl_2Pu(NO_3)_6$, $K_2Pu(NO_3)_6$, $(C_5H_5NH)_2Pu(NO_3)_6$ in addition to $Cs_2Pu(NO_3)_6$ (Anderson, 1949). These materials are less in a dissolver solution of irradiated fast neutron reactor fuel. However, further investigation concerning the double salt of Pu nitrate for the U crystallization process will required experimentally.
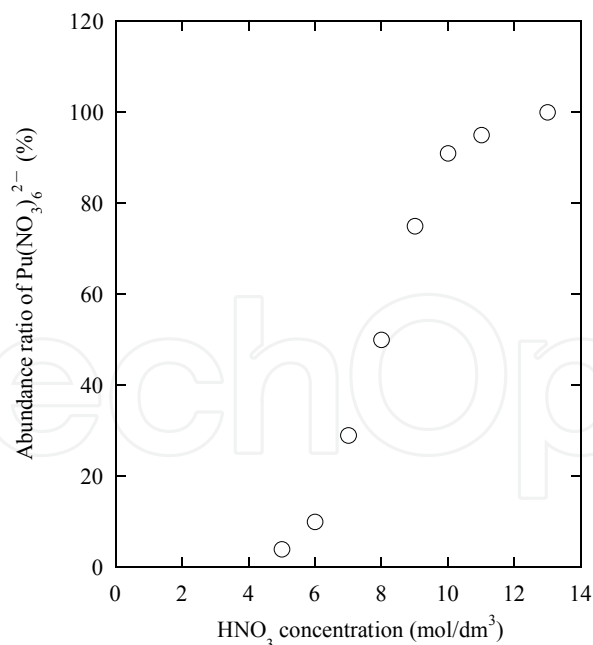

Fig. 8. Abundance ratio of $Pu(NO_3)_6^{2-}$ in HNO_3 solution

Among alkali earth metals, Ba behavior is examined in the cooling batch crystallization. The DFs of Ba was 4.7 after the crystal washing. In the precipitates formation experiments, $Ba_{0.5}Sr_{0.5}(NO_3)_2$ was observed using simulated high level liquid waste solution (Izumida &

Kawamura, 1990). On the other hand, the DF of Sr was decontaminated with the uranyl nitrate solution containing Sr and Ba after the UNH crystal was washed (Kusama et al., 2005). The solubility of Ba is 0.4 g/dm³ in 400 g/dm³ of uranyl nitrate solution with 5 mol/dm³ HNO_3. Therefore, Ba is assumed to precipitate as $Ba(NO_3)_2$ in the U crystallization process. The solid impurities are not removed by the crystal washing with a HNO_3 solution.

Insoluble residues consist of Zr and the elements of platinum group such as Ru in a nuclear fuel reprocessing. Zirconium and Mo precipitate in the form of zirconium molybdate in the dissolution process (Adachi et al., 1990; Lausch et al., 1994; Usami et al., 2010). This compound tends to form at high temperature and with low HNO_3 concentration in the solution. The DF of Zr was high after the crystal washing and Zr remained in the mother liquor. The feed solution was cooled and the acidity in the feed solution increases in the course of U crystallization. Therefore, zirconium molybdate would be difficult to crystallize at low temperature and with high HNO_3 concentration in the mother liquor.

The behavior of Ce, Pr and Eu in the rare earth elements was evaluated in the U crystallization experiments. The DFs of these elements achieved to approximately 10^2 after the crystal washing. Their solubility in the HNO_3 solution was so high that there was no precipitation as solid impurities. Therefore, they remained in the mother liquor during the U crystallization and these elements in the mother liquor that was attached to the surface of the UNH crystal were washed away with the HNO_3 solution.

4. Crystallization apparatus for continuous operation

4.1 Concept of crystallization apparatus

The crystallizer is designed for continuous operation adoption high throughput and equipment scale-up and is developed for the U crystallization in the NEXT (Washiya et al., 2010). Figure 9 shows a schematic diagram of annular type continuous crystallizer. A rotary-driven cylinder has a screw blade to transfer UNH crystal slurry and annular shaped space is formed as crystallization section in between the rotary cylinder and outer cylinder. A dissolver solution of irradiated fast neutron reactor fuel is fed into the annular section from the lower part of the equipment, and the coolant is supplied into the cooling jacket located on the outside cylinder. The dissolver solution is cooled down gradually and is transferred to the outlet in the upper side of the equipment. The UNH slurry is obtained in the annular section and is discharged by the guide blade attached to the rotary cylinder. The mother liquor is separated from the UNH crystal and is discharged from the nozzle located in the more upper side than solution level. The discharged UNH slurry is still accompanied with a little solution. Hence, it needs to be dried by the crystal separator as centrifugal dewatering process.

