VIII-Ⅱ-1. Project Research

Project 9

PR9

Application Studies on Effective Use of F-Elements

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1. Objectives and Allotted Research Subjects

Studies on actinide nuclides with careful management are being more important for reprocessing, disposal, partitioning, and transmutation processes in the nuclear fuel cycle. Hot laboratory of KURRI is one of core facilities in Japan, in which actinides especially transuranic elements (Pu, Am, Cm, and so on) can be treated. In our series of past research projects, separation, purification, and synthesis procedures were found to be effective for other elements, for example, rare metal refining. In this context, the actinide studies are expanded for fundamental and application studies on f-elements. Allotted research subjects are as the followings.

- ARS-1 Molecular dynamics simulation of molten salts containing f-elements (N. Ohtori *et al*.)
- ARS-2 Assessment study on chemical properties of actinides in molten salts (M. Myochin *et al.*).
- ARS-3 Absorption spectrophotometric study on titanium in molten salts. (T. Uda et al.)
- ARS-4 Study on complexation of actinides in aqueous solutions (T. Sasaki *et al*.).
- ARS-5 Spectroelectrochemical analysis of actinide ions in molten salts and hydrate melts (A. Uehara *et al.*)
- ARS-6 Study on chemical isotope effect of actinides and fission product elements (T. Fujii *et al.*).
- ARS-7 Systematic study on bonding characteristics of trivalent actinides with ligands (A. Shinohara *et al*.).
- ARS-8 Electrochemical study of uranium in pyrochemical reprocessing system (Y. Sakamura *et al.*).
- ARS-9 XAFS analysis on halogenides containing actinides and FP elements (H. Matsuura *et al*.).
- ARS-10 Fundamental and application studies on effective use of f-elements (Y. Ikeda *et al*.).
- ARS-11 Fundamental study on electrolytic formation/dissolution of f-element compounds in molten salts (T. Goto *et al*.).
- ARS-12 Study on neutron capture cross sections of long-lived nuclides by activation method (S. Nakamura *et al*.).

2. Main Results and Contents

ARS-1, 2, 3, 8, 9, and 11 studied the chemical behavior of actinides, lanthanides, FP elements, and structural material elements in molten salts, the results of which are to be dedicated to the development of nuclear fuel cycle or general industrial use. MD calculations of LiCl-KCl containing small amount of $TbCl_3$ was performed in ARS-1 and the structural information around Tb ions was obtained. In ARS-2, reduction from UO_2^{2+} to UO_2^{+} or U^{4+} in alkali chloride melts was studied. An applicability of tungsten as a reductant was confirmed. ARS-3 studied the effect of fluoride ion and oxide ion on the Ti^{3+} dissolved in chloride molten salt using the method for development of coherent electrodeposition of Ti^0. ARS-8 studied the reduction rate of UO_2 in LiCl and discussed the reduction mechanism of UO_2 using an one-dimensional diffusion layer model. In ARS-9, the local structure of Nd ions in molten chlorides was studied by extended X-ray absorption fine structure (EXAFS). All the samples were prepared at KURRI and XAFS analysis was performed at BL11XU, SPring-8. ARS-11 studied electrochemical behavior of Al ion in molten LiCl-KCl and LiCl-KCl-CsCl. The diffusion coefficient of Al(III) was determined. ARS-5 and 10 studied the U chemistry in low temperature or room temperature melts. Coordination circumstance and redox reaction of U ions in Ca chloride hydrate melt was clarified in ARS-5 by spectroscopic and electrochemical methods. In ARS-10, the electrochemical behavior of $(EMI)_2UO_2Cl_4$ (EMI: 1-ethyl-3-methylimidazoliun), in the mixture of EMICl and $EMIBF_4$ was studied and the basic electrochemical data were obtained. ARS-4, 6, and 7 studied aqueous chemistry of actinides and FP elements. ARS-4 studied Th solubility in the presence of humic substances. Dependence of the Th solubility on pH_c was clarified. ARS-6 studied Sr complexation by ab initio method. Optimized geometries of hydrated Sr species were calculated. ARS-7 studied precipitation properties of the hydroxide complexes of various FP elements. A multitracer produced at KURRI using UO_2 was supplied for ARS-7. Nuclear physical properties of TRUs were investigated in the study, ARS-12. By activation method using KUR, the thermal-neutron capture cross section of ^{237}Np was newly evaluated.

3. Summaries of the achievements

In this research, by using various unique facilities of KURRI for f-element 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 f-elements. The results are useful either for scientific purpose or for technological purpose for nuclear science and general industry.

採択課題番号 23P9　　ｆ－元素の有効利用に関わる基礎及び応用研究　　プロジェクト
（京大・原子炉）山名　元

PR9-1 Molecular Dynamics Simulation of Molten (Li-K)Cl Containing $TbCl_3$

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INTRODUCTION: Molten salts are hopeful solvents for lanthanides and actinides in reprocessing of nuclear fuel. However, knowledge of chemical stability of ionic species in melts is still inadequate to maximize their potential abilities. Information on local structure around ionic species in melts may provide useful measures for their stability in melts. Molecular dynamics (MD) simulation is a powerful tool to elucidate such the structures microscopically. In particular, recent MD simulations with polarizable ionic model (PIM)[1-4] have brought much progress in understanding of structure in ionic melts: they have successfully revealed more reliable pictures of local structures in UCl_3[2] and $LaCl_3$[3] melts and molten alkali chlorides containing $LaCl_3$[4] which are comparable with those from XRD and EXAFS studies. In this work, we have performed MD calculations of molten mixtures of lithium and potassium chlorides containing small amount of $TbCl_3$ in order to obtain the structural information around Tb ions.

CALCULATIONS: All the MD calculations have been carried out by using *NVT* condition[5]. The total ion numbers N were about 1700 in the cell volume V determined from the experimental density[6] at simulated temperature, T = 973 K. The ratios of LiCl to KCl in simulated melts were set at 25:75, 50:50, and 75:25 in mol%. Each melt was added with 1 mol% $TbCl_3$. as a solute. The potential parameters used in the present works were taken from the ref. [7].

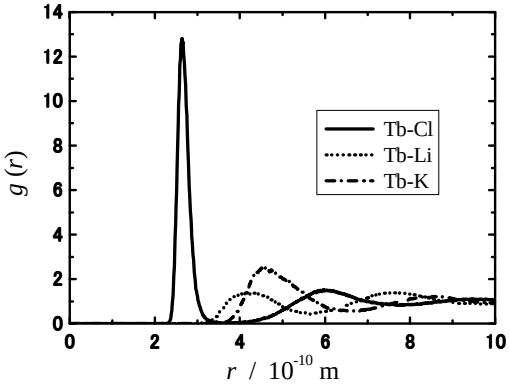

Fig. 1. Radial distribution function, obtained by the MD simulation, between Tb and the other ions in molten (Li-K)Cl at 973 K.

RESULTS: Figure 1 shows the obtained radial distribution functions between Tb and the other ions at the ratio of LiCl:KCl = 50:50 mol%. The first peak was observed at 2.64 Å in that for Tb and Cl pair. Although the peak position didn't depend on the composition of solvent melts, the angular distribution function clearly suggests that the first coordinated shell around Tb ion by Cl ions may become more regular octahedron with increasing KCl ratio as illustrated in Fig. 2.

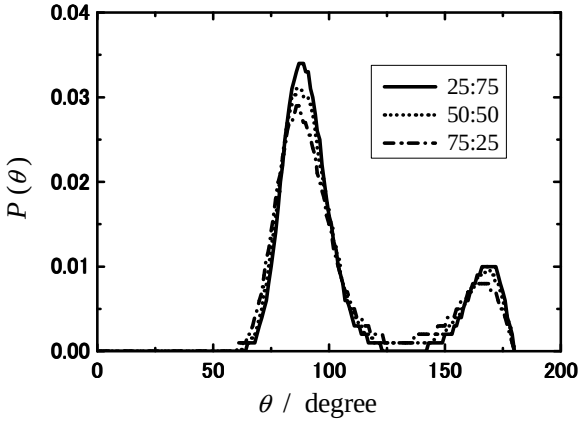

Fig. 2. The calculated angular distribution function of Cl-Tb-Cl in the first coordinated shell around Tb ion in molten (Li-K)Cl at 973 K.

