

CO9-1 Extraction chromatography and solvent extraction of Eu using TEHDGA

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INTRODUCTION: The disposal of high level radioactive liquid waste produced from nuclear power plants is one of the main problems surrounding nuclear energy. To solve this problem, partitioning and transmutation technologies for high-level radioactive liquid waste generated from the reprocessing of spent nuclear fuel from nuclear power plants is being developed. The Japan Atomic Energy Agency (JAEA) has proposed the "SELECT Process" which involves the separation and transmutation of radioactive nuclides as a method of managing radioactive waste [e.g. 1]. The SELECT process consists of four steps, in which various extractants are used to separate minor actinides (MA) and rare earth elements (REE) from the spent nuclear fuel solution. In this study, we focused on europium (Eu), which is a REE that has two radioisotopes, ¹⁵⁴Eu and ¹⁵⁵Eu with a half-life of 8.6 years and 4.8 years respectively [2]. TEHDGA (Tetra-2-ethylhexyldiglycolamide), is a new extractant synthesized at JAEA that has both excellent extraction and separation performance for minor actinides and REE. In order to understand its chemical behavior and to compare its efficiency during different extraction methods, solvent extraction and extraction chromatography were carried out using TEHDGA on Eu.

EXPERIMENTS: The organic phase was prepared by diluting the extractant TEHDGA with a 4:1 mixed solution of n-dodecane and 1-octanol to adjust the concentration to 0.01, 0.02, 0.04 and 0.10 M. 1 ppm Eu was dissolved in 1.5 M HNO₃ for the aqueous phase. The phases were stirred for 30 mins to reach equilibrium and then separated by centrifugation. Back extraction was performed with a 0.1 M HNO₃ solution. To prepare the resin for extraction chromatography, 1 g of TEHDGA was dissolved in 50ml of ethanol (99.5% purity) to make a 0.001 M solution. 1 g of styrene divinylbenzene was added to the solution and the ethanol was evaporated. For the extraction chromatography experiment, 1.5 M HNO₃ was added to the resin and then transferred into a column. The column was attached under another column which introduced the feed solution to the resin filled column. A valve was attached between the columns to regulate the flow to ensure the resin filled column would not be saturated by the feed solution and to not disturb the resin. 10 ml of 1.5 M Eu(NO₃)₂ solution was introduced to the upper column and the eluted solution was collected in increments of 1 ml. For the batch experiment, a separate batch of resin was prepared with the same method and was shaken for

15 mins with 1.5 M Eu(NO₃)₂ and the liquid was collected. Europium concentration from all experiments were measured by Inductively Coupled Plasma Quadrupole Mass Spectrometry (ICP-QMS) at Kyoto University.

RESULTS AND DISCUSSIONS: A slope 2 correlation between the TEHDGA concentration and Eu concentration was observed (Fig. 1). This suggests that a TEHDGA : Eu = 2 : 1 complex forms in this acidity, and the following equation can be obtained.



A breakthrough curve was obtained with the extraction chromatography (Fig 2). After 5ml, the relative concentration of Eu maintains a flat peak, suggesting the resin became saturated with Eu. The number of theoretical plates was calculated as 12.2, and the height equivalent of one theoretical plane (HETP) as 2.5 mm. From the batch experiment, this value was proven to be reasonable.

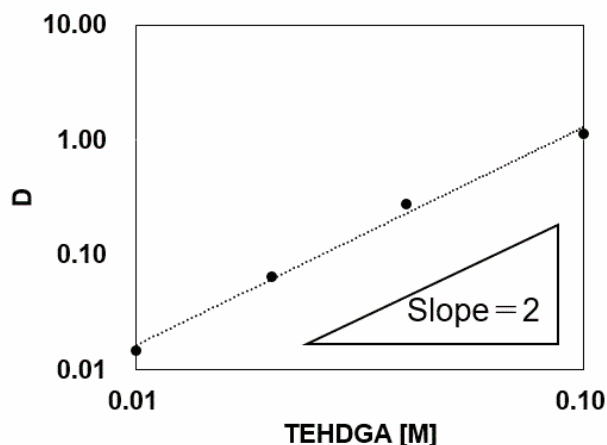


Fig. 1. Dependence of D on TEHDGA concentration for Eu.

