

I-1. PROJECT RESEARCHES

Project 7

Chemical and electronic properties of Actinide compounds and their applications

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INTRODUCTION: Actinides exhibit characteristic chemical and electronic properties originating from 5f electrons, and their chemistry is important for nuclear fuel-cycle technology, separation science, radiochemistry, and medical-nuclide production. This project integrates actinide separation chemistry, data-driven extractant design, decay-product separation, and actinyl-ion coordination chemistry by using the hot-laboratory infrastructure of KURNS. In the present period, three submitted studies were summarized: machine-learning-assisted evaluation of extractants for minor actinide separation, Ra-228 recovery from Th resources for Ac-225 production, and bifunctional monoamide-diamide resins for selective adsorption of actinyl ions.

EXPERIMENTS: URhSi and URhGe single crystals were prepared by arc melting and examined by single-crystal X-ray diffraction. The OECD/NEA IDEaL database was linked to regression workflows with clustering of DGA, BTP, CMPO and related extractants. La extraction by D₂EHFA/n-dodecane was measured with ADA buffers as a model for Ac chemistry. Precise ¹⁰¹Ru-NQR measurements of URu₂Si₂ were continued under uniaxial [100] stress. For Ac-225 production, 6.0 g ThO₂ was processed using PVPP in 8 M HNO₃ to recover Ra-228 and recycle Th. Silica-supported DMAA-TMMA resin was synthesized and tested for U(VI), Ce(III) and Th(IV) adsorption in nitric acid.

RESULTS: URhSi and URhGe were confirmed to have TiNiSi-type structures, but Rh and Si/Ge sites are interchanged and the Rh-Si network in URhSi is strongly deformed, implying different 5f ground states and interlayer coupling. Class-specific machine-learning regressions gave higher accuracy than whole-dataset models, showing that extractant class and descriptors carry chemical significance. In D₂EHFA extraction, high distribution ratios were accompanied by pH decrease due to proton release, and ADA did not sufficiently suppress the pH shift. Ru-NQR under 0.23 GPa [100] stress showed no linewidth anomaly around the 18 K hidden-order transition, indicating no magnetic moment appears under this condition. PVPP adsorbed Th with a capacity of 0.140 g-Th/g-PVPP and recovered 96.6% of Ra-228 from a Th-Ra mixed solution; residual Th was reconverted to porous ThO₂. DMAA-TMMA and DMAA-TPMA resins enhanced U(VI) adsorption over a monoamide resin, with higher U(VI) than Ce(III) uptake and high Th(IV) affinity for DMAA-TMMA.

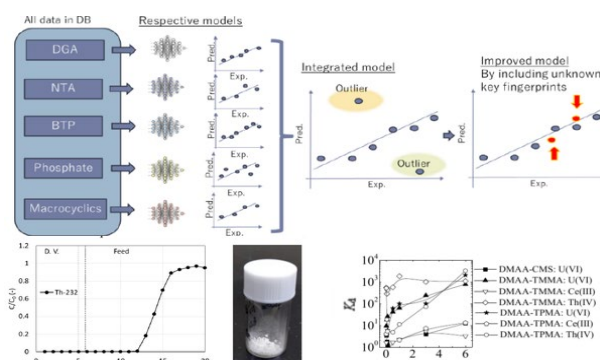


Fig. 1. Representative results: machine-learning workflow for MA extractants (top), PVPP-based Th/Ra separation and reconverted ThO₂ (bottom left), and adsorption behavior of monoamide-diamide resins toward U(VI), Ce(III), and Th(IV) in nitric acid (bottom right).

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Crystal Structure and Characterization of Actinide Intermetallic Compounds

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INTRODUCTION: Strongly correlated electrons in actinide compounds are the origin of various phenomena such as heavy fermion formation and exotic superconductivity coexisting with magnetic orderings. These phenomena are based on specific ground states of 5f electrons located in the crystal lattice. It is therefore critically important to determine atomic arrangements around the uranium site of interest. In this study, we focus on intermetallic uranium compounds showing ferromagnetic superconductivity. URhSi and URhGe are known to crystallize in the orthorhombic TiNiSi-type structure. Despite the very similar ferromagnetic properties, only the latter shows superconductivity.[1,2] In this study we reinvestigate the crystal structure of these compounds to precisely characterize the local atomic arrangements.

EXPERIMENTS: The samples were synthesized by arc-melting starting materials under an argon gas atmosphere. Small single crystals suitable for single-crystal X-ray diffraction were extracted from the arc-melted ingot. X-ray diffraction was measured using monochromated Mo K α radiation with an imaging plate detector.

