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INTRODUCTION: The randomly cross-linked heterogeneous and macromolecule properties of humic substances (HSs) as natural organic matter would be influenced by radiation, in soils, sediments, and natural waters. When the HS in underground water contacts with a radioactive waste package at repository site, the chemical property of HS should be altered by gamma irradiation and the ability of complex formation may be decreased. The acid dissociation constant and the apparent formation constant of radionuclides with HS changes depending on the solution conditions such as pH, metal and HS concentrations, and ionic strength. In the present study, the HS samples irradiated by Co-60 gamma-ray source were characterized by potentiometric titration.

EXPERIMENTS: The gamma-ray irradiation was performed in the gamma-ray irradiation facility in Kyoto university research reactor institute (KURRI) with TBq ⁶⁰Co source. Aqueous solution of Aldrich humic acid abbreviated to HS (Sigma-Aldrich Co.) sealed into glass vessels without air removing were set at positions of 1 kGy/h for high dose rate. The applied doses were 0 - 500 kGy by controlling the irradiation period between 0 - 500 h. The initial concentration of proton-exchanging sites C_R in meq/g for HS is known value. Each sample solution containing 1 meq/dm³ of HS was prepared by dissolving the solid humic substance in 0.1 M NaOH and then 0.1 M HClO₄ to neutralize alkali solution. The ionic strength was controlled by 0.1 M NaClO₄. After irradiation, the solution pH values were slightly decreased, then the pH was readjusted to ca. 8. On the other hand, no pH shift has been observed under no gamma-irradiation condition.

The titration was conducted using an automatic titrator, equipped with a microburette, combination glass electrode, and polyethylene centrifuge tubes in a water bath at 298 ± 0.5 K under a nitrogen gas atmosphere. A combined glass electrode was used to measure the pH, and the reference electrode was filled with a mixed solution of 3.6 M NaCl and 0.4 M NaClO₄ in order to prevent precipitation of KClO₄ at the junction of the electrode and the solution. The calibration of the glass electrode for conversion of the millivolt readings into pH was conducted with a blank titration using 0.1 M HClO₄ and 0.05 M NaOH + 0.05 M NaClO₄ standard solutions. The millivolt readings of the glass electrode were compared with $-\log[H^+]$ (= pH) calculated from the added NaOH concentration assuming NaOH was completely dissociated under the titration conditions.

RESULTS: The experimental titration of HS at $I = 0.1$ (NaClO₄) was conducted from an initial pH of ca. 2.5 to 10.5. As shown in Fig. 1, the fitted values of (R⁻) increased with increasing pH_c. These curves showed no clear point of neutralization, which suggested polyelectrolytic properties and heterogeneity of functional groups for each binding site.

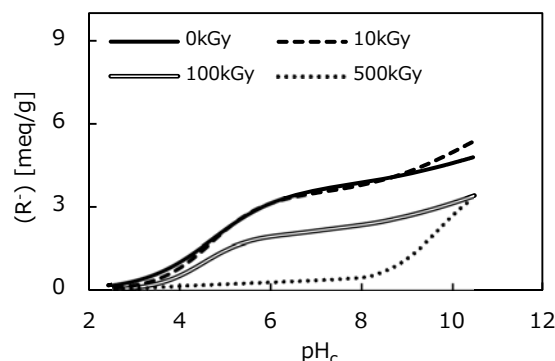


Fig. 1 Irradiation dose effect on the the total carboxylic and phenolic group concentrations of HS, (R⁻).

The plots as a function of pH_c were fitted by non-linear least-squares fitting analysis according to Eqs. (1) and (2).

$$[R^-] = 10^{-pH_c} - 10^{(pH_c - pK_w)} - \frac{c_{Na}V_{ini} + c_{Na}V_{add} - c_{ClO_4}V_{ini} - c_{ClO_4}V_{add}}{V_{ini} + V_{add}} \quad (1)$$

$$[R^-] = (R^-)^j \quad (2)$$

where c_{Na} and c_{ClO_4} are the concentrations of sodium and perchlorate ions in the initial test solution, c'_{Na} and c'_{ClO_4} are the concentrations of the titrant solutions, V_{ini} is the initial volume, V_{add} is the added titrant volume. At a given I , the [R⁻] in eq/dm³ is defined by the sum of two dissociated functional groups of HS (R⁻) in meq/g and j g dissolved in V mL solution. The fitted curves reproduced the experimental data well, and some general parameters of acid dissociation [1] could be determined as summarized in Table 1.

Table 1 Fitted parameters for HS

Dose	C^{W_1}	C^{W_2}	$\frac{\log K_1}{1 - m_1}$	$\frac{\log K_2}{1 - m_2}$	m_1	m_2
kGy	meq/g	meq/g				
0	3.56	2.82	4.70	10.84	0.42	0.71
500	0.29	3.83	3.78	9.70	0.47	0.24

REFERENCE:

[1] Kirishima, A., Ohnishi, T., Sato, N., Tochiyama, O.: *Talanta*, **79** (2009) 446.

