CO9-1

Preparation method of NaCl–UCl_3 salt

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INTRODUCTION: NaCl(66 mol%)–UCl_3(34 mol%) salt (m.p. 796 K) is a promising candidate for a fuel salt of molten chloride salt fast reactor [1]. Reprocessing of the used fuel salt is crucial for effective utilization of nuclear resources. A reasonable reprocessing process for the used fuel salt is expected to be developed by applying pyrochemical technologies which have been established for recycling the used metallic fuel [2–3]. In this study, a chlorination of U metal by $CdCl_2$ in NaCl was studied to prepare NaCl–UCl_3 salt which will be used to obtain the basic properties for developing the pyrochemical reprocessing process of the used fuel salt.

EXPERIMENTS: The preparation of NaCl–UCl_3 salt was performed in a glove box filled with purified Ar gas. A mixture of NaCl(1.515 g)–$CdCl_2$(3.655 g) salt was loaded in Ta crucible (13 mm inner diameter, 35 mm height). Then, the mixture was melted at 823 K together with U metal rod (φ6 mm, 34.426 g) for overnight to convert NaCl–$CdCl_2$ melt to NaCl–UCl_3 melt by proceeding the following chemical reaction.

$$2U + 3CdCl_2 \rightarrow 2UCl_3 + 3Cd \qquad (1)$$

A largely negative value of Gibbs energy of reaction (1) (ΔG = –577 kJ at 823 K) indicates that $CdCl_2$ initially added would be consumed to form UCl_3 and Cd when excess amount of U metal is supplied. Thus, in the present experimental condition, it was expected to form NaCl(1.515 g, 66.1 mol%)–UCl_3(4.588 g, 33.9 mol%) salt and Cd metal (2.238 g) with almost no remaining $CdCl_2$.

(a) Formed Cd metal

(b) Recovered salt

Fig. 1. Pictures of (a) formed Cd metal and (b) recovered salt after the experiment.

RESULTS: After the experiment, the resulting salt, the Cd metal formed, and the U metal rod were recovered (Fig. 1). The weight loss of the U metal rod was 3.218 g which was close to the amount of U metal (3.170 g) to consume all $CdCl_2$ according to reaction (1). The weight of recovered salt was 6.109 g, which agreed well with the expected value (6.103 g = 1.515 g + 4.588 g). The amount of recovered Cd metal (1.505 g) was smaller than the calculated value (2.238 g), which might be explained by that a part of the formed Cd metal would evaporate during the experiment due to its relatively low boiling point (1040 K). These results indicated the feasibility of the method to prepare NaCl–UCl_3 salt with the expected composition using chlorination of U metal by $CdCl_2$ in NaCl. The detailed composition of the obtained NaCl–UCl_3 salt will be quantitatively analyzed in near future.

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CO9-2

Characterization of tetravalent actinide hydroxide coprecipitated solid phase

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INTRODUCTION: Safety assessment of geological disposal requires a reliable prediction of radionuclide migration behavior under repository conditions. Tetravalent actinides such as Th(IV), U(IV), and Pu(IV) easily precipitate to form amorphous hydroxide ($M(OH)_4(am)$) and play a role in controlling their solubility in groundwater. Under considerable time span during the safety assessment, $M(OH)_4(am)$ is expected to transform into more thermodynamically stable crystalline oxide: $MO_2(cr)$ [1]. Although previous studies have investigated to reveal the state of $M(OH)_4(am)$ and the process of their transformation to $MO_2(cr)$ for each actinide [2,3], multiple nuclides would coprecipitate under actual disposal conditions. In the case of the coprecipitated solid phase consisting of multiple nuclides with different stabilities, the solubility-limiting solid phase and its transformation process may be different from those consisting of a single nuclide. In this study, coprecipitated solid phases of Th(IV) and Zr(IV) amorphous hydroxide were prepared and aged under elevated temperature conditions. The solid-phase state was investigated using powder X-ray diffraction (PXRD) to interpret the solubility.

