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Preparation and characterization of dicesium tetravalent plutonium hexanitrate

Masaumi Nakahara[a,*], Kazunori Nomura[a], Tadahiro Washiya[b], Takahiro Chikazawa[c], Izumi Hirasawa[d]

[a] *Nuclear Fuel Cycle Engineering Laboratories, Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki 319-1194, Japan*
[b] *Advanced Nuclear System Research and Development Directorate, Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki 319-1194, Japan*
[c] *Energy Project and Technology Center, Mitsubishi Materials Corporation, 1002-14 Mukouyama, Naka-shi, Ibaraki 311-0102, Japan*
[d] *Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

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ABSTRACT

In experiments on U crystallization in a dissolver solution containing Cs, there is concern that Cs and Pu(IV) nitrate complex are deposited on the UNH crystal in the dissolver solution at the time of the U crystallization. The characteristics of generation of Cs and Pu(IV) nitrate complex with dissolver solution of MOX fuel were examined. This complex was obtained as a precipitate by mixing dissolver solution of MOX fuel and $CsNO_3$ solution, and was identified as dicesium tetravalent plutonium hexanitrate, $Cs_2Pu(NO_3)_6$ by concentration analysis and XRD. The precipitate has a tendency to be generated at high HNO_3 concentrations. Thermal analysis shows that the precipitate is stable below 245 °C, and a weight loss of $10.29 \pm 0.23\%$ is observed between 245 and 297 °C. This result indicates the decomposition of $Cs_2Pu(NO_3)_6$ to $Cs_2PuO_2(NO_3)_4$. With these properties, the UNH crystal should melt at the condition between 60 and 100 °C and be separable from the Cs complex by filtration. This suggests a new method of crystal purification allowing higher decontamination of UNH crystal in the U crystallization process.

1. Introduction

Japan Atomic Energy Agency (JAEA) has been developing advanced aqueous reprocessing for fast reactor fuel cycle systems. This process is called “New Extraction System for Transuranium (TRU) Recovery (NEXT)”, and consists of a high efficiency dissolution process, a crystallization process for recovering a part of the U, a simplified solvent extraction process using tri-*n*-butylphosphate (TBP) as an extractant of U, Pu and Np co-recovery, and an Am and Cm recovery process using extraction chromatography [1].

In this study for NEXT, a part of the U in the dissolver solution derived from irradiated fast reactor mixed oxide (MOX) fuel is recovered as uranyl nitrate hexahydrate (UNH) crystal merely by cooling the dissolver solution, taking advantage of the temperature dependence of the solubility of U in the HNO_3 solution. Dissolver solution with high concentrations of materials from irradiated fast reactor MOX fuel contains greater amounts of Pu and fission products (FPs), and among FPs, Cs is one of the most common elements in the irradiated fast reactor MOX fuel. Thus, the behavior of Pu and FPs, especially Cs, was studied under the operating conditions for U crystallization.

In the previous experiments of U crystallization with U and simulated FPs (non radioactive nuclides), the decontamination factor (DF) of Cs for the UNH crystal after crystal washing was about 10^2 [2]. However, the Cs behavior in the dissolver solution of irradiated MOX fuel is different from the above results; it depends on the Pu valence in the feed solution. The Pu valence in the feed solution was changed to Pu(IV) by NO*x* bubbling, which brought about a reasonable DF of Pu after washing UNH crystal [3]. With Pu(IV) in the feed solution, little Pu attached to the UNH crystal, and the surface of UNH crystal was contaminated with the mother liquor containing Pu. On the other hand, the DF of Cs was low even after washing the UNH crystal; that is, Cs was hard to separate from the UNH crystal. This suggests not only that mother liquor containing Cs attached to the UNH crystal surface, but also that some kind of Cs complex precipitate is formed under the conditions of crystallization. In contrast, U crystallization experiments were conducted with the dissolver solution containing irradiated fast reactor MOX fuel, in which Pu valence was changed to Pu(VI) by boiling the feed solution [4]. If Pu(VI) exists in the dissolver solution, the DF of Pu extremely is low even after washing the UNH crystal. The color of the obtained crystal was orange, contrasting with the yellow crystal in Pu(IV) feed solution. The Pu(VI) seems to be co-crystallized with U(VI) in the $UO_2(NO_3)_2$–$PuO_2(NO_3)_2$–HNO_3–H_2O solution because of chemical similarity between U(VI) and Pu(VI). In the case of Pu(VI), the DF of Cs was about 10^2 after crystal washing. This suggests that little Cs was accompanied with the UNH crystal, and the only surface of UNH crystal was contaminated with mother liquor containing Cs. In the series of our U crystallization experiments, it has been found that the DF of Cs is low in the presence of

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* Corresponding author. Tel.: +81 29 282 1111; fax: +81 29 282 9290.
E-mail address: nakahara.masaumi@jaea.go.jp (M. Nakahara).

