

CO9-1 Nuclides sorption onto rock samples in the presence of humic acid

T. Sasaki, Q. Zhao, T. Saito¹, R. Tonna, N. Sato², A. Kirishima², D. Akiyama², K. Takamiya¹, T. Kobayashi, S. Sekimoto¹

Graduate School of Engineering, Kyoto University

¹ Institute for Integrated Radiation and Nuclear Science, Kyoto University

² Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

INTRODUCTION: Safer handling of high-level radioactive wastes (HLW) produced from nuclear recycling is a major scientific and engineering challenge. Although the possibility of early failure of HLW packages after repository closure is low, the radionuclides (RNs) could leach to the biosphere. The sorption reaction of RNs onto host rock would be exploited as an effective barrier to inhibit the migration. Simulation-, field-, and laboratory-based studies have demonstrated that the sorption of RNs would be significantly affected by natural organic matters, such as humic acid (HA) molecules in groundwater, by complexation or colloidal formations [1,2]. In addition, the gamma rays stemming from the decay of RNs penetrate through the steel canisters of HLW with a long-term gamma irradiation field will be generated near the packages. The gamma irradiation would affect the chemical properties of HA, subsequently leading to interactions between HA and RN. Nevertheless, the effect of gamma-irradiated HA on the sorption of RN has not been clarified yet.

This study was aimed at elucidating the dependence of gamma-irradiated HA solutions on the sorption of RNs. It can enable the prediction of radionuclide migration and help establish a sorption coefficient database. For this purpose, this research was conducted on investigating the impact of gamma irradiation on the complexation of HA with non-radioactive Cs and Eu, including the apparent formation constant and the complexation affinity in terms of molecular-weight fractions.

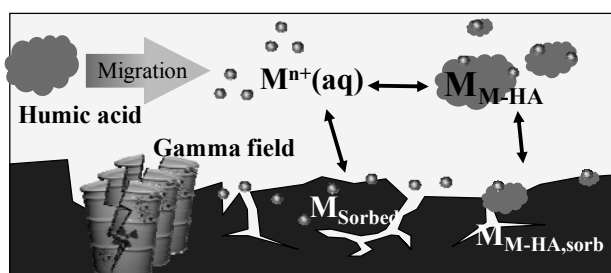


Fig. 1 Typical sorption and complexation of RNs (M) in the presence of humic acid and a groundwater systems.

EXPERIMENTS: The pH of the irradiated HA solution was adjusted to around 8. Stock metal solution was added to the HA solution to obtain an initial metal con-

centration of ca. 10^{-8} mol/dm³. The rock powder was put into a polycarbonate tube. The metal–HA solutions were either not aged or aged for a few months prior to the following process, named as the co-sorption and pre-contact systems. Samples were placed horizontally and shaken gently at room temperature. After a contact time of 1 month, the supernatant was filtered through a membrane filter with a pore size of 0.20 μ m. The filtrates were analyzed using a total organic carbon analyzer and ICP-MS for TOC and metal concentrations, respectively. For comparison, the metal concentration was also measured by using a 10 kDa pore size filter. Recovery experiments were also carried out for the loss of HA and metal ions in the metal–HA system using a 0.20 μ m pore size filter under the same experimental conditions [3].

RESULTS: Batch sorption experiments were performed to evaluate the effect of gamma-irradiated HA on the sorption reactions of Cs and Eu at neutral pH. The purified Aldrich HA in solution was irradiated by a ⁶⁰Co source at KURNS of gamma rays up to 100 kGy. The irradiation reduced the sorption coefficients of the HA molecules.

In the absence of HA, the sorption coefficient of trivalent Eu ions was as high as the reported values. In the presence of non-irradiated HA, the sorption of Eu complexed with HA was suppressed owing to the formation of neutral or negatively charged complexes in aqueous phase. Although the ratio of HA- and non-complexed species was more than 10, the ratio in the solid phase was less than 1. The ratio was evaluated based on the difference in metal and TOC concentration solutions filtered by a different pore size filter. The result indicated the ratios decreased with dose, suggesting that the metal complexation affinity of the decomposed fragments of HA was lower than that of the non-irradiated one.

On the other hand, the Cs sorption was not affected by HA and the gamma irradiation dose, probably due to a weak complexation ability of monovalent cation with HA. And, it indicates an insignificant contribution of HA to Cs sorption onto the rock surface. This new method to evaluate the molecular-weight distribution of species in liquid and solid would provide more quantitative findings of the impact of HA on the sorption of metal ions onto rock sample. Further experimental investigation of the sorption mechanism will provide more detailed insight into the different impacts of HA on RNs.

REFERENCES:

- [1] J.F. McCarthy *et al.*, T.C.J. Yeh, Water Resour. Res. 32 (1996), 1223–1238.
- [2] J.F. McCarthy *et al.*, Hydrol. 30 (1998), 49–77.
- [3] Qi Zhao *et al.*, J. Hazard. Mater., Vol. 428, 128211, 2022.

CO9-2 Solid phase transformation of lanthanide oxide to hydroxide in aqueous solutions

T. Kobayashi, R. Nanjo, Y. Sato, T. Sasaki, R. Motokawa¹, S. Sekimoto², K. Mori², K. Takamiya²

Graduate School of Engineering, Kyoto University

¹ Japan Atomic Energy Agency

² Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: For the safety assessment of high-level radioactive waste disposal, it is important to establish a robust prediction of the migration behavior of radionuclides under relevant disposal conditions. Actinides with long-half-lives behave as polyvalent metal ions and easily hydrolyzed to form amorphous hydroxide precipitates at neutral pH of groundwater. The sparingly soluble amorphous hydroxides are considered to play as solubility-limiting solid phases to dominate the migration behavior of actinides [1]. However, due to decay heat from the high-level waste, the amorphous hydroxides are possibly transformed into more thermodynamically stable solid phases during the long-time migration scenario. On the other hand, some of crystalline oxides known as stable solid phases are reported to be partly converted to hydroxides in aqueous solutions under certain conditions [2]. Although it is necessary to elucidate the stable state of solid phase in long-term disposal system, there are still some open questions on the stability of hydroxide-oxide solid phases in aqueous solutions. In the present study, we focus on the trivalent lanthanum oxide-hydroxide solid phases as chemical analogous of trivalent americium and curium. Lanthanum crystalline oxide was prepared and aged in aqueous solutions at 90 °C. After given aging periods, the solid phases were investigated by X-ray and neutron diffraction techniques.