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INTRODUCTION: Safety assessment of radioactive waste disposal requires to predict the solubility limit of radionuclides under relevant repository conditions. Isosaccharinic acid (ISA), a degradation product of cellulose found in low- and intermediate-level radioactive waste, is known to form strong complexes with radionuclides [1]. Therefore, ISA has been considered to potentially enhance the solubility of radionuclides, which possibly affects the safety assessment of radioactive waste disposal. Although several literatures have investigated the interaction of ISA with radionuclides, uranium is one of the elements, on which only very few studies have proposed the dominant ISA complexes and their formation constants. Under reducing geochemical conditions in the repository system, tetravalent state (U(IV)) is the most relevant oxidation state for uranium. Due to the strong hydrolysis reaction, U(IV) easily precipitates as sparingly soluble amorphous hydrous oxide (UO₂(am, hyd)) in the neutral to alkaline pH range [2]. The formation of soluble U(IV)-ISA complex potentially increases the apparent solubility of uranium, which can mobilize uranium in the repository system. In the present study, we focused on the solubility of U(IV) in the presence of ISA at hydrogen ion concentrations (pH_c) of 6–12 and total concentration of ISA ([ISA]_{tot}) of 10⁻³ to 10⁻¹ mol/dm³ (M). Based on the solid phase analysis and slope analysis of the solubilities, dominant U(IV)-ISA complex was revealed, and the formation constant was determined by the thermodynamic analysis of the solubility data.

EXPERIMENTS: Calcium isosaccharinate (Ca(ISA)₂) was synthesized from α-lactose and converted to NaISA stock solution. A stock solution of U(IV) was electrochemically prepared by reducing 0.06 M uranyl nitrate. Portions of concentrated NaOH solution was then added into the U(IV) stock solution to precipitate amorphous U(IV) hydrous oxides (UO₂(am, hyd)). The precipitate was washed several times and finally suspended in 20 mL of 1 mM Na₂S₂O₄ solution at around pH_c = 10. Sample solutions at specific pH_c and [ISA]_{tot} were prepared by an undersaturation method. Before adding a portion of suspended stock solution of UO₂(am, hyd) to each sample tube, pH_c was adjusted using HCl/NaOH and [ISA]_{tot} was adjusted by appropriate amount of NaISA stock solution. The ionic strength (*I*) of each sample solution was set to *I* = 0.5 using the 5 M NaCl stock solution. The sample solutions kept in polypropylene tubes were placed in glass bottles and stored under the Ar atmosphere to avoid the

oxidation of U(IV) during the experiment. After aging a given period, the pH_c was measured and supernatant was filtrated through 10 kDa membranes. U(IV) concentration in the filtrate was determined by ICP-MS and solid phase was examined by XRD after drying the samples.

RESULTS: U(IV) solubility after 3–10 weeks in the presence of 10⁻³–10⁻¹ M ISA was measured in the pH_c range of 6–12 after ultrafiltration through 10 kDa membranes. A steady state was confirmed to be achieved within 3 weeks. In the presence of ISA with a concentration higher than 10^{-2.1} M, U(IV) solubility was found to be higher in comparison with systems in the absence of ISA, depending on the pH_c and ISA concentration. U(IV) solubility was observed to be almost constant against pH_c at pH_c 6–12, indicating that four OH⁻ ions are involved in the U(IV)-ISA complex, provided that UO₂(am, hyd) is the solid phase. The slope of U(IV) against [ISA]_{tot} at around pH_c 7.2 and 10.0 was approximately 2, indicating that two ISA molecules were involved in the formation of the U(IV)-ISA complex. It is noted that no significant peak except that of NaCl(cr) was observed in the XRD patterns of the solid phase, suggesting that the initial UO₂(am, hyd) was not transformed during the experiment. The formation of U(IV)-ISA complex was then described by the equation; U⁴⁺ + 4OH⁻ + 2ISA⁻ ⇌ U(OH)₄(ISA)₂²⁻. Taking the U(IV)-ISA complex formation constant (β₁₄₂), hydrolysis constants of U(IV) (β_{1*m*}) [3], and solubility product of UO₂(am, hyd) (K_{sp}) [3] into account, U(IV) solubility ([U(IV)]) can be described as

$$[U(IV)] = [U^{4+}] + \sum_m [U(OH)_m^{4-m}] + [U(OH)_4(ISA)_2^{2-}]$$

The solubility data in the neutral to alkaline pH range were analyzed to determine the complex formation constants β₁₄₂ in the least squares fitting analysis. The formation constant was determined to be log β₁₄₂ = 50.8 ± 0.1. The increase of the U(IV) solubility in the presence of ISA was quantitatively well explained by the formation of U(OH)₄(ISA)₂²⁻.

REFERENCES:

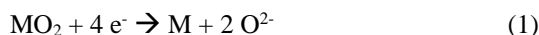
- [1] Hummel W *et al.* Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands. Elsevier, North-Holland, Amsterdam (2005).
- [2] Baes C. F., Mesmer R. E. The Hydrolysis of Cations. John Wiley & Sons, New York (1976).
- [3] Guillaumont R *et al.* Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, North-Holland, Amsterdam (2003).

CO9-3 Electronic Absorption Spectra of Tellurium in LiCl-KCl Eutectic Melt

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INTRODUCTION: The electrolytic reduction technique in LiCl-Li₂O melts has been developed for pyrochemical reprocessing of spent oxide fuels. At the cathode, actinide oxides are reduced to their metals:



where M denotes actinides such as U and Pu. Similar to oxygen, chalcogen fission products such as Se and Te are dissolved into the melt in the form of divalent anion.

Recently, the authors have been studied electrochemical behaviors of Na₂Se and Na₂Te in LiCl-KCl eutectic melt to extract Se and Te from molten salts [1,2]. It was indicated that the deposition of Te proceeded in two steps at the anode: the oxidation of Te²⁻ to Te₂²⁻ occurred followed by the oxidation of Te₂²⁻ to Te, which was similar to the electrochemical behaviors of S [3] and Se [1]. To verify the redox mechanism of Te, a spectroscopic study was conducted in this study. The absorption spectra of Na₂Se in LiCl-KCl melt have been already reported [4].