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Table 1
Experimental condition.

RUN no.	Dissolver solution of MOX fuel			$CsNO_3$ solution	
	HNO_3 (mol/dm^3)	U (g/dm^3)	Pu (g/dm^3)	HNO_3 (mol/dm^3)	Cs (g/dm^3)
RUN1	2.8	20.0	70.0	2.9	81.0
RUN2	5.3	19.0	70.0	4.9	80.0
RUN3	8.1	20.0	70.0	7.7	79.0

Pu(IV). Yakimov et al. [5] reported that Cs is crystallized as $CsNO_3$ or $Cs_2UO_2(NO_3)_4$ in the $CsNO_3$–$UO_2(NO_3)_2$–H_2O system. However, Cs concentration in the feed solution was much lower than the saturation concentration of $CsNO_3$ or $Cs_2UO_2(NO_3)_4$. The DF of Cs was relatively high after crystal washing in the $UO_2(NO_3)_2$–HNO_3–H_2O system [2]. Meanwhile, Staritzky and Truitt [6] reported that a pale green complex forms after mixing solutions of $CsNO_3$ and $Pu(NO_3)_4$ with high HNO_3 concentrations, which they inferred to be $Cs_2Pu(NO_3)_6$. Hence, the Cs might form into a double salt with Pu(IV), and be crystallized as $Cs_2Pu(NO_3)_6$ under the conditions of our crystallization experiments.

In the NEXT process, U is recovered from the dissolver solution under the crystallization condition where the Pu valence in the feed solution is adjusted to Pu(IV). The DF of Cs would be low even after washing the UNH crystal because of the precipitation of $Cs_2Pu(NO_3)_6$. Therefore, the properties of $Cs_2Pu(NO_3)_6$ are important for achieving the purification of the UNH crystal in the U crystallization process. However, there is little experimental data on the properties of $Cs_2Pu(NO_3)_6$.

This paper reports on our experimental studies of the generation properties of $Cs_2Pu(NO_3)_6$ in HNO_3 solution, on the structure of this complex as characterized by X-ray diffraction (XRD), and on its thermal properties as measured by thermogravimetry (TG), which are relevant for the UNH crystal purification process. These experiments were conducted at the Chemical Processing Facility (CPF) of Nuclear Fuel Cycle Engineering Laboratories (NCL), JAEA.

2. Experimental

2.1. Reagents and procedure

Table 1 summarizes the experimental conditions. HNO_3 and $CsNO_3$ (purity 99.99%) were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Dissolver solution was prepared by dissolution of the MOX fuel with 8 mol/dm^3 HNO_3 solution at 100 °C, and the Pu valence in the dissolver solution was stabilized to Pu(IV) by NOx bubbling. The dissolver solution was finally divided into portions whose volumes were all 20 cm^3 and whose HNO_3 concentrations were 3, 5 and 8 mol/dm^3, respectively. Also, 20 cm^3 portions of $CsNO_3$ solution were prepared, mixing $CsNO_3$ powder in HNO_3 solutions whose concentrations were 3, 5 and 8 mol/dm^3, respectively.

The $CsNO_3$ solution was added to the dissolver solution little by little while stirring with a magnetic stirrer at 20 °C for about 120 min. The precipitate produced out of the solution was separated from the mother liquor by suction filtration with a glass filter. Then, the precipitate was washed with 8 mol/dm^3 HNO_3 solution in order to remove the mother liquor, and was dried at room temperature in a glove box.

2.2. Analysis

The acidities of the dissolver solution and $CsNO_3$ solution were determined by titration (COM-980Win, Hiranuma Sangyo Co., Ltd.) and the Pu valence in the dissolver solution was confirmed as Pu(IV) by spectrometry (Ubest-55, JASCO Corporation) of the ultraviolet (UV)–visible region. The concentrations of U and Pu were measured by colorimetry and the concentration of Cs was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES; ICPS-7500, Shimadzu Corporation). The precipitate was measured in a solution prepared by the dissolution of the precipitate in 1 mol/dm^3 HNO_3 solution. The structure of the precipitate obtained in these experiments was characterized by XRD (RINT 2000/PC, Rigaku Corporation) under CuKα radiation. Thermophysical properties were measured by TG (DTG-50, Shimadzu Corporation), in which the sample was heated to 400 °C at a heating rate of 5 °C/min in a purified Ar atmosphere.