EXPERIMENTS: Lanthanum oxide (La_2O_3) were purchased from the manufacturer and heat at 1000 °C for 2 hours to remove possible residual hydroxides. Then given amount of La_2O_3 was added in a sample solution. The sample solution was prepared by D_2O and the initial pH was adjusted to pH 8 by DCI/NaOD with small portion of pH buffer (TAPS). The ionic strength (I) was set to $I = 0.1$ by adding appropriate amount of NaClO_4 . After the sample solution with the solid phase was heated at 90 °C for 1, 3, 7 hours, the solid phase was separated and dried. In order to prevent the possible contamination of proton (H) and possible transformation by atmospheric H_2O , preparation of sample solution, aging, and drying were performed in an Ar glove box. The X-ray diffraction patterns were collected by Smartlab (Rigaku). The neutron diffraction pattern was collected by the versatile compact neutron diffractometer (VCND) located at the B-3 beam port of the Kyoto University research reactor (KUR) [3]. A Cu monochromator with 40 mm diameter was used to monochromatize the neutron wavelength of 1.0Å. The beam size was approximately 10 mm in width and 30 mm in height. The beam flux was 1.3×10^5 n/s·

cm^2 during the operation at the power of 5 MW on KUR.

RESULTS: Figure 1 shows the X-ray and neutron diffraction patterns of initial La_2O_3 and the solid phase after aging at 90 °C for 1 hour. The X-axis represent the lattice plane spacing d ($d = \lambda/2 \sin \theta$, $\lambda = 1.54$ Å for X-ray diffraction and $\lambda = 1.0$ Å for neutron diffraction). By comparing the XRD patterns before and after the aging, peaks corresponding to La_2O_3 disappeared and those corresponding to $\text{La}(\text{OH})_3$ appeared. This indicated that the initial La_2O_3 almost completely converted to crystalline $\text{La}(\text{OH})_3$ even after 1 hour. The XRD patterns of the solid phases after 3 and 7 hours aging were found to show no significant difference to that after 1 hour. Figure 1 also shows the neutron diffraction patterns of before and after the aging. The pattern seems to include both peaks corresponding to La_2O_3 and $\text{La}(\text{OH})_3$. Further confirmation is needed by the measurement of longer aging periods.

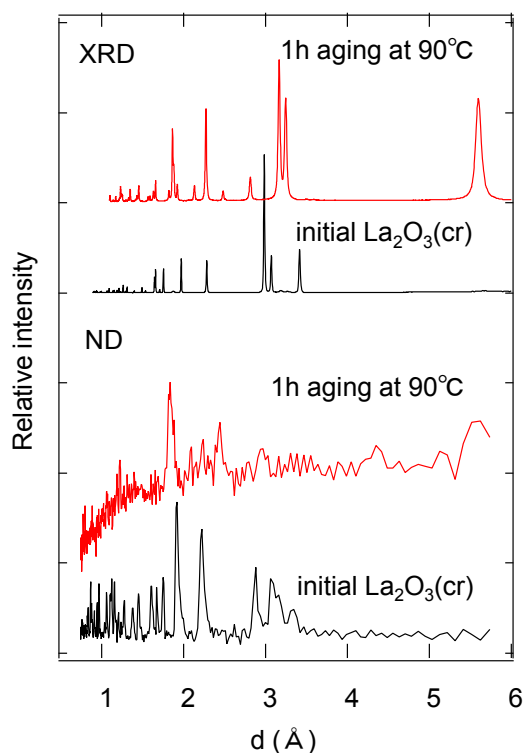


Fig. 1. X-ray and neutron diffraction patterns of initial La_2O_3 and the solid phase after aging at 90 °C for 1 hour.

REFERENCES:

- [1] 包括的技術報告:わが国における安全な地層処分の実現—適切なサイトの選定に向けたセーフティケースの構築—, NUMO-TR-20-03 (2021).
- [2] Md.Moniruzzaman *et al.*, J. Nucl. Radiochem. Sci., 20,32-42 (2020).
- [3] K. Mori *et al.*, JPS Cnf.Proc., 33, 011093 (2021).

CO9-3 Electrochemical U dissolution from U-Ru alloy in LiCl-KCl-UCl₃ melt

T. Murakami¹, Y. Sakamura¹, K. Uozumi¹ and K. Takamiya²

¹Central Research Institute of Electric Power Industry
²Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: Electrochemical dissolution of actinides in molten chloride salt is performed in electrorefining process of spent metallic fuels. Since part of actinides exists as alloys with noble metal fission products in spent metallic fuels [1], for the purpose of achieving a high dissolution ratio of actinides from the spent metallic fuels, it is necessary to accumulate the basic knowledge on the actinide dissolution from actinide-noble metal alloys. As one of actinides-noble metal alloys, this study focused on U-Ru alloy and electrochemical dissolution of U from U-Ru alloy was investigated in LiCl-KCl-UCl₃ melt.

EXPERIMENTS: All experiments were performed in an Ar atmosphere glove box. Cyclic voltammetry, one of the electrochemical measurements, was performed using a Ru metal plate and a W wire as the working electrode in LiCl-KCl eutectic salt containing 0.16 mol% UCl₃ at 723, 773 and 823 K. The counter electrode was a glassy carbon rod. The reference electrode was Ag/AgCl electrode which was composed of a Ag wire immersed in LiCl-KCl-AgCl melt loaded in a pyrex glass tube.

