

VIII-II-1. Project Research

Project 4

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1. Objectives and Allotted Research Subjects

Studies on actinide elements are categorized into two subjects, that is, a) engineering studies with the standpoint of nuclear fuel cycle, and b) fundamental studies with the standpoint of physics and chemistry. National laboratories are directed to the engineering vocation, while university laboratories are permissible to concentrate on the basic research. The principal objective of the present project research is to provide scientific and technological basis of physics and chemistry of actinide elements. Thus it covers various experimental studies of actinides and transactinides, on nuclear properties, radiochemical and other chemical properties, process chemistry, and material properties, and so on. Allotted research subjects are as the followings.

- ARS-1 Study on neutron capture cross sections of long-lived nuclides by activation method (S. Nakamura *et al.*)
- ARS-2 Isotope production and application by using actinides (S. Shibata *et al.*)
- ARS-3 Study on coordination chemistry of actinide elements (Y. Ikeda *et al.*)
- ARS-4 Spectroelectrochemical analysis of actinide ions in molten salts (A. Uehara *et al.*)
- ARS-5 Study on chemical isotope effect of actinides and fission product elements (T. Fujii *et al.*)
- ARS-6 Physicochemical properties of actinide elements and nuclear materials (H. Moriyama *et al.*)
- ARS-7 Thermodynamic study of actinide complexes in aqueous solution (T. Sasaki *et al.*)
- ARS-8 Fundamental study on solid-state properties of perovskite type oxides (S. Yamanaka *et al.*)
- ARS-9 Assessment study on chemical properties of actinides in molten salts (M. Myochin *et al.*)
- ARS-10 Electrochemical study of uranium in pyrochemical reprocessing system (M. Kurata *et al.*)
- ARS-11 Basic study for “atom at a time chemistry” of heavy actinide and trans-actinide elements (A. Shinohara, *et al.*)

2. Main Results and Contents

Nuclear physical properties of TRUs were investigated in the study, ARS-1 and ARS-2. In ARS-1, by activation

method using KUR (analytical part was performed in this year), the effective neutron capture cross-section of the $^{243}\text{Am}(n,\gamma)^{244\text{g}}\text{Am}$ reaction was newly evaluated. In ARS-2, ^{237}Np and $^{241,243}\text{Am}$ samples were prepared by precipitation method as neutron-irradiation target for measurements of neutron-induced fission cross-sections. ARS-3, ARS-4, ARS-6, ARS-9, and ARS-10 studied the chemical behavior of actinides and lanthanides in molten salt and ionic liquid systems, the results of which are to be dedicated to the development of reprocessing technique. ARS-3 studied electrochemical reactions of uranyl chloride complexes in an ionic liquid. Cyclic voltammograms of $\text{UO}_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$ in 1-butyl-3-methylimidazolium chloride (BMICl) were obtained. ARS-4 studied redox behavior of Np ions in a chloride melt, NaCl-2CsCl. Redox potentials of the $\text{Np}^{4+}/\text{Np}^{3+}$ and Np^{3+}/Np couples were determined. ARS-6 studied separation efficiency of Am from Ce in a LiCl-KCl/Ga system. The separation factor was obtained to be ~ 100 . ARS-9 studied chemical behavior of U in molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic. Redox behavior of UO_2^+ and UO_2^{2+} was investigated. ARS-10 studied anodic dissolution of U-Zr alloys. Potentiostatic electrolyses were performed to investigate U and Zr co-deposition in LiCl-KCl- UCl_3 -ZrCl₄ melts. In ARS-5, isotope fractionation of Sr in a solid-liquid reaction was studied. Isotope separation factors in Sr^{2+} - SrCO_3 system were evaluated. In ARS-7, hydrolysis of Zr and Th was studied. Precipitants were analyzed by XRD and TG/DTA. In ARS-8, physicochemical characteristics of (Sr,Ba)-Mo-O ternary compounds were investigated. Temperature dependence of thermal conductivities was discussed. In ARS-11, chemical behavior of transactinides was studied. Solvent extraction behavior of mendelevium in 2-thenoyltrifluoroacetone (HTTA)/HCl/ CCl_4 system was studied.

3. Summaries of the achievements

In this research, by using various unique facilities of KURRI for actinide research, new and characteristic chemical and nuclear physical data were obtained. These new information encompass solid chemistry, molten salt and solution chemistry, as well as nuclear reactions of actinides. The results are useful either for scientific purpose or for technological purpose for actinide management in the nuclear fuel cycle.

PR4-1 Measurements of Neutron Capture Cross Sections for Radioactive Nuclei

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INTRODUCTION: A series of experiments with the activation method has been conducted to measure thermal-neutron capture cross-sections and resonance integrals of Minor Actinides (MAs), ex. ²³⁷Np and ²⁴¹Am. Americium-243 is one of the important MAs, because it has long half-life (7370yr) and products higher Cm isotopes via neutron capture reaction, i.e. ²⁴⁴Cm, ²⁴⁵Cm, ²⁴⁶Cm and so on. This work reports the measurements for the effective neutron capture cross-section of the ²⁴³Am(*n,γ*)^{244g}Am reaction.

EXPERIMENTS: Adequate amount of a high-purity ²⁴³Am standardized solution (999Bq) was prepared for an irradiation sample. The amount of ²⁴³Am was measured with an alpha spectrometer, EG&G ORTEC SOLOIST alpha spectrometer. The irradiation for the ²⁴³Am sample was performed for 1 hour at the Pn-2 of the KUR in 2005. Wires of Au/Al and Co/Al alloys were irradiated together with the Am sample to monitor neutron flux components at the irradiation position. A high-purity Ge detector was used to measure the γ rays emitted from the Am sample and wires to obtain their induced activities. **Figure 1** shows an example of γ-ray spectrum of ²⁴³Am sample. **Figure 2** shows the decay scheme of ²⁴⁴Am[1]. Decay γ rays emitted from ^{244g}Am (10.1h) were observed at the energies of 154, 744 and 898 keV. However, 538-keV γ ray was not observed because of its small emission probability.

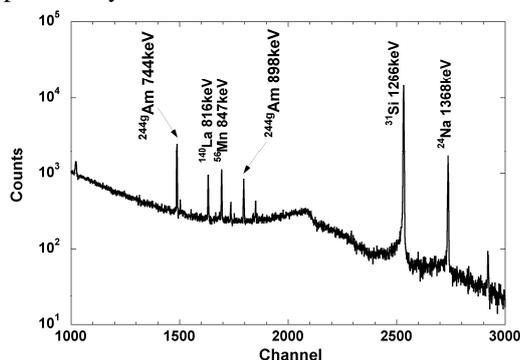


Fig. 1. An example of γ-ray spectrum of ²⁴³Am sample.

ANALYSES AND RESULTS: When analyzing the spectral data, there was the problem that the γ-ray emis-

sion probabilities have about 30% errors[2]. As seen in Fig.2, the ²⁴⁴Am ground state decays to the 6⁺ state of ²⁴⁴Cm by the probability of 100% via β⁻ decay. There is no transition from the isomer to ground states of ²⁴⁴Am.