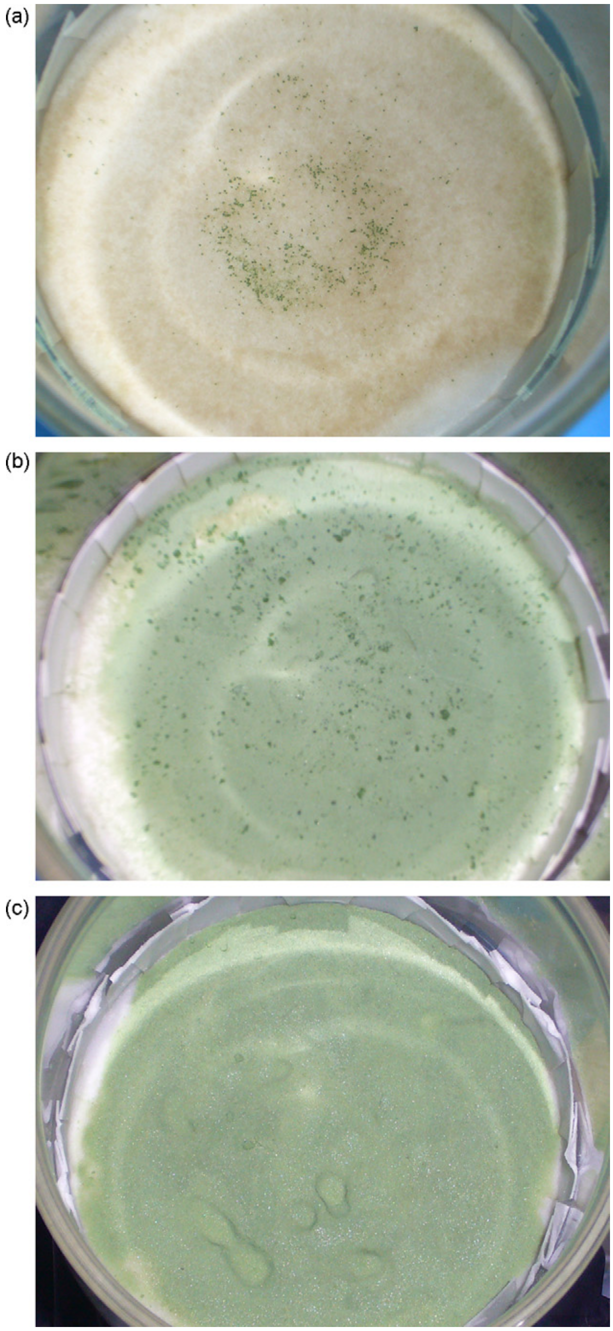

Fig. 1. Appearance of the Pu and Cs complex after separation from the mother liquor: (a) 3 mol/dm^3 HNO_3 solution; (b) 5 mol/dm^3 HNO_3 solution; (c) 8 mol/dm^3 HNO_3 solution.

3. Results and discussion

Fig. 1 shows the appearance of the washed precipitate from 3, 5 and 8 mol/dm^3 HNO_3 solution after separation in these experiments. The precipitates were separated from the mother liquor by filtration, dried at room temperature, and weighted. The precipitate was a pale green complex, generated in greater amounts with increase in the concentration of HNO_3 in the solution, specifically 0.17, 3.59 and 4.62 g in RUN1, RUN2 and RUN3, respectively. The concentration of U in the precipitate was under the lower measurable limit (<0.03 g/dm^3) of our analytical method. The precipitate was composed of Pu and Cs, and had the formula $Cs_nPu(NO_3)_m$, in which the n and m were estimated to be 2.0 ± 0.1 and 6.2 ± 0.3, i.e.

Table 2
Concentration of HNO_3 and metal in the mother liquor.

RUN no.	HNO_3 (mol/dm^3)	U (g/dm^3)	Pu (g/dm^3)	Cs (g/dm^3)	Temperature (°C)	System
RUN1	2.8	10.8	31.5	37.4	20	U–Pu–Cs–HNO_3–H_2O
RUN2	5.1	10.0	4.7	10.1	20	U–Pu–Cs–HNO_3–H_2O
–	6.5	–	3.4	3.8	28	Pu–Cs–HNO_3–H_2O [7]
RUN3	7.9	10.2	1.0	5.7	20	U–Pu–Cs–HNO_3–H_2O

$Cs_{2.0\pm0.1}Pu(NO_3)_{6.2\pm0.3}$. It was thus confirmed that this complex is $Cs_2Pu(NO_3)_6$ has been reported in the literature [7].