RESULTS: We confirmed that URhSi and URhGe crystallize in the TiNiSi-type structure. Overall structural characteristics can be understood as follows: TiNiSi-type structure is derived from the ordered hexagonal AlB₂-type (known as ZrBeSi-type) structure. Here, uranium occupies the triangular site, while Rh and Si(Ge) form a honeycomb-like network. Indeed, these characteristics are well preserved in URhSi and URhGe. However, surprisingly, Rh and Si(Ge) sites are swapped with each other. Furthermore, Rh-Si network is strongly deformed in URhSi. As a result, the layered structure is no longer maintained, and interlayer coupling becomes significant. Note that all the existing experimental study on the crystal structure of these compounds consistently reported similar structural parameters for these compounds. The present results strongly suggest that the 5f ground state under the crystal field in URhSi and URhGe is different from one another. Moreover, the interlayer coupling in URhSi suggests modification on the conduction band. The ferromagnetism of these compounds might therefore have different origins. Further investigations on the evolution of the ferromagnetic interaction in the URh(Si,Ge) alloy are in progress.

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Development and Validation of a Machine Learning Scheme for Actinide Separation Chemistry

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INTRODUCTION: Minor actinides in spent nuclear fuel pose major heat and toxicity challenges despite their small quantities, motivating efforts to separate them from rare earth elements to reduce repository burden. While selective extractants are crucial, their compatibility with organic solvents strongly affects performance, making solvent choice equally important. This study combines systematic extraction experiments with chemoinformatics and machine learning to accelerate solvent and extractant screening, focusing especially on fluorinated solvents. Molecular features are mapped into Hansen solubility space to predict solubility and extraction behavior. To address the greater complexity of extractant design, the work builds data-driven models using curated databases and clustering to compensate for sparse data. Rather than inventing new ligands, the strategy optimizes side chains of established extractant frameworks such as DGA, BTP, and CMPO as shown in Fig. 1. Results indicate that medium-length straight alkyl chains favor fluorinated solvents and that tuning with co-components can further enhance performance. Overall, the study advances toward a unified predictive model for americium extraction by integrating chemical insight with machine learning.

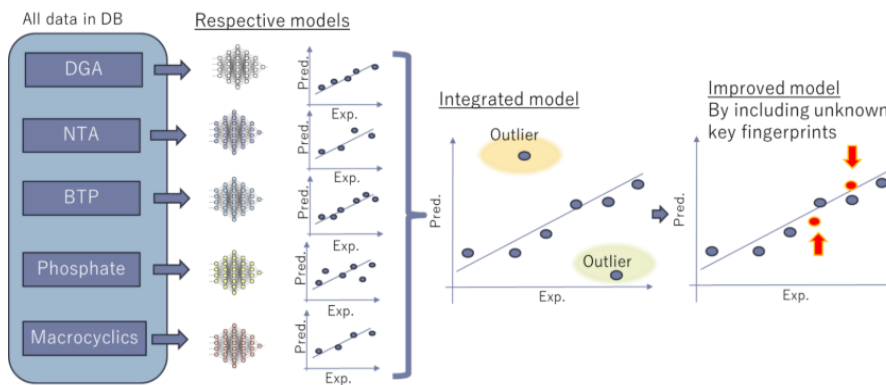


Fig. 1. Approach to identify the model to find a candidate MA extractant

RESULTS: The OECD/NEA IDEaL database was connected to machine learning workflows and performed a variety of regression analyses on extractant performance (Fig. 2). By clustering extractants into several groups and conducting regressions separately for each group while varying kernel types, we found that group-specific models achieve higher accuracy than models trained on the entire dataset. This indicates that extractant class and descriptor choice strongly influence regression performance and may reflect underlying chemical significance. Moreover, even extractants that are poorly fitted by regression—or appear as outliers—can provide valuable insights, suggesting opportunities to discover new extractants and identify key molecular features beyond conventional model predictions.