RESULTS: Since W forms no alloy with U, a cathodic current, c1, and the corresponding anodic current, a1, observed at around -1.4 V (vs. Ag/AgCl) in Fig. 1 were ascribed to U metal deposition and the dissolution of the deposited U metal (reaction 1), respectively,



Another cathodic and anodic current couple (c2 and a2) was seen at around -0.2 V, corresponding to the U³⁺/U⁴⁺ redox reaction (U⁴⁺ + e⁻ = U³⁺).

Fig. 2 shows cyclic voltammograms of the Ru plate electrode in the melt at 723, 773 and 823 K. In addition to the cathodic and anodic current couples ascribing to U metal deposition and dissolution (c1 and a1) and U³⁺/U⁴⁺ redox reaction (c2 and a2), several cathodic and anodic currents were observed. Taking into account that five alloy phases, U₂Ru, URu, U₃Ru₄, U₃Ru₅ and URu₃, exist in U-Ru binary system [2], it was considered that the cathodic currents corresponded to U³⁺ reduction on the Ru plate to form U-Ru alloys and the anodic currents were due to the U dissolution from the formed U-Ru alloys (reaction 2),



The results of Fig. 2 also indicated that most part of U could be anodically dissolved from U-Ru alloy by keeping the anode potential at more positive potential than -1.0 V at the electrorefining process. As the future study, it is necessary to investigate the anodic dissolution behavior of U from U-noble metal fission products alloys other than U-Ru alloy to evaluate the electrolysis condition of electrorefining process with a high dissolution

ratio of U from spent metallic fuels.

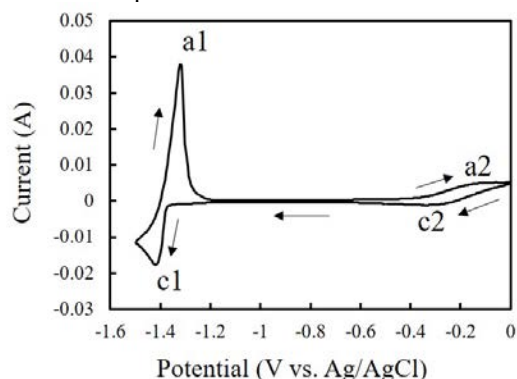


Fig. 1 Cyclic voltammogram of the W wire electrode (1 mmφ, immersion depth of 7 mm into the melt) in LiCl-KCl-0.16mol%UCl₃ melt at 773 K. Scan rate was 50 mVs⁻¹.

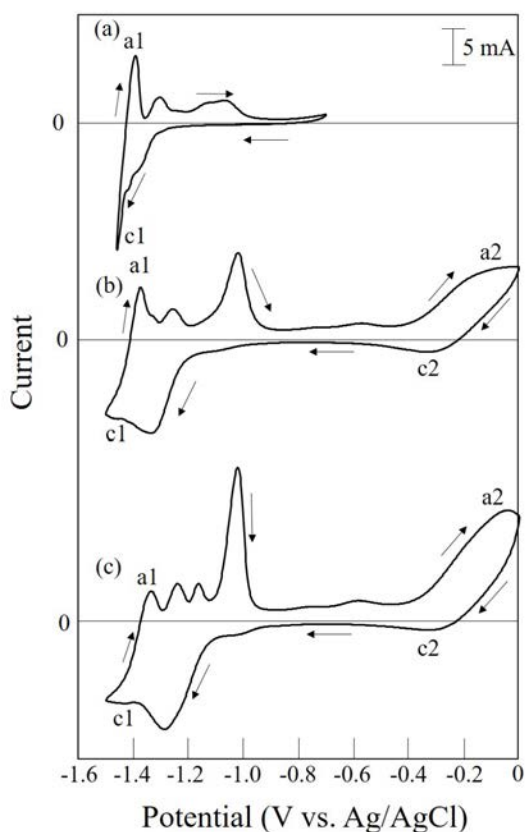


Fig. 2 Cyclic voltammograms of the Ru plate electrode in LiCl-KCl-0.16mol%UCl₃ melt at (a) 723 K, (b) 773 K and (c) 823 K. Scan rate was 20 mVs⁻¹. The effective electrode dimension was (a) 1×2×7 mm, (b) and (c) 1×2×8 mm.

REFERENCES:

- [1] K. Inagaki *et al.*, Trans. Am. Nucl. Soc., **110** (2014) 786-787.
- [2] T. B. Massalski ed., BINARY ALLOY PHASE DIAGRAMS SECOND EDITION, ASM International, Materials Park, OH (1990).

CO9-4 The solvent extraction behavior of Eu and Tb in nitric acid solution using TDdDGA

M. Ikeno, C. Saiga, S. Takahashi, C. Kato, T. Matsumura¹, H. Suzuki¹, S. Fukutani² and T. Fujii

Graduate School of Engineering, Osaka University

¹Nuclear Science and Engineering Center, Japan Atomic Energy Agency

²Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: For the long-term use of nuclear power plants, it is essential to make further progress in the technology for the processing of radioactive waste contained in the spent nuclear fuel. In response to this situation, JAEA has developed the “SELECT process” as a part of the technology for separation and transmutation of radioactive nuclides from radioactive liquid waste [e.g. 1]. In this process, several extractants suitable for different applications have been considered for the extraction of minor actinides (MAs) and rare earth elements (REEs) from radioactive liquid waste. More detailed studies to expand knowledge of the chemical extraction behavior between these extractants and radioactive elements are needed. We focused on europium (Eu), which is a radioactive element contained in the spent nuclear fuel. Europium concentration in the spent nuclear fuel can be up to ~0.52 g/L [2] and the isotopes ¹⁵⁴Eu and ¹⁵⁵Eu have a half-life of 8.6 years and 4.8 years respectively [3] posing as a threat to the recycling process. In order to understand its chemical behavior during the extraction reaction, a new extractant, *N,N,N',N'*-tetradodecyldiglycolamide (TDdDGA) was used to with the solvent extraction method to determine its chemical properties. In addition, terbium (Tb), which is also a lanthanide and has similar properties to Eu, was studied and the results were compared.