EXPERIMENTS: LiCl-KCl-Na₂Te mixture (Te: 0.51 wt%) was prepared by heating a quartz crucible containing LiCl-KCl eutectic (59:41 mole ratio, Aldrich-APL) and Na₂Te (99.9% purity, Alfa Aesar) at 773 K.

LiCl-KCl eutectic (4.077 g) was loaded in a rectangular cylinder quartz cell (10 x 10 mm) used for absorption spectrometry and heated to 723 K in an electric furnace. The experimental apparatus was previously described in detail by Nagai et al. [5] The following steps were carried out and then the absorption spectrum of the melt was measured by using an UV/Vis/NIR spectrophotometer (V-570, JASCO).

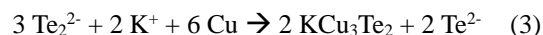
- (1) 0.118 g of the LiCl-KCl-Na₂Te mixture was added.
- (2) 0.064 g of the LiCl-KCl-Na₂Te mixture was added.
- (3) 0.099 g of the LiCl-KCl-Na₂Te mixture was added.
- (4) 0.030 g of Te (99.9999% purity, Nilaco) in an Al₂O₃ tube was immersed in the melt.
- (5) The Te was removed from the melt.
- (6) A Cu rod (φ2 mm) was immersed in the melt.

RESULTS: Fig. 1 shows absorption spectra of the melt during the steps (1)-(4). The absorption peak at ~500 nm corresponding to Te²⁻ ions was increased by adding the LiCl-KCl-Na₂Te mixture (steps (1)-(3)). The Te concentration in the melt after step (3) was determined to be 0.027 wt% by ICP-AES analysis. After Te was added into the melt by step (4), the absorption peak remarkably increased within 1.0 h, which was visually confirmed as shown in Figs. 2a and 2b. The Te concentration in the melt after 1.5 h immersion of the Te was 0.039 wt%. In addition, the peak position was slightly shifted to the shorter wavelength. Therefore, it was suggested that

about 40% of Te²⁻ was reacted with Te to form Te₂²⁻.



After the Cu rod immersion (step (6)), the absorption peak gradually decreased and the melt turned light brown as shown in Fig. 2c. The Te concentration in the melt was decreased to 0.017 wt% after the Cu rod was immersed for 2.0 h, which might be due to the deposition of KCu₃Te₂ [2].



The results of this spectroscopic study are considered to be consistent with the results of the electrochemical measurement [2]. However, the mass balance of Te in the melt should be examined in detail in future work.

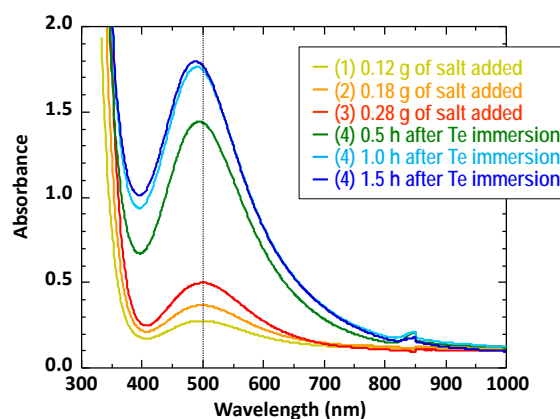


Fig. 1 Absorption spectra of LiCl-KCl-Na₂Te melt during steps (1)-(4).

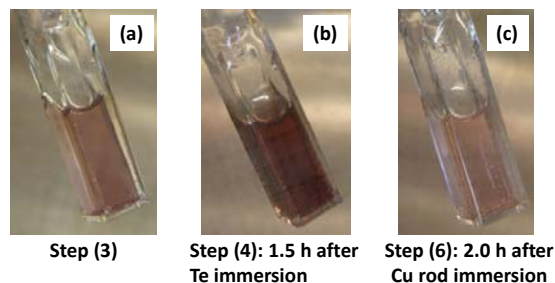


Fig. 2 The quartz cell containing LiCl-KCl-Na₂Te melt after steps (3), (4) and (6).

REFERENCES:

- [1] Y. Sakamura, T. Murakami and K. Uozumi, Proc. The 48th Symposium on Molten Salt Chemistry, p. 1, Niigata Univ., Japan, Nov. 24-25, 2016, in Japanese.
- [2] Y. Sakamura, T. Murakami and K. Uozumi, Proc. The 49th Symposium on Molten Salt Chemistry, p. 84, Kansai Univ., Japan, Nov. 30 - Dec. 1, 2017, in Japanese.
- [3] D. Warin, Z. Tomczuk and D.R. Vissers, J. Electrochem. Soc., **130** (1983) 64-70.
- [4] Y. Sakamura, T. Murakami, K. Uozumi, A. Uehara and T. Fujii, KURRI Progress Report 2016, p. 15, 2017.
- [5] T. Nagai, T. Fujii, O. Shirai and H. Yamana, J. Nucl. Sci. Technol., **41** (2004) 690-695.

CO9-4 Solvent Extraction of Uranium(VI) from Concentrated Calcium Chloride to Organic Solution

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INTRODUCTION: The extraction distribution of trivalent actinides and lanthanides between tri-butyl phosphate (TBP) and nitric acid solutions has been studied [1] and their extraction behavior has been systematically elucidated. When the concentrated electrolyte solutions such as calcium nitrate hexahydrate were used as an aqueous solution, distribution of lanthanide ions were enhanced because of the water-deficiency by which we can expect magnified appearance of ligand solvation and hydration [2,3]. We have reported that the coordination structure of UO_2^{2+} in concentrated CaCl_2 determined by X-ray absorption fine structure (XAFS) analyses changed significantly depended on the concentration of Cl^- [4]. In this study, extraction behavior of UO_2^{2+} depended on the concentration of CaCl_2 as well as H^+ was compared with the local structure of UO_2^{2+} in those solvents.