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[1] P. A. Madden, R. Heaton, A. Aguado and S. Jahn, J. Mol. Struct.:THEOCHEM, **771** (2006) 9-18.
[2] Y. Okamoto, P. A. Madden and K. Minato, J. Nucl. Mater. 344 (2005) 109-114.
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[4] Y. Okamoto, S. Suzuki,H. Shiwaku, A. Ikeda-Ohno, T. Yaita and P. A. Madden, J. Phys. Chem. A, **114** (2010) 4664–4671.
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[6] G. J. Janz, in *NIST Molten Salts Database*, Ver. 2.0, (NIST SRD 27, 1992).
[7] M. Salanne, C. Simon, P. Turq and P. A. Madden, J. Phys. Chem. B, **112** (2008) 1177-1183.

採択課題番号 23P9-1　融体中での f-元素の分子動力学計算と実験系の照合研究　プロジェクト（新潟大・理）大鳥範和、石井良樹（京大・原子炉）深澤一仁、上原章寛、藤井俊行、山名　元（オックスフォード大学）Paul A. Madden

PR9-2 Reduction from UO_2^{2+} to UO_2^{+} or U^{4+} in Alkali Chloride Melts by using Tungsten

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INTRODUCTION: In the pyro-metallurgical method for reprocessing spent oxide fuels, it is necessary to once reduce from those oxides to metallic state. The currently proposed reduction process is electro-reduction technique, which electrolytically reduces UO_2 and PuO_2 to their metallic states, and those product metals are dissolved into melt. However, this dissolution is likely to cause appreciable amount of un-reduced oxides, which leads to the formation of actinyl ions dissolved in the melt. Therefore, the reduction of actinyl ions to lower valence states, such as trivalent and tetravalent ions, is desired before the refining operation. In this study, we made researches on the reduction from UO_2^{2+} to UO_2^{+} or U^{4+} in alkali chloride melts by using tungsten as a reductant.

EXPERIMENAL: All operations were carried out in a glove box filled with dry Ar gas. An anhydrous reagent of LiCl–KCl eutectic was purchased from Aldrich-APL L.L.C. and was used without further treatment. The uranyl source material containing UO_2^{2+} was prepared by dissolving the U_3O_8 powder with purging dry Cl_2 gas into the LiCl–KCl eutectic melt. In the spectrum measurements, the reagent of LiCl–KCl eutectic was put into the quartz tube which had a welded optical measurement cell at the bottom of tube. After measuring the background absorption spectrum of the pure melt, a portion of the uranyl source material was added into the melt and the spectrum of UO_2^{2+} was measured. And the tungsten mesh was immersed into the melt, and the valence change of uranyl ions was monitored until the spectrum was steady and the changed spectrum was recorded. After then, dry Cl_2 gas was purged into the melt in presence of the tungsten mesh, and the spectrum was measured after the remaining Cl_2 in the melt was removed by dry Ar gas purging.

RESULTS: In this experiment before the reductive operation, the absorption spectrum of the initial sample of UO_2^{2+} in LiCl–KCl eutectic at 500 °C was observed as shown in Fig. 1(a). When the tungsten mesh was immersed into the melt, the spectrum changed and other peaks were observed in the wavenumber range below 23000 cm^{-1} and small absorptions at 12500 and 15500 cm^{-1} as shown in Fig. 1(b). This spectrum is agreed with that of UO_2^{+} in LiCl–KCl eutectic.[1] This indicates that UO_2^{2+} reduced to UO_2^{+} by using the tungsten. However, in the spectrum in Fig. 1(b), the absorption peak of U^{4+} at 8500 cm^{-1} was slightly observed. In a word, there is a little possibility of the reduction from UO_2^{2+} to U^{4+}. By Cl_2 purging into the melt in presence of the tungsten mesh, the absorption peaks of UO_2^{2+} and UO_2^{+} decreased and another peaks appeared at 15000, 8500 and 5000 cm^{-1} as shown in Fig. 1(c). This spectrum was a good agreement with that of U^{4+} in LiCl–KCl eutectic.[2]

To identify the reductions from UO_2^{2+} to U^{4+}, these reaction paths were examined. When the tungsten was immersed into the melt, the reduction of UO_2^{2+} to UO_2^{+} was observed. This reduction of UO_2^{2+} to UO_2^{+} proceeded by the oxidation of tungsten, and can be given by following reaction 1. In the spectrum in Fig. 1(b) which can be slightly observed the peak of U^{4+} at 9000 cm^{-1}, the absorption of the produced WCl_2 by this reaction 1 was not observed. It is thought that the product of WCl_2 reacted as following reaction 2. The $WOCl_4$ could not be observed in the melt, and seemed to vaporize easily from the melt without remaining. We observed that the volatile compound was coagulated as red powder on the upper area of the cell. After then, purging Cl_2 into the melt in presence of the tungsten mesh, this coagulated powder grew to be needle-shape crystals on the upper area of the cell. The growth of these crystals was proved to proceed with increasing the amount of $WOCl_4$ by the reductions of UO_2^{+} and UO_2^{2+} to U^{4+} by following reactions 3 and 4, respectively.

$$2UO_2Cl_2 + W \rightarrow 2UO_2Cl + WCl_2 \quad (1)$$
$$7UO_2Cl_2 + 2WCl_2 \rightarrow 6UO_2Cl + UCl_4 + 2WOCl_4\uparrow \quad (2)$$
$$2UO_2Cl + 4W + 11Cl_2 \rightarrow 2UCl_4 + 4WOCl_4\uparrow \quad (3)$$
$$UO_2Cl_2 + 2W + 5Cl_2 \rightarrow UCl_4 + 2WOCl_4\uparrow \quad (4)$$

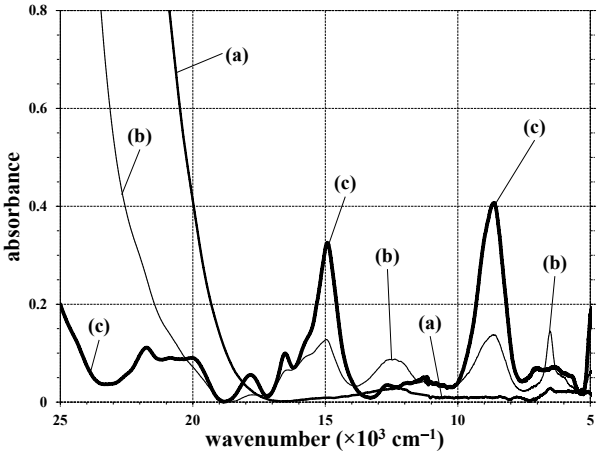

Fig.1. Absorption spectra of uranium ions before tungsten mesh immersion: (a), after tungsten mesh immersion: (b), and after additional dry Cl_2 gas purging: (c) in LiCl–KCl eutectic at 500 °C.

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[1] D. A. Wenz, *et al.*, Inorg. Chem., **3** (1964) 989-992.
[2] G. Landresse, Anal. Chim. Acta, **56** (1971) 29-37.

採択課題番号 23P9-2　アクチニド元素の溶融塩中での化学的性質の評価研究　プロジェクト
（原子力機構）小藤博英、永井崇之、岡本芳浩、明珍宗孝（京大・原子炉）上原章寛、藤井俊行

PR9-3 Caracterization of Dissoved Titanium Ion in Chloride Molten Salt

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INTRODUCTION:

The information on dissolved ions in molten salt is important for development and optimization of materials processing using molten salt electrolysis. The valence number of electrode active ions is an essential parameter. If active ions are complex ion, the structure of ions (for example, the kind of coordinating ion and its number) is also important. Nagai and his co-workers developed a method for in-situ measurement of absorption spectrum of dissolved ion in high temperature molten salt and applied it to some actinides for development of recycling process for nuclear fuels [1]. This method is useful to investigate the valence number and the complex of dissolved ions in molten salt. In this study, we investigated the effect of fluoride ion and oxide ion on the trivalent titanium ion dissolved in chloride molten salt using the method for development of coherent electrodeposition of metallic titanium.