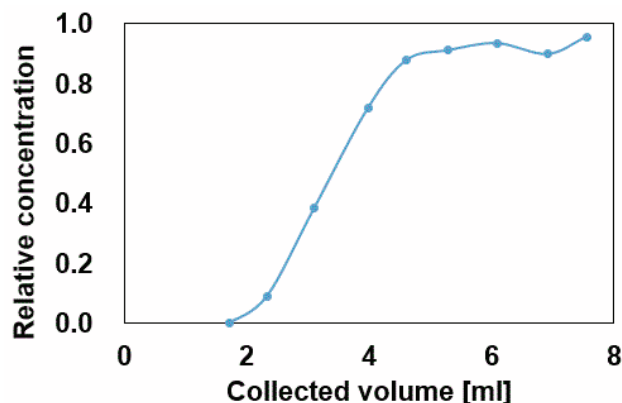


Fig. 2. Eu elution curve of extraction chromatography. Concentration is normalized to the starting Eu solution.

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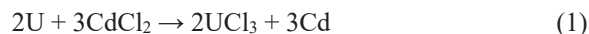
CO9-2 Electrochemical Behavior of U in NaCl-CaCl₂ Melt at 823 K

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INTRODUCTION: The mixture of NaCl and CaCl₂ is one of the promising candidates as the base salt for molten chloride salt fast reactor from the viewpoints of melting point, solubility of actinides, applicability to reprocessing, restraining of radioactive elements formation by irradiation and so on. Electrochemical properties of actinides in the melt are required for constructing a reprocessing process of the spent molten chloride fuel salt. However, reports on electrochemical measurements of actinides in NaCl-CaCl₂ melt [1, 2] are very limited. Thus, this study investigated electrochemical behavior of U to evaluate the redox potential of U in eutectic NaCl-CaCl₂ melt at 823 K.

EXPERIMENTS: All experiments were performed in a glove box filled with purified Ar gas. Eutectic NaCl-CaCl₂ melt containing UCl₃ was prepared as follows. NaCl (23.4 g), CaCl₂ (48.1 g) and CdCl₂ (0.587 g) were loaded in an alumina crucible and melted at 823 K. A U metal rod (36.0 g) was immersed in the melt for overnight to form UCl₃ in the melt,



Gibbs energy of reaction 1 is -577 kJ at 823 K [3] suggesting that almost all of CdCl₂ was consumed to dissolve U. Thus, the resulting concentration of UCl₃ in the melt was calculated to be 0.255 mol% based on reaction 1. The remained U metal rod was recovered after the completion of the reaction.

Electrochemical measurements were performed in the prepared melt at 823 K. The working electrode was W wire (1 mmφ). The Ag/AgCl reference electrode was used, of which potential was -1.255 V (vs. Cl₂/Cl⁻). Glassy carbon rod (3 mmφ) was used as the counter electrode.

RESULTS: Fig. 1 shows cyclic voltammogram of W wire electrode in the melt. A cathodic current, c1, increasing from around -2.5 V (vs. Cl₂/Cl⁻) was ascribed to U metal deposition (reaction 2),



The corresponding anodic current, a1, was due to the dissolution of the deposited U (reverse reaction of reaction 2). A broad cathodic (c2) and anodic (a2) current couple at around -1.2 V was considered to correspond to the following reaction,



The additional cathodic (c3) and anodic (a3) currents might be due to U adsorption and desorption, respectively.