EXPERIMENTS: Solvent extraction experiments, concentrated CaCl_2 containing uranyl ion was used as aqueous solution, and dodecane containing TBP was used as organic solution. After equilibrium was attained, two phases were separated, and concentration of uranyl ion was measured by using absorption spectrometer. X-ray absorption fine structure XAFS measurement was performed at BL27B beam line in KEK. Sample solution was sealed in polyethylene bag. For the analysis of XAFS spectra, Win XAS 3.1 and FEFF 8 was used.

RESULTS: In the present report, effect of H^+ in concentrated CaCl_2 on the coordination number and bond distances of UO_2^{2+} determined by XAFS was investigated based on the results of the solvent extraction of UO_2^{2+} in the electrolyte by TBP. These figures show that the coordination numbers of Cl and H_2O to UO_2^{2+} were plotted as a function of H^+ concentration ratio. Here, total concentration of Cl^- was adjusted to be 13 M by adding water or CaCl_2 . In the absence of H^+ , about two Cl and two H_2O coordinate to UO_2^{2+} equatorial sphere to be $\text{UO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ whereas five H_2O coordinate to UO_2^{2+} in 1 M HClO_4 aqueous solution [4]. Two water molecules coordinated to UO_2^{2+} was exchanged by two TBP to be extracted into organic phase as $\text{UO}_2\text{Cl}_2(\text{TBP})_2$ resulted in higher extraction percentage. When H^+ concentration increases, coordination number of H_2O significantly decreased to one, and that of Cl slightly increased to three. It was suggested that the uranyl ion forms tri-chloro complex, which is ionic species, at high concentration of

H^+ would be formed. The extraction percentage decreased because of the ionic formation in aqueous phase.

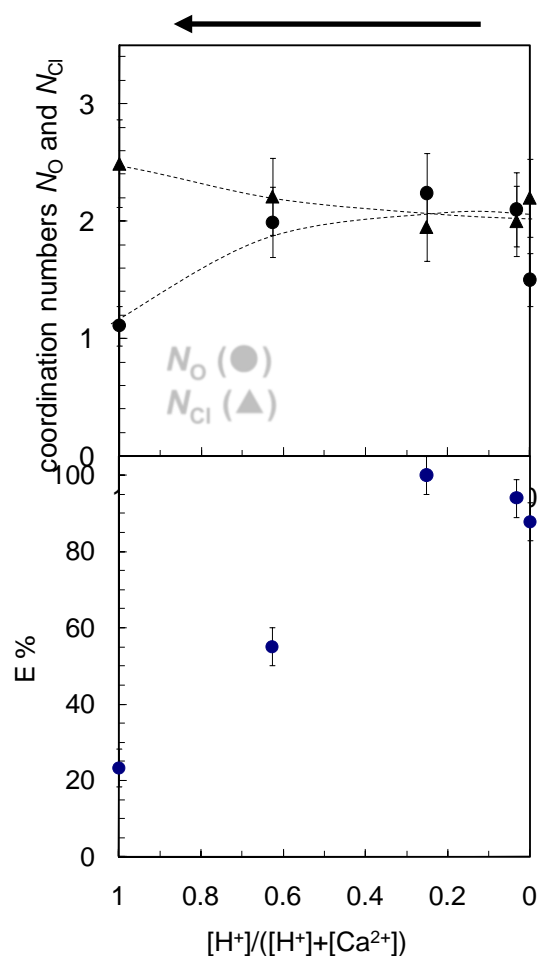


Figure 1. Coordination number of Cl and H_2O to UO_2^{2+} equatorial sphere calculated based on the R-space after Fourier transform. Extraction percentage of UO_2^{2+} between various H^+ concentration in 12 M Cl electrolyte and 0.2 M tributyl phosphate in dodecane.

REFERENCES:

- [1] G.F. Best, et al., *J. Inorg. Nucl. Chem.* **12** (1959) 136-140.
- [2] E. Akatsu, et al., *Anal. Chim. Acta.* **62** (1972) 325-335.
- [3] H. Yamana, et al., *J. Alloys Comp.* **271-273** (1998) 707-711.
- [4] A. Uehara, et al., *NEA/NSC/DOC* **15** (2009) 197-203.

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INTRODUCTION:

After the LOCA of Fukushima Daiichi NPS, the melted core reacted with coolant at high temperature forming fuel debris containing fuel and structural materials such as zirconium. Under high temperature condition in the pressure vessel, several kinds of FPs and TRU were possibly released into the cooling water mixed with seawater and the air from the melted core and its fine debris. Information on the radionuclide behavior in fuel debris and surface seawater will be helpful to analyze the forthcoming analysis data about the contents of minor FPs and TRU in contaminated water, and to manage associated secondary wastes. First, the simulated fuel debris composed of uranium and zirconium oxides with main structural materials such as steel and concrete was prepared by heat treatment in reductive or oxidative conditions. Then the dissolution behavior of typical gamma-ray fission products and neutron activated nuclides as well as uranium in solid solutions was investigated by neutron irradiation and following leaching in the non-filtrated seawater. Dissolution behavior of MA was also studied by the used of MA doped simulated fuel debris.

