XAS Investigation of Eu Sorption at Oxide-Water Interfaces Affected by the Siderophore Desferrioxamine B

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Introduction

The U.S. Department of Energy (DOE) must decommission and decontaminate a large number of surplus facilities containing approximately 180,000 metric tons of metal, mostly carbon steel and stainless steel. Common contaminants of these DOE facilities are the actinides and lanthanides. Previous studies have confirmed that the passivity layer formed on the steel surfaces is highly radioactive and is a complex mixture of oxides [1]. Decontaminating these metal surfaces requires dissolving the surface oxide layers and solubilizing the contaminants. Hence, chelators and strong acids that can dissolve iron oxides are potential candidate decontamination agents. Among these candidates, siderophores, the naturally occurring chelators, are the focus of this study because of their high affinities for iron and actinides and because they are less environmentally hazardous than other organic and inorganic acids.

To evaluate the feasibility of using siderophores for decontamination, it is necessary to develop a better understanding of (1) the interaction between siderophores and actinides and iron oxides, (2) the surface chemical properties that foster dissolution, and (3) the conditions that maximize dissolution. Therefore, it is important to identify the local structure and coordination chemistry of adsorbed species at the solid-water interface in order to develop molecular-scale predictions of the efficacy for the removal of actinides by siderophores. This direct structural information can be obtained only from the results of microscopic studies, such as x-ray absorption spectroscopy (XAS) analysis.

Methods and Materials

Several solids were used in this study to simulate the passivity layers on steel surfaces. These solids included hematite (α-Fe_2O_3) and Cr-substituted iron oxides (3.5% and 15% Cr-substituted hematite), synthesized on the basis of methods from Schwertmann [2] and Busca et al. [3]. These solids have different crystalline structures, morphologies, and surface characteristics, as analyzed by x-ray diffraction (XRD); color measurement; magnetic susceptibility; scanning electron microscopy (SEM); potentiometric titration; Brunauer, Emmett, and Teller (BET) surface area measurement; infrared absorption spectroscopy (IR); the thermogravimetric method (TG); and differential thermal analysis (DTA).

Eu sorption samples were prepared in a glove box under argon gas with a total Eu concentration of 10^{-4} M and with 0.01 M sodium nitrate as the background electrolyte. The solution pH was adjusted to 7, and the solid concentrations were adjusted to have 20 m^2/L of solid surface areas in each sample. These samples were then put in a shaker to equilibrate for 24 h at room temperature before 10^{-3} M of the siderophore, desferrioxamine B (DFB), was added. Samples were to equilibrate for another 24 h at pH 7 before centrifuging. The paste form of the centrifuged samples was than stored in bottles under argon gas and loaded into the sample cells prior to XAS data collection. Eu XAS spectra were collected at the L_{II} edge at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) sector 13 at the APS by using a wavelength dispersive spectrometer (WDS).

Results

The extended x-ray absorption fine structure (EXAFS) spectra and radial distribution functions (RDFs) of selected Eu sorption samples and model compounds are shown in Figs. 1 and 2, respectively. It was found that adsorbed Eu formed similar local structures at the oxide-water interfaces in the presence of DFB, regardless of the different characteristics of the adsorbents. Nevertheless, the structural environment of adsorbed Eu with DFB was different from that of adsorbed Eu without DFB. XAS results suggested that adsorbed Eu formed both monodentate and bidentate inner-sphere complexes on the solid surfaces but only bidentate inner-sphere complexes in the presence of DFB. The macroscopic kinetic study of Eu desorption and iron dissolution by DFB (experiments conducted in parallel to the microscopic study) showed that Eu was desorbed from solid surfaces by DFB but reached a plateau within 2 h of the reaction time. Iron dissolution by DFB, on the other hand, was retarded by the adsorbed Eu. These results indicated that the weaker bonded monodentate inner-sphere complexes that Eu formed on oxide surfaces could be removed by DFB, while bidentate inner-sphere complexes remained on the solid surfaces under the experimental conditions used in this work. Furthermore, the results also suggested that Eu bidentate surface complexes occupied the surface reaction sites on the solid surfaces, thereby blocking the sites from the access of DFB, which caused the decrease of Fe dissolution within the reaction time in this study.

Discussion

The surface coverage of Eu on solids ranges from 2.1 to 3.3 μmol/m^2 for samples without DFB and from 1.0 to