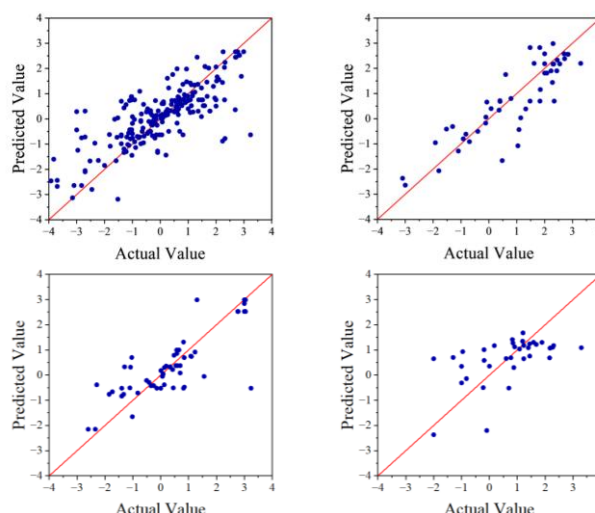


Fig.2 Result of regression with respective clusters: (1) all, (2)DGA, (3)BTP, and (4)CMPO

Solvent extraction of ^{228}Ac by D_2EHPA under pH range.

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INTRODUCTION: Actinium is the earliest element in the actinide series, which has 29 isotopes excluding metastable states, and is considered similar to lanthanum in chemical properties. In terms of oxidation state, actinium has only trivalent state like the elements after americium in the actinide series. Most isotopes of actinium are produced by nuclear reactions and have short half-lives of a few seconds to a few minutes. ^{225}Ac , one radioisotope of actinium, is used in targeted alpha therapy and has been reported to be highly effective to the cancer therapy, especially for prostate cancer [1]. ^{228}Ac , one of the thorium series, reaches radiolytic equilibrium with the parent nuclide ^{228}Ra in about 30 hours. Therefore, once separated, the same amount of ^{228}Ac can be collected again [2]. ^{228}Ac emits photons over a wide energy range and its emission rate is very high. With these properties, ^{228}Ac is expected to facilitate basic research on actinium, such as chelate chemistry, which is also required for labeling. Previously, the extraction behavior of ^{228}Ac and La by D_2EHPA in the pH range is evaluated using shaking time, extractant concentration dependence, and pH as indicators for study basic coordination chemistry of actinium.

In this study, the ADA buffer concentration dependence has been investigated using La for the suitable extraction condition investigation.

EXPERIMENTS: The buffer ADA is used as the aqueous phase, and n-dodecane (nDD), one of hydrocarbonate solvents with properties such as nonflammability, chemical stability and low viscosity, were used as the organic phase. Initially, La was dissolved in the aqueous phase. Under the various ADA concentration condition, La in the aqueous phase was extracted into the organic phase by complexation with D_2EHPA . The distribution ratio was used as an index to evaluate how much La in the aqueous phase was extracted into the organic phase.

RESULTS: In regions where the D_2EHPA concentration is high—that is, where the partition coefficient is large—the pH decreases (Fig. 1). This is thought to be due to the effect of proton release by D_2EHPA . Proton release resulting from complexation between D_2EHPA and La causes the pH to decrease. The problem is that the pH decrease cannot be suppressed due to the buffer effect of ADA.

This suggests that ADA is hardly dissociated into protons, meaning that its buffer function is not being fully exerted.

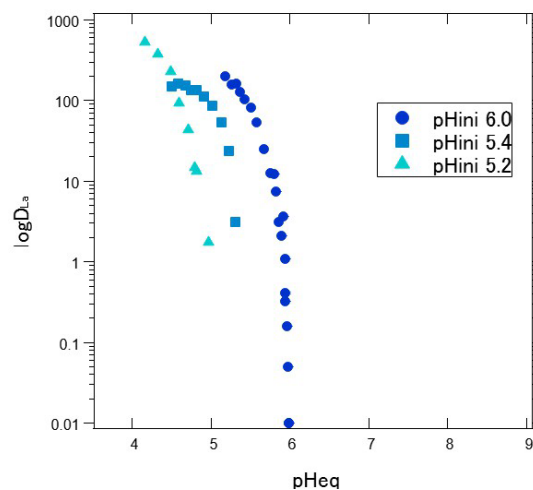


Fig. 1. pH Dependence of the Distribution Ratio D_{La} at Equilibrium

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Study of Heavy Fermion Superconductor URu₂Si₂ NQR/NMR under uni-axial stress

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INTRODUCTION: Understanding of "Hidden ordering" in URu₂Si₂ is fairly progressed recently [1], whereas the definitive answer is still missing. This issue is very exciting since the hidden ordering is supposed to be new spontaneous symmetry breaking. Considering the recent experimental

results, a few possible space groups of hidden order symmetry have been selected previously [2,3]. If the hidden order symmetry is once determined, the corresponding multipolar order parameter is spontaneously determined.

