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Microscopic analyses of complexes formed in adsorbent for Mo and Zr separation chromatography

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ABSTRACT

Molybdenum and zirconium obstruct the efficient recovery of minor actinides (MA(III): Am(III) and Cm(III)) by extraction chromatography; hence, the removal of these elements prior to MA(III) recovery is desirable. The use of an adsorbent impregnated with bis(2-ethylhexyl) hydrogen phosphate (HDEHP) for Mo and Zr decontamination was evaluated in this report. The adsorption/elution and column separation experiments showed that Mo and Zr in the simulated HLLW were selectively adsorbed on the particles, and that Mo was eluted by H₂O₂. EXAFS analysis and SAXS patterns of the adsorbent containing Zr revealed that the Zr-HDEHP complex had a crystal-like periodic structure similar to the structure of the precipitate produced in the solvent extraction system. Micro-PIXE analysis revealed that distribution of the residual Zr on the adsorbent was uniform.

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1. Introduction

Separation of MA(III) contained in high-level liquid waste (HLLW) from the other fission products is desirable because of their strong decay heat and radiation energy. In recent years, extraction chromatography has been proposed as a candidate [1] for the recovery of MA(III) from HLLW. The adsorbent used for this technique is prepared by impregnating an extractant onto a styrene-divinylbenzene copolymer coating around a porous silica particle (SiO₂-P) [2]. Currently, two column separation operations are required to recover MA(III) by extraction chromatography: MA(III) and lanthanides (Ln(III)) are recovered from the HLLW by the first column, and MA(III) are separated from Ln(III) by the second column [3]. Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and bis(2-ethylhexyl) hydrogen phosphate (HDEHP) extractants are used with the adsorbents of the first and second columns, respectively. Molybdenum and zirconium inhibit the group separation of MA(III) and Ln(III) by the CMPO/SiO₂-P adsorbent [4]. We propose a Mo and Zr adsorption removal method using a HDEHP/SiO₂-P adsorbent packed column, which is

expected to show highly selective extraction behavior toward these two species from a highly acidic medium.

In this paper, we report the adsorption and elution behavior of Mo and Zr at various nitric acid concentrations using the HDEHP/SiO₂-P adsorbent. The distribution and chemical state of non-eluted elements in the particles were evaluated through EXAFS, SAXS, and micro-PIXE analyses.

2. Experimental

2.1. Adsorbent

Porous SiO₂ (particle diameter: 50 μm, pore diameter: 50 nm) was coated with a styrene-divinylbenzene copolymer (cross-linking degree of 15%), followed by impregnation with 20 wt% of the HDEHP extractant, as detailed previously [1]. These HDEHP/SiO₂-P particles were used as the adsorbent for Mo and Zr in the following experiments.

2.2. Adsorption and elution experiments

Batch adsorption experiments were carried out using Mo(VI), Zr(IV), and Nd(III) in a nitric acid medium on the HDEHP/SiO₂-P

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adsorbent. For each cation, a feed solution with a concentration of 20 mmol/dm³ (mol/dm³ = M) was prepared. A glass vial was filled with 0.2 g of the adsorbent and 4 cm³ of the feed solution, and then shaken mechanically for 3 h at 298 K. After separation of the solid and liquid phases, the cation concentration was measured by UV–vis spectrophotometry. In order to evaluate the adsorption performance, the distribution coefficient K_d was obtained by Eq. (1), where

$$K_d = \frac{C_{\text{aq-ctrl}} - C_{\text{aq}}}{C_{\text{aq}}} \times \frac{V}{W} \quad (1)$$

C is the cation concentration [mM], and the indexes *aq* and *ctrl* correspond to the aqueous phase and control respectively. V is the volume of the solution [cm³], and W is the dry weight of the adsorbent [g].

The separation apparatus consisted of a Pyrex glass column (ϕ 10 mm \times h 150 mm) with a cooling water jacket, plunger pump, pressure gauge, and fraction collector. In the column separation experiment, 7.85 cm³ of the sample solution containing Mo(VI) or Zr(IV) in 3.0 M HNO₃ was loaded onto the column at a constant flow rate of 5 cm³/min. Then, a washing solution and an eluent were successively introduced onto the column. The effluent from the column was fractionally collected every 3 cm³. Cation concentrations in each fraction were analyzed by UV–vis spectrophotometry, and elution curves of the cations were obtained.

2.3. Micro-PIXE analysis

Micro-PIXE analysis was carried out on the adsorbent under various conditions in order to evaluate the distribution of cations inside the particles, before and after the batch elution operation. In advance with the analysis, contamination of the sample particles was checked by SEM-EDX analysis. The experiment was performed with a light-ion microbeam line connected to a 3 MV single-ended accelerator at the Takasaki Ion Accelerators for Advanced Radiation (TIARA) facility, at the National Institute for Quantum and Radiological Science and Technology, Japan. The proton beam energy used was 3 MV, and the beam spot size and projection area were 1 \times 1 μm^2 and 150 \times 150 μm^2 respectively. The particle fixed on a carbon fiber was set in vacuum environment, and characteristic X-ray from the particle was detected by a lithium-drifted silicon detector. Energy resolution of the detector at 2.3–10.5 keV is 110–220 eV. The distance from the particle and the detector was 18 mm. 2 dimensional mapping of Si, Mo and Zr were obtained by analyzing X-ray spectra. Quantitative evaluation were not carried out in this study.