4.2 Continuous operation with uranyl nitrate solution using annular type continuous crystallizer

The continuous operation experiments were evaluated with a uranyl nitrate solution (Washiya et al., 2010). The feed solution of 450 g/dm³ U concentration in 5 mol/dm³ HNO_3 was cooled at 0°C at 20 rph. Afterwards, amount of the crystal stay was increased gradually, and it reached to steady state in 1−2 h. The moisture content in the UNH slurry obtained from the outlet of the slurry was about 40%. The UNH crystal size was

approximately 600 μm and is considered to appropriate size for solid-liquid separation. The U concentration in the mother liquor was reached to steady state within 2 h, and crystal ratio of U was about 84%.
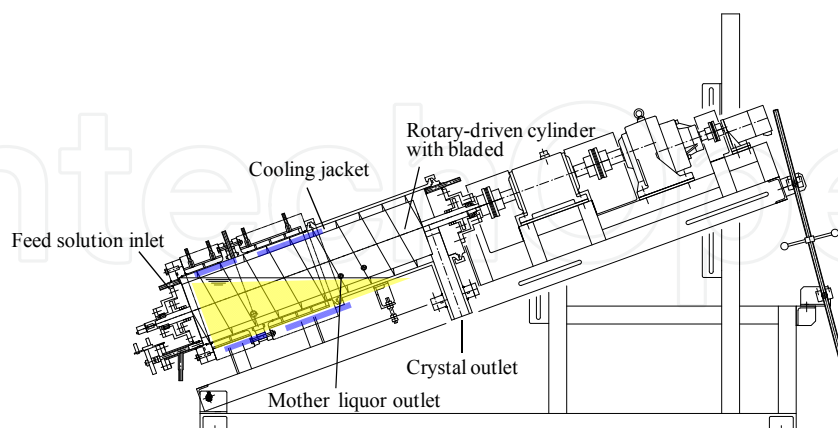

Fig. 9. Schematic diagram of annular type continuous crystallizer

To extract operational failure events comprehensively concerning to the U crystallizer and to clarify their importance, failure mode analysis was carried out by applying Failure Mode and Effects Analysis (FMEA). Significant failure events were identified with failure causes, their effects and probability of these failures were predicted by making use of operation experience. All failure events were evaluated by cause, primary and secondary effects and scored them. As results, crystal accumulation, blockage of mother liquor discharge nozzle, blockage of crystal discharge nozzle were selected as important specific failure events. To investigate how to detect non-steady condition, these three experiments were carried out with screw rotation speed decline, crystal outlet blockage and mother liquor outlet blockage. Also, the resume procedure after non-steady state was examined sequentially to consider countermeasures for each non-steady event (Shibata et al., 2009). The accumulation of UNH crystals can be detected by the torque of the cylinder screw, the liquid level in the annular section and other instruments. These experimental results show that it is possible to recover from non-steady state when the cause of the phenomena such as blockage of crystal outlet is removed by an appropriate operation. The fundamental performance of crystallizer annular type was investigated with uranyl nitrate solution. The experiment will be carried out to confirm the system performance on integrated crystallization system consisting of the engineering-scale crystallizer, crystal separator and related systems.

5. Purification of uranyl nitrate hexahydrate crystal product

5.1 Principal of crystal purification

Generally, crystalline particles produced in crystallizers are often contaminated by the mother liquor which appears on the surface or inside the bodies of the crystals. The UNH crystal recovered from a dissolver solution of irradiated fast neutron reactor fuel is washed away with a HNO_3 solution. Although the TRU elements and FPs on the surface of the UNH crystal are decontaminated by the crystal washing, the inclusions within the crystal and the solid impurities are not removed from the UNH crystal. Therefore, crystal purification method is studied for the purpose of further increasing decontamination performance. One