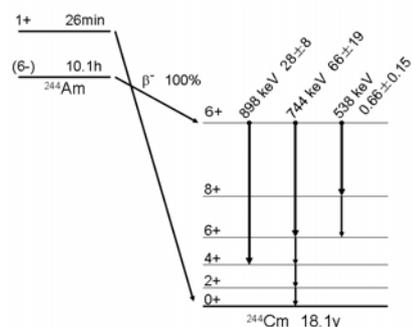


Fig. 2. Decay scheme of ²⁴⁴Am to ²⁴⁴Cm.

Using this scheme[1], emission probabilities were derived straightforward from the ratios of γ-ray yields for 154, 744 and 898 keV. The results are listed in **Table1**.

Table 1. Results of emission probabilities.

E _γ (keV)	This Work	T.O.I. 8 th	Ref.[1]
154	18.2 ± 0.9	16 ± 5	—
538	—	0.66 ± 0.15	0.4
744	70.4 ± 0.8	66 ± 19	72
898	29.6 ± 0.8	28 ± 8	28

The ²⁴³Am(*n,γ*)^{244g}Am reaction rate was obtained with the amount of ²⁴³Am sample, the γ-ray yields as well as these emission probabilities. The thermal-neutron flux was obtained as (2.09 ± 0.08) × 10¹³ n/cm²s and the epi-thermal index[3] was 0.033 ± 0.003 at the irradiation position. The effective neutron capture cross-section was calculated from the reaction rate and the thermal-neutron flux, and obtained as 5.3 ± 0.3 b. the present result was about 28% smaller than 7.3 b estimated with the evaluated data. In the past, the effective cross-section for the ²⁴³Am(*n,γ*)^{244m+g}Am reaction had been measured with the alpha spectroscopy, and found as 174.5 ± 5.3 b [4]. From these values, the effective cross-section for the formation of ^{244m}Am can be derived as 169.2 ± 5.3 b.

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- [4] M.Ohta *et al.*, *J.Nucl.Sci.Technol.*, **43**, 1441(200).

PR4-2 Target Preparation of ^{237}Np and $^{241,243}\text{Am}$ by Precipitation Method

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INTRODUCTION: Nuclear properties of minor actinide (MA) nuclides which are produced in a nuclear reactor by neutron capture reaction of nuclear fuel elements are important parameters in safety evaluation of FBR cycle. It is difficult to measure the nuclear properties such as cross sections of neutron capture and fission because of in-purities included in MA samples. In the measurement of nuclear properties of MA's, preparation of an MA sample is very important to obtain correct data. The sample preparation should be carried out just before the examination because in-purities are produced by nuclear decay of various nuclides included in the sample material. In this work, MA samples (^{237}Np and $^{241,243}\text{Am}$) were prepared by precipitation method [1, 2] as neutron-irradiation target for measurements of neutron-induced fission cross-sections.

EXPERIMENTS: ^{237}Np : The original solution of 200 μg acidic solution includes 1.0 mg of ^{237}Np and also includes ^{239}Pu , ^{241}Am , and ^{243}Cm as in-purities. The in-purities were separated from ^{237}Np using anion exchange column (Muromac 1X8). A part of the original solution (40 μL) was poured into the column, and 1 mL of the mixed solution (9 M HCl and 0.05 M NH_4I) was injected twice to the column to elute uranium, plutonium, and other in-purities. And neptunium was eluted by 0.1 mL of the mixed acid (4 M HCl and 0.1 M HF) twice. NH_4OH was added to the eluting solution to precipitate neptunium, and the precipitation was filtered by Anodisc. ^{241}Am and ^{243}Am : The original solution contains 1.02 mg of ^{241}Am and 1.0 mg of ^{243}Am in about 500 μg and 700 μg acidic solutions, respectively. The in-purities of solutions were isotopes of americium, curium and their daughter isotopes. The separation scheme for both isotopes is the same. A part of original solution (20 μL for ^{241}Am , 100 μL for ^{243}Am) was poured to the anion exchange column (Muromac 1X8), and americium was eluted from the column by injecting 1 mL of 9 M HCl. Americium was precipitated by adding NH_4OH and filtered by Anodisc.

The precipitation filtered on the Anodisc was dried up, and alpha-particle spectroscopy was carried out to determine the amount of intended MA and in-purities.

RESULTS: The alpha-particle energy spectrum of the prepared ^{237}Np target is shown in Fig. 1. There appears energy peaks originated in ^{239}Pu as an in-purity. But the amount of ^{239}Pu in the target is less than 10% compared with that in the original solution. The alpha-particle energy spectra of $^{241,243}\text{Am}$ are shown in Fig. 2. In this figure,

the upper and lower panels represent the spectrum of ^{241}Am and ^{243}Am , respectively. In the case of ^{241}Am , the peak of ^{242}Cm (6.1 MeV) was found in the original solution, but there is no peak in the spectrum shown in this figure. It was found that the in-purities were separated effectively for each target preparation.

And, from the width of each energy peak, the prepared targets are found to be thin enough to detect fission fragments emitted from the target using PPAC fission chamber.

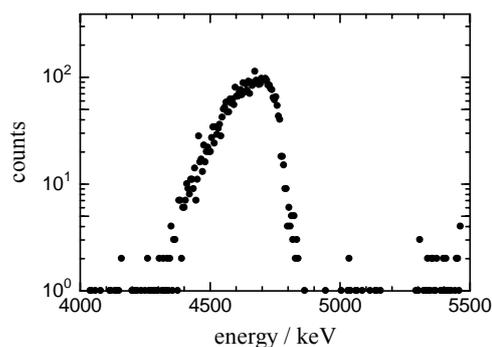


Fig. 1. The alpha-particle spectrum of the prepared ^{237}Np target.

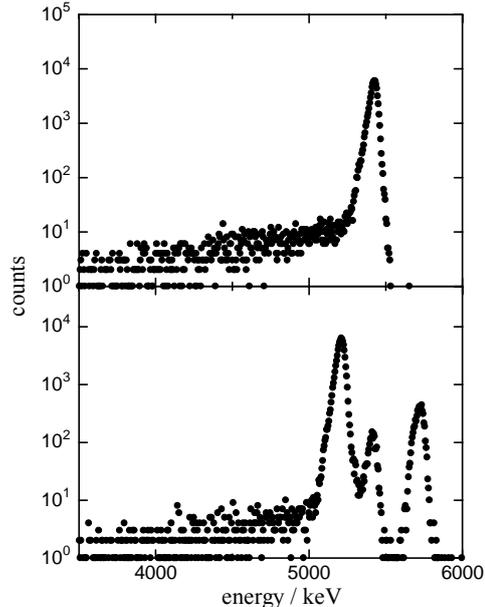


Fig. 2. The alpha-particle spectra of ^{241}Am (upper panel) and ^{243}Am (lower one) targets.