EXPERIMENTAL:

Several types of $\text{UO}_2\text{-ZrO}_2$ solid solution samples with different Zr concentration were prepared by heat treatments under reducing and oxidizing atmospheres. The sample was vacuum-sealed in quartz tube and irradiated for 20 min using the pneumatic transferring system (Pn-2) at KUR. For reducing the high radioactivity of short-lived nuclides, the sample was left for a given period, and then suspended in 30 ml of deionized water. After the aging time in the atmospheric condition at R.T., a 10 mL of supernatant was transferred to new sample tube after filtration with 0.45 μm (Advantec) or 10 kDa (Microcon, Millipore) membranes, followed by evaporation of the solution at 363 K in order to prepare a solidified point-like gamma source. For MA doped sample, similar preparation techniques were applied by using U_3O_8 powder doped with ^{237}Np , ^{243}Am . Gamma- and alpha ray spectrometry were performed using a Ge detector (GMX15P4, Ortec) and Si-detector (7401, Camberra) to determine the nuclides leached.

RESULTS:

Figure 1 shows the typical γ -ray spectrum of the UO_2 sample after thermal neutron irradiation at KURRI. The γ -ray peaks from FP nuclides, Cs-137, Ba-140, Zr-95, I-131, and Ru-103 were observed.

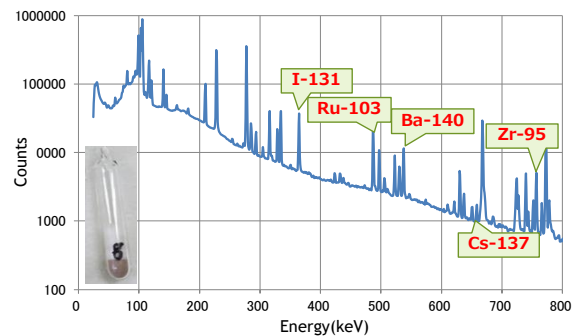


Fig.1 γ -ray spectrum of the uranium oxide sample after neutron irradiation at KURRI.

The leaching ratio of FPs for MCCI debris ($\text{UO}_2\text{-CaCO}_3\text{-SiO}_2$ component), which was prepared at 1200 °C under an aerobic condition of 2% oxygen + Ar, was determined. The UO_2 was partly oxidized to U_3O_8 , and CaUO_4 (cubic), CaUO_4 (trigonal), Ca_3UO_6 were formed with increasing the initial Ca/U ratio. One example of the leaching ratio was shown in Figure 2. The r_M values for all of FPs were higher than uranium, probably due to the facilitation of Ca leaching from the debris.

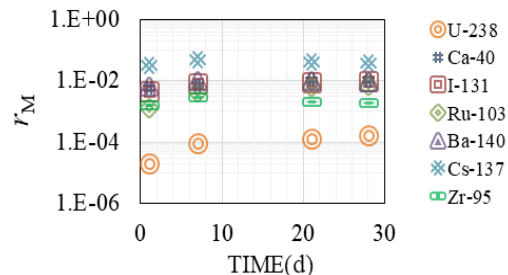


Fig.2 The leaching ratio r_M of oxidized MCCI debris.

The leaching ratio of Pu and Am was suppressed in the very low extent (0.02 % or less). The leaching of Am is expected to be suppressed to very low extent regardless of the oxidation state of Am in the solid phase since the solubilities of both Am(III) and Am(IV) are very low at the pH of seawater. The R_U value was about 0.1 % during the leaching test. From this result, it is considered that the uranium dissolution from the simulated fuel debris was governed by the solubility limitation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{am})$ or maybe their intermediate phase as discussed in our previous study [1].

REFERENCE:

- [1] T. Sasaki, Y. Takeno, A. Kirishima, N. Sato, J. Nucl. Sci. Technol., **53** (2016) 303-311.

CO9-6 Search for the Vacuum Ultraviolet Photons from $^{229\text{m}}\text{Th}$ Reacted with HF Gas

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INTRODUCTION: Thorium-229m is the extremely low energy isomeric state in ^{229}Th and the excitation energy was reported to be 7.8 ± 0.5 eV [1]. The energy corresponds to vacuum ultraviolet photon ($\lambda = 160$ nm). Because of the low excitation energy, $^{229\text{m}}\text{Th}$ is expected to change the decay mode: internal conversion or gamma-ray transition, depending on its chemical condition. Recently, it was reported that the $^{229\text{m}}\text{Th}$ neutral atom decays by internal conversion with a half-life of 7 μs , and that the $^{229\text{m}}\text{Th}^{2+}$ ion in the isolated system decays with a half-life of longer than 60 s [2, 3]. It suggests that $^{229\text{m}}\text{Th}^{2+}$ ion may decay by mainly gamma-ray transition (photon emission). However, the photons from $^{229\text{m}}\text{Th}$ have never been observed; photon detection for $^{229\text{m}}\text{Th}$ would provide valuable information to elucidate the interesting decay mechanism of $^{229\text{m}}\text{Th}$. To observe the photons, in this study we performed following experiments: First, we prepared $^{229\text{m}}\text{Th}$ as recoil products (high valence $^{229\text{m}}\text{Th}^{2+}$ ions). Subsequently, $^{229\text{m}}\text{Th}$ ions were directly reacted with hydrogen fluoride gas. Since the lowest binding energy of the outermost electron in ThF_4 is 8.3 eV [4] which is larger than the $^{229\text{m}}\text{Th}$ excitation energy, 7.8 eV, it is expected that $^{229\text{m}}\text{Th}$ is not able to decay by internal conversion. Finally, the $^{229\text{m}}\text{Th}$ sample was subjected to the photon detection.