EXPERIMENTS: For the HNO₃ concentration dependency, TDdDGA was used as the extractant and a mixed solution of n-Dodecane and 1-Octanol was used as solvents to adjust the TDdDGA concentration to 0.01, 0.02, 0.04 and 0.10 M. For the aqueous phase, 1 ppm of Eu or Tb was added to HNO₃ 1.5 M. Both phases were stirred for 30 mins to reach equilibrium. The solution was separated by centrifugation and the aqueous phase was exchanged with a 0.1 M HNO₃ solution and back extraction was performed. The Eu and Tb concentrations of the aqueous phase before and after both extractions were measured by Inductively Coupled Plasma Quadrupole Mass Spectrometry (ICP-QMS) at Kyoto University, and the distribution ratios were determined. Furthermore, fluorescence spectra were measured to observe the com-

plex structure in the organic solutions after fore extraction. All experiments were carried out at room temperature.

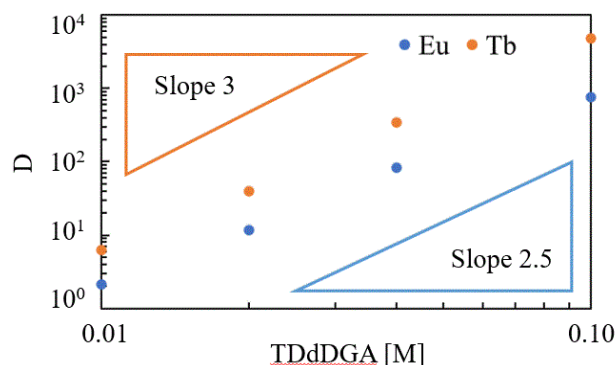


Fig 1. Dependence of D on TDdDGA for Eu and Tb. Tb has a higher D compared to Eu.

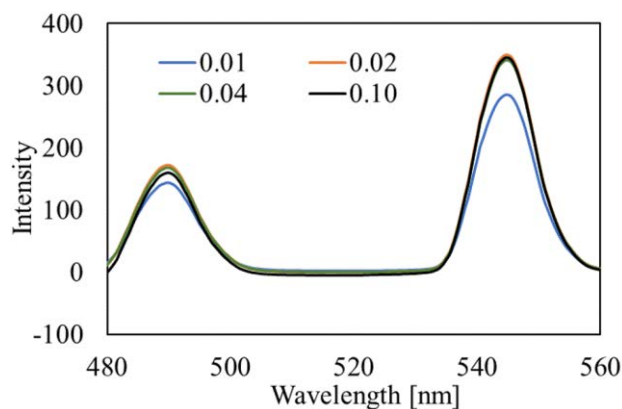


Fig 2. Fluorescence spectra of Tb with various TDdDGA concentrations.

RESULTS AND DISCUSSIONS: The solvent extraction and fluorescence spectra results are shown in Figs 1 and 2. Terbium was consistently up to 10 times higher in distribution ratios at all extractant concentrations compared to Eu. From the extraction reaction and slope analysis, it is suggested that a TDdDGA : Eu = 3 : 1 complex had formed and the complex structure did not change with the increase in extractant concentration. For Tb, it was also suggested that a complex of TDdDGA : Tb = 3 : 1 formed. However, since the fluorescence spectra intensity increased between TDdDGA 0.01 M and above, this indicates the existence of multiple complex structures can be formed with Tb and that there is a distinct difference between 0.01 M and 0.02 M or higher.

REFERENCES:

- [1] T. Matsumura., *Kino Zairyo* **40** 60-71 (2020).
- [2] JAEA-Review, 2008-037 (2008).
- [3] G. Audi. *et al.*, *Nucl. Phys. A*, **729** 3-128 (2003).

CO9-5 Solid-liquid extraction of Ca, Sr, Ba, Ra with crown ether toward the chemical study of nobelium

E. Watanabe,^{1,2} Y. Kasamatsu,^{1,2} R. Nakanishi,^{1,2}
S. Otaka,^{1,2} K. Takamiya³ and A. Shinohara^{4,5}

¹Graduate School of Science, Osaka University

²RIKEN Nishina Center for Accelerator-Based Science

³Institute for Integrated Radiation and Nuclear Science,
Kyoto University

⁴Institute for Radiation Science, Osaka University

⁵Osaka Aoyama University

INTRODUCTION: Nobelium (No) is an actinide element with atomic number 102. While other f-block elements are stable at +3 or higher valence states in aqueous solutions, No is considered to form +2 valence state stably because of its electronic configuration $[\text{Rn}]5f^{14} 7s^2$. Previous ion-exchange experiments have reported that No exhibits 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 II elements from the viewpoint of molecular structure in the solution and its electronic structure.

We focus on solid-liquid extraction using crown ether. Sr resin, commercially available crown-ether supported resin, has extraction selectivity for alkaline earth ions, and this selectivity is sensitive to change by type of acid of a liquid phase and its concentration [3,4].

This study aims to investigate the extraction behavior of No^{2+} in the Sr resin system and the bonding properties of No^{2+} -crown complexes. To obtain a distribution coefficient (K_d) of ^{255}No , which has a half-life of 3.5 min, chemical reaction in the extraction systems must rapidly reach chemical equilibrium. In this study, solid-liquid extraction experiments of ^{47}Ca , ^{85}Sr , ^{133}Ba , and ^{226}Ra were conducted to investigate the applicability of Sr resin extraction system for ^{255}No experiments.

EXPERIMENTS: 0.5–2 mL of HNO_3 or HCl solutions containing the radiotracers ^{47}Ca , ^{85}Sr , ^{133}Ba , and ^{226}Ra were contacted with 50–500 mg of Sr resin and shaken for 1–1440 minutes. ^{47}Sr , ^{85}Ba , and ^{133}Ra are produced by AVF cyclotron at RIKEN Nishina Center and had no carrier (no matrix elements), while ^{47}Ca was produced by neutron irradiation to $^{\text{nat}}\text{CaO}$ powder at KURNS and had carrier about 1 mg / mL Ca dissolved. After extraction experiments, only the liquid phase was taken by centrifugation, and the γ rays of each nuclide were measured with a Ge semiconductor detector. A sample without resin was also prepared. K_d was calculated by the equation

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

where A_s and A_{STD} are radioactivities of the aqueous phase of the extraction sample and the control sample, respectively; V is the volume of the aqueous phase (mL);

and w is the mass of the dry resin (g). The A values for each nuclide were appropriately corrected considering their respective half-lives.

