CO9-1

Characterization of Zr(IV)-Ce(IV) coprecipitated hydroxide solid phases

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INTRODUCTION: In safety assessments for the geological disposal of high-level radioactive waste, solubility-limiting solid phase under a relevant groundwater condition is selected for each radionuclide. In the case of radionuclides that behave as tetravalent metal ions, their respective hydroxides are regarded as the solubility-limited solid phases [1]. On the other hand, in actual disposal environments, various elements not only radioactive but also non-radioactive leached from the waste form to coexist in groundwater. Therefore, when tetravalent metal ions precipitate as hydroxides, there is a possibility of forming co-precipitated solid phases with different elements. This study focuses on the state of the coprecipitated solid phase composed of cerium as a lanthanide and zirconium as an analog of a tetravalent actinide. The mother solutions are mixed with given molar ratios, and the coprecipitated hydroxide solid phase is generated under different temperature and pH conditions. The structure of the coprecipitated solid phase is investigated using X-ray diffraction.

EXPERIMENTS: The coprecipitated hydroxide solid phase was prepared by an oversaturation method. Acidic Ce(III) hydrochloride ([Ce] = 0.6 M) solution and acidic Zr(IV) hydrochloride ([Zr] = 0.6 M) solution were first mixed in given molar ratio ([Zr]/[Ce]=10/0, 7/3, 5/5, 3/7, and 0/10). After adjusting the ionic strength (I) to $I = 0.1$ with $NaClO_4$, small aliquots of 8 M NaOH was added to adjust the pH to 8 or 12 to form coprecipitated hydroxide solid phases. The sample solution was then aged at 25 or 70 °C for one month and the pH and Eh were measured. A portion of the coprecipitated solid phase was separated by centrifugal sedimentation, vacuum dried, and the diffraction pattern was measured using a powder X-ray diffractometer (MiniFlex600, RIGAKU).

RESULTS: In the case of [Zr]/[Ce]=10/0, no significant XRD peaks were observed except at pH=12 and 70°C, indicating that the solid phase was amorphous. On the other hand, at pH=12 and 70°C, peaks corresponding to ZrO_2(monoclinic) and ZrO_2(tetragonal) were observed. In the case of [Zr]/[Ce]= 0/10, although Ce(III) was used as an initial solution, but no diffraction peaks of Ce_2O_3 or $Ce(OH)_3$ were observed and only CeO_2(cubic) was observed. Considering the observed pH and Eh values, it was considered that Ce(III) was oxidized to Ce(IV) during the aging period at pH 8 and 12. In the diffraction patterns of the coprecipitated hydroxide solid phases ([Zr]/[Ce]=7/3, 5/5, 3/7), peaks corresponding to CeO_2(cubic) and ZrO_2(tetragonal) were observed. Both peaks became sharper at higher temperatures after the aging periods, indicating a temperature dependence of crystallization. Furthermore, since there was almost no peak shift in the CeO_2(cubic) peak due to changes in the mixing ratio with Zr, it was concluded that Zr was hardly dissolved in CeO_2(cubic). In this experiment, a Ce(III) hydrochloride was used as the initial solution. As a result, Zr(IV) may not easily enter the $Ce(OH)_3$ or Ce_2O_3 initially formed by the rapid addition of NaOH, and the Ce(III) solid phase may have subsequently been oxidized to CeO_2(cr).

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Chemical extraction of Uranium from NaCl-UCl_3 melt

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INTRODUCTION: Chloride salts have been attracting widespread attention as a fuel of molten salt fast reactor [1]. It is necessary to develop a process to recycle the used chloride fuel salt for the effective utilization of the nuclear fuel resources. Therefore, pyrochemical reprocessing process has been proposed for recycling the used salt with NaCl-$CaCl_2$ base salt, where reductive extraction of actinides (An) from the used salt is one of the main steps: An in the used salt are chemically reduced and extracted into liquid Bi by using Na or Ca as a reducing agent (reaction 1) [2].

$$An^{3+} + 3Na_{\text{in liq. Bi}}\ (\text{or } 3/2Ca_{\text{in liq. Bi}}) \rightarrow An_{\text{in liq. Bi}} + 3Na^{+}\ (\text{or } 3/2Ca^{2+}) \qquad (1)$$

In this study, to experimentally investigate the preliminary feasibility for applying the pyrochemical reprocessing process to the used salt with NaCl base salt, reductive extraction test of U from NaCl-UCl_3 salt was performed.