EXPERIMENTS: In the previous experiment [5] performed in the similar manner, disturbing photon emission from the daughter nuclides of ^{233}U and ^{232}U was observed. Therefore, in this study, we purified ^{233}U by anion-exchange method using HCl solution and then, immediately prepared electrodeposited ^{233}U sample. To obtain $^{229\text{m}}\text{Th}$ ions as recoil products, the ^{233}U sample was set in the Collection Apparatus for Recoil Products (CARP) [6]. The schematic diagram of CARP is shown in Fig. 1. In collecting $^{229\text{m}}\text{Th}$ ions, He gas or He/HF mixture gas were guided into the CARP and the required voltage was applied to guide $^{229\text{m}}\text{Th}$ ions onto the copper plate. After $^{229\text{m}}\text{Th}$ was collected for several hours, the copper plate was taken and set in the photon detection chamber to perform photon detection. In the photon detection, we used the photomultiplier tube (PMT, HAMAMATSU R6836), which detects 4-10 eV photons. The PMT was cooled to about 10°C and set in vacuum.

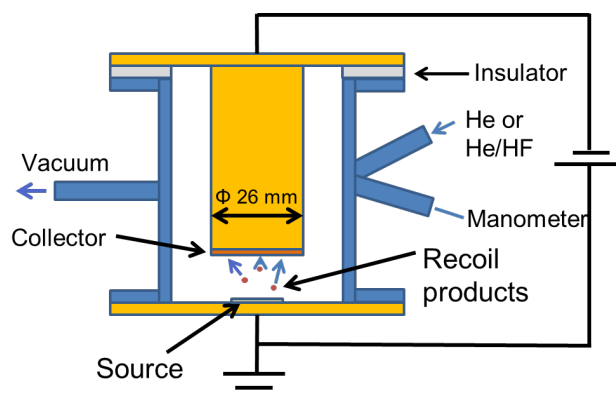


Fig. 1. Schematic diagram of CARP. Recoil products are stopped in the gas and are guided onto the collector (Cu plate) by the voltage applied between the source and the collector.

RESULTS: As a result, disturbing photon emission observed in the previous experiment [5] became negligibly small. In the previous experiment [5], decaying photon emission was observed for both the samples: collected under He gas and the sample under He/HF gas. Under He gas, $^{229\text{m}}\text{Th}$ recoils are considered to be soon neutralized and therefore the nuclide decays by internal conversion (no photons), which contradicts the result. Thus, we concluded that the observed photons originate from β -ray emitting daughter nuclides (Cherenkov) not from $^{229\text{m}}\text{Th}$. In this study using fresh ^{233}U , by contrast, no significant photons were detected for the ^{229}Th sample collected under He gas. This result means that the influence of the daughter nuclides (disturbing photon emission) was removed; we achieved low background ultraviolet photon detection for $^{229\text{m}}\text{Th}$ sample. However, for ^{229}Th sample collected under He/HF mixture gas, photon emission was also not observed. Under the present experimental conditions, $^{229\text{m}}\text{Th}$ ions might not be reacted with HF gas sufficiently. Highly charged ion is easily and rapidly oxidized in air. Pure fluorine gas should be used although it is difficult.

REFERENCES:

- [1] B. R. Beck *et al.*, LLNL-PROC-415170 (2009).
- [2] L. von der Wense *et al.*, *Nature* **533** (2016) 47-51.
- [3] B. Seiferle *et al.*, *Phys. Rev. Lett.*, **118** (2017) 042501.
- [4] N. Trautmann, *J. Alloys Compd.*, **213/214** (1994) 28.
- [5] Y. Yasuda *et al.*, *KUR Progress Report* **2016** (2017) 98.
- [6] Y. Shigekawa *et al.*, *Rev. Sci. Instrum.*, **87** (2016) 053508.

CO9-7 Investigation of Coprecipitation with Sm Hydroxide Using KUR Multitracer

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INTRODUCTION: Chemistry researches on actinide and transactinide elements at the uppermost end of the periodic table are very important in inorganic chemistry. Owing to strong relativistic effect on the electronic shells of heavy elements, their chemical properties would be unique in the periodic table. It is, however, difficult to perform chemical experiment with heavy actinide and transactinide elements because these atoms must be produced at accelerators using heavy-ion induced nuclear reactions with low production rates. Furthermore, these elements have short half-lives. Thus, we need to establish new experimental methods or apparatuses specified for these elements. For such a purpose, it is important to perform fundamental chemical experiments (with and without apparatuses) using the lighter elements whose chemical properties are known.

We previously reported the coprecipitation method with Sm hydroxide for heavy elements [1]. Indeed, suitable experimental condition for element 104, Rf, was successfully determined through fundamental experiments using homologues of Rf: Zr, Hf, and Th [2]. In the previous coprecipitation experiment [1], multitracer produced by spallation reaction of Ta in RIKEN was used to investigate the coprecipitation properties of various elements. In this work, precipitation properties of the elements contained in KUR multitracer were studied. The KUR multitracer was produced by neutron-induced fission reaction of ²³⁵U. Thus, the product nuclides are different from those in RIKEN multitracer. We expect to obtain complementary data by this experiment.

EXPERIMENTS: The KUR multitracer sample was prepared by irradiating thermal neutrons on UO₂ powder which is mixed with RbCl at KUR [3]. Fission products implanted in NaCl were dissolved in 0.01 M HCl and were separated from the UO₂ powder by a suction filtration. A portion of the sample was subjected to γ -ray measurement by a Ge detector, and count rates of γ -ray

peaks and their time dependences were measured.

In the precipitation experiment, 20 μ L (20 μ g) of Sm standard solution (1 M HNO₃) was added into the multitracer solution. After mixing it, 2 mL of basic solution was added to generate hydroxide precipitate. In the present experiment, we used dilute NH₃ solution, concentrated NH₃ solution, 0.1, 1, 6, and 12 M NaOH solutions as the basic solutions to observe the dependence of the precipitation yield on the concentration of the basic solution. Subsequently, the solution was stirred for 10 s and was soon filtrated with a polypropylene membrane filter. To check the complete precipitation of the samples, precipitate samples with stirring for 10 min after adding the basic solution were also prepared. The samples were then dried on heater at 100 degree C and were assayed for γ -ray measurements. Supernatant solutions were evaporated to dryness and were also subjected to measurements. The coprecipitation yields were determined from the results of the γ -ray measurements.