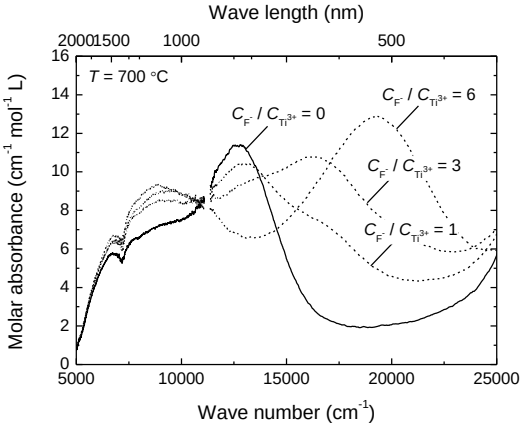
EXPERIMENTS:

We measured the absorbance of $TiCl_3$ dissolved in NaCl-KCl equimolar molten salt to obtain the absorption spectrum of Ti^{3+}. And then, we investigated the effect of F^- and O^{2-} on Ti^{3+} by repeating measurement of absorance and addition of NaF and Na_2O, respectively. The samples used in this study were mixtures of NaCl, KCl, NaF, Na_2O and $TiCl_3$ which were prepared by melting the reagents in a closed stainless container. The titanium trichloride ($TiCl_3$) was synthesized by the reported technique [2].

RESULTS:

Figure 1 shows the absorption spectra of the trivalent titanium ion in NaCl-KCl equimolar molten salt at 700 °C. The chloride complex of Ti^{3+} has an absorption peak at around 786 nm. We confirmed that the shape of the spectrum was drastically changed by adding F^- as shown in Fig. 1 (a). This change gradually proceeded by adding NaF until the ratio of the concentration of F^- to that of Ti^{3+} (C_{F-} / C_{O2-}) was over about 6. These results indicate that Ti^{3+} dissolved in NaCl-KCl molten salt reacted with F^- to form fluoride complex with 6 coordinate ions (TiF_6^{3-}), which may be more stable than chloride complex of Ti^{3+}. On the other hand, by adding O^{2-}, the shape of the spectrum of Ti^{3+} was not changed but the spectrum was slightly shifted upward as shown in Fig. 1 (b). We considered that this increase of absorbance is due to the decrease of the dissolved Ti^{3+} because the molar absorbance shown in Fig. 1 (b) is an apparent value obtained by division of the nominal mole of Ti^{3+} by the volume of the molten salt. We also confirmed that black particles were suspended in the molten salt after adding O^{2-}. The particles were identified to be TiOCl by XRD. Therefore, we considered that when O^{2-} is introduced to the NaCl-KCl molten salt containing Ti^{3+}, Ti^{3+} reacts with O^{2-} and Cl^- to form TiOCl.

(a)



(b)

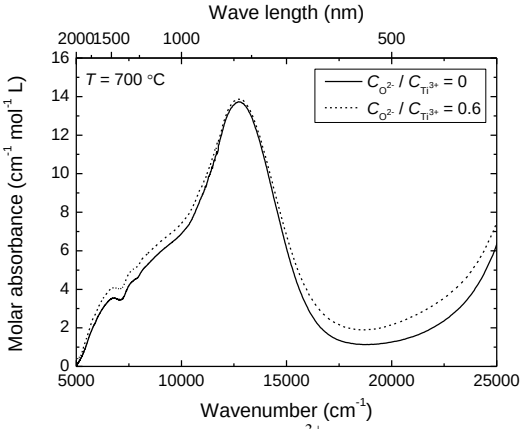


Fig. 1. Absorption spectra of Ti^{3+} in NaCl-KCl equimolar molten salt. Solid line attributes the absorption by chloride complex of Ti^{3+}. The broken lines corresponds the absorption spectra after adding anion, (a) F^- and (b) O^{2-}.

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[1] T. Nagai, T. Fujii, O. Shirai and H. Yamana, J. Nuc. Sci. Tech., **41** (2004) 690-695.
[2] H. Sekimoto, Y. Nose, T. Uda, H. Sugimura, High Temp. Mater. Proc., **30** (2012) 435-440.

採択課題番号 23P9-3　溶融塩中の吸収分光測定を用いたチタン製錬に関する研究　プロジェクト
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（京大原子炉）上原　章寛、藤井　俊行、山名　元

PR9-4 Thorium Solubility in the Presence of Humic Substances

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INTRODUCTION: The amount of radionuclide potentially mobilized in radioactive waste repository system is related to its solubility in groundwater. For tetravalent actinide, the solubility under relevant geological condition is rather limited because of strong hydrolysis reaction. However, in the presence of inorganic and organic complexing ligands, the 'apparent' solubility of tetravalent actinide may be influenced by forming complexes and compounds. For the reliable assessment of their migration behaviour, it is important to clarify dominant species and evaluate the solubility of tetravalent actinide quantitatively. Among various kinds of complexing ligands, humic acid (HA) prevails in groundwater and has strong complexation capability. HA consists of aromatic rings and hydrocarbon chains, has negatively charged functional groups, such as carboxyl and phenolic groups, and would strongly coordinate with tetravalent actinide with these functional groups. In the present study, we investigate the solubility of thorium(IV) in the presence of HA under different pH and ionic strength conditions to evaluate the impact of HA to the solubility of thorium(IV).

EXPERIMENTAL: A stock solution of thorium perchlorate was prepared from $Th(NO_3)_4{\cdot}4H_2O$ and a stock solution of purified humic acid (Aldrich HA) was obtained after purification. The initial Th concentration of sample solutions was set to be 10^{-6} mol/dm^3 (M) and the initial concentrations of humic acid were set to be from $5.28{\cdot}10^{-6}$ to $5.28{\cdot}10^{-3}$ eq/L. The hydrogen ion concentration (pH_c) was adjusted from 4 to 12 with $HClO_4$/NaOH and the ionic strength (I) was adjusted to be 0.1 and 1.0 by adding appropreate amount of $NaClO_4$. The sample solutions were kept in an Ar glove box. After given periods, the pH_c of each sample solution was measured using combination glass electrodes (9611-10D Horiba Ltd.) and the supernatant was filtrated through 0.45 μm syringe filter and 3k Da ultrafiltration membranes (ca. 2 nm pore size). Th concentrations after each filtration were determined by ICP-MS (HP4500, Hewlett Packard). The detection limit was around 10^{-10} M.

RESULTS: Th solubility in the presence of HA after 144 days is shown in **Fig. 1**. A dashed curve represents the solubilituy of $Th(OH)_4$(am) in the absence of HA [1]. In the presence of $5.28{\cdot}10^{-3}$ eq/L HA, the solubility values after filtration through 0.45 μm remain initial Th concentration level, while those after filtration through 3k Da show considerably low values. This trend is in good agreement with the size distribution of purified HA itself, and rather different from the size distribution of Th hydrolysis species. Therefore, it is considered that Th forms a complex with HA and the complex was filtered out by 3k Da membranes. In the presence of $5.28{\cdot}10^{-5}$ eq/L HA, similar trend is shown. In the acidic pH_c, the solubility values after filtration through 0.45 μm membranes are slightly lower than those in neutral and alkaline pH_c. Under acidic pH_c condition, HA is considered to release less protons and agglomerate to form larger species. The Th-HA complex may agglomerate in a similar manner and filtered out even by 0.45 μm. The trend is observed under the condition of I = 1.0 more clearly, suggesting that co-existing cation (Na^+) may affect the agglomeration of HA. Thus, we confirmed that HA coordicate with tetravalent Th to change the 'apparent' solubility of $Th(OH)_4$(am). It is also indicated that size distribution of the Th-HA complex is highly important, since Th-HA complex is thought to increase in size and filtered out by small size filters such as 3k Da membranes under certain condition. For the quantitative discussion of Th solubility in the presence of HA, and evaluation using thermodynamic data, further investigation is needed.