EXPERIMENTS: In the experiment, amorphous hydroxide coprecipitates of Th(IV) and Zr(IV) ($(Th,Zr)(OH)_4(am)$) were prepared by an oversaturation method. Mother solutions of Th hydrochloric acid ([Th] = 0.1 M) and Zr hydrochloric acid ([Zr] = 0.1 M) were mixed in a given molar ratio, and the pH was adjusted to 8 or 12 with NaOH. The sample solutions containing the coprecipitated solid phase were settled at 25 or 70 °C for one month. The supernatant of each sample solution was then ultrafiltered (10 kDa membrane), and the metal ion (Th, Zr) concentrations in the filtrate were quantified by ICP-MS. In addition, a portion of the coprecipitated solid phase was dried in a glove box, and the diffraction pattern was measured by a powder X-ray diffractometer (PXRD).

RESULTS: In the PXRD pattern, diffraction peaks corresponding to ZrO_2 (monoclinic) were observed in the case of the sample prepared from only Zr mother solution, and diffraction peaks corresponding to ThO_2 (cubic) were observed when prepared from only Th mother solution. On the other hand, in the samples co-precipitated from a Th and Zr mixed solution, the peaks tended to become broader as the [Th]/[Zr] ratio approached 5/5. This suggests that the coprecipitated solid phase would be more stable as amorphous, consisting of small particles. The solubilities of Th and Zr in the coprecipitated solid phase were found to decrease with decreasing [Th]/[Zr] at the same pH. It is known that when the size of the solid phase particles is sufficiently small, the solubility increases inversely proportional to the particle size due to the particle size effect [3]. Therefore, the solubility of coprecipitated $(Th,Zr)(OH)_4(am)$ was interpreted, taking into account the particle size effect on solubility based on the results of PXRD.

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CO9-3

Neutron Irradiation of Zn-Coated Stainless Steel Foil

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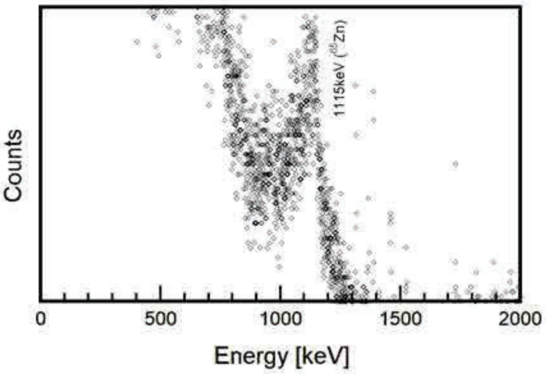
INTRODUCTION: One of the methods to control the accumulation of ^{58}Co and ^{60}Co, which are generated in the nuclear reactors, is to inject Zn into the cooling water. The Zn injection increases ^{65}Zn concentration via the neutron capture of a stable isotope ^{64}Zn. Hence, preparing ^{64}Zn depleted materials is required. In our previous study[1,2], the isotope separation of Zn has been tested by employing solvent extraction and liquid chromatography with a macrocyclic polyether, 1-aza-15-crown-5-ether. Possible magnitudes of isotope fractionation have been found. In the present study, electroplating of Zn onto a stainless steel (SUS304H) foil as a mechanism of depressing ^{58}Co and ^{60}Co was performed. Fragments of the Zn-coated foil were irradiated by neutrons at KUR, and ^{65}Zn generation has been confirmed.

EXPERIMENTS: All chemicals used were analytical grade. A sample solution of 0.1 mol dm^{-3} (M) $Zn(NO_3)_2$ was prepared. A stainless steel foil was immersed in the solution and electroplating of Zn onto the foil was performed. As a working electrode, a SUS304H foil of 0.02 mm in thick(5mm in width x 40 mm in length) was used. A reference electrode of Ag/AgCl and a counter electrode of Pt wire were used. The electroplating was run at -1.4 V for 10 to 100 min. After the electroplating, the foil was rinsed by water and dried at room temperature. The dried foil was then cut into pieces of 10mg each. One of the pieces was irradiated in a pneumatic irradiation system of the Kyoto University Research Reactor, where the thermal neutron flux is 2.3 x 10^{13} n/cm^2/sec. After the irradiation, gamma spectrometry was performed.