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INTRODUCTION: Recently, some research groups have investigated application of ionic liquids (ILs) instead of conventional molten salts as media of pyro-reprocessing processes for spent nuclear fuels. We have studied electrochemical reactions of uranyl chloride complexes in 1-butyl-3-methylimidazolium chloride (BMICl) to get basic data for such an application of ILs.

EXPERIMENTS: As uranyl chloride complexes, we used $\text{UO}_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$ and $\text{Cs}_2\text{UO}_2\text{Cl}_4$, which were prepared according to previous procedures [1, 2]. 1-Butyl-3-methylimidazolium chloride (BMICl, Kanto Chemical Co., Inc.) was used without further purification. In order to remove water and volatile impurities, BMICl was kept for more than 3 h under reduced pressure at 120 °C. Sample solutions for experiments were prepared by dissolving uranyl chloride into BMICl, and the residual water in sample was removed by the similar manner as mentioned above.

RESULTS: We measured UV-visible spectra of samples prepared to examine the chemical forms of uranyl species in BMICl. Absorption spectra of samples were found to be almost consistent with that for $\text{UO}_2\text{Cl}_4^{2-}$ [3], indicating that the uranyl species in BMICl exist as $\text{UO}_2\text{Cl}_4^{2-}$. Electrochemical measurements by cyclic voltammetry (CV) were carried out by using an electrochemical analyzer (BAS, ALS model 660B) in glove box under an Ar atmosphere. Temperatures of sample solutions were controlled at 80 ± 1 °C by a hot plate. A glassy carbon (BAS, diameter = 1 mm) and a platinum wire were used as a working electrode and a counter electrode, respectively. As a reference electrode, an Ag/AgCl electrode (BAS, RE-1B) was used and connected with a CV cell (BAS, VC-2) by a liquid junction filled with BMIBF_4 as used as medium. All potentials

reported here are versus Ag/AgCl. We measured cyclic voltammograms of sample solutions in the potential range $-1.0 \sim -0.4$ V at various scan rates. Figure 1 shows typical cyclic voltammograms for BMICl dissolving $\text{Cs}_2\text{UO}_2\text{Cl}_4$. Peaks of one redox couple are found to be observed around -0.73 V and -0.65 V, respectively. The potential difference between two peaks (ΔE_p) is 78 mV, which is almost consistent with theoretical ΔE_p value (70 mV) for the reversible one electron transfer reaction at 80 °C. Similar phenomena were also observed in sample solution prepared by dissolving $\text{UO}_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$ into BMICl.

From these results, it is concluded that the uranyl species in BMICl is present as $\text{UO}_2\text{Cl}_4^{2-}$ and is reduced quasi-reversibly to $\text{UO}_2\text{Cl}_4^{3-}$.

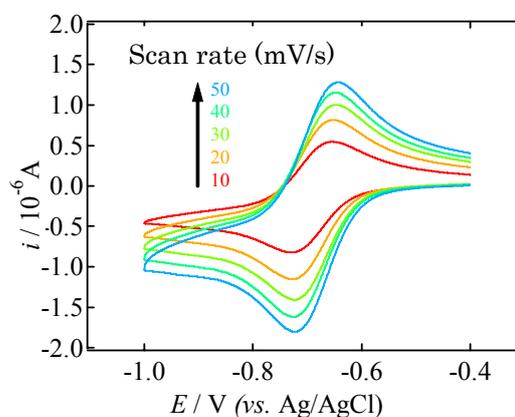


Fig. 1. Cyclic voltammograms of solution prepared by dissolving $\text{Cs}_2\text{UO}_2\text{Cl}_4$ into BMICl. $[\text{UO}_2^{2+}] = 1.3 \times 10^{-2}$ mol kg^{-1} . Temp. = 80 °C.

Initial scan direction: cathodic.

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PR4-4 Electrochemical Study of Neptunium Ions in Molten NaCl-CsCl Eutectic

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INTRODUCTION:

In the dry reprocessing process for the spent nuclear fuels by the oxide electro-winning method, the spent fuel is dissolved into molten NaCl-CsCl eutectic salt. In our group, the redox potential and absorption spectra of uranium and plutonium ions in molten NaCl-CsCl eutectic have been reported[1]. It is important to study chemical behavior of uranium and plutonium ions as well as minor actinides (MAs; Np, Am, Cm etc.) in order to recover from high level wastes. For Np, which is one of the long-lived MAs, electrode reaction of Np in the molten LiCl-KCl eutectic has been studied by several authors [2-4]. In the present study, cyclic voltammograms for the redox of the $\text{Np}^{4+}/\text{Np}^{3+}$ and Np^{3+}/Np couples in molten NaCl-CsCl eutectic were obtained to determine the standard redox potential, and absorption spectra of NpO_2^+ , Np^{4+} and Np^{3+} were measured to study coordination circumstance of neptunium ions in the melts at the temperature range between 823 and 923 K.

EXPERIMENTAL:

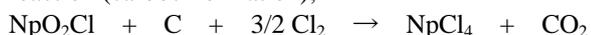
All the experiments were carried out in a glove box filled with dry argon whose humidity and oxygen impurity was continuously kept less than 1 ppm.

In this experiment, Ar gas atmosphere in the sample cell was maintained to the supplied gas conditions that the flow rates of Cl_2 , O_2 , and Ar were controlled by the metal sealed mass flow controller 5400-50SCCM (Kofloc Co. Ltd.). 2 graphite rods of 3 mm in diameter were used as working and counter electrodes, and a reference electrode was an Ag/Ag^+ electrode composed a PYREX tube, about 1 g of 4.85 mol% AgCl in NaCl-CsCl eutectic, and an Ag wire.

A single beam spectrophotometer V-350 (JASCO Co. Ltd.) was used for the absorption spectrophotometry over the wave number range from 5×10^3 to $25 \times 10^3 \text{ cm}^{-1}$. An electrochemical measurement system, HAG-5001 (Hokuto Denko Co. Ltd.) was used for the measurement of the formal redox potential of the $\text{Np}^{4+}/\text{Np}^{3+}$ couple.

RESULTS:

The Np^{4+} was prepared from NpO_2Cl by passing through Cl_2 gas coexistent with carbon rod as following reaction (carbochlorination);



Absorption spectrum corresponding to Np^{4+} observed as shown in Fig. 1 was similar to that in LiCl-KCl[5].

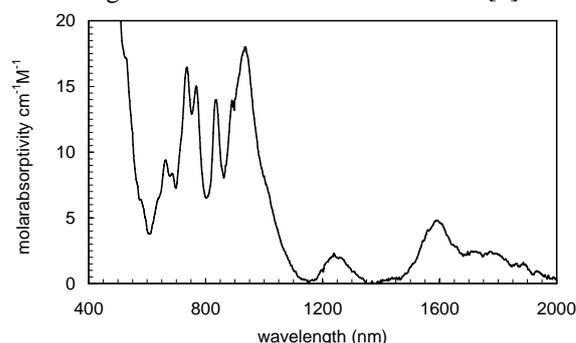


Fig. 1. Absorption spectrum of Np^{4+} in NaCl-CsCl eutectic at 923K.