EXPERIMENTS: In this study, the local symmetry of Ru site is determined in the hidden order state without uni-axial stress and with uni-axial stress along the [100] and [110] directions [4], by means of precise Ru-NQR measurements. These measurements again support the 4-fold symmetry at Ru site in the hidden order state without uni-axial stress. Furthermore, certain cases can be excluded from the previously proposed possible ones. In this year, the Ru-NQR measurements under uni-axial stress [100] direction are continued.

RESULTS: Fig. 1 shows the T-dependence of ¹⁰¹Ru NQR linewidth W_{1Q} at zero field under uni-axial stress σ along [100] direction of 0.23GPa. As ¹⁰¹Ru is $I=5/2$ nuclei, there are two NQR peaks are observed *i.e.* ν_{1Q} ($I = \pm 3/2 \leftrightarrow I = \pm 1/2$) and ν_{2Q} ($I = 5/2 \leftrightarrow I = \pm 3/2$). In the present case, the linewidth for ν_{1Q} results are presented. The T-dependence of W_{1Q} shows no anomaly at the hidden ordering around 18K in the case under [100] stress. This indicates that no magnetic moment appears at the hidden order phase transition under [100] stress.

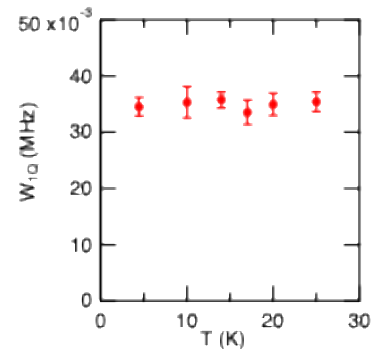


Fig. 1. T-dependence of ¹⁰¹Ru NQR linewidth W_{1Q} at zero field under uni-axial stress $\sigma[100]=0.23$ GPa.

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Fundamental Study on Extraction/Separation of Actinides and Their Decay Products for Medical Nuclide Production

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INTRODUCTION: Targeted alpha therapy using Ac-225 has been shown to be effective in treating cancer, and research using Ac-225 is currently being actively conducted. To improve the production capacity of Ac-225, a method has been proposed that utilizes naturally abundant Th-232 to generate Ra-229 via the (n,γ) reaction of Ra-228 using thermal neutrons, and then produces Ac-225 through the decay of Ra-229. However, the amount of Ra-228, a decay product of Th-232, present in natural ThO₂ is extremely limited. Therefore, it is necessary to efficiently separate this trace amount of Ra-228 from the large quantities of Th-232. In previous studies, a method was developed to recover the non-adsorbed Ra-228 by adsorbing Th-232 using polyvinylpyrrolidone (PVPP) [1]. In this study, the effectiveness of Ra-228 separation using PVPP was evaluated by conducting a series of processes from ThO₂ conversion to Ra-228 separation. Furthermore, a fundamental study on reconversion of the used Th into a porous oxide form to facilitate the subsequent re-separation of Ra-228 after equilibrium was performed to achieve more efficient recovery of Ra-228 from Th resources.

EXPERIMENTS: The primary conditions for this series of processes, such as reaction temperature and concentration of nitric acid, are the same as those in previous experiments [1-3]. However, due to the increased amount of ThO₂, certain conditions, such as the amount of adsorbent, have been modified accordingly. In this study, 6.0 g of ThO₂ was treated to evaluate Ra-228 separation using PVPP. Since previous Th adsorption experiments on PVPP were performed using trace amounts of Th-232, a breakthrough experiment of Th on PVPP was conducted to determine the adsorption capacity. The feed solution consisted of 20 mL of 8 M HNO₃ solution in which 2.0 g of thorium nitrate was dissolved. The bed height of PVPP was 93 mm (1.8 g) and the flow rate was set to 0.25 mL/min. After the separation of Ra-228, Th in solution was recovered as thorium oxalate using 0.05 M oxalic acid and then reconverted to a porous oxide form by heating at 630°C for 2 h.

RESULTS: Fig. 1 shows the breakthrough curve of Th-232 on PVPP. The Th adsorption capacity on PVPP under the present conditions was determined to be 0.140 g-Th/g-PVPP. Based on this result, the column separation conditions were optimized, resulting in a recovery ratio of 96.6% for Ra-228 from a Th-Ra mixed solution using PVPP. As described above, the effectiveness of Ra-228 separation using PVPP in the target fabrication process was demonstrated. Moreover, the conversion of Th remaining after the separation of Ra-228 into a porous oxide form was successfully achieved as shown in Fig. 2.