EXPERIMENTS: The reductive extraction test was carried out in a glove box filled with purified Ar gas. The dark brown NaCl (66 mol%)-UCl_3 (34 mol%) salt (m.p. 796 K) had been prepared by chlorinating U metal using $CdCl_2$ as the chlorination agent in NaCl at 823 K (reaction 2) [3].

$$2U + 3CdCl_{2\,\text{in NaCl}} \rightarrow 2UCl_{3\,\text{in NaCl}} + 3Cd \qquad (2)$$

The prepared NaCl-UCl_3 (1.642 g) was melted at 821 K in alumina crucible. To proceed with the reductive extraction reaction (reaction 3), Bi-0.4wt%Na alloy and Bi metal were added to the melt in three parts.

$$U^{3+} + 3Na_{\text{in liq. Bi}} \rightarrow U_{\text{in liq. Bi}} + 3Na^{+} \qquad (3)$$

The total amounts of the added Bi-0.4wt%Na alloy and Bi metal was 19.379 g and 17.611 g, respectively. According to phase diagram of NaCl-UCl_3 system [4], solid NaCl would be deposited when the concentration of UCl_3 in the melt decreases below around 30 mol% along with the progress of the reductive extraction reaction (reaction 3). To collect the deposited NaCl, MgO tube (6 mm in diameter) was inserted in the melt during the experiment, since NaCl is expected to be deposited preferentially on the surface of MgO of which crystal structure is same as that of NaCl.

RESULTS: After the reductive extraction experiment, MgO tube was removed from the melt. It was found that the surface of the MgO tube was covered by solid deposits together with small amount of brown NaCl-UCl_3 adhered salt (Fig. 1). The solid deposits were considered to be NaCl. The deposits will be analyzed by SEM-EDX in the future. The obtained results might suggest the possibility to construct a simple pyrochemical reprocessing process: Actinides would be recovered together with the NaCl base salt at the reductive extraction step, leaving fission products in the used salt. Then, the recovered actinides could be chlorinated in the recovered NaCl base salt to produce the recycled fuel salt.

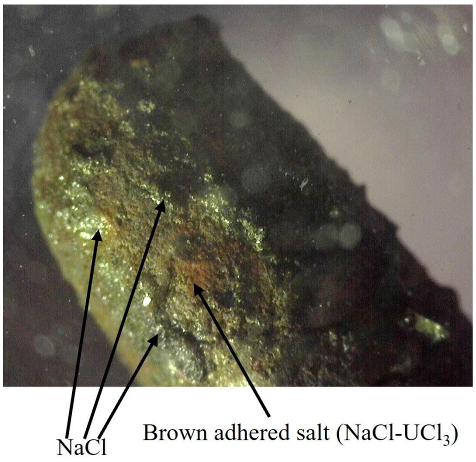

Fig. 1. Photograph of the surface of MgO tube after reductive extraction of U from NaCl-UCl_3 melt at 821 K.

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CO9-3

Coprecipitation of Ca and Sr with europium oxalate for chemical research on element 102, nobelium

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INTRODUCTION: Element 102, nobelium (No), is an actinide element. Nobelium preferentially exists as the +2 oxidation state in aqueous solutions [1] and exhibits similar chemical behavior to that of alkaline-earth metal ions, unlike the other actinides. Furthermore, it was reported that chemical properties of No were similar to those of Sr [2,3]. On the other hand, in our previous research, the coprecipitation behavior of nobelium was observed to be closer to that of Ca[4]; while the No^{2+} ions were almost quantitatively coprecipitated with calcium oxalate (~100%), Sr^{2+} ions showed about 40% co-precipitation yield under the same conditions. It was difficult to compare the differences of relative yields between Ca and No because both Ca and No (co-)precipitated with almost 100% yield. Therefore, other carrier elements are required to compare relative yields of Ca and No. In this study, we aim to compare the behaviors of No with that of Ca and Sr in oxalate coprecipitation systems. To achieve this, coprecipitation experiments of No must be carried out under conditions where the co-precipitation yield of Ca is not quantitative. For this purpose, a different carrier element was used instead of Ca. We selected europium (Eu) as the new carrier element and conducted the coprecipitation experiments of Ca and Sr with europium oxalate towards the future coprecipitation experiment of nobelium.

EXPERIMENTS: ^{85}Sr tracer was produced in the ^{nat}Rb (d,xn) ^{85}Sr reaction at the RIKEN AVF cyclotron and chemically separated from the target material to ensure its carrier-free state. In addition, ^{47}Ca was produced by thermal neutron irradiation of a ^{nat}CaO target at 5 MW for 1 h using a pneumatic irradiation system of Kyoto University Research Reactor, and it contained macro ^{nat}Ca as a carrier. Oxalate (4–200 mM) and europium nitrate (2 mM) solutions were used, and pH was adjusted to 1.5 with nitric acid and sodium hydroxide solution. Then, 5 mL of each solution was mixed at room temperature with 10 μL of a ^{47}Ca or ^{85}Sr tracer solution in 10^{-2} M nitric acid and stirred for 3 min. The precipitates were subsequently collected by suction filtration, and the radioactivity of ^{47}Ca or ^{85}Sr in the precipitates was quantified using a Ge semiconductor detector.