RESULTS: Figure 1 shows the K_d values in 3.5 M HNO_3 as a function of shaking time. For Sr, Ba, and Ra, the extraction equilibrium was reached within 1 min. On the other hand, it took about 5 minutes for Ca to reach chemical equilibrium. This difference may be caused by the fact that only the Ca sample contained a macro amount of carriers. It is important to examine the change in the K_d values of ^{255}No for shaking times 1–5 min.

In both nitric and hydrochloric acid systems, the K_d values of Ca are significantly lower than that of Sr, Ba, and Ra. Since ionic radius and available coordination number of Ca^{2+} is small, the extracted species, $\text{Ca}^{2+}(\text{NO}_3)_2$ -crown, may have lower stability.

We will obtain the K_d values of ^{255}No in Sr resin system using the batch-type solid-liquid extraction apparatus developed in our previous study [5]. We also plan to conduct an X-ray absorption spectroscopy study to obtain the detailed molecular structure of the extracted Ca^{2+} -crown complexes.

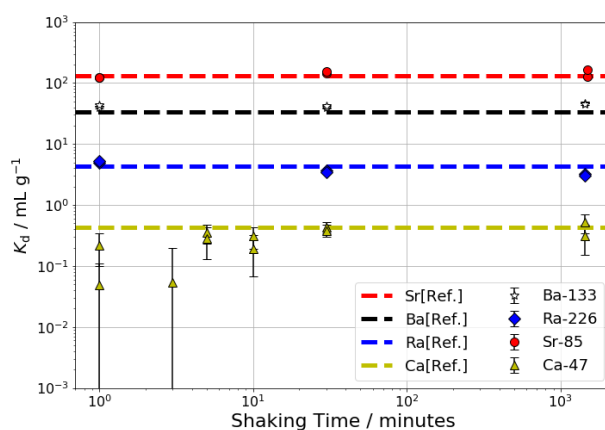


Figure 1. The K_d values of ^{47}Ca , ^{85}Sr , ^{133}Ba , ^{226}Ra in Sr resin / 3.5 M HNO_3 system (dashed lines indicate the values obtained in reference [3]).

REFERENCES:

- [1] R. Silva *et al.*, *Inorg. Chem.*, **13** (1974) 2233.
- [2] H. Ninomiya, Master thesis, Osaka University (2019).
- [3] E. P. Horwitz *et al.*, *Solv. Extr. Ion Exch.*, **10** (1992) 313.
- [4] D. V. Filosofov *et al.*, *Solv. Extr. Ion Exch.*, **33** (2015) 496.
- [5] Y. Kasamatsu *et al.*, *Radiochim. Acta*, **103** (2015) 513.

CO9-6 Determination of Uranium in Fallout Using Fission-Track Analysis

K. Takamiya, N. Toe, M. Inagaki, S. Sekimoto, Y. Oki and T. Ohtsuki

Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: A large amount of radioactive materials were released to the environment by the severe accident of Fukushima Daiichi Nuclear Plant in 2011. One of the major radioactive components of the released materials are radio-caesium, but there contained a small amount of uranium [1]. Insoluble radioactive particles which is one of the important chemical forms of fallout materials were found in the environment, and a part of them also contain uranium component [2]. The radioactivity of uranium in fallouts is so large to affect human health, but the uranium is an important fingerprint of melted nuclear fuel of the power plant. In the case of radio-caesium, the quantity in insoluble particles can be determined by measurement of gamma-ray spectrum, but it is difficult to determine the uranium component because of their low radioactivity. Fission track method is one of the useful techniques to determine a small amount of fissile materials [3]. In the present work, a standard environmental sample which contains uranium were subjected to the fission-track analysis to investigate experimental conditions for determination of the uranium in fallout materials.

EXPERIMENTS: The standard environment sample of IAEA-384 which contains comparable amount of uranium as soils in Japan has been irradiated by neutrons to produce fission tracks on a polycarbonate detector (BARYOTRAK, Fukubi Chemical Industry). Several mg of the fine particles of the sample were scattered on the detector surface and wrapped by a paraffin film to fix particles on the detector. Samples with detectors were irradiated by neutrons using TC-Pn irradiation facility at the power of 1 MW on KUR. The irradiation time varies from 1 to 60 min. After the irradiation, sample particles were removed from the detector together with the film. Fission tracks were etched in the detector with a solution of 8 mol/L sodium hydroxide at 70°C for 1 hour. Detectors were washed by pure water and the etched tracks were observed by using optical microscope.

RESULTS: Examples of image of fission tracks are shown in Fig. 1. The upper and lower panels indicate the images obtained by irradiation for 10 and 60 min, respectively. Fission tracks were produced all over the surface of both detectors. There found several clusters of tracks in both images but not in the image of 1-min irradiation. The clusters might indicate existence of highly concentrated uranium. Because the concentration of uranium in fallout materials released from the nuclear power plant is expected to be higher than that of the sample used in the present work, it was found that the fallout materials con-

taining uranium can be clearly identified from soil and other natural particles by fission-track analysis. In the case of identification of fallout materials from the nuclear power plant, the irradiation time shorter than 10 min might be effective because cluster of tracks can be produced by only the fallouts but not by soil and other natural particles.

In the near future, we will try to determine the uranium concentration in fallout materials using fission-track analysis. And this method could be applied to detection of insoluble particles produced by nuclear incident such as explosion of an atomic bomb.