Based on the results of the cyclic voltammetry, galvanostatic electrolysis at -10 mA was performed for 10 seconds to deposit U metal on the W wire electrode. Then, the applied current was set at 0 mA to measure the redox potential of the U metal on the W in NaCl-CaCl₂-0.255mol%UCl₃ melt. By using the measured redox potential ($E = -2.466$ V), the formal standard redox potential ($E^{0'}$) was calculated to be -2.325 V according to the following Nernst equation of reaction 2,

$$E = E^{0'} + \frac{RT}{3F} \ln C_{\text{UCl}_3} \quad (4)$$

R is gas constant, T is temperature in Kelvin, F is faraday constant, C_{UCl_3} is the concentration of UCl₃ in the melt. The obtained formal standard redox potential in NaCl-CaCl₂ melt (-2.325 V) was higher than that in LiCl-KCl melt (-2.466 V [4]). The difference in the formal standard redox potential indicated the stability of U³⁺ could depend on the cations of the solvent.

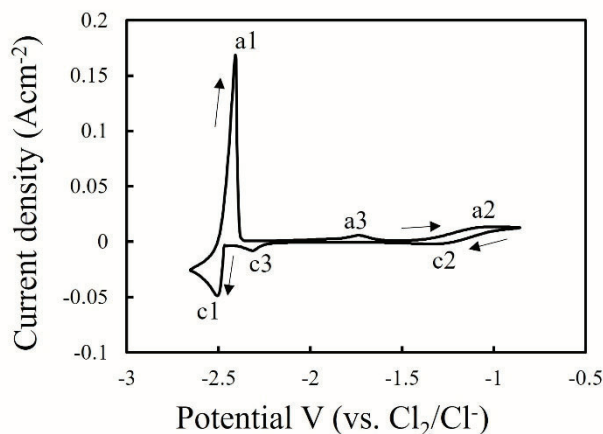


Fig. 1. Cyclic voltammogram of the W wire electrode in NaCl-CaCl₂ melt containing 0.255 mol% UCl₃ at 823 K. Scan rate was 50 mV·s⁻¹.

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CO9-3 Solid phase analysis of (Zr,Ce)O₂ solid solutions in aqueous systems

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INTRODUCTION: It is important to understand the solubility behavior of (Zr,U)O₂ solid solution in aqueous systems for the management of nuclear fuel debris generated in the Fukushima Daiichi Nuclear Power Plant accident since (Zr,U)O₂ solid solution is one of the possible major components of the debris. Many studies have been dedicated to establishing a robust thermodynamic model to quantitatively explain the solubility of ZrO₂ and UO₂, while less is known for the solubility of mixed systems. In the present study, we focused on (Zr,Ce)O₂ solid solution as an analog of (Zr,U)O₂ solid solution. In the phase diagram of (Zr,Ce)O₂ solid solution at 1000 °C, for example, pure ZrO₂ exhibits a monoclinic phase, and tetragonal ZrO₂ and cubic CeO₂ phases appear with increasing Ce molar ratio [1]. This trend is similar to that observed in the phase diagram of (Zr,U)O₂ solid solution [2]. In this study, (Zr,Ce)O₂ solid solution was prepared with the molar ratio of Zr/Ce = 7/3 at 1000 °C and characterized using powder X-ray diffraction (XRD). Then, the solid phase was placed into aqueous sample solutions under reducing conditions ranging from pH 0.8 to 8.0 for several months. After the immersion of given periods, the solid phase was separated, dried and investigated by powder XRD to elucidate the change in the state of solid phase and discuss their solubility behavior.

EXPERIMENTS: Acidic stock solutions of Zr(IV) nitrate and Ce(IV) nitrate were prepared and mixed with the molar ratio of Zr/Ce = 7/3. Portions of concentrated polyvinyl alcohol (PVA) were added to the mixed solution and heated to dryness at 200 °C. The dried powder was then heated at 1000 °C for 4 hours in a muffle furnace to synthesize (Zr,Ce)O₂ solid solution. The preparation method is known as a polymeric steric entrapment method, which enables synthesizing of metal oxide solid solution at a lower temperature [3]. The powder XRD pattern of the synthesized solid phase is shown in Fig. 1. Diffraction peaks corresponding to tetragonal ZrO₂ and cubic CeO₂ were observed in the pattern, indicating that the solid phase is a mixture. This solid phase was put into polypropylene sample tubes and aqueous solutions ranging from pH 0.8 to 8.0 with the ionic strength (*I*) of *I* = 0.5 by NaClO₄ were added to the sample tubes. It is noted that to enhance the dissolution of Ce in the solid phase, 1 mM Sn(II)Cl₂ was added as a reducing chemical. After several months, the solid phase was separated, dried in a vacuum dedicator, and investigated using powder XRD.