Table 2 shows the concentrations of HNO_3, U, Pu and Cs in the mother liquor in these experiments. The solubility of $Cs_2Pu(NO_3)_6$, which was reported by Anderson [7], is also listed in this table. The concentration of Pu decreases as that of HNO_3 increases in the mother liquor. The nitrate ion complex of Pu(IV) in HNO_3 solutions may be expressed as $Pu(NO_3)_n{}^{4-n}$ ($n = 1-6$). Lipis et al. [8] plotted the molar extinction coefficients evaluated at selected Pu(IV) absorption peaks as a function of HNO_3 concentration and used them to determine the nitrate coordination number of Pu(IV). The range of HNO_3 concentration where each of the complexes are stable was found to be as follows: $Pu(NO_3)^{3+}$, <1.5 mol/dm^3; $Pu(NO_3)_2{}^{2+}$, 1.5–2.1 mol/dm^3; $Pu(NO_3)_3{}^{+}$, 2.1–3.8 mol/dm^3; $Pu(NO_3)_4$, 3.8–5.6 mol/dm^3; $Pu(NO_3)_5{}^{-}$, 5.6–7.1 mol/dm^3; and $Pu(NO_3)_6{}^{2-}$, >7.1 mol/dm^3. This stability range for $Pu(NO_3)_6{}^{2-}$ is in general agreement with the conclusions of Ryan [9], who studied the nitrate complex of Pu(IV) by ion exchange and spectrophotometric methods. From the difference in the absorption peaks at 609 and 744 μm, the abundance of the $Pu(NO_3)_6{}^{2-}$ complex has been determined as a function of HNO_3 concentration; specifically, the concentration of $Pu(NO_3)_6{}^{2-}$ has been reported to be 4, 10, 29 and 50% in 5, 6, 7 and 8 mol/dm^3 HNO_3 solutions, respectively. Veris et al. [10] reported that Pu(IV) forms three major nitrate complexes, which they observed and identified by absorption spectroscopy, ^{15}N nuclear magnetic resonance (NMR) and extended X-ray absorption fine structure (EXAFS) as $Pu(NO_3)_2{}^{2+}$, $Pu(NO_3)_4$ and $Pu(NO_3)_6{}^{2-}$. Based on the difference in the absorption peaks, $Pu(NO_3)_6{}^{2-}$ was found to increase with increase in the concentration of HNO_3 in accordance with the following reactions ($n = 1-6$):

$$Pu(NO_3)_{n-1}^{5-n} + NO_3{}^{-} \leftrightarrow Pu(NO_3)_n^{4-n}. \tag{1}$$

On the other hand, $Cs_2Pu(NO_3)_6$ is generated by the following reaction:

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

A higher ratio of $Pu(NO_3)_6{}^{2-}$ is advantageous for the formation of $Cs_2Pu(NO_3)_6$. The production of the precipitate $Cs_2Pu(NO_3)_6$ increased with increase in the concentration of HNO_3 in the mother liquor. Likewise, as shown in reaction (2), although the formation of $Cs_2Pu(NO_3)_6$ might make $Pu(NO_3)_6{}^{2-}$ decrease momentarily in the mother liquor, this shift of chemical equilibrium will subsequently bring about an increase in the ratio of $Pu(NO_3)_6{}^{2-}$ in the mother liquor again by reaction (1). As a result, it will contribute to further generation of $CsPu(NO_3)_6$.

The XRD pattern of the obtained precipitate is shown in Fig. 2. Though the precipitate did not contain a significant amount of U, most of the observed peaks of the XRD agree extremely well with the peaks of $Cs_2U(NO_3)_6$ [11]. This suggests that the precipitate has a crystal structure which replaces U in $Cs_2U(NO_3)_6$ with Pu(IV).