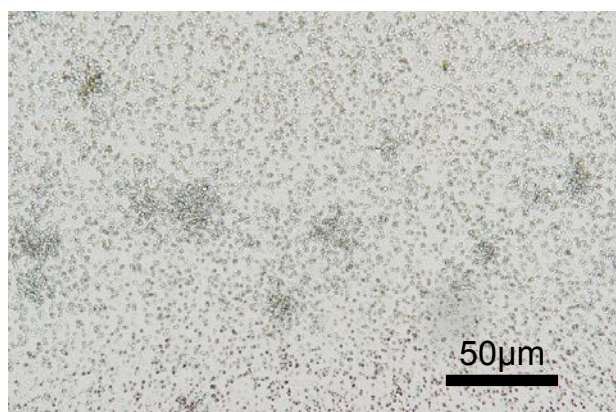
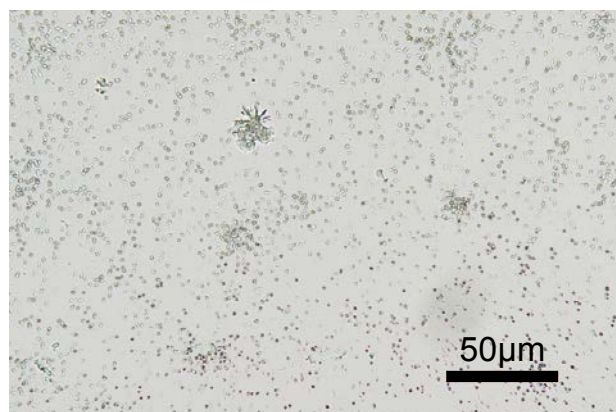


Fig. Tracks produced on the surface of the detector by irradiation of IAEA-384. Upper and lower panels show images observed by irradiations for 10 and 60 min, respectively.

REFERENCES:

- [1] Y. Shibahara *et al.*, *J. Radioanal. Nucl. Chem.* **303**, 1421-1424 (2015).
- [2] Y. Abe *et al.*, *Analytical Chemistry* **86**, 8521-8525 (2014).
- [3] F. Esaka *et al.*, *Analytical Chemistry* **87**, 3107-3113 (2015).

CO9-7 Measurement of X-ray of Pd-103 with a CdZnTe semiconductor detector

T. Kubota¹, S. Fukutani², and Y. Shibahara²

¹Agency for Health, Safety and Environment, Kyoto University

²Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: Palladium-107 is one of long half-life nuclides in high level radioactive waste. It undergoes only beta decay with a half-life is 6.5×10^6 y. Its migration in the environmental and the following inner exposure is a concern for safety assessment [1]. In the assessment with radiochemical methods, Pd-103 would be used as a tracer with an appropriate length of half-life; however, its low gamma ray emission rate is unfavorable. Nevertheless, the emission rate of X-ray around energy of 20 keV from Pd-103 is much higher, which provides the possibility to make quantitative analysis. The acquisition of photon energy spectra is usually used by a Ge(Li) semiconductor detector. However, it cannot measure such low energy region. In this report the photon spectrum of Pd-103 was acquired with a CdZnTe (CZT) semiconductor detector which can detect low-energy photon.

EXPERIMENTS: Pd-103 was produced from Pd-104 through photo nuclear reaction. The powder of PdCl₂ was encapsulated in a quartz tube under vacuum [2]. The PdCl₂ sample was irradiated with high-energy photons generated from the bombardment of platinum with electrons of 30 MeV at KURNS-LINAC. The CZT detector, GR1TM from Kromek Ltd, can be used without cooling and its detector size was 1cm³ [3]. The calibration of the detector was conducted with reference sources containing Am-241, Cd-109, Co-57, Co-60, and Cs-137.

RESULTS: Figure 1 shows the photon spectrum of the reference sources. The CZT detector can measure the low energy photon of 10 keV without interfere by noise. The energy resolution was 1.6 % at 662 keV of Cs-137. The high peak of X-ray from Am-241 and Cd-109 was shown around 20 keV and is overlapped with a small peak probably from Cs-137. This spectrum yields an energy calibration curve in Figure 2, showing its high linearity in a wide energy range. Figure 3 shows the photon spectrum of PdCl₂ two weeks after irradiation. The peak of 357 keV of Pd-103 was hardly shown in the spectrum due to its low emission rate. The large peak shown around 300 keV was identified as Rh-101m of 307 keV produced from Pd-102 through photo nuclear reaction. The large peak shown around 20 keV can be considered as mixed X-ray from Pd-103 and Rh-101m. The purification of Pd-103 from Rh-101m can provide the X-ray source of Pd-103, suitable for radiochemical tracer.

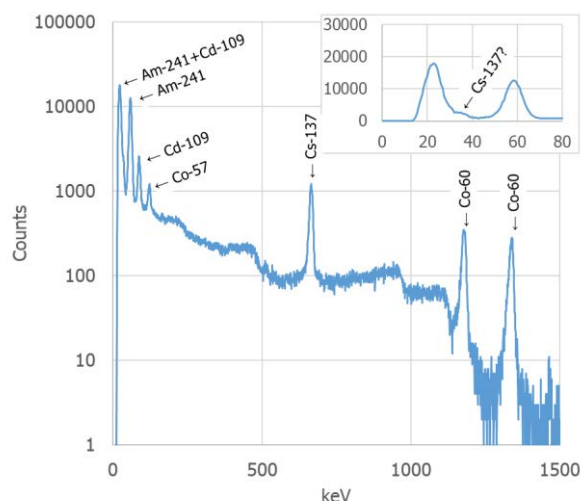


Figure 1 Photon spectrum obtained from mixed reference sources.

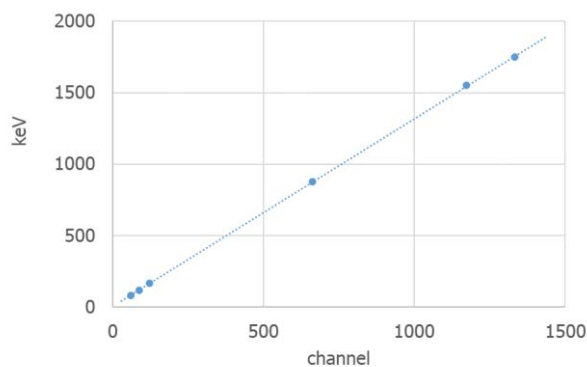


Figure 2 Energy calibration curve evaluated with mixed reference sources.