RESULTS AND DISCUSSION: Figure 1 shows the powder XRD patterns of the solid phase after the immersion of the sample solution at pH 1.1 and after the

immersion without Sn(II). It is noted that a peak corresponding to cubic CeO₂ at 2θ = 29° in the diffraction patterns of pH 1.1 with Sn(II) became more clear compared to that in the patterns without Sn(II) and before immersion. This suggests the possible transformation of the solid phase by contacting the reducing aqueous solution. For more detailed analysis, the diffraction patterns were analyzed using Rietveld refinement. For the initial synthesized solid phase, the obtained lattice parameter as cubic CeO₂ was slightly smaller than that of pure cubic CeO₂, indicating a portion of Zr incorporated into the cubic phase to form a cubic CeO₂-based solid solution. Similarly, ZrO₂ was considered a tetragonal ZrO₂-based solid solution, which agreed with the reported phase diagram [1]. The lattice parameters of the solid phase after the immersion without Sn(II) were the same as those of the solid phase before the immersion. In contrast, the lattice parameter of cubic CeO₂ was found to increase after the immersion at pH 1.1 with Sn(II). The composition of cubic CeO₂-based solid solution changed to decrease the Zr ratio in the solid solution. Since the change is only observed in the presence of Sn(II), the redox reaction of Ce(IV) in the solid phase may be involved. Further studies are needed to clarify the solubility behavior of (Zr,Ce)O₂ solid solution.

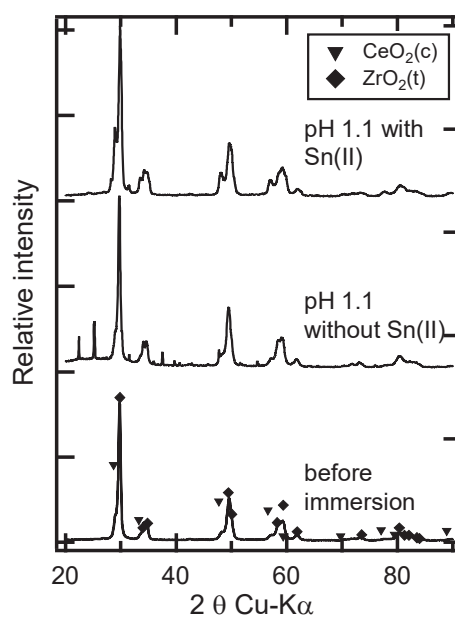


Fig. 1. Powder XRD patterns of (Zr,Ce)O₂ solid solution before and after the immersion in aqueous systems.

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CO9-4 Solid-liquid extraction and precipitation experiments of ^{47}Ca for the chemical study of nobelium

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INTRODUCTION: Element 102, nobelium (No) is a member of actinide elements. While other f-block elements stably exist at +3 or higher valence states in aqueous solutions, No is reported to form +2 valence state stably because of its electronic configuration: $[\text{Rn}]5f^{14} 7s^2$. In previous ion-exchange experiments, No is reported to exhibit similar chemical behavior to that of Ca^{2+} and Sr^{2+} [1]. Our group has recently suggested that No^{2+} shows different behavior from alkaline earth metal ions, in the samarium hydroxide coprecipitation [2]. Further systematic studies are needed on the No^{2+} comparing with group 2 elements.