Cyclic voltammogram for the redox of the $\text{Np}^{4+}/\text{Np}^{3+}$ couple was observed in the temperature between 823 and 923 K. Figure 2 shows that the typical cyclic voltammograms for the redox of the $\text{Np}^{4+}/\text{Np}^{3+}$ couple measured at the potential scanning rate from 0.05 to 0.5 Vs^{-1} . It was found that the electrode reaction was controlled by the diffusion of Np^{4+} . The diffusion coefficient of Np^{4+} in NaCl-CsCl eutectic at 923 K calculated was $1.98 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which was smaller than that in LiCl-KCl eutectic[3].

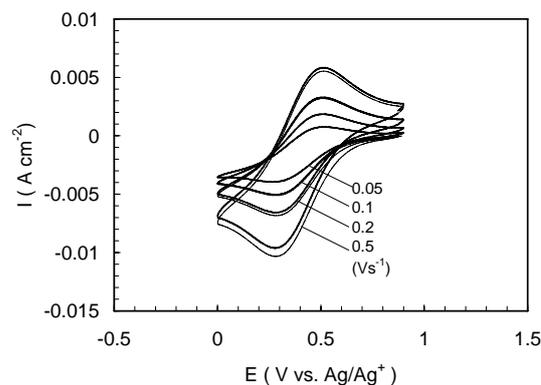


Fig. 2. Cyclic voltammogram for the redox of the $\text{Np}^{4+}/\text{Np}^{3+}$ couple in NaCl-CsCl eutectic at 923K.

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PR4-5 Chemical Separation of TRU Elements and Fission Products and Their Isotopic Fractionations in the Separation Process

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INTRODUCTION: Strontium has four naturally occurring isotopes: ^{84}Sr (isotopic abundance= 0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.02%), and ^{88}Sr (82.56%). These isotopic abundances have natural variations. Isotope fractionations of strontium in chemical exchange reactions have been investigated by various research groups. For example, solvent extraction system using a macrocyclic compound as an extractant gives a large isotope separation factor [1]. The reported distinguishable isotope separation factors suggest that fractionation of Sr isotopes may be detectable even in simple chemical reactions. In this context, we focused on a simple solid-liquid system. Strontium carbonate was selected as the solid phase and a solution containing hydrated Sr^{2+} ion was selected as the liquid phase. The isotope fractionation in the precipitation reaction between these two phases was studied.

EXPERIMENTAL: 1g of strontium carbonate and 10 mL of 0.05 M sodium carbonate were put in a PP tube. The tube was sealed, and then it was gently shaken at 298K. After a possible aging, SrCO_3 was precipitated. The precipitant was separated by centrifugation, and the supernatant was filtered by a PTFE membrane (0.20 μm pore size). Sr concentration in the solution was analyzed by ICP-AES. The solid-liquid equilibrium was attained within 3 days. The sample aged 25 days was used for isotopic analysis.

The sample diluted with H_2O was once loaded on a cation-exchange column (DOWEX 50WX8), then it was rinsed by 0.1 M HNO_3 . Sr was collected in 8 M HNO_3 . Again, the collected solution was loaded on a column filled with Sr resin (Eichrom), then it was rinsed by 8 M HNO_3 . Sr was collected in 0.05M HNO_3 .

Sr in this elution fraction was enriched to be ~70ppm Sr in 1M HNO_3 . 1 μL aliquot was put onto a rhenium single filament with a tantalum activator. The total amount of Sr loaded on the filament was 70 ng. Similar procedure was performed for our starting material and a Sr standard (SRM-987). Isotopic ratios were determined by multi-collector thermal ionization mass spectrometry (Finnigan, MAT262).

RESULTS: The precipitation reaction of SrCO_3 is written as,



The solubility of SrCO_3 in Na_2CO_3 was shown in Fig. 1. The reported solubility [2] was shown together. It can be seen that our result agree with the reported solubility.

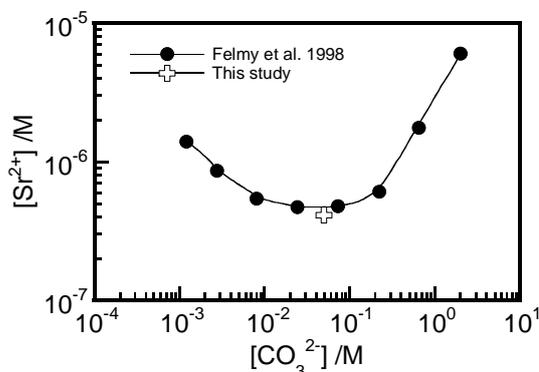


Fig. 1. Solubility of SrCO_3 in Na_2CO_3 .

In the present study, we checked the isotopic difference in the equilibrium constant of reaction 1. The isotope fractionation factor $\alpha_{86,m}$ ($m=84, 87, \text{ or } 88$) is defined as,

$$\alpha_{86,m} = \frac{([\text{mSr}]/[^{86}\text{Sr}])_{\text{liquid}}}{([\text{mSr}]/[^{86}\text{Sr}])_{\text{solid}}} \quad (2)$$

The isotope enrichment factor $\epsilon_{86,m}$ is defined as,

$$\epsilon_{86,m} = \alpha_{86,m} - 1 \quad (3)$$

$([\text{mSr}]/[^{86}\text{Sr}])_{\text{solid}}$ can be substitute as $[\text{mSr}]/[^{86}\text{Sr}]$ of the starting material. The obtained $\epsilon_{86,m}$'s are shown in Fig. 2 with 2σ analytical errors. Heavier isotopes were preferentially fractionated into the liquid phase. The marine environment is a carbonate system, in which some samples showed Sr isotope fractionations (~0.4 ‰ for $\epsilon_{86,88}$). [3] Our results may be correlated with these isotope fractionations.

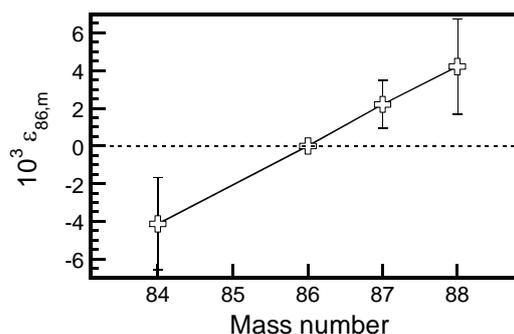


Fig. 2. Isotope enrichment factor.

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INTRODUCTION: Reductive extraction, which uses molten salt and liquid metal as solvents, is expected to be useful for the separation and recovery of minor actinides (MAs).¹⁾ Recently, Conocar *et al.* reported that the separation factors of Pu and Am from Ce and Sm were very high in the system of LiF-AlF₃/Al-Cu.²⁾ Also, by measuring the electromotive force of Pu and Ce, Laplace *et al.* reported that the separation factors of these elements were different in different metals and that solvent metals were ordered from the most selective to the less selective one as Al > Ga > Bi > Zn > Cd.³⁾ Similar results were obtained in our calculations of the separation factors.⁴⁾ In the present study, the separation factors of Am from Ce were measured in the LiCl-KCl/Ga system at 773K, for comparison.