RESULTS: As shown in Fig. 1, clear gamma spectrum was obtained for the Zn-coated foil. A characteristic gamma-ray of 1115.5 keV emitted from ^{65}Zn was found. This indicates that, even by using ^{64}Zn depleted materials, the Zn coating onto the stainless steels may be possible.



F ig. 1. Gamma spectrum of a Zn-coated stainless steel foil irradiated at KUR

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CO9-4

Development of a barium malonate coprecipitation method for the chmiecal study of element 102, nobelium

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INTRODUCTION: Nobelium (No, Z = 102) is an actinide element and has distinctive properties among f-block elements in that it is stable as a divalent cation in aqueous solutions [1]. Previous studies compared the behavior of No with that of transition metals and group 2 elements and concluded that No behaves like group 2 elements as a hard acid. However, due to low production rates and short half-lives of No nuclides, chemical researches on No are very limited. In our group, extraction and coprecipitation methods for heavy elements [2] have been developed and applied to No. As a result, we found that No exhibits soft acid behavior. For further chemical study of No, we plan to investigate the complexation of No^{2+} with oxalic and malonic acids, which are expected to form covalent bonding involving its d- and f-orbitals. These dicarboxylic acids function as chelating ligands, forming stable precipitates with numerous metal ions including group 2 elements. The objective of this study is to investigate the chemical properties of No by comparing chemical bonding properties and ligand size effect on malonate complexation for No and group 2 elements. This paper presents the (co-)precipitation experiments of group 2 elements in malonic acid.

EXPERIMENTS: A) Malonic acid precipitation experiment with macro amounts of group 2 elements. Malonic acid buffer solution at pH = 7 was prepared by dissolving malonic acid (1.370 g) and disodium malonate (3.973 g) in distilled water (200 mL). 10 µL each of ^{47}Ca, ^{85}Sr, or ^{133}Ba were added to the metal (Ca, Sr, or Ba) chloride solution at room temperature and stirred for 5 min to form precipitate. After suction filtration, radioactivity of ^{47}Ca, ^{85}Sr, or ^{133}Ba in the filtrate and collected precipitate were determined by gamma-ray measurement with a Ge detector to evaluate the precipitation yield. B) Coprecipitation experiment of ^{47}Ca and ^{85}Sr with barium malonate. Coprecipitation experiments of ^{47}Ca and ^{85}Sr with Ba selected as the carrier element were performed and the behavior was compared with the precipitation behavior. The ^{47}Ca used in the experiments was produced by thermal neutron irradiation of a ^{nat}CaO target at 5 MW for 1 h at KURNS.

RESULTS: In the precipitation experiments, Ca and Sr were unreactive with malonate ions, while Ba formed crystalline precipitates and chemical reactions reached to equilibrium state within 1 min. From chemical simulation based on the malonate complexes formation constants and dissociation constants of malonic acid, the equilibrium concentration products for Ca and Ba malonate at pH 3 and Sr malonate at pH 4 exceeded their solubility products, suggesting thermodynamically favorable precipitation. The low yields of Ca and Sr are due to their slow reaction kinetics. In the coprecipitation experiments, Ba was selected as the carrier element under malonic acid conditions of pH 7. The co-precipitation yields of Sr were higher than those of Ca with largely different ionic radius from that of Ba. Reaction kinetics of Ca and Sr were fast in the presence of carrier element Ba (faster kinetics). Neutral metal complex concentrations at equilibrium are estimated from chemical simulations, and their proportion reflects coprecipitation efficiency qualitatively. These findings suggest that complex stability in solution influences coprecipitation behavior, and the stability of the No–malonate complex can be examined using the barium malonate coprecipitation method.

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