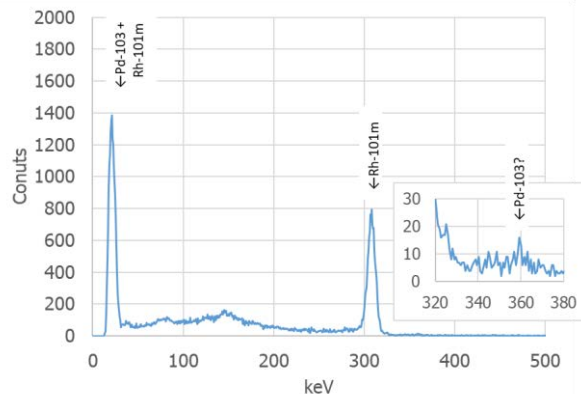


Figure 3 Photon spectrum obtained from irradiated palladium.

REFERENCES:

- [1] K. Iwata *et al.*, Proc. 18th Workshop on Environmental Radioactivity, (2017) 163-166.
- [2] T. Kubota *et al.*, KURNS Progress Report (2018) 209.
- [3] M. Kowatari *et al.*, Radiation Protection Dosimetry (2015), Vol. 167, pp. 348-352.

CO9-8 Effect of Coexistence of Adsorptive Metal Ions on γ -Ray Irradiation for Crown Ether Resin in HNO_3

M. Nogami¹, M. Katsuyama¹, M. Yokota¹, and N. Sato²

¹Faculty of Science and Engineering, Kindai University

²Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: We have been investigating the applicability of crown ether resins to radioactive liquid wastes treatment. In our earlier study, silica-supported resins consisting of dibenzo-18-crown-6 (DB18C6) (Fig. 1) has been found to adsorb e.g. Pd(II) and Ag(I) in nitric acid media[1]. It has also been revealed that γ -ray irradiation to DB18C6 resin in HNO_3 caused opening of crown ether ring (Fig. 2), resulting in the formation of structure obtaining plural hydroxyl groups without selectivity to the above-mentioned metal ions[2]. These results suggest that coexisting adsorptive metal ions on γ -ray irradiation for crown ether resins may suppress the ring opening, because these metal ions would be captured by DB18C6 resin in a manner of getting stuck in the crown ether ring. In the present study, therefore, γ -ray irradiation behavior to DB18C6 resin in HNO_3 containing Pd(II) and Ag(I), respectively, was investigated.

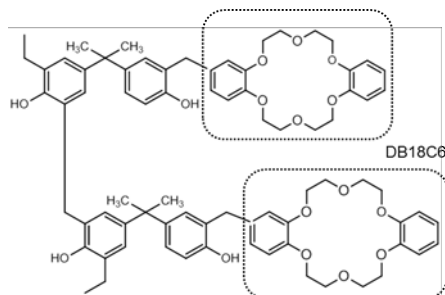


Fig. 1. Chemical structure of DB18C6 resin

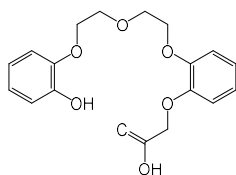


Fig.2. An expected ring opening of DB18C6 by irradiation in HNO_3

EXPERIMENTS: DB18C6 resin was synthesized by following the earlier study[1]. 0.5 mol/dm^3 (=M) HNO_3 containing 10 mM Pd(II) or Ag(I), and 0.5 M HNO_3 as the reference were used as the sample solutions followed by the preparation of in total four irradiation samples shown below :

- (i) DB18C6 resin + 10mM Pd(II) in 0.5 M HNO_3
- (ii) DB18C6 resin + 10mM Ag(I) in 0.5 M HNO_3
- (iii) DB18C6 resin + 0.5 M HNO_3
- (iv) silica support + 10mM Ag(I) in 0.5 M HNO_3

where solid/liquid ratio for every sample was 1 g/5cm^3 . γ -Ray irradiation was carried out similarly to the earlier study (max. 54 kGy)[3]. The irradiated samples underwent solid-liquid separation and concentrations of metal ions for supernatant liquid of samples (i), (ii) and (iv) were measured using ICP-OES. Adsorptivities were evaluated by the distribution ratio, K_d .

RESULTS: In this study, phenomena of interest except irradiation procedure itself were observed for the relationship between DB18C6 resin and metal ions. For Sample (ii), white turbidity was generated in the glass sample tube after preparation of the solution. Afterwards, the turbid compounds were precipitated and white lumps were deposited on the dark brown DB18C6 resin. The concentration of Ag in the supernatant after deposition of white lumps was found to be 0.8 M, meaning that more than 90 % of Ag disappeared from the liquid phase before irradiation. Such a precipitation was not observed in our earlier study, and it is probably because the initial concentration of Ag(I) was 10 times lower (1 mM) than that of this study[1]. On the other hand, such a precipitation was not seen in Sample (iv), either. These results indicate that a precipitation reaction occurred between DB18C6 resin and Ag(I). Ag has been expected to be adsorbed onto DB18C6 resin in the form of Ag(I). However, the expectation should be re-evaluated.

Eventually, the concentration of Ag in the supernatant of Sample (ii) after irradiation was decreased to 0 mM. The result can be expressed as ∞ by evaluating by K_d . K_d value of neat DB18C6 resin for Ag(I) at 0.5 M HNO_3 was ca. 9[1]. Although the direct comparison is impossible because the experimental conditions were not completely identical, it is likely that the irradiated DB18C6 resin still captures Ag in a certain chemical form.

For Sample (i), the concentration of Pd in the supernatant after irradiation was found to be 2.7 mM, which is equivalent to $K_d \approx 13$. K_d value of neat DB18C6 resin for Pd(II) at 0.5 M HNO_3 was ca. 75[1]. Although the direct comparison is impossible due to the similar reason for Ag(I), adsorptivity of DB18C6 resin for Pd(II) is found decreased after irradiation. These results suggest that the opening of crown ether ring by irradiation takes place even under coexistence of Pd(II).