crystal purification method, the grown crystalline particles are purified by heating up to as high as the melting point of the crystal and introducing the mother liquor to the outside of the crystal, which is exhaled along defects and grain boundaries (Zief & Wilcox, 1967; Matsuoka & Sumitani, 1988). This phenomenon is called "sweating" and is applied to organics and metals. The mother liquor and melt in the crystal are discharged by Ostwald ripening and increase in the internal pressure (Matsuoka et al., 1986). The incorporated liquid is expelled from grooves along defects and grain boundaries. It was reported that countless grooves were observed in the organic crystal after sweating (Matsuoka & Sumitani, 1988). The purification of the *p*-dichlorobenzene (*p*-DCB) and *m*-chloronitrobenzene (*m*-CNB) crystalline particles by sweating was experimentally investigated (Matsuoka et al., 1986). The purity of 99.99% was obtained by a single sweating stage at temperatures about 1°C below the melting points of the pure crystals after the duration of 90 or 120 min of sweating. In the batch operation, the UNH crystal purification experiments were carried out with the dissolver solution of MOX fuel containing simulated FPs (Nakahara et al., 2011). Although the DFs of solid impurities such as $Ba(NO_3)_2$ and $Cs_2Pu(NO_3)_6$ did not change in the sweating process, that of Eu increased with increases in temperature and time. In the batch experiments, the DF of Eu increased to approximately 2.4 times after 30 min at 60°C. There results indicated that liquid impurities such as Eu were effectively removed by the sweating method, but solid impurities such as Pu, Cs and Ba were minimally affected in the batch experiments.
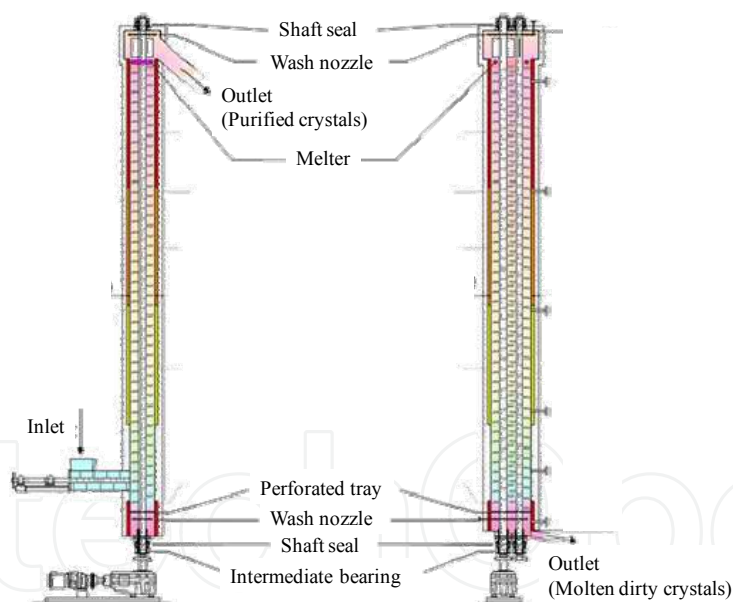

Fig. 10. Schematic diagram of KCP

5.2 Concept of crystal purification apparatus

The crystal purification apparatus, Kureha Crystal Purifier (KCP), has been applied in industrial plants using organic matter (Otawara & Matsuoka, 2002). The schematic diagram of KCP is shown in Figure 10. The apparatus has been developed in the following fashion: feed stock is charged as solids at the bottom of the column, the heating unit is set at the top of the column, and it is possible to contact the melt with crude crystal countercurrently. The KCP features high purity, high yield, energy savings, little maintenance, and a long, stable

operation (Otawara & Matsuoka, 2002). The crude crystal is supplied at the bottom of the column and then is carried to the upper side of a column by a double screw conveyor, and then part of the crystal is molten by a heating unit at the top of the column and the melt trickles downward among the crude crystal. The apparatus performs countercurrent contact between the crystal and reflux melts in the course of being conveyed upward, and the crude crystal is washed by a portion of the melt. Therefore, higher DFs of liquid impurities will be obtained by the KCP, because the liquid impurities were washed with melt in addition to sweating effect. The pure crystal product exits from the top of the column.