The TG curve of the precipitate, shown in Fig. 3, was obtained in this study. This TG curve shows that there are two steps in the thermal decomposition of this precipitate. There was no observable weight loss below 245 °C, but a sharp weight loss began at around 245 °C. This decomposition reaction was completed by 297 °C, and the next sharp weight loss was observed between 315 and 380 °C. Gel'man et al. [12] reported that $Cs_2U(NO_3)_6$ is gradually oxidized to a pale yellow amorphous powder with the composition $Cs_2UO_2(NO_3)_4$ above 100 °C. At 253 °C, partial fusion takes place and two phases appear, a pale yellow solid phase consisting chiefly of $CsNO_3$, and a melt whose composition is $Cs_2UO_2(NO_3)_4$. When the melt is heated above 260 °C, it gradually decomposes with the evolution of NO_2. The final product after decomposition is a mixture of $CsNO_3$ and UO_3. Assuming that the precipitate of Cs decomposed in the same way as $Cs_2U(NO_3)_6$ in the experiment, the obtained precipitate is a result of the first step of the decomposition of $Cs_2Pu(NO_3)_6$ as follows:

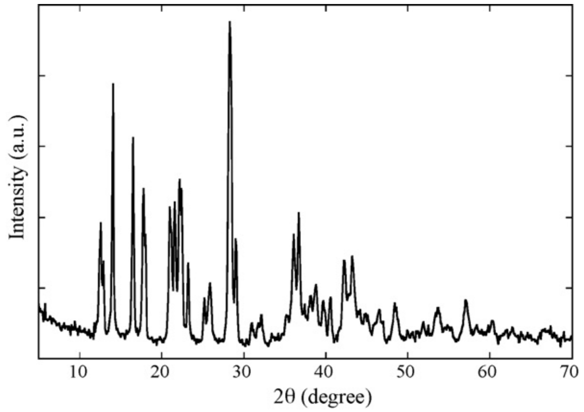

Fig. 2. XRD pattern of the Pu and Cs complex.

$$Cs_2Pu(NO_3)_6 \rightarrow Cs_2PuO_2(NO_3)_4 + NO_2 + NO + 1/2O_2. \tag{3}$$

The calculated weight loss by the reaction (3) is 10.49%, which is in good agreement with the observed weight loss seen in the first step of the TG curves, 10.29 ± 0.23% at 245 °C. When the sam-

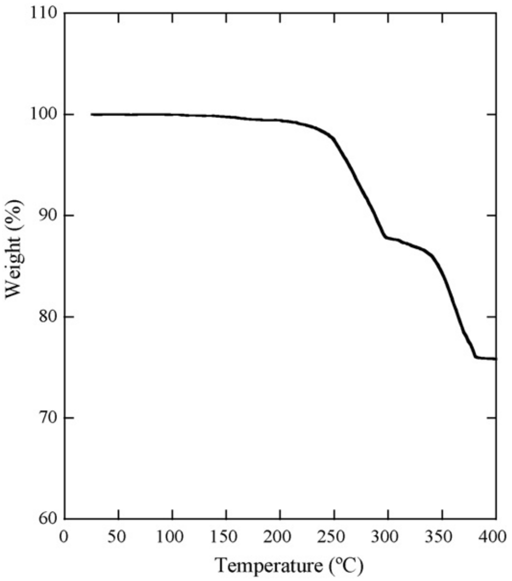

Fig. 3. TG curve of the Pu and Cs complex with a heating rate of 5 °C/min.

ple is heated above 297 °C, it gradually decomposes, and finally the sample becomes a mixture of $CsNO_3$ and PuO_2. In this reaction, the weight loss is calculated to be 14.12%, and the observed weight loss of the sample in the second step is 13.79 ± 0.61%. This result indicates that the above reaction occurred. Since the UNH crystal melts at 60.2 °C, a precipitate containing Cs, $Cs_2Pu(NO_3)_6$, which is anticipated to exist under the conditions of the U crystallization, will be stable at the melting point of UNH crystal. Therefore, according to this result, the precipitate of Cs can be separated from the UNH crystal due to their different melting points.

4. Conclusions

The characteristics of generation of dicesium tetravalent plutonium hexanitrate, $Cs_2Pu(NO_3)_6$ with dissolver solution of MOX fuel were investigated in our experimental facility, CPF. This complex was obtained as a precipitate by mixing dissolver solution of MOX fuel and $CsNO_3$ solution, which was identified as $Cs_2Pu(NO_3)_6$ by concentration analysis and XRD. The precipitate has a tendency to be generated at high HNO_3 concentrations. There was no observable weight loss below 245 °C, and at this temperature, the weight loss began. The subsequent observed weight loss was 10.29 ± 0.23%, which indicates the transformation of $Cs_2Pu(NO_3)_6$ to $Cs_2PuO_2(NO_3)_4$. We propose a new crystal purification method for better decontamination of UNH crystal, based on the difference in melting points of $Cs_2Pu(NO_3)_6$ and UNH crystal. In this method, the UNH crystal could be melted at the condition between 60 and 100 °C and separated from the Cs complex in the solid state by filtration.

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