EXPERIMENTS: Eutectic LiCl-KCl was obtained from the APL Engineered Materials Inc., Ga and Ce metals from Nilaco Corporation, Ce (III) standard solution from Wako Pure Chemical Industry, Ltd., and radioactive tracers of Am-241 and Ce-139 from the Isotope Products Laboratories (IPL). The radioactive tracers in a nitric acid medium were transformed to their fluorides with known amounts of Ce by using a hydrofluoric acid solution. The precipitates were then dried in a vacuum at room temperature, and were loaded in an alumina crucible together with 25g of eutectic LiCl-KCl and 35g of Ga metal. The system was then heated to 773K (± 5 K) and the equilibrium distributions were controlled by adding small amounts of Li-Ga alloy and/or GaCl₃. After attainment of equilibrium, samples were taken from each phase, and were subjected to gamma-ray spectroscopy. In some cases, the lithium concentration in the gallium phase was also measured by atomic absorption spectrometry. All experiments with high purity reagents were performed in a globe box under argon atmosphere containing < 0.5ppm of O₂ and < 0.2ppm of H₂O.

RESULTS: In Fig. 1, the log D_M values for Am are plotted as a function of the log D_{Ce} values. In the first run of this experiment, the separation factor of Am and Ce was obtained to be about 60. This value seems not so high compared with those reported in the other systems such as the LiCl-KCl/Bi at 773K.¹⁾ For one of the

reasons, it may be considered that such oxychlorides as MO⁽ⁿ⁻²⁾⁺ affect the distribution coefficients. In fact, it was observed that the mass balance of Am and Ce was low (about 30%) in the run No.1, possibly due to the formation and precipitation of their oxychlorides and/or oxides. By assuming the formation of CeOCl, the molality scale concentration of the oxygen anion ($[O^{2-}]$) may be obtained to be larger than $10^{-4.65}$ by taking the literature value of the solubility products $K_s(\text{CeOCl}) = [\text{Ce}^{3+}][O^{2-}] = 10^{-7.45}$ with the present Ce^{3+} concentration of $[\text{Ce}^{3+}] = 10^{-2.8}$.⁵⁾ In the second run, on the other hand, ZrCl₄ was added to the molten salts phase as the oxide ion scavenger in order to avoid the formation of oxychlorides, and the separation factor of Am and Ce was obtained to be about 100. In this case, the mass balance of Am and Ce was observed to be kept high (about 100%).

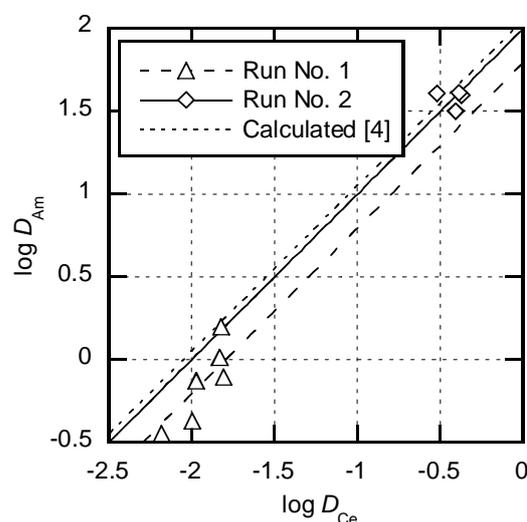


Fig. 1. Distribution coefficients of Am as a function of that of Ce in the LiCl-KCl/Ga system at 773K.

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PR4-7 Solid Phase Precipitates in M(IV)-OH-oxalate Ternary Aqueous System

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INTRODUCTION: Characterization of the solid phase in aqueous solution, as well as thermodynamic studies of the soluble species in the aqueous phase, is important in order to understand the low solubility. In the presence of oxalic acid (H₂Ox), the Th(IV) ion precipitates as Th(ox)₂ under acidic conditions. However, the solid phase has not been characterized at neutral pH. On the other hand, the solid phase for Zr(IV) has been reported not to consist of Zr(ox)₂ but rather of Zr(OH)₂(ox) under acidic conditions. A comparison of these results suggests that the chemical composition of solid phases may be attributed to competitive reactions between hydrolysis and complexation. In the present investigation, the solid phases are formed in aqueous solutions in the presence of oxalic acid at several different pH_c. The solid phases were analyzed by some methods.

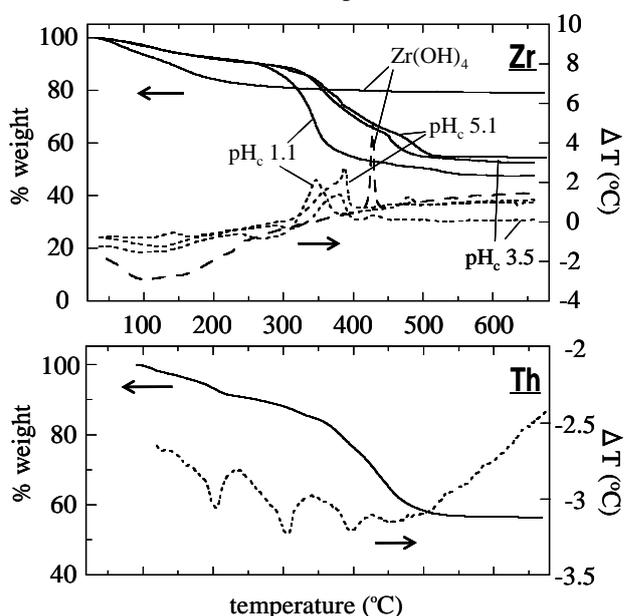
EXPERIMENTAL: Solid phase samples were prepared by the oversaturation method [1]. After drying the solid phase at 60°C, X-ray diffraction patterns were measured, and the TGA/DTA system was used. The heating rate was +5°C/min and the maximum temperature was about 700°C. Elemental analysis revealed that the weight percentage of the carbon and hydrogen in the solid phase were measured. After dissolution of the precipitate by a mixture of perchloric and nitric acids at 180°C and 120 psi for 60min, the concentration of metal and sodium ions was measured by ICP-AES.

RESULTS: The X-ray diffraction patterns of the solid phase precipitated at pH_c 1.1 and 5.1 were broad corresponding to amorphous materials. The results of the TGA and DTA are shown in Fig. 1 together with that for Zr(OH)₄. The broad endothermic peak around 100°C and the sharp exothermic peak around 420°C for the Zr(OH)₄ were attributed to the dehydration reaction and the crystallization, respectively. There are at least two stages of the decomposition of the zirconium-oxalate precipitate. The percentage of weight loss below 300°C corresponds to the dehydration, and the decomposition of oxalate salt and crystallization of zirconium oxide is thought to occur at 300-500°C. The TGA curves for the precipitates formed at pH_c 3.5 and 5.1 are similar over the entire temperature range. On the other hand, a greater weight loss for the precipitate at pH_c 1.1 was shown. This suggests that the original precipitate at pH_c 1.1 contains a larger amount of oxalic acid. Considering the weight percentages of C, H, Zr and Na from the elemental analysis of the solid phases precipitated under various experimental conditions, the composition of the solid phase as Zr:OH:carboxylate can be deduced assuming the solid phase consists of Zr(OH)_n(ox)_{(4-n)/2} and H₂O,

Na⁺, ClO₄⁻ and free oxalate ion. Thus, the value of *n* in Zr(OH)_n(ox)_{(4-n)/2} was determined to be in good agreement with the results of elemental analysis. In our previous work, zirconium hydroxide did not precipitate at pH_c < 2 when [Zr]_{ini} was 10⁻² M in the absence of organic acid [1]. However, under the present conditions at a similar pH_c, the solid phase was observed and found to consist of a mixture of oxalate and OH ions.

