Chemistry

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Sorption of Eu(III) by a Smectite Thin Film by XAFS and Voltammetry

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Introduction

Sorption of actinides(III) on smectite should be studied to elucidate the migration behavior of actinides(III) in backfill materials of geologic disposal facility. We propose the method using smectite thin film for the sorption experiments to avoid uncertainty caused by change in pH and chemical species of actinides(III) during the experiments.

Reversibility of adsorption of Eu(III), an alternative of actinides(III), was examined by cyclic voltammetry (CV), where cyclis voltammograms of Eu(III)/Eu(II) were measured, and chemical forms of Eu(III) sorbed on smectite film were measured by X-ray absorption fine structure (XAFS).

Experimental

Smectite and Eu solution

Smectite ($Na_{0.33}(Si_{3.67}Al_{0.33})Al_2O_{10}(OH)_2$) was obtained from Kunimine Kogyo Co. Ltd., Japan, and originated from Tsukinuno, Japan. The Na^+ form of the smectite was used in the experiments. Eu solutions were prepared by diluting a $Eu(NO_3)_3$ stock solution in the DDI water to obtain Eu concentrations from $1.0x10^{-4}$ mol·L^{-1}. The pH of the Eu solutions were adjusted from 5.8 to 7.8 with a 1 M NaOH and 1 M HCl solutions.

Sorption experiments and analysis

A 30 µl solution of 1g smectite·L^{-1} was placed on a glassy carbon plate. A smectite film attached to electrode was made by drying the above sample for overnight at room temperature. The smectite film attached to electrode was immersed in the 20 ml NaCl solution of 0.025 mol·L^{-1} containing $1.0x10^{-4}$ mol·L^{-1} Eu for 2 hours at 25 °C. The solution had been purged with Ar during the sorption experiments since 20 minutes before the start. The cyclic voltammetry (CV) measurements were carried out in an undivided electrode cell. Working electrode, the counter electrode and the reference electrode were glassy carbon covered with smectite film, Pt and a saturated calmel electrode (SCE), respectively.

After the sorption and voltammetric experiments, the smectite films attached to electrodes were separated from the electrolyte solutions, followed by washing with the DDI solution. The Eu-L-edge X-ray absorption spectra were measured for the wet smectite film attached to electrodes at Photon Factory of High Energy Research Organization beam line 27B. Spectra were measured in fluorescence mode for all samples using 9-element Ge array detector interfaced to single-channel analyzers. XAFS analysis was performed by using the REX-2000 of Rigaku, Japan. Least squares fitting of the nearest shell was carried out to determine the coordination number (CN) and bonding distance (R).

Results

Voltammetry analysis

The cyclic voltammograms of the Eu sorbed on the smectite film showed reduction peak of Eu(III) and oxidation peak Eu (II). On the contrary, no peak was detected in 0.025 mole·L^{-1} electrolyte solution without Eu. The peak current intensity of Eu(III)/Eu(II) decreased with increasing pH in the Eu solutions.

XAFS of Eu sorbed on smectite films

The XAFS spectrum of Eu sorbed on smectite film at pH 5.9 resembled that dissolved in solution at pH 5. In RSF high intensity at R around 2 was obtained for Eu sorbed on the smectite film and dissolved in the solution. The bonding distance (R) between center Eu and the first nearest neighbor oxygen atoms was 2.43 Å, and coordination number (CN) was 8.4. These values were in good agreement with those of Eu in the solution of pH 5. At pH 7 the XAFS spectrum and RSF of the sorbed Eu were similar to those of $Eu(OH)_3$. R between center Eu and the first nearest neighbor oxygen atoms was 2.48 Å, and CN was 5.46. These values did not agree with Eu in the solution of pH 5, but with $Eu(OH)_3$.

Conclusions

CV and XAFS analysis indicate that decrease in the intensity of the peak current was caused by the change of the chemical species of the sorbed Eu(III) from $Eu(III)^{3+}$ to Eu hydroxides. It is concluded that the present method using a thin film of smectite with CV and XAFS was effective to study the sorption behavior of redox sensitive elements on smectite.

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