2.4. X-ray analyses

The structures of the complexes found in the adsorbent after the elution operation were investigated by X-ray diffraction (XRD), small angle X-ray scattering (SAXS), and extended X-ray absorption fine structure (EXAFS) analyses. The precipitate generated in the third phase of the solvent extraction system using 0.1 M HDEHP in dodecane was also investigated for comparison. The SAXS and EXAFS experiments were carried out at the BL10C and BL27B beam lines, respectively, at the Photon Factory in the High Energy Accelerator Research Organization, Japan.

3. Results and discussion

3.1. Adsorption/elution experiments

Fig. 1 shows the distribution coefficients of Mo(VI), Zr(IV), and Nd(III) as a function of nitric acid concentration.

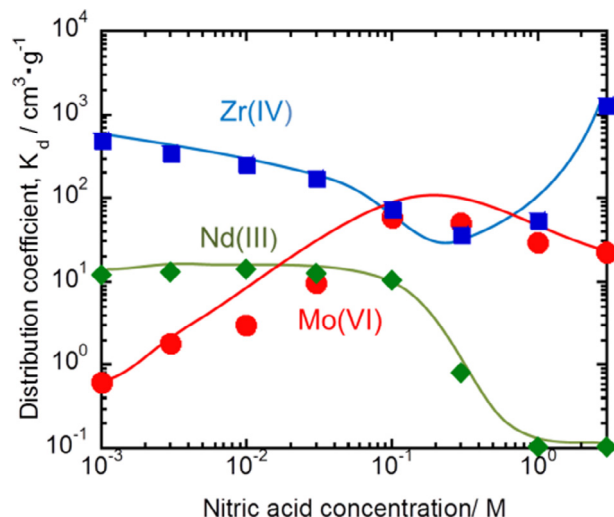


Fig. 1. Distribution coefficients of Nd(III), Mo(VI), and Zr(IV). ([Metal] = 20 mM, Contact time: 180 min, Temperature: 298 K).

The distribution coefficient of Nd(III) significantly decreased with increasing nitric acid concentration above 0.1 M. It has been reported that six molecules of HDEHP extract one trivalent cation by forming a chelate complex after the release of three H⁺ ions [5]. Therefore, the reaction progress is hindered under highly acidic conditions.

On the other hand, the adsorption behavior of Mo(VI) and Zr(IV) was distinctly different from that of Nd(III). The chemical state of Mo(VI) in solution is known to be pH dependent: MoO₂²⁺ for pH = 0–2 and MoO₄²⁻ for pH > 2 [3,6,7]. The local maximum in the distribution coefficient was a result of the change in the extraction reaction for Mo(VI) resulting from by the change in its chemical state.

The distribution coefficient of Zr(IV) also showed distinct acid–base dependence and was larger than that of Mo(VI) at most concentrations. These distribution coefficients indicate that Zr(IV) is difficult to elute from the HDEHP/SiO₂-P adsorbent by changing only the concentration of nitric acid, while Mo(VI) is expected to be discharged from the adsorbent by washing with a less acidic solution.

Column separation experiments were carried out in order to confirm the elution performance of Mo(VI) and Zr(IV). The elution curves of Mo(VI) and Zr(IV) with several eluents are shown in Figs. 2 and 3, respectively. In these column experiments, several solutions (0.5 M C₂H₂O₄, 1 M CH₃COONH₄, 1 M CH₃COOH, 50 mM DTPA, 50 mM IDA, and 0.5 M H₂O₂) were examined as eluents for Mo(VI) and Zr(IV) in order to select the appropriate eluent for each cation. Table 1 shows the recovery ratios of Mo(VI) and Zr(IV) calculated from the elution curves.

For Mo(VI), a recovery ratio of more than 90% was achieved when using 0.5 M C₂H₂O₄, 1 M CH₃COONH₄, 50 mM DTPA, and 0.5 M H₂O₂ solutions as the eluent from the HDEHP/SiO₂-P adsorbent. The 0.5 M C₂H₂O₄ and 1 M CH₃COONH₄ solutions were desirable as they allowed for rapid elution and afforded a sharp elution curve. The chemical states of the eluted species were [MoO₄][C₂O₄] and [MoO₄]₂[C₂O₄] for the C₂H₂O₄ solution, and [(NH₄)₂][MoO₄] for the CH₃COONH₄ solution. This was because the adsorbed MoO₂²⁺ from a less acidic solution was converted into MoO₄²⁻ with an increase in pH of the eluents passing through the column [7,8].

In contrast, the Zr(IV) was not discharged by any eluents. As discussed above, elution of Zr(IV) from HDEHP/SiO₂-P by a change in the acidity was not expected. In order to chemically remove the charged Zr(IV) from the adsorbent, the chemical states of Zr(IV)

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