RESULTS: The coprecipitation yield of ^{85}Sr increased monotonically from 10.9 ± 1.8% to 90.1 ± 3.1% in the oxalate concentration range of 2–50 mM and did not reach either 0% or 100%. These yields are suitable for direct comparison of the coprecipitation yield of nobelium. In addition, the Sr yields sensitivity to oxalate concentration suggests that the coprecipitation behavior of Sr involves complex formation. In the coprecipitation experiments for Ca, the coprecipitation yield improved with increasing oxalate concentration above 25 mM; however, the yield was lower than that of Sr. This behavior is different from that predicted based on calcium oxalate precipitation. This maybe suggest that high concentration of Ca ions in the non-carrier-free tracer solution influences the co-precipitation behavior of Ca with europium oxalate.

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Investigation of Group 1 Element Adsorption on $K_2Zn_3[Fe(CN)_6]_2$ Toward the Chemical Characterization of Francium

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INTRODUCTION: Francium (Fr), the element with the highest atomic number among the Group 1 elements, is theoretically predicted to exhibit ionization potentials and electron affinities that deviate from the trends observed in its lighter congeners due to significant relativistic effects [1–3]. However, as Fr has no stable isotopes and is subject to substantial experimental constraints, direct empirical data supporting these theoretical calculations are extremely limited. The objective of this study was to establish an experimental methodology to quantitatively evaluate the chemical properties of Fr and the influence of relativistic effects. Specifically, focusing on the monovalent cation adsorption properties of complex salts composed of ferrocyanide ions and transition metal ions, we developed a method to estimate the standard Gibbs energy ($\Delta G°$) for the adsorption reactions of Rb^+ and Cs^+ onto $K_2Zn_3[Fe(CN)_6]_2$. Furthermore, we evaluated the feasibility of applying this method to experiments involving the short-lived Fr.

EXPERIMENTS: For the experiments using ^{86}Rb, a hydrochloric acid solution of Rb_2CO_3 containing ^{86}Rb produced via neutron irradiation at the Pn-2 facility of the KUR was employed. For ^{137}Cs, a commercially available ^{137}Cs solution was used. First, $K_2Zn_3[Fe(CN)_6]_2$ was synthesized following a previously reported method [4] and immersed in a KCl solution to saturate the interstitial sites with K^+ ions. This solid phase was then mixed and shaken with solutions containing $^{86}Rb^+$ or $^{137}Cs^+$, followed by solid-liquid separation via vacuum filtration. The radioactivity of ^{86}Rb or ^{137}Cs in each phase was measured using a Ge detector to calculate the adsorption rate. In this study, we first investigated the time required to reach adsorption equilibrium and subsequently conducted adsorption experiments to calculate $\Delta G°$. Additionally, assuming Fr experiments where handling at tracer levels (ultra-low concentrations) is mandatory, we examined the concentration dependence of $\Delta G°$ in the low-concentration region using Cs^+.

RESULTS: It was confirmed that the adsorption of Rb^+ and Cs^+ reached equilibrium within approximately 3 minutes. This indicates that the current system is sufficiently applicable to experiments targeting Fr isotopes with half-lives ranging from several minutes to several tens of minutes (e.g., ^{223}Fr). The maximum adsorption capacity per unit mass of $K_2Zn_3[Fe(CN)_6]_2$ was determined using a Langmuir plot, and subsequently, the equilibrium constants and standard Gibbs energies were estimated using Kielland plots. As a result, the $\Delta G°$ values for Rb^+ and Cs^+ were found to be -4.51 ± 0.42J/mol and -10.98 ± 1.15 kJ/mol, respectively, which are consistent with the observed adsorption rate trends.

On the other hand, the $\Delta G°$ obtained from the Cs^+ experiments in the low-concentration region was -2.2 ± 0.4 kJ/mol, showing a positive deviation compared to the values estimated from high-concentration data. This discrepancy is likely due to the increased relative contribution of adsorption site heterogeneity and physical adsorption, in addition to the chemical ion-exchange reaction, in the low-concentration regime. Moving forward, we plan to optimize the experimental conditions to minimize the contribution of physical adsorption, aiming for a smooth transition to Fr experiments.

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