In this study, we investigated precipitation behaviors of Ca, Sr, and Ba maleate and acetylacetonate to find suitable conditions for coprecipitation experiment of No.

In addition, we consider that the complexes of No having clear molecular structure in the solution should be selected to investigate the chemical properties of No because in the discussion on the data of No theoretical supports are of significant importance. We focus on solid-liquid extraction using crown ether, and have indeed performed extraction experiments with Sr resin which is commercially available crown-ether supported resin. The crown ether has extraction selectivity for alkaline earth ions, and this selectivity is sensitive to ligand ions in the aqueous solutions such as Cl^- and NO_3^- [3,4]. In addition, we plan to use the other type of crown ether resins which have reaction groups. In this study, we performed extraction experiment of Ca using crown ether resin having nitro or carboxyl group for future No extraction experiment.

EXPERIMENTS: In precipitation experiment, first 20 mL of aqueous solutions containing Sr, Ba or Ca (5 mg) were mixed with 20 mL of 0.5 M potassium maleate or 1 M acetylacetonate in ethanol, and shaken for 10-1440 min. Then, the precipitate was filtrated on a polypropylene membrane filter. For Ca sample, ^{47}Ca radiotracer was added. ^{47}Ca was produced by neutron irradiation to ^{nat}CaO powder at KURNS and chemically purified before the precipitation experiments.

In solid-liquid extraction, 0.5 mL of 2 M HCl solutions containing ^{47}Ca tracer was contacted with 50 mg of nitro or carboxyl resins for 1-30 min. After that, the resin and solution was separated through a filter unit. We synthesized the resins used in this experiment.

After the precipitation and extraction experiments, the samples were subjected to γ -ray measurement with a Ge semiconductor detector to measure the amount of ^{47}Ca . precipitation yields were estimated from the counts. In extraction, the distribution coefficients, K_d , were calculated by the equation

$$K_d = (A_{\text{STD}} - A_s)V / A_s w,$$

where A_s and A_{STD} are radioactivities of the aqueous phase of the extraction sample and the control sample which was obtained in the extraction without the resin. V is the volume of the aqueous phase (mL), and w is the mass of the dry resin (g).

RESULTS: In the precipitation experiment, almost 0% yields were obtained under all experimental conditions. When pH of the solution was higher, we were able to see the formation of precipitates for Sr and Ba; however, we cannot exclude the possibility of formation of hydroxide precipitates in high pH solutions. In conclusion, we did not find suitable experimental conditions to investigate the maleate and acetylacetonate precipitation of No.

In extraction experiment, the K_d values of ^{47}Ca were almost constant for shaking time from 1 to 30 min. This result indicates that the chemical reactions involved in the present complexation and extraction are sufficiently fast for the investigation of extraction behavior of ^{255}No whose half-life is about 3 min. Though the K_d values for nitro resin were slightly lower than those for carboxyl resin, the all values were similar and indeed range in 3-9 g/mL. For detailed discussion, further experiments in various concentrations of HCl and other acids are needed. In addition, we plan to perform extraction experiments using radiotracers of other group 2 elements. Based on the obtained data, we want to find suitable experimental conditions for extraction of No.

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CO9-5 Stability of Cyclic Monoamide Extractants for U(VI) with Longer Side Chains against γ -Ray Irradiation in HNO_3

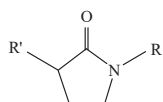
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INTRODUCTION: Uranium is the predominantly major component in spent fuels, and novel extractants with high selectivity and capacity for U(VI) and radiation stability in nitric acid media are desired in the world. Our attention as candidate extractants has been paid for 1,3-dialkyl-2-pyrrolidone (DRP) (Fig. 1), one of cyclic monoamide compounds, and previously stability against γ -ray irradiation for DRPs with straight and relatively shorter R and R', i.e., 1,3-dibutyl-2-pyrrolidone (DBP : R, R' = -C₄H₉) and 1,3-dihexyl-2-pyrrolidone (DHP : R, R' = -C₆H₁₃), was investigated[1]. In this study, DRPs with relatively longer R and R', i.e., 1,3-dioctyl-2-pyrrolidone (DOP : R, R' = -C₈H₁₇), 1,3-didodecyl-2-pyrrolidone (DDP : R, R' = -C₁₂H₂₅), and 1,3-di(2-ethylhexyl)-2-pyrrolidone (DEhP : R, R' = -C₈H₁₇) was similarly studied.