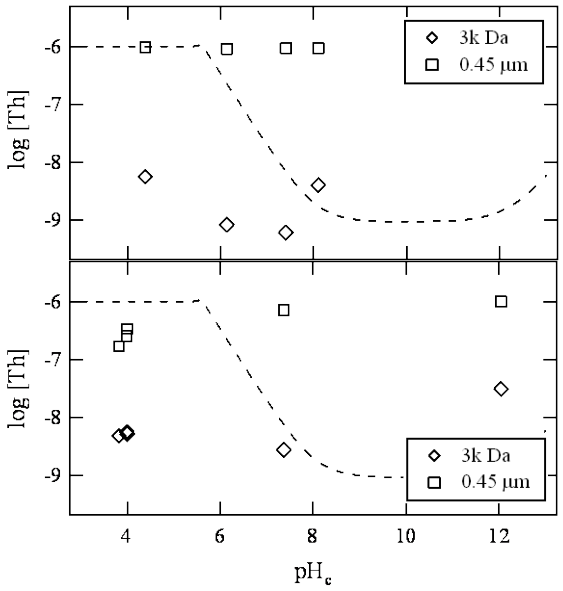

Fig. 1. Th solubility in the presence of $5.28{\cdot}10^{-3}$ eq/L HA (upper) and $5.28{\cdot}10^{-5}$ eq/L HA (lower) after filtration through 0.45 μm (□) and 3k Da(◇). The initial Th concentration is 10^{-6} M, and a dashed curve represents the solubility of $Th(OH)_4$(am) in the absence of HA [1].

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[1] Kobayashi, T., Sasaki, T., Takagi, I., Moriyama, H., *J. Nucl. Sci. Technol*. **48** (2011) 993–1003.

採択課題番号 23P9-4　　アクチニド元素の水溶液内錯生成反応に関する研究　　プロジェクト
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PR9-5 Electrochemical Characteristics of Uranium Ions in Calcium Chloride Hydrate Melts

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INTRODUCTION:

The calcium chloride hexahydrate, $CaCl_2 \cdot 6H_2O$, and similar hydrate melts are of considerable interest as solvents with properties intermediate between those of aqueous solution and molten salts. In view of the activity coefficients, viscosity and structural property, it is considered that water molecules in $CaCl_2 \cdot 6H_2O$ melts are strongly coordinated to the calcium ion and there are no free water molecules to dissociate to form H^+ and OH^-. As a result, this material has advantages such as inorganic-based melt and low melting temperature. In the present study, coordination circumstance and redox reaction of uranium ions such as U^{4+} and UO_2^{2+} in $CaCl_2 \cdot nH_2O$ hydrate melt (n = 6 – 10) have been investigated by spectroscopic and electrochemical methods. The chemical behavior of uranium ion in the hydrate melt was compared with that in the other solvents such as high temperature [1] or room temperature [2] molten salts, organic solvents [3] and relatively low concentration solution of hydrochloric acid [4].

EXPERIMENTAL:

For the electrochemical measurements, a three-electrode system was used. A pyro-graphite carbon (Toyo Tanso Co. Ltd.) of 3 mm diameter was used as a working electrode, and the silver|silver chloride (Ag|AgCl) electrode was used as a reference electrode. This reference electrode, in which was put an aqueous solution containing 1 M LiCl along with a Ag wire of 1 mm diameter coated by AgCl. For voltammetric operation, the platinum mesh electrode was employed as a counter electrode. Electrochemical measurement systems, Hz-5000 (Hokuto Denko Co.) were used for the cyclic voltammetry and the linear sweep voltammetry. Controlled-potential electrolysis was carried out in order to identify the electrode reaction. In this experiment, a rotating carbon electrode was employed as a working electrode to enhance the efficiency of the electrolysis. The counter electrode was also a platinum mesh electrode, and the counter phase was separated by glass filter membrane from the objective phase to avoid cyclic redox reaction. After the electrolysis, absorption spectra were measured. A self-registering spectrophotometer UV-1000 (Shimadzu Co.) was used for the measurements over the wavelength from 400 to 900 nm.

These measurements were carried out at 300 ± 2 K.

RESULTS:

Influences of the water content on chemical status of UO_2^{2+} and U^{4+} in $CaCl_2 \cdot nH_2O$ were also studied by electrochemical and spectroscopic methods. Visible absorption spectra of U^{4+} in $CaCl_2 \cdot nH_2O$ changed drastically along with the water content. This suggested the strong influence of water content on the coordination status of U^{4+} in the melt. Cyclic voltammograms of U^{4+} in $CaCl_2 \cdot nH_2O$ indicated that the U^{4+}/U^{3+} redox couple was quasi-reversible reaction and that the formal redox potential for the U^{4+}/U^{3+} couple was almost independent of the hydration number n to be 0.790 ± 0.010 V vs. Ag|AgCl reference electrode (1M LiCl) at 298 K. Diffusion coefficients of U^{4+} depended not only on the hydration number n but also on the temperature in the melts. The oxidation peaks of voltammogram were attributed to the oxidation of U^{4+} to uranyl ions by the water molecules. The results of the cyclic voltammogram of UO_2^{2+} in $CaCl_2 \cdot nH_2O$ showed that there are various reductions from UO_2^{2+} to lower valence states including the formation of UO_2^{+} and solid UO_2. The UO_2^{+} formed in $CaCl_2 \cdot 6H_2O$ was identified spectrophotometrically after the controlled potential electrolysis. On the other hand, it is reported that UO_2^{+} formed electrochemically in diluted acidic solutions such as 0.1M HCl disproportionates spontaneously to form U^{4+} and UO_2^{2+}. These results indicate that the UO_2^{+} in $CaCl_2 \cdot 6H_2O$ was more stable than that in the acidic solutions. It was also found that UO_2^{+} disproportionated to form UO_2^{2+} and UO_2 in $CaCl_2 \cdot 6H_2O$.

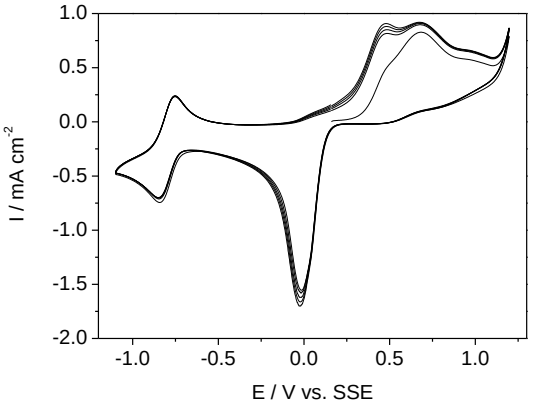

Fig. 1. Cyclic voltammogram of U^{4+} in $CaCl_2 \cdot 6H_2O$ containing 0.05 M UCl_4. Potential scanning rate is 0.02 V s^{-1}.

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採択課題番号 23P9-5　　溶融塩及び水和物溶融体中における　　プロジェクト
アクチノイドイオンの分光電気化学的研究

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（京大院工）深澤一仁、宇多健詞

PR9-6 Chemical Isotope Effect of Actinides and Fission Product Elements

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INTRODUCTION: Strontium 90 (^{90}Sr) is known as one of fission products, and it has a large fission yield. In order to know the chemical behavior of Sr complexes, we study the highly precise isotopic analysis of Sr [1]. The analytical technique will be helpful to understand the fractionation mechanism of Sr isotopes in environmental samples and so on. In parallel with the analytical studies, quantum chemical calculations are performed to check the validity of analytical results. The equilibrium constant of the isotope exchange reaction can be theoretically obtained as the reduced partition function ratio (RPFR) of isotopologues. The RPFR value is usually calculated through harmonic vibration analysis. In this study, we report some *ab initio* calculations of hydrated Sr^{2+} complexes.