5.3 Continuous operation with uranyl nitrate solution using kureha crystal purifier

The crystal purification experiments with the KCP were carried out using the UNH crystal recovered from uranyl nitrate solution containing Sr of SUS304L (Yano et al., 2009). Although the DF of liquid impurities, Eu, in the static system was approximately 2.4 at 60°C for 30 min, the DF of Sr was 50 by the KCP. The liquid impurities such as Sr was removed from the UNH crystal not only by the sweating phenomenon but also by washing with U reflux melt, which was produced by the melter at the top of the column of the KCP. On the other hand, the DF of solid impurities, SUS304L, achieved a value of 100 with the KCP. In the static system, the solid impurities remained in the UNH crystal after the sweating operation. In the KCP, the solid impurities were removed from the UNH crystals due to upward movement of the crude crystals from the double screw conveyors; the UNH crystals and solid impurities, which have different densities and particle sizes, separate from each other by gravity and mixing.

6. Conclusion

Experimental studies on the behavior of TRU elements and FPs in the dissolver solution of irradiated fast neutron reactor core fuel were carried out to develop a crystallization method as a part of an advanced aqueous reprocessing. The experimental results show high HNO_3 concentration in the feed solution increased with increasing the UNH crystal ratio in the U crystallization process. Among coexistent elements, Zr, Nb, Ru Sb, Ce, Pr, Eu, Am and Cm remained in the mother liquor at the time of U crystallization. Therefore, portions of these elements in the mother liquor that was attached to the surface of the UNH crystal were washed away with HNO_3 solution. Cesium exhibited different behavior depending on whether Pu was present. Although a high DF of Cs was obtained in the case of uranyl nitrate solution without Pu(IV), Cs was hardly separated at all from the UNH crystal formed from the dissolver solution of irradiated fast neutron reactor core fuel in the case of high Cs concentration in the feed solution. It is likely that a double salt of Pu(IV) and Cs, $Cs_2Pu(NO_3)_6$ precipitated in the course of U crystallization process. Since Ba precipitated as $Ba(NO_3)_2$, its DF was low after the UNH crystal was washed. Neptunium was not removed from the UNH crystal because Np was oxidized to Np(VI) in the feed solution and thus co-crystallized with U(VI). The experimental data on the behavior of TRU elements and FPs will be actually utilized in fast neutron reactor fuel reprocessing. The continuous crystallizer and the KCP were developed, and the apparatus performance was examined with the uranyl nitrate solution containing simulated FPs. In the future, the integrated crystallization system performance will be confirmed for part of U recovery in the NEXT process.

7. Acknowledgment

8. References

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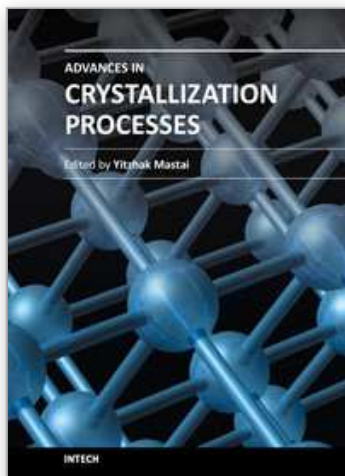
Advances in Crystallization Processes

Edited by Dr. Yitzhak Mastai

ISBN 978-953-51-0581-7

Hard cover, 648 pages

Publisher InTech

Published online 27, April, 2012

Published in print edition April, 2012

Crystallization is used at some stage in nearly all process industries as a method of production, purification or recovery of solid materials. In recent years, a number of new applications have also come to rely on crystallization processes such as the crystallization of nano and amorphous materials. The articles for this book have been contributed by the most respected researchers in this area and cover the frontier areas of research and developments in crystallization processes. Divided into five parts this book provides the latest research developments in many aspects of crystallization including: chiral crystallization, crystallization of nanomaterials and the crystallization of amorphous and glassy materials. This book is of interest to both fundamental research and also to practicing scientists and will prove invaluable to all chemical engineers and industrial chemists in the process industries as well as crystallization workers and students in industry and academia.

How to reference

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Masaumi Nakahara (2012). Separation of Uranyl Nitrate HexahydrateCrystal from Dissolver Solution of IrradiatedFast Neutron Reactor Fuel, Advances in Crystallization Processes, Dr. Yitzhak Mastai (Ed.), ISBN: 978-953-51-0581-7, InTech, Available from: http://www.intechopen.com/books/advances-in-crystallization-processes/separation-of-uranyl-nitrate-hexahydrate-crystal-from-dissolver-solution-of-irradiated-fast-neutron

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