(R, R': hydrocarbon group)

Fig. 1. Chemical structure of DRP.

EXPERIMENTS: Among the above-mentioned five DRPs, only DDP is present as solid at room temperature and the other four are liquid. For the sample for γ -ray irradiation to DRPs, solutions consisting of 30 vol% DRP in *n*-dodecane as the organic phase and 3 or 6 mol/dm³ (= M) HNO_3 as the aqueous phase were prepared in a Pyrex tube (O/A=1 (v/v)). Irradiation was carried out by the ⁶⁰Co source up to ca. 1.1 MGy at room temperature under ambient atmosphere similarly to the earlier study[1]. Organic phases of the irradiated samples were then analyzed by ¹H NMR using CDCl₃ and tetramethylsilane (TMS) as solvent and internal standard material, respectively. The residual ratios of DRPs were calculated by the area ratio of each signal in DRPs with that of TMS.

RESULTS: In a ¹H NMR spectrum, neat DRP shows several signals, e.g., (A)1.7, (B)2.2, (C)3.3 ppm for DEhP. The residual ratios for DEhP irradiated with 3 and 6 M HNO_3 , respectively, were calculated from each signal and are shown in Fig. 3 together with the relationship between the position of hydrogen in the structure of DEhP and that of the signal. It can be seen for both HNO_3 concentrations that the residual ratios are decreased linearly and similarly with increasing dose up to ca. 1 MGy. Also, there is little difference in the residual ratio among the position (A) through (C).

In case of DHP[1], the residual ratios of ca. 50 % were obtained after irradiation with 6 M HNO_3 at ca. 0.75 MGy, which is similar to the result for DEhP. However, unlike the case for DEhP, the residual ratios at pyrrolidone ring (corresponding to the positions (B) and (C) in Fig. 2) were apparently lower than those at the side chains. On the contrary, for the sample irradiated with 3 M HNO_3 , nearly no decomposition occurred after irradiation at ca. 0.8 MGy, which is a different trend compared with DEhP.

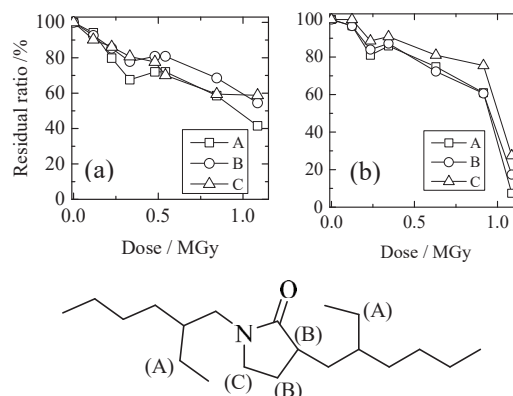


Fig.2. Dependence of residual ratio of DEhP on dose; (a) 3 M HNO_3 , (b) 6 M HNO_3 and chemical structure of DEhP.

The results for DOP and DDP obtained in a similar manner to DEhP are shown in Table 1. Summarizing these results, in general, the samples irradiated with 3 M HNO_3 are more stable than those irradiated with 6 M HNO_3 . This is in accordance with the results for water-soluble *N*-butylpyrrolidone (NBP) which has similar chemical structure to DRPs[2].

The relationship between the chemical structure of DRP and the stability remains unclear and further investigation would be necessary.

Table 1. Relationship between dose and residual ratio of DOP and DDP.

DRP	Dose / MGy	[HNO_3] / M	Residual ratio / %
DOP	0.79	3	65
DOP	0.83	6	40
DDP	0.71	6	60

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