COMPUTATIONAL DATAILS: The orbital geometries and vibrational frequencies of hydrated Sr(II) complexes were calculated by using the conventional Hartree-Fock (HF) approximation and the density functional theory (DFT) as implemented by the Gaussian03 code [2]. The DFT method employed here is a hybrid density functional consisting of Becke's three-parameter non-local hybrid exchange potential (B3) with Lee-Yang-and Parr (LYP) non-local functionals (B3LYP). The 6-31++G** basis set was chosen for H and O, and LanL2DZ was chosen for Sr. The former is an all-electron basis, while the latter is an effective core potential (ECP) basis.

RESULTS: The hydrated Sr^{2+} species is generally thought to be present as eight-coordinated $Sr(H_2O)_8^{2+}$. The structure was converged to be the square antiprism with 2.69 Å Sr-O bond length [3]. This agreed with literature data determined by a combination of the extended X-ray absorption fine structure (EXAFS) spectrometry and molecular dynamics (MD) [4]. Isotope fractionation of a Sr carbonate complex shown in Fig. 1 was estimated in the present study. The coordination number was set to be eight. Carbonate ion was treated as a bidentate ligand. This model complex was unstable and deformed into $[SrCO_3(H_2O)_5]H_2O$ with the 6th water molecule moving out of the inner coordination shell.

The isotope enrichment factor due to the intramolecular vibrations can be evaluated from RPFR [5], $(s/s')f$,

$$\ln (s/s')f = \Sigma[\ln b(u_i') - \ln b(u_i)] \quad (1)$$

where

$$\ln b(u_i) = -\ln u_i + u_i/2 + \ln (1 - e^{-ui}) \quad (2)$$

and

$$u_i = h\nu_i/kT \quad (3)$$

ν stands for vibrational frequency. The subscript i stands for the ith molecular vibrational level with primed variables referring to the light isotopologue. The isotope enrichment factor due to the molecular vibration can be evaluated from the frequencies (ν) summed over all the different modes.

The $\ln(s/s')f$ values of hydrated Sr(II) species were estimated by quantum chemical calculations. The results are shown in Table 1. Carbonate showed larger $\ln(s/s')f$ value compared with that of the hydrated Sr ion. This suggests that heavier Sr isotopes enrich in carbonate. These values may be useful to estimate the degree of isotope fractionation.

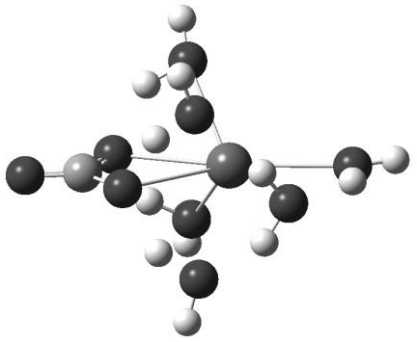

Fig. 1. Equilibrium geometry of $SrCO_3(H_2O)_6$.

Table 1 $\ln(s/s')f$ (‰) of hydrated Sr^{2+} species for an isotope pair, ^{86}Sr-^{88}Sr.

	HF	B3LYP
$Sr(H_2O)_8^{2+}$	1.424	1.416
$SrCO_3(H_2O)_6$	1.640	1.507

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採択課題番号 23P9-6　アクチニド元素及び FP 元素の化学同位体効果に関する研究　プロジェクト（京大・原子炉）藤井俊行、福谷　哲、山名　元

PR9-7 Investigation on the Properties of Hydroxide Precipitation 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. It is because the chemical properties of these elements would be unique, which is caused by strong relativistic effect on the shell electrons. It is, however, difficult to perform chemical experiment with heavy actinide and transactinide elements because these 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 and test them using the elements whose chemical properties are known.
We have ever developed the preparation method of a coprecipitate sample with Sm which has high energy resolution in the α spectrometry by using membrane filters [1]. In this work, precipitation properties of the hydroxide complexes of various elements were studied by this method using multitracer produced with Kyoto University Reactor (KUR) aiming at the precipitation experiment of heavy actinide and transactinide elements.

EXPERIMENTS: The KUR multitracer sample was prepared by irradiating thermal neutrons on UO_2 powder which is mixed with NaCl at KUR [2]. Fission products implanted in NaCl were dissolved in 0.01 M HCl and were separated from the UO_2 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, 200 μL of water and 20 μL (20 μg) of Sm standard solution (1 M HNO_3) were added into 20–40 μL of the multitracer solution. After mixing it, 2 mL of basic solution was added to generate hydroxide precipitate. In the present experiment, we used dilute NH_3 solution, concentrated NH_3 solution, 0.1, 1, 6, and 12 M NaOH solutions as the basic solutions to observe the dependence of the precipitation yield on the component 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 5 min in water bath after adding the basic solutions 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 precipitation yields were determined from the results of the γ-ray measurements.

RESULTS: Main nuclides identified from the γ-ray energies and their half-lives were ^{24}Na, ^{91}Sr, ^{95,97}Zr, ^{99}Mo, ^{103}Ru, ^{105}Rh, ^{131m,132}Te, ^{131,133}I, ^{140}Ba, ^{140}La, ^{141,143}Ce, and ^{151}Pm. To obtain correct precipitation yields, we exclude the nuclides whose decays are affected by their parent or daughter nuclide from determining the yields.
The precipitation yield for each nuclide is shown in Table 1. The yields of alkaline metal element were almost 0 %, and those of lanthanide elements were almost 100 %. It would indicate that chemical properties which are inherent in each element influence the coprecipitation yields with Sm. For some elements such as Zr and Ru, interesting dependences of the yields on the component of the basic solution were observed. For further discussion, precipitation properties of these elements, not coprecipitation properties, should be studied.

Table 1. Precipitation yields of multitracer.

Nuclide	dil.NH_3	conc.NH_3	0.1M NaOH
Na-24	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Sr-91	43.3 ± 0.8	74.6 ± 1.2	5.6 ± 0.2
Zr-97	100.0 ± 3.7	100.0 ± 15.6	100.0 ± 0.8
Ru-103	89.0 ± 9.9	50.7 ± 6.9	98.1 ± 5.7
Rh-105	100.0 ± 0.8	60.8 ± 1.2	100.0 ± 1.0
Te-132	79.8 ± 5.6	68.4 ± 0.6	95.4 ± 0.7
I-131	16.0 ± 0.6	9.9 ± 0.5	8.2 ± 0.2
I-133	20.5 ± 0.3	18.4 ± 0.3	11.8 ± 0.1
Ba-140	15.2 ± 1.9	100.0 ± 1.0	2.6 ± 0.0
Ce-143	100.0 ± 1.1	100.0 ± 1.1	100.0 ± 1.0
Pm-151	100.0 ± 1.5	100.0 ± 1.4	100.0 ± 24.3

	1M NaOH	6M NaOH	12M NaOH
Na-24	0.0 ± 0.0	0.2 ± 0.1	0.2 ± 0.0
Sr-91	1.3 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
Zr-97	84.2 ± 5.1	–	–
Ru-103	82.6 ± 4.2	15.2 ± 0.6	9.0 ± 0.3
Rh-105	100.0 ± 1.7	77.2 ± 2.4	74.5 ± 2.0
Te-132	35.1 ± 0.5	32.1 ± 1.4	23.5 ± 0.7
I-131	1.4 ± 0.1	1.7 ± 0.1	3.1 ± 0.1
I-133	4.0 ± 0.0	3.7 ± 0.2	5.9 ± 0.2
Ba-140	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
Ce-143	100.0 ± 1.7	100.0 ± 2.8	100.0 ± 2.2
Pm-151	100.0 ± 12.4	100.0 ± 16.0	100.0 ± 28.3