REFERENCES:

- [1] M. Nogami *et al.*, J. Radioanal. Nucl. Chem., **303** (2015) 1549-1553.
- [2] M. Oya *et al.*, ICIE2018, Yogyakarta, Indonesia (2018) ADS-2P.
- [3] N. Miyata *et al.*, KURRI Progress Report 2010 (2011) 258.

CO9-9 Fundamental study on reactor production and separation and purification of β -radioactive materials including Ce-141 for nuclear medicine therapy

T. Yamamura¹, K. Washiyama², C. Tabata¹, R. Okumura¹, K. Ogawa³

¹Institute for Integrated Radiation and Nuclear Science, Kyoto University

²Advanced Clinical Research Center, Fukushima Medical University

³Pharmaceutical Sciences Department, Kanazawa University,

(B-1) ^{146}Nd (17.2%) (n, γ) ^{147}Nd (11.0d) \rightarrow ^{147}Pm (2.6y), ^{148}Nd (5.8%) (n, γ) ^{149}Nd (1.73h) \rightarrow ^{149}Pm (53.1h), (B-2) ^{168}Er (26.8%) (n, γ) ^{169}Er (9.4d), ^{170}Er (14.9%) (n, γ) ^{171}Er (7.5h) \rightarrow ^{171}Tm (1.9y) are possible.

We need several discussions with researchers in this community and trial-error-based experiments of ^{177}Lu production was put ahead of the present study. The experimental study will be executed in the next KUR machine time.

INTRODUCTION:

Recent investigations on the targeted alpha therapy (TAT) revealed its efficacy in the case of ^{225}Ac [1] and also the difficulty in the production of ^{225}Ac . Depending on the target disease and patient's condition, cancer drugs based on β -ray emitting radionuclides (RI's) such as ^{177}Lu is still competitive in the efficacy of ^{225}Ac [2]. However, Japan is also very far behind in the production of β -ray emitting RI's that can be produced by neutron irradiation reactions. The author has taken part in the IAEA International Conference "Technical Meeting on State of the Art Research Reactor Based Radioisotope and Radiopharmaceutical Production" on March 22-26, 2021 as the only Japanese participant [2]. It was a valuable opportunity to share best practices in each country, especially information on the production and supply of ^{177}Lu and the recent ^{166}Ho radiopharmaceuticals, in addition to the traditional ^{90}Y .

For irradiation using the present KUR and the forthcoming Fukui reactor, several requirements holds on the (n, γ) reaction candidates. The reaction have a certain neutron absorption cross section, the isotope abundance ratio of the target nuclide in nature be large, the β -ray energy available for therapy be large, and the half-life be in the range of several days to 20 days. The target and nuclide combinations that satisfy these conditions (Table 1) are (A) ^{140}Ce (88.5%)(n, γ) ^{141}Ce ($T_{1/2} = 32.5\text{d}$), ^{142}Ce (11.1%)(n, γ) ^{143}Ce (33.0h) \rightarrow ^{143}Pr (13.6d). If the conditions (4) allow for the lifetime of the daughter nuclide to be 1-2 years, then

EXPERIMENTS:

The experiments planned were as follows: RI production using a hydraulic transport tube, which has the highest neutron flux in the reactor at the Combined Research Laboratory of Kyoto University. Ce (50 μg), Nd (50 μg), and Er (50 μg) of atomic absorption standard solutions are dropped into a small quartz beaker, evaporated and dried under an IR lamp, sealed in a polyethylene bag, and placed in an Al irradiation vessel. During the 1-week cooling period, (A) ^{143}Pr and (B-1) ^{149}Pm are produced and are separated from the target by chemical manipulation and purified as carrier-free material. On the other hand, since (A) ^{141}Ce and (B-2) ^{169}Er have half-lives in the good range in spite of not carrier-free, the amount produced and radioactivity be checked.

REFERENCES:

- [1] Clemens Kratochwil, *et al.*, J. Nucl. Med., 57 (2016) 1941; doi.org/10.2967/jnumed.116.178673
- [2] Richard P. Baum, *et al.*, J. Nucl. Med., 57 (2016) 1006. https://doi.org/10.2967/jnumed.115.168443
- [3] T. Yamamura, RI production for medical applications in Japanese Research Reactors, JRR-3, KUR and future reactor, Technical Meeting on State of the Art Research Reactor Based Radioisotope and Radiopharmaceutical Production, IAEA EVT1904823 (2021) .

Table 1 Classifications of RI's based on several requirements on the (n, γ) reaction candidates.

Classification based on half-life	Elements	Starting nuclide		Product nuclide				Side / Following reactions
		Nuclide	σ [barn]	Nuclide (Mass number)	γ [keV]	β [MeV]	Half-life	
Objective of this study (moderate;10-40 d)	Ce	140 (88.5%)	0.58	141	145	0.4, 0.6	32.5 d	Ce-138 (0.25%) \rightarrow Ce-139 (137.6d)
		142 (11.1%)	0.95	143	293, 57	1.1, 1.4 \rightarrow 0.9	33 h \rightarrow 13.57d	Ce-143 \rightarrow Pr-143
	Nd	146 (17.19%)	1.4	147	91, 531	0.8, 0.9	10.98 d	
		Er	168 (26.8%)	169	169	110	0.3	9.40 d
			6	171	308, 296, 112	1.1, 1.5	7.52 h	
Too short (<3d) #	La	139 (99.9%)	9.0	140	1596, 487	1.4, 2.2	40.2 h	
	Y	89 (100%)	1.25	90	?	2.3	64.1 h	
Too long (>40d)	Tb	159 (100%)	23.1	160	879, 299, 966	0.6, 1.7	72.3 d	
	Tm	169 (100%)	105	170	84	1.0	128.6 d	
	Sc	45 (100%)	15	46	889, 1121	0.4	83.82 d	