RESULTS: The product nuclides were identified from the γ -ray energies and the half-lives. To obtain correct precipitation yields, we exclude the nuclides whose decays are affected by their parent or daughter nuclide from the analysis of the coprecipitation yield. Especially, the ⁹¹Sr and ¹⁵¹Pm nuclides are of great importance for the establishment of the experimental method: Sr is comparative data for element 102, No, and Pm is near to Sm in the periodic table (Radioactive isotopes of Sm were not observed in both RIKEN and KUR multitracer). The coprecipitation experiment was succeeded and now the data are under analysis. The coprecipitation yields would be shown later.

REFERENCES:

- [1] Y. Kasamatsu *et al.*, *Appl. Radiat. Isot.* **118** (2016) 105-116.
- [2] Y. Kasamatsu *et al.*, *J. Nucl. Radiochem. Sci.* **14** (2014) 7-11.
- [3] K. Takamiya *et al.*, *J. Nucl. Radiochem. Sci.*, **1** (2000) 81-82.

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INTRODUCTION: It is of great importance to develop resins with selectivity to uranium(VI) species in nitric acid media. As a part of this purpose, we have previously investigated the change in chemical structure and adsorptivity to metal ions of a cyclic monoamide resin consisting of poly-*N*-vinyl- ϵ -caprolactam (VEC) with a 7-membered ring and polyvinylpyrrolidone (PVPP), another cyclic monoamide resin with a 5-membered ring by γ -ray irradiation in HNO_3 . The manner of structure change in these two resins has been found basically identical, namely, starting from the cleavage of the monoamide ring by the addition of oxygen atom originating from HNO_3 , followed by the formation of chain monoamides by the continuous addition of oxygen. These compounds have multiple coordinative oxygen atoms, but the change in the adsorptivity has been found different resulting probably from the number of atoms in the ring[1-3]. For these two resins, the functional carbonyl groups are located relatively close to the main polymer chain. In the present study, a resin consisting of 1-(4-vinylbenzyl)piperidin-2-one (VBPP) was newly synthesized. It has a 6-membered cyclic piperidine ring with a spacer between the functional carbonyl group and the main polymer chain. γ -Ray irradiation in HNO_3 was performed to this resin to reveal the change in chemical structure and adsorptivity.

EXPERIMENTS: VBPP was synthesized by reacting piperidin-2-one with copolymer beads of chloromethylstyrene and divinylbenzene by following the literature[4]. γ -Ray irradiation to VBPP was carried out using 6 M HNO_3 similarly to the earlier study (max. 0.95 MGy)[1]. The irradiated VBPP was separated from the supernatant liquid and washed using distilled water to avoid further degradation by HNO_3 . Adsorptivities of the irradiated VBPP to metal ions at equilibrium were obtained by a batch method. Samples of the conditioned resin (wet 0.15 g) and 3 cm³ of 0.1 - 6 M HNO_3 solutions containing 1 mM Pd(II), Zr(IV), or Mo(VI) were shaken at 298K in a thermostatic shaking bath for 24 h. After shaking, samples of the supernatant were taken and the concentrations of the metal ions were measured using ICP-OES. Adsorptivities were evaluated by the distribution ratio, K_d .

RESULTS: Adsorptivities of VBPP irradiated in 0.1 M HNO_3 at various dose to the examined metal ions are shown in Fig. 1. The K_d values for Re(VII) are found decreased with increasing dose. On the other hand, those for Pd(II) and Zr(IV) are found decreased with increasing dose. These tendencies were also observed for

the samples with the other examined HNO_3 concentrations. It has been revealed that the irradiated VEC and PVPP showed increasing adsorptivities to Pd(II) and Zr(IV), and these are in accordance with the results in this study.

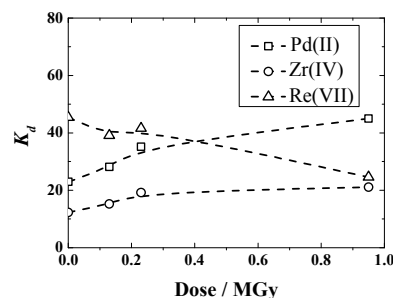


Fig. 1. Adsorptivity of VBPP irradiated in 0.1 M HNO_3 at various dose to metal ions in HNO_3

For the IR spectra of irradiated VBPP, a new peak generated at around 1730 cm⁻¹ probably attributed to a carboxyl group. In addition, no water-soluble degraded compounds were observed for the supernatant liquid separated from the irradiated VBPP by ¹H and ¹³C NMR analyses.

The above results indicate that the structure change in VBPP by γ -ray irradiation in HNO_3 occurred mainly in piperidine ring similarly to those for PVPP and VEC and that the “spacer” part underwent little influence (Fig. 2). Water-soluble degraded compounds were observed for PVPP and VEC, e.g., oxalic acid for PVPP and succinic acid for VEC, respectively. The reason why such compounds were not generated in VBPP is unclear so far.