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採択課題番号 23P9-7 3価アクチノイドと配位分子との化学結合性の系統的研究　　プロジェクト
（阪大院・理）笠松良崇、塩原直也、横北卓也、小森有希子、吉村　崇、高橋成人、篠原　厚、（京大炉）高宮幸一

PR9-8 Mechanism of Electrolytic Reduction of UO_2 Pellet in Molten LiCl and LiCl-KCl

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INTRODUCTION: The electrolytic reduction process of actinide oxides in molten LiCl salt bath at 923 K has been developed for the nuclear fuel reprocessing. UO_2 and MOX can be reduced to the metallic form by the following cathode reaction:

$$MO_2 + 4\ e^- \rightarrow M + 2\ O^{2-}\ ,\ (M = U \text{ and } Pu). \quad (1)$$

Since salt-soluble FPs of alkali and alkaline-earth metals accumulate in the LiCl, their effect on UO_2 reduction was experimentally studied at KURRI [1]. UO_2 pellets were reduced by potential-controlled electrolysis in various LiCl salt baths containing up to 30 mol% of KCl. The reduction progressed from the outside toward the center of the UO_2 pellet. It was found that the reduction rate was remarkably decreased after the additions of KCl, which was attributed to the decrease in the solubility of Li_2O in the salt bath with increasing the KCl concentration [2]. In this study, the reduction mechanism of UO_2 was discussed using an one-dimensional diffusion layer model.

CALCULATION MODEL: The reduction mechanism of UO_2 pellets is considered as follows. The diffusion of O^{2-} ions from the inside of UO_2 pellet to the bulk salt determined the reduction rate. At first, the surface of UO_2 pellet is reduced to metal. The reduced U metal layer has gaps because the density of UO_2 is about 60% that of U metal, and the molten salt then permeates into the gaps. The O^{2-} ionized at the U metal/UO_2 interface is discharged to the bulk salt through the molten salt pass by diffusion. The O^{2-} concentration seems to be the solubility limit at the vicinity of the U metal/UO_2 interface since charge transfer of Eq. (1) is fast at high temperature. Therefore, the O^{2-} solubility to determine the driving force of diffusion strongly affects the reduction rate.

To simulate how the reduction progresses, an one-dimensional diffusion layer model was designed as shown in Fig. 1. The assumptions are as follows.

a) The cathode potential is negative enough to reduce UO_2 to U metal and charge transfer is fast. Thus, the diffusion of O^{2-} through the salt is the rate determining step.

b) The U metal formed in the beginning of electrolysis shrinks to give a dense outer layer, L_1 [1]. Inside the dense outer layer, the volume shrinkage of U metal does not occur to give a porous inner layer, L_2. ϕ_1 and ϕ_2 are effective porosities of L_1 and L_2, respectively.

c) In the δ_2 layer next to the UO_2/U metal interface, the value of diffusion coefficient of O^{2-}, D_1, might be smaller than the value at a low concentration, D_0, because the viscosity would increase with increasing the O^{2-} concentration. There is a diffusion layer, δ_1, outside of L_1.

Then, the following equation can be derived from the mass balance of O^{2-} ions.

$$\frac{i}{2F} = D_1\phi_2\frac{C_0-C_1}{\delta_2} = D_0\phi_2\frac{C_1-C_2}{L-L_1-\delta_2} = D_0\phi_1\frac{C_2-C_3}{L_1} = D_0\frac{C_3-C_4}{\delta_1} \quad (2)$$

Here, i is the current density, F is the Faraday constant and C_i is the concentration of O^{2-} at each interface.

RESULTS AND DISCUSSION: The relationship between the thickness of U metal layer and square root of the electrolysis time was calculated for LiCl and LiCl-10mol% KCl systems using Eq. (2) and the values of parameters appropriately determined considering the literature [1, 2]. Fig. 2 shows the calculated results along with the experimental results [1]. The values of D_0 for LiCl-10mol%KCl, ϕ_1 and ϕ_2 were mainly adjusted to best fit the experimental results. The negative deviation from the parabolic relation was reproduced by assuming both the shrinkage of outer U metal layer and the smaller diffusion coefficient of O^{2-} in a high concentration range. For improving the simulation, it is strongly desired to clarify the dependence of diffusion coefficient of O^{2-} on KCl and O^{2-} concentrations as well as the configuration of pore in U metal products.

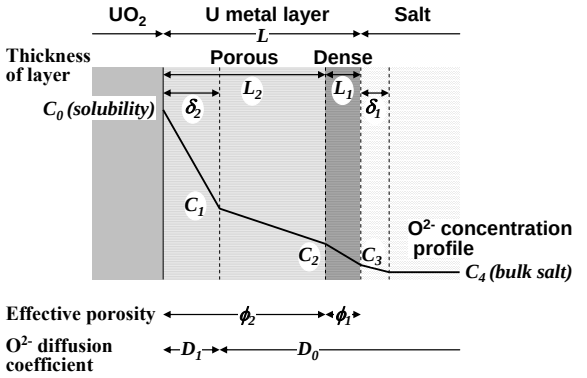

Fig. 1. Schematic view of one-dimensional diffusion layer model for electrolytic reduction of an UO_2 pellet.

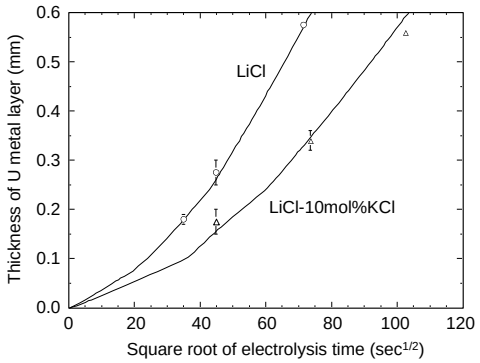

Fig. 2. Dependence of thickness of U metal layer on electrolysis time: comparison of calculated results (solid lines) with experimental values [1].

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採択課題番号 23P9-8　　溶融塩化物中でのウランの酸化還元挙動に関する乾式再処理基礎研究　　プロジェクト

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PR9-9 Local Structural Analysis of Neodymium Cation in Molten Various Chlorides

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INTRODUCTION: It is very essential to grasp the chemical behaviour of fuel elements and fission products in each step of processes in order to make realization of pyrochemical reprocessing of nuclear fuel. Neodymim is one of the fission products as well as the rare earth element having divalent cation through the electrochemical reaction[1]. It seems to be existing the simple relationship between the structural model and electrochemical properties of molten salts, however, even the variation of redox potential depending on various electrolytes has not been well explained scientifically. To obtain the information on the local structure of neodymium cation in various molten electrolytes, the systematic characterization using extended X-ray absorption fine structure (EXAFS) has been carried out.

EXPERIMENTS: Since the concentration of neodymium in electrolytes is 1 to 5 molar %, the EXAFS measurements have been carried out using high enegy X-ray generated at BL11XU, SPring-8, Japan. The samples of mixture melts have been molten in a quartz vessel kept in an argon circulated glove box and sealed in the quartz cells in a funnel or a rectangular type (X-ray path: 1.5 mm or 10 mm, respectively) under vacuum condition. EXAFS spectra of neodymium K- Edge (43.571 keV) of these samples heated at 923 K by an electric furnace[2] on the beamline have been obtained by a quick scan of transmission mode. The data analyses have been done using WinXAS 3.0[3] and FEFF 8.01[4] and the curve fitting analyses introduced 3rd and 4th cumulants have been performed since anharmonic oscillation effect cannot be ignored on the spectra at high temperature.