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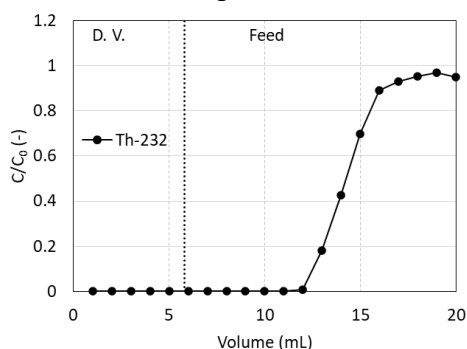


Fig. 1. Breakthrough curve of Th-232 on PVPP.



Fig. 2. ThO₂ (reconverted).

Effect of Chain Length of Bifunctional Monoamide-Diamide Resin on Adsorptivity to Actinyl Ions

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INTRODUCTION: Development of highly selective compounds for hexavalent actinide species (actinyl ions, An(VI), AnO_2^{2+}) has been important. We have been focusing on monoamide compounds which coordinate with An(IV) and (VI) species in nitric acid media. It is known that diamide compounds are used for separating not only An(IV) and (VI) species but also An(III) and lanthanide(III) (Ln(III)) ones. To increase the possibility of coordination of carbonyl oxygen atoms with an AnO_2^{2+} ion from the spatial viewpoint, bifunctional resins consisting of both monoamide and diamide compounds have recently been synthesized. As a result, adsorptivity to U(VI) was found to become improved compared with that of resins consisting of exclusive monoamide structure as expected[1]. In this study, effect of the chain length of diamide structure in the bifunctional resin on the adsorptivity was investigated.

EXPERIMENTS: In the previous study, *N,N*-dimethylacrylamide (DMAA) and *N,N,N',N'*-tetrapentylmalonamide (TPMA) were used as monoamide and diamide, respectively. In this study, *N,N,N',N'*-tetramethylmalonamide (TMMA) were used instead of TPMA (Fig. 1). The bifunctional resin was synthesized similarly to the previous study using two steps, where chlorine atoms of polychloromethylstyrene (CMS) were substituted by TMMA [1], and the final silica-supported resin (Silica DMAA-TMMA) was obtained. Adsorptivity of the resin was examined by a batch method using U(VI), Ce(III), and Th(IV) up to 6 mol/dm³ (= M) HNO_3 at room temperature.

RESULTS: Dependence of K_d values of each resin for U(VI), Ce(III), and Th(IV) (representative of An(IV)) on HNO_3 concentration is shown in Fig. 2. The values of DMAA-TMMA and DMAA-TPMA for U(VI) are basically identical, increasing with increasing concentration of HNO_3 . The adsorptivity of both resins are significantly improved compared with the monoamide resin (DMAA-CMC). Besides, the K_d values for U(VI) are higher than for Ce(III), suggesting that, as expected, bifunctional monoamide-diamide resins may improve adsorptivity to An(VI) by suppressing the adsorption for Ln(III). On the other hand, it was also clarified that DMAA-TMMA have higher selectivity for Th(IV).

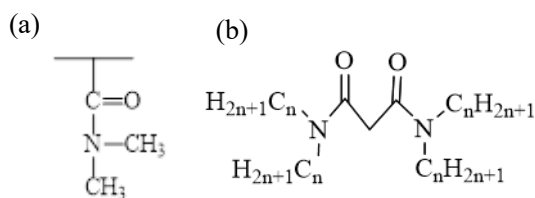


Fig. 1. Chemical structures of (a) DMAA and (b) diamides (TMMA (n=1), TPMA (n=5)).

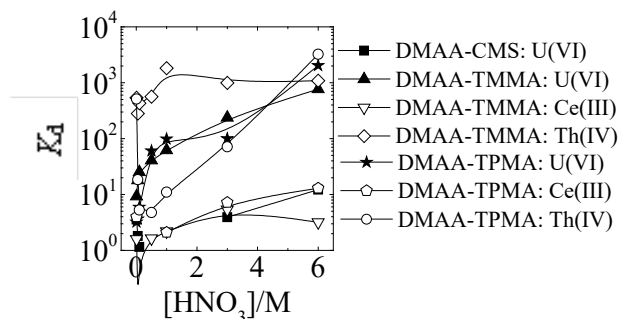


Fig. 2. Adsorptivity of monoamide-diamide resins to U(VI), Ce(III), and Th(IV) in HNO_3 .

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