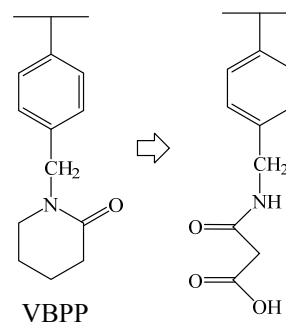


Fig.2. Expected major route of change in chemical structure of VBPP by γ -ray irradiation in HNO_3

REFERENCES:

- [1] N. Miyata *et al.*, KURRI Progress Report 2010 (2011) 258.
- [2] M. Nogami *et al.*, J. Radioanal. Nucl. Chem., **296** (2013) 423-427.
- [3] T. Nishida *et al.*, KURRI Progress Report 2013 (2014) 295.
- [4] M. Nogami *et al.*, Prog. Nucl. Energy, **50** (2008) 462-465.

CO9-9 Electrochemical Behavior of Zirconium in Molten Chloride Coexisting Fluoride and Oxide to Develop Processing Nuclear Fuel Debris

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INTRODUCTION: In order to develop processing nuclear fuel debris caused by nuclear accident of the Fukushima Daiichi Nuclear Power Plants with huge earthquake and tsunami 2011, We proposed selective fluorination and molten salt electrolysis to separate uranium from nuclear fuel debris. Process scheme is as follows; 1) selective fluorination; UF_4 was fluorinated from nuclear fuel debris using HF[1], 2) selective dissolution; UF_4 was dissolved in molten bath and 3) molten salt electrolysis; uranium ions were reduced in molten bath, and uranium metal or oxide was deposited on electrode. However coexisted zirconium can be fluorinated with uranium and zirconium oxide will be remained at the upstream process. Therefore, electro-reduction of uranium cannot be made because standard redox potential of zirconium is more positive than uranium. Zirconium electrochemistry due to the presence fluoride ions and oxide should be investigated to reduce zirconium concentration in molten bath.

EXPERIMENTS: All the electrochemical experiments using molten LiCl-KCl have been performed in an electric furnace which is built inside a glove box filled with on argon atmosphere using an electrochemical analyzer. Electrochemical analysis has been performed according to both Cyclic voltammetry and differential pulsed voltammetry by using the electrodes as follows: working electrode: tungsten, counter electrode: glassy carbon and reference electrode: silver wire dipped in molten LiCl-KCl + AgCl inside the borosilicate tube. Silica glass was used as a crucible. To observe the oxide addition effect, 0 and 10 times amount of Li_2O to the concentration of zirconium (0.1 mol%) was added to the molten bath. Constant-voltage and constant-current electrolysis has been carried out during 2000 sec to obtain a sample of characterization for SEM/EDX and XRD by using the electrodes as follows: cathode: tungsten, anode and reference electrode: silver wire dipped in molten LiCl-KCl + AgCl inside the borosilicate tube. All measurements have been performed at 823.15 K. Sweep rate was 50 mV/s and sweep potential range was -0.2 to -1.7(V vs. Ag/AgCl).

RESULTS AND DISCUSSION: As shown in Fig. 1, cyclic voltammetry of cathodic sweeps and anodic sweeps was observed mainly zirconium reduction peaks and oxidation peaks[2]. Increasing current density from -0.8 (V vs. Ag/AgCl) and reduction potential of Zr^{4+}/Zr^{2+} was observed at -1.4 to -1.0 (V vs. Ag/AgCl). Reduction potential of Zr^{2+}/Zr^0 was also observed at -1.6(V vs. Ag/AgCl). The potential of zirconium reduction to metal was not negatively shifted, while, the potential of zirconium to divalent was negatively shifted and the current of zirconium to divalent further decreasing by increasing measurement cycle. It was considered that structure of zirconium ions complex was changed by addition of oxide. Furthermore, this fact suggested that the substance with poor electrical conductivity such as ZrO might be deposited on the electrode. In the constant current electrolysis, it was confirmed that a difference in the voltage change was observed to compare containing Li_2O sample and Li_2O free sample. In the case of Li_2O free sample, the current increases or decreases drastically. It can be expected that zirconium ions concentration in molten bath decreases and the behavior of deposition of zirconium metal changes according to formula of $ZrCl_4 + 2Li_2O = ZrO_2 + 4LiCl$ [3].

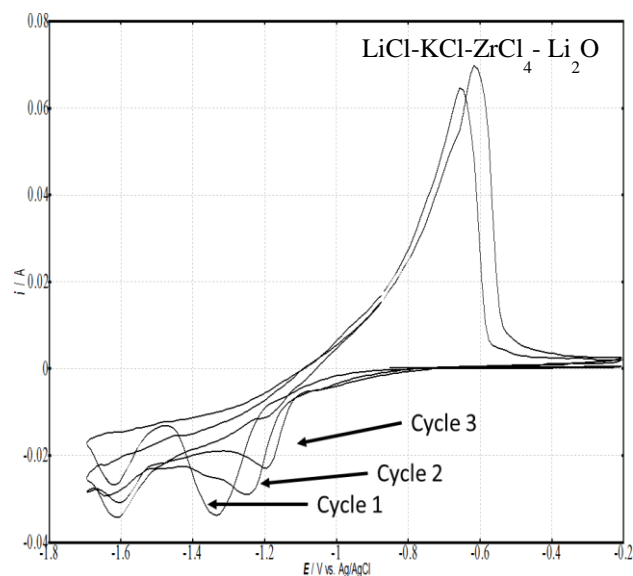


Fig.1 CV for molten LiCl-KCl containing 0.1 mol% $ZrCl_4$ and containing 1 mol% Li_2O

REFERENCES:

- [1] T. Ono, N. Sato, A. Nezu, T. Uchiyama, H. Matsuura, *ECS, Trans.*, **75**, 87, 2016
- [2] M. Iizuka, CRIEPI Report T98001, 23, 1998
- [3] Y. Sakamura, T. Kato, M. Kurata, H. Moriyama, CRIEPI Report T96073, 7, 1997