RESULTS and DISCUSSION: By utilization of X-ray from an undulator beamline, even such as highly diluted solution with the highly X-ray absorbing element, i.e. $NdCl_3$-$BaCl_2$-LiCl (1:10:89), could be measured within 5 minutes to obtain decent quality of spectrum. It is epoque making that the similar concentration of the electrolytes will be able to evaluated by EXAFS. Various structural parameters obtained by assuming 6-coodinated structure for the mixtures of 1 mol % of neodymium in 10 mol % of LiCl exchanged with KCl, CsCl, $CaCl_2$, and $BaCl_2$ are shown in Fig. 1. With reference to the inter-ionic distance between Nd^{3+} and Cl^- in molten pure LiCl, those with K and Ca do not so much variated but that with Cs gets shorten and that with Ba gets expanded. These tendencies are partly following to the structural information obtained for rare earth trichlorides in various alkali cationic chlorides[5,6]. Although the structural information obtained by EXAFS is limited to the 1st coordination sphere around neodymium cation, it is found that even in such diluted solution of neodymium, the local structure has been influenced by the cation existing in 2nd coordination sphere from neodymium. The tendency observed in the melts containing Ba^{2+} which has larger cationic size is one of the useful informations to explain the anomalous tendencies observed in UV-Vis spectroscopy and electrochemical behaviour[7,8].

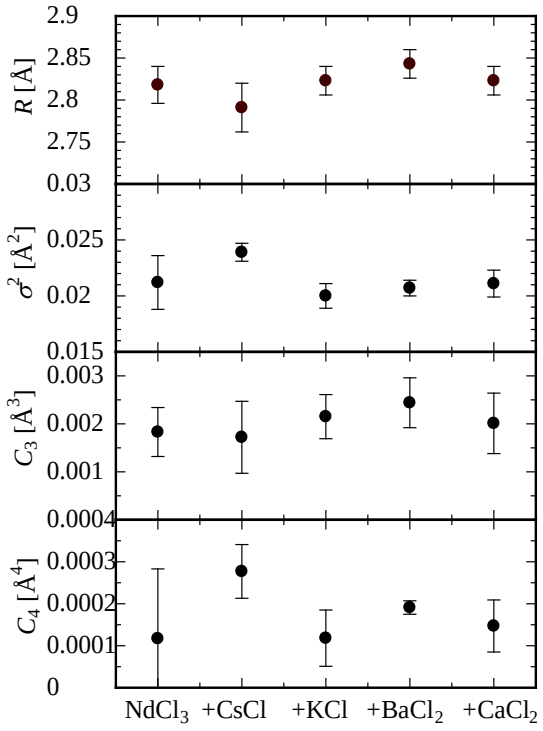

Fig. 1. structure parameters obtained by curve fitting analysis for neodymium in various melts.

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採択課題番号 23P9-9アクチニド元素及び FP 元素含有ハロゲン化物の XAFS 構造解析 プロジェクト
（東工大・原子炉研）松浦治明、赤塚　洋、根津　篤
（京大・原子炉）上原章寛、山名　元、藤井俊行

PR9-10 Electrochemical and Spectroelectrochemical Studies on $[UO_2Cl_4]^{2-}$ in 1-Ethyl-3-methylimidazolium Based Ionic Liquids - Identification of Uranyl(V) Species -

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INTRODUCTION: Room temperature ionic liquids (ILs) are expected to be useful media for recovering uranium from spent nuclear fuels and solid wastes contaminated with uranium[1], *e.g.*, as media for extraction and electrolytic deposition. Hence, the extraction behavior of uranyl species from aqueous to IL phase, the electrochemical behavior of uranyl species in ILs, and so on have been studied[2-5]. In the present study, we have examined the electrochemical behavior of uranyl(VI) species, $(EMI)_2UO_2Cl_4$, in the mixture of EMICl and $EMIBF_4$ (EMI = 1-ethyl-3-methylimidazoliun) to obtain the basic data for evaluating application of ILs to pyro-reprocessing process. We used the mixture of EMICl and $EMIBF_4$ as the reaction media, because this mixture is liquid at room temperature.

EXPERIMENTS: 1-Ethyl-3-methylimidazolium chloride and $EMIBF_4$ were commercially available from Kanto Chemical Co., Inc. The former was repeatedly (at least 4 times) treated with activated charcoal in acetonitrile, followed by filtration and vacuum evaporation, and the latter was used without further purification. The $[EMI]_2[UO_2Cl_4]$ was prepared by the similar method reported previously. UV-visible absorption spectra of solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ into $EMIBF_4$/Cl ($[Cl^-] = [BF_4^-] = 3.54 \times 10^{-1}$ M) were measured by using SHIMADZU UV-3150 spectrophotometer. Cyclic voltammetric (CV) measurements of sample solutions were carried out at 25 ºC under a dry Ar atmosphere using BAS ALS660B. A conventional three-electrode system was utilized, *i.e.*, a Pt disc working electrode (surface area (*S*): 0.020 cm^2), a Pt wire counter electrode and an Ag/Ag^+ reference electrode (0.01 M $AgNO_3$, 0.1 M tetra-*n*-butylammonium perchlorate in acetonitrile) connected to the sample solution through a glass frit filled with the solvent ionic liquid. The Fc/Fc^+ couple was used as the reference redox system. All potentials reported here are *versus* Fc/Fc^+. Dissolved O_2 in the sample solutions was removed by passing Ar gas through for at least 10 min prior to starting the CV measurements. The ohmic drop in this experiment was compensated by subtracting the cyclic voltammogram of the blank $EMIBF_4$/Cl solution from that of $[UO_2Cl_4]^{2-}$ in the same solvent.

RESULTS: The cyclic voltammograms of the EMICl and $EMIBF_4$ mixture dissolved $[EMI]_2[UO_2Cl_4]$ (6.06×10^{-2} M) were measured. One redox couple is observed around -1.0 V *vs*. Fc/Fc^+. It was found that the values of $(E_{pc} + E_{pa})/2$ (E_{pc} and E_{pa} are peak potentials for cathodic and anodic peaks, respectively) are constant (-0.989 V *vs*. Fc/Fc^+) regardless of the scan rates, and that a plot of i_{pc} (the peak currents of cathodic peaks) against $v^{1/2}$ gives a linear relationship with slope of 8.21. Furthermore, we estimated the standard rate constant (k^0) based on the kinetic parameter (ψ) proposed by Nicholson. The k^0 value was estimated as $(2.7\sim2.8) \times 10^{-4}$ cm/s in the range of scan rates from 50 to 300 mV/s. The estimated value is in the range of the k^0 value ($(4.0 \sim 9.9) \times 10^{-3} > k^o > (2.7 \sim 6.6) \times 10^{-7}$) for the quasi-reversible reaction on the basis of the reversibility factor (Λ) of Matsuda and Ayabe. These results suggest that the electrochemical reaction of $[UO_2Cl_4]^{2-}$ocuurs quasi- reversibly. In order to examine the reduction product, we carried out spectroelectrochemical studies using optically transparent thin layer electrode (OTTLE) cell in the range from 0 to -1.306 V. The isosbestic point is found to be observed around 350 nm. In addition, from the Nernstian plot, the electron stoichiometry (*n*-value) and the formal potential were evaluated as 0.99 and -0.99 V, respectively. These results indicate that $[U^{VI}O_2Cl_4]^{2-}$ is reduced to $[U^{V}O_2Cl_4]^{-}$ in the mixture of EMICl and $EMIBF_4$ and the resulting $[U^{V}O_2Cl_4]^{-}$ species are relatively stable.

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採択課題番号 23P9-10　　f-元素の有効利用に関わる基礎及び応用研究　　プロジェクト
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PR9-11 **Electrochemical Behavior of f-elements Compound**

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INTRODUCTION: Molten salts are promising media for separation and recovery of the spent nuclear fuel. To realize the process, clarifying the physicochemical properties of f-elements in molten salts is required. Although cesium is known as an important fission product, little has been reported about its effect on the molten salts. From the background, we have examined the influence that the existence of the cesium ion gave to other multi valence ions in molten LiCl-KCl. In this report, aluminum ion was selected as model of a multi valence cation (f-elements) and electrochemical behavior of aluminum ion in molten LiCl-KCl and LiCl-KCl-CsCl were investigated.