It is notable that the ratio of *n* in the solid phase decreases gradually with the decreasing pH_c. In the presence of an excess of oxalic acid, no precipitate was observed at pH_c 1 to 6, and zirconium formed soluble species such as 1:3 and 1:4 complexes with oxalate ion [2]. The composition of the precipitate formed at pH_c 7.4 was similar to that of the hydroxide with less oxalate.

For Th(IV), the solid phase was estimated to be Th(ox)₂·2H₂O, and not ternary precipitate by analysis of the TGA and DTA curves (Fig. 2). There were three decomposition stages corresponding to dehydration (200°C), formation of Th(CO₃)₂ (300°C) and formation of ThO₂ (400°C). In the present case, the TGA and DTA curves at pH_c 0.8 (Fig. 2) were similar to those at pH_c 2.9, indicating formation of Th(ox)₂·2H₂O. Since the constant of formation of thorium complex with oxalate ion is lower than that of zirconium [3], Th oxalate precipitate could not be re-dissolved. On the other hand, the Zr oxalate precipitate was re-dissolved. It should be noted that this precipitate could be dissolved at pH_c 4, due to the formation of the anionic oxalate complexes.



Figs.1 and 2. TGA and DTA curves of Zr and Th solid phases precipitated in the presence of oxalic acids.

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INTRODUCTION: In irradiated nuclear fuels, a number of fission products (FPs) are produced and they significantly affect the fuel characteristics. Therefore, the behavior of FPs and the properties of their compounds are very important for evaluation of the fuel characteristics. In the high-burnup oxide fuels, it has been reported that some FPs dissolve in the fuel matrix and others form oxide or metallic inclusions. The gray oxide phase of (Sr,Ba)-(U,Pu,Zr,RE,Mo)-O compounds have been observed as the oxide inclusions; especially we focused on (Sr,Ba)-Mo-O ternary compounds [1] because they would take various chemical forms under the different oxygen potentials.

EXPERIMENT: High-density sintered samples of SrMoO₄ and BaMoO₄ were prepared by spark plasma sintering (SPS). Powders of SrMoO₄ and BaMoO₄ were put into a graphite die, and then SPS was performed at 1073 K for 10 min under an inert atmosphere. SrMoO₃ and BaMoO₃ were prepared by reduction of SrMoO₄ and BaMoO₄ under 4 % H₂-Ar gas-flow atmosphere at 1523 K. To prepare sintered samples for characterizations, the obtained powders were put into a graphite die and given SPS at 1673 K for 1 min under an inert atmosphere. To examine the sample purity and determine the lattice parameter, powder x-ray diffraction (XRD) data were collected in air at room temperature. The sample density was calculated from the sample size and weight at room temperature. The thermal conductivity (κ) was calculated from the heat capacity (C_p), thermal diffusivity (α), and density (d) using the relationship of $\kappa = \alpha C_p d$. The heat capacity data were obtained from the SGTE database. The thermal diffusivity was measured by the laser flash method in a vacuum above room temperature.

RESULTS: Figure 1 shows the crystal structures of (Sr,Ba)MoO₃ and (Sr,Ba)MoO₄. (Sr,Ba)MoO₃ take the cubic perovskite type structure, while (Sr,Ba)MoO₄ take the tetragonal scheelite structure. The numbers of atoms per unit cell are 5 and 24 for (Sr,Ba)MoO₃ and (Sr,Ba)MoO₄, respectively. Therefore, it can be said that

the structure of (Sr,Ba)MoO₄ is more complex than that of (Sr,Ba)MoO₃.

Figure 2 shows temperature dependence of the thermal conductivities (κ) of (Sr,Ba)MoO₃ and (Sr,Ba)MoO₄, in the temperature range from room temperature to 700 K. Clearly, κ values of (Sr,Ba)MoO₃ are quite high compared with those of (Sr,Ba)MoO₄. The values are 30 Wm⁻¹K⁻¹ at room temperature, which is approximately 10 times higher than those of (Sr,Ba)MoO₄.

A part of the present results has been reported in Proceedings of MS&T08 and is now being prepared for publication (Transactions of the Atomic Energy Society of Japan).

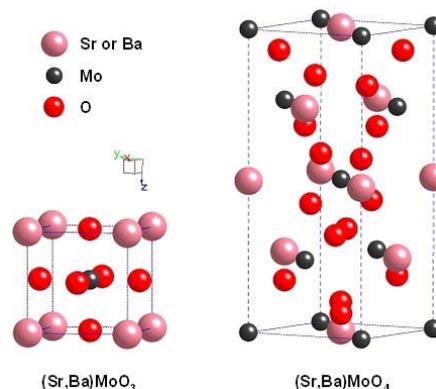


Fig. 1. Crystal structures of (Sr,Ba)MoO₃ (cubic perovskite) and (Sr,Ba)MoO₄ (tetragonal scheelite).

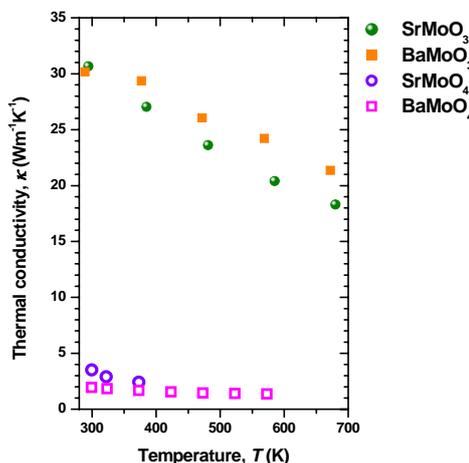


Fig. 2. Temperature dependence of the thermal conductivities of (Sr,Ba)MoO₃ and (Sr,Ba)MoO₄.

REFERENCE:

[1] K. Kurosaki et al., Proc. MS&T08, 313-318, (2008).

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INTRODUCTION: A pyrochemical process by using alkaline molybdate melt has been studied as a candidate reprocessing process for spent oxide fuels. This alkaline molybdate melt of $\text{Na}_2\text{MoO}_4\text{-MoO}_3$ mixtures can characteristically dissolve uranium dioxide, UO_2 , in a short time^[1]. It was confirmed by the XPS analysis of the coagulation salt samples that the uranium ions in the melt after dissolving the UO_2 pellet were tetra-valent ions. However, the chemical circumstances of uranium ions dissolved in alkaline molybdate melts have not been studied. Since the melting point of Na_2MoO_4 is high and it reacts with the measurement quartz cell, the absorption spectrophotometry has not ever been reported.

In this study, the absorption spectra of uranium ions in molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic at 550 °C were measured by the UV/Vis/NIR spectrophotometry, and the cyclic voltammetry was carried out in this pure eutectic. The melting point of this eutectic is lower than that of Na_2MoO_4 , and the corrosion damage of the quartz cell can be avoided.

EXPERIMENTS: All operations were conducted in a glove box with a dry argon atmosphere. The $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic salt was prepared by melting the mixed anhydrous reagents of Li_2MoO_4 and Na_2MoO_4 at 750 °C. The UO_2 powder was dissolved into molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic by adding MoO_3 . Then this source material containing uranium ions was added into the measurement melts used in the absorption spectrophotometry.

In the absorption spectrophotometry, about 8 g of the prepared $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic salt was put into the quartz tube which had a welded transparent optical measurement cell at the bottom of tube. Then they were heated to 550 °C. After taking the background absorption spectrum of the pure eutectic at 550 °C, a portion of the source material containing uranium ions was added into the melt and the absorption spectrum of uranium ions in the $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic was measured.

In the cyclic voltammetry, about 8 g of the prepared $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic was put into the quartz tube and heated to 550 °C. After melt was complete, a working electrode, a counter electrode and a reference electrode were all inserted into the measurement cell. Two platinum wires of 1 mm in diameter were used as the working and counter electrodes. The reference electrode utilized was composed of a Pyrex tube with $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic and a platinum wire.

RESULTS: Absorption peaks of uranium ions in molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic were found at 700, 910, 1470, and 1690 nm, as shown in Fig. 1. These observed spectra of uranium ions were similar to those of the uranyl penta-valent ion, UO_2^+ , in molten chlorides^[2]. Therefore, it indicates that the uranium ions in the molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic existed as UO_2^+ when UO_2 was dissolved into the melt. To confirm the stability of UO_2^+ , in molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic, oxygen gas was purged into the melt. After purging oxygen gas, the absorption peaks of UO_2^+ decreased and UO_2^+ was thought to be oxidized to the uranyl hexa-valent ion, UO_2^{2+} .

In the measured voltammograms in a pure melt as shown in Fig. 2, it was confirmed that alkali metals deposited at -0.7 V (vs. reference electrode) and oxygen generated from the melt at 1.0 V. The cyclic voltammetry in molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic was possible to measure like the electrochemical measurement in molten chlorides, but it was confirmed the potential window of molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic was narrower than those in molten chloride mixtures.

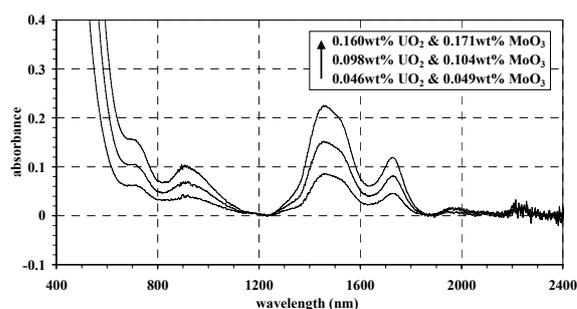


Fig. 1. Absorption spectra of uranium ions in molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic at 823K.

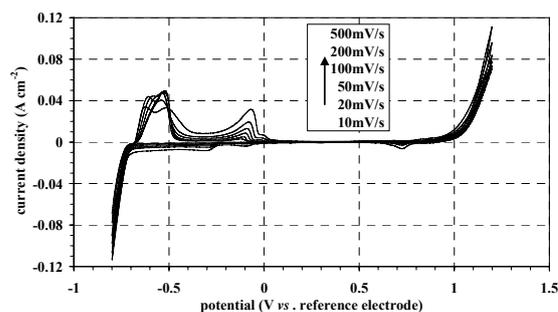


Fig. 2. Cyclic voltammograms in pure molten $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$ eutectic at 823K.

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PR4-10 Electrochemical Codeposition of U and Zr in LiCl-KCl-UCl₃-ZrCl₄ Melts

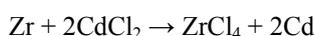
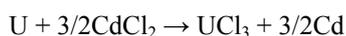
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INTRODUCTION: Electrorefining process is the major step of pyrochemical reprocessing of spent metallic fuel (U-Pu-Zr). The spent metallic fuel is loaded in the anode basket in LiCl-KCl melt. According to the reduction potentials of actinides on the solid cathode and the liquid cadmium cathode (LCC), uranium is selectively deposited on the solid cathode, and uranium, plutonium and minor actinide are recovered in LCC simultaneously. When electrorefining process is operated at high current density and high recovery rate of actinides (e.g., U: >99.5 %, Pu: >99.9 %, MA: >99.9 %), a portion of zirconium should be oxidized at the anode to form zirconium ions in the melt. Formed zirconium ions are reduced at the solid cathode and LCC with actinides. Therefore, it is inevitable to study the effect of zirconium ion on the performance of electrorefining process. However, electrochemical behavior of Zr [1] or actinides [2] in LiCl-KCl melt containing only respective ion has been investigated but not in the melt containing both zirconium and actinides ions. Then, in this study, potentiostatic electrolyses were performed to study the U and Zr codeposition in LiCl-KCl-UCl₃-ZrCl₄ melts.

EXPERIMENTS: All the experiments were conducted in an argon glove box under atmospheric pressure. High purity LiCl-KCl eutectic melts containing UCl₃ and ZrCl₄ was used as an electrolyte at 773 K. In order to prepare the melts, CdCl₂ was added into LiCl-KCl melts in which uranium or zirconium metal was immersed. Then, UCl₃ or ZrCl₄ was formed chemically in the melts according to the following reactions,

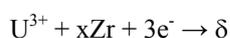


The working electrode was a Ta or Zr plate. The counter electrode was Zr plate. The reference electrode was Ag/AgCl electrode consisting of a silver wire immersed in LiCl-KCl eutectic melts containing 1.0 wt% AgCl, which was placed in a pyrex tube with thin bottom to maintain electrical contact with the electrolyte. Samples obtained after potentiostatic electrolyses were analyzed by XRD. The concentration of UCl₃ and ZrCl₄ in the melts was analyzed by ICP-AES.

RESULTS: Potentiostatic electrolyses at -1.6 V (vs. Ag⁺/Ag) were performed using Ta plate as the substrate in LiCl-KCl-UCl₃(0.13 mol%)-ZrCl₄(0.065 mol% or 0.24

mol%) melts. Since the standard electrode potential at 773 K for U³⁺/U and Zr⁴⁺/Zr is reported to be more positive than -1.6 V, it is considered that uranium and zirconium ions are reduced simultaneously at -1.6 V. From the XRD pattern of Fig. 1(a), it was shown that δ phase was formed in the high ZrCl₄ concentration melts (ZrCl₄/UCl₃ = 0.24/0.13 mol%). δ phase is a nonstoichiometric alloy in the U-Zr binary system, of which composition range is from 22 at%U to 34 at%U. In the low ZrCl₄ concentration melts (ZrCl₄/UCl₃ = 0.065/0.13 mol%), uranium and zirconium metals were deposited as shown in Fig. 1(b). On the other hand, in the case of potentiostatic electrolysis at -1.6 V using Zr plate as the substrate, δ phase was formed on the substrate even in the low ZrCl₄ concentration melts (ZrCl₄/UCl₃ = 0.050/0.13 mol%) as shown in Fig. 1(c).

Obtained results of potentiostatic electrolyses described above might indicate that δ phase would be formed only when uranium ion was reduced on zirconium metal.



Further investigation will be conducted on the detail condition for δ phase formation.

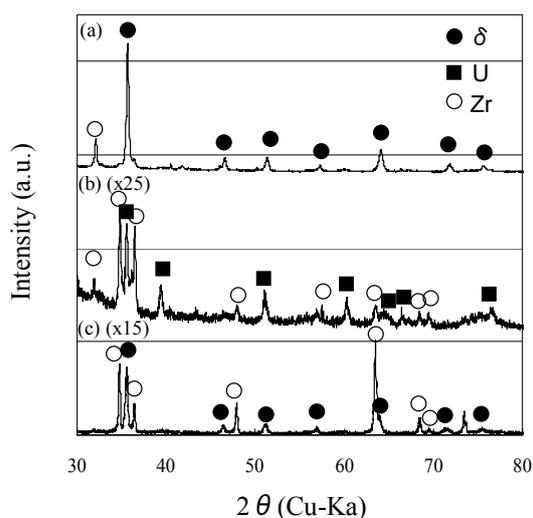


Fig. 1. XRD patterns of the samples obtained after potentiostatic electrolysis at -1.6 V. (a) on Ta substrate in the melts (ZrCl₄/UCl₃ = 0.24/0.13 mol%), (b) on Ta substrate in the melts (ZrCl₄/UCl₃ = 0.056/0.13 mol%) and (c) on Zr substrate in the melts (ZrCl₄/UCl₃ = 0.050/0.13 mol%).

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PR4-11 Chromatographic and Solvent Extraction Behavior of Mendelevium(III)

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INTRODUCTION: It is expected that the chemical properties of the heavy actinides and transactinide elements are deviated from the periodical trend since the influence of relativistic effect [1]. However, the chemistry of the heavy actinides and transactinide are limited because of the short lifetimes and small production rate of the nuclei, thus the chemical properties of these complexes have still unexplored. We study about the chemical behavior of the heavy and super heavy elements with the chemistry of the homologous elements and development of the chemical apparatus for the heavy and super heavy elements [2,3]. In this work, we report on the solvent extraction behavior of mendelevium by 2-thenoyltrifluoroacetone (HTTA) in HCl/CCl₄.

EXPERIMENTS: Mendelevium and thulium isotopes, ²⁵⁵Md ($T_{1/2} = 27$ min) and ¹⁶²Tm ($T_{1/2} = 21.7$ min) were produced in the ²⁴⁸Cm(¹¹B,4n)²⁵⁵Md and ^{nat}Gd(¹¹B,xn)¹⁶²Tm reactions using the RIKEN K70 AVF Cyclotron. Reaction products recoiling out of the target were stopped in a helium gas flow, attached to KCl aerosols generated by sublimation of KCl powder, and then transported to a chemistry laboratory.

1) Chromatography. The aerosol was collected on a naflon sheet. The products were dissolved in 50 μ L of 0.05 M HNO₃ and then the solution was chromatographed on a Ln resin column with a flow rate of 1.4 mL/min of 0.05 M HNO₃. The solution (fraction 1) eluted within 1 min, and the fraction 2 eluted from 1 to 2 min were collected into plastic tubes, respectively. The solutions eluted with 0.7 M and 6.6 M of HNO₃ were collected as the fraction 3 and 4, respectively. Each eluate was dried up on tantalum plates. The residue on the tantalum plate was measured by alpha spectrometry using silicon semiconductor detectors.

2) Solvent Extraction. The aerosol was collected on a polyester or naflon sheet. The products were dissolved in 100 or 200 μ L of NH₄Cl/HCl at pH 2.85, 3.00, 3.05, 3.08, 3.26, 3.36, 3.38, or 3.53. The equal volume of HTTA (0.1 M) in CCl₄ was added. The mixture was shaken for 20 min. After centrifuging for 1 min., the aqueous and organic phases were separated, and then dried up on tantalum plates. The residue was subjected to alpha spec-

trometry using Si semiconductor detectors and γ -ray spectrometry using Ge detectors. Distribution ratio (D) was obtained from radioactivities of each phase. The loss of radioactivities by sublimation of TTA complexes was corrected for the organic phase.

RESULTS: The alpha particle spectrum of the transported products showed the existence of ²⁵⁵Md, and the other isotopes ²⁵⁴Fm, ¹⁴⁹Tb were founded. In the column chromatography, ²⁵⁵Md was eluted with 6.6 M of HNO₃ and adsorbed in 0.05 M and 0.7 M of HNO₃. ²⁵⁴Fm was eluted both with 0.7 M and 6.6 M of HNO₃. This suggests that Md(III) is strongly coordinated with HDEHP in the resin compared with Fm(III) because Md(III) has the smaller ionic radius than Fm(III). The distribution ratios D of ²⁵⁵Md and ¹⁶²Tm against the pH of the aqueous phase in the solvent extraction are shown in Figure 1. The linear regression analysis of the data in Figure 1 gave the slope value ca. 3 in the range pH 2.8-3.4, although the D value was reached almost constant in the range pH 3.4-3.6. This suggests that the three TTA coordinate to the metal ion in the range pH 2.8-3.4 and hydrolysis of the complex was occurred at higher pH region. The D values of Md(III) and Tm(III) were very similar all over the pH region in this study.

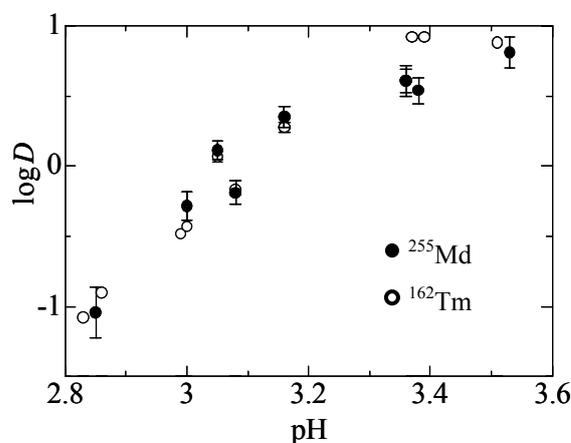


Figure 1. Extractions of ²⁵⁵Md and ¹⁶²Tm from NH₄Cl/HCl with 0.1 M HTTA in CCl₄.

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