EXPERIMENTS: The LiCl-KCl-CsCl eutectic (LiCl-KCl-CsCl=57.5:13.3:29.2 mol %) was used as an electrolyte. $AlCl_3$ was directly added to the melt as an Al(Ⅲ) ion source. A Chromel-Alumel thermocouples were used for temperature measurement. The temperature was maintained within 1±K by a temperature control unit. All experiments were conducted in an argon atmosphere with a continuous gas refining instrument. A tungsten wire electrode covered with a high purity alumina tube was used as a working electrode for investigating electrochemical behavior of aluminum ions. The reference electrode was a silver wire immersed in LiCl-KCl-CsCl containing 1 mol% of AgCl, placed in a Pyrex glass tube with a thin bottom to maintain electrical contact with the melt. The potential of this reference electrode was calibrated with reference to that of a Li^+/Li electrode, which was prepared by electrodepositing Li metal on W wire. All potentials are given in reference to Li^+/Li electrode potential. A potentio/galvanostat was used for electrochemical measurement. Diffusion coefficient of aluminum ions was determined by means of electrochemical measurement. Micro Raman measurement was performed for analyzing the liquid structure and coordination of aluminum ion in molten salts.

RESULTS: Figure 1 shows a typical cyclic voltammograms (CV) obtained at 0.1 Vs^{-1} in the eutectic LiCl-KCl-CsCl melt containing Al(Ⅲ) ions on a tungsten electrode. The peaks A and A' are attributed to the reduction of Al(Ⅲ) to Al and the oxidation of Al to Al(Ⅲ) respectively.

$Al(Ⅲ)+3e^- \rightarrow Al$ (1)

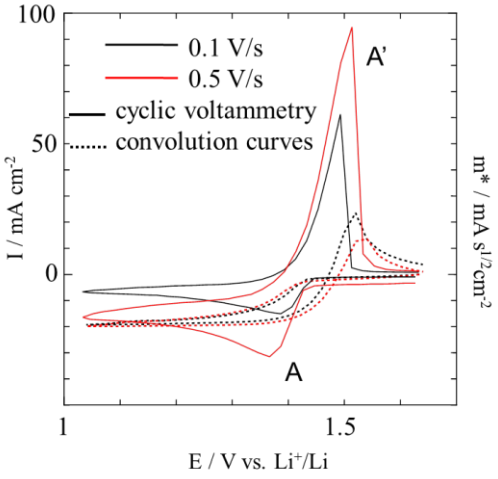
$Al \rightarrow Al(Ⅲ)+3e^-$ (2)

Detail analysis of the voltammogram CV was performed by using the convolutional analysis as shown in Fig.1. By analyzing the convoluted curves, it can be observed that the direct and reverse scans are not identical. This indicated that the reduction of Al(Ⅲ) on a tungsten electrode was not reversible reaction and the electrochemical couple of Al(Ⅲ)/Al was typically characteristic of a soluble-insoluble exchange.

According to the theory of convolution, the diffusion coefficient is calculated using the equation(3):

$$m^* = nFCD^{0.5} \quad (3)$$

where m^* is the limiting current of the convoluted curve of the corresponding cyclic voltammogram. The diffusion coefficient of Al(Ⅲ) in LiCl-KCl-CsCl at 603 K was estimated to be 4.0×10^{-8} cm^2 s^{-1}. The diffusion coefficient was 3 orders lower than that in LiCl-KCl. This implied the coordination of aluminum ion in the molten salts was affected by the existence of the cesium ion. These results were also supported by the Raman spectra of aluminum ion which largely changed greatly by the presence of cesium ions.



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採択課題番号 23P9−11　　溶融塩中における f−元素化合物の電気化学的形成・溶解に関する基礎研究　　プロジェクト

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PR9-12 Measurements of Neutron Capture Cross Sections for Radioactive Nuclei

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INTRODUCTION: As a part of the research projects, a series of cross-section measurements has been carried out for minor actinides to obtain basic data for studies on nuclear-fuel cycles and nuclear transmutation. Neptunium-237 is one of important isotopes because it contributes to the long-term radiotoxicity of nuclear wastes. However, there still exist large discrepancies among reported data of the thermal-neutron capture cross section (σ_0) as shown in **Figure 1**. Then, the present work reports the measurement for the thermal-neutron capture cross-section of ^{237}Np.

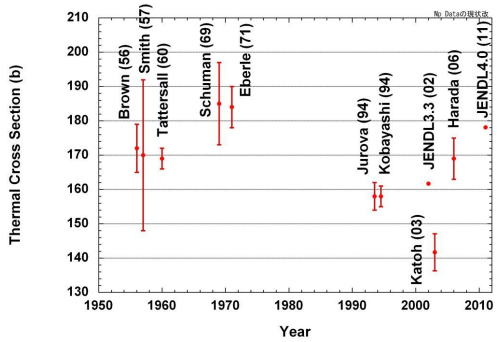

Fig.1. Situation of the reported data of σ_0 for ^{237}Np

EXPERIMENT: A standardized solutions of ^{237}Np (200Bq) were irradiated together with neutron monitors in the pneumatic tube (Pn-2) of the KUR in the latter half of 2010. The reactor power was 1 MW. The ^{237}Np samples were irradiated for 600sec, and another one together with a Gd shield (25μm in thickness) for 300 sec. After the irradiations, induced activities of samples were measured with a high purity Ge detector. **Figure 1** shows the neutron fluxes obtained from the measurements of the irradiated neutron monitors. The thermal neutron flux was 4.4×10^{12} n/cm^{2}sec at the irradiation position of the Pn-2.

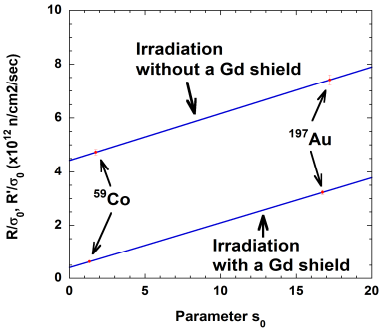

Fig.2. neutron flux components at Pn-2

ANALYSIS AND DISCUSSION: The reaction rates of ^{237}Np samples were calculated with γ-ray yields, efficiencies, decay data and γ-ray emission probabilities. However, there are still discrepancies among the data of the γ-ray emission probabilities (Iγ). The data of the emission probability for984-keV γ-ray emitted from ^{238}Np have been reported as shown in **Table 1**. These data are in good agreement with each other.

Table 1 984-keV γ-ray emission probability

Author	Year	984-keV Iγ (%)
Harada *et al.*	2006	25.2±0.5
Rengan *et al.*	2006	25.2±0.5
Chang et al.	1990	25.19±0.21
Lederer	1981	27.8
Winter *et al.*	1972	25.4

On the other hand, there are still discrepancies among reported data of Iγ for 984-keV γ-ray emitted from ^{233}Pa as listed in **Table 2**.

Table 2. 312-keV γ-ray emission probability

Author	Year	312-keV Iγ (%)
Harada *et al.*	2006	41.6±0.9
Singh and Tuli	2005	38.5±0.4
Schukin *et al.*	2004	37.5±0.24
Lucva *et al.*	2000	37.8±0.6
Woods *et al.*	2000	38.7±0.4
Gehrke *et al.*	1979	38.6±0.5

Then, when the combinations of Iγ data were changed, their influences on the σ_0 were examined. When the influences were examined about the data by Kobayashi and Katoh, their results are modified as shown in **Table 3**.

Table 3. influences on the σ_0 by the Iγ data

Author	Pa: 38.6% Np: 27.8%	41.6 25.2	38.5 25.2
This Work	-	198±8	183±7
Katoh('03)	141.7±5.4	169±6	156±6
Kobayashi('94)	158±3	196±4	181±3

The present work is in good agreement with the data by Kobayashi. From reviewing data, the discrepancies among the σ_0 of ^{237}Np would be caused by the Iγ data used for the analyses. The data of the σ_0 should be settled by experimental further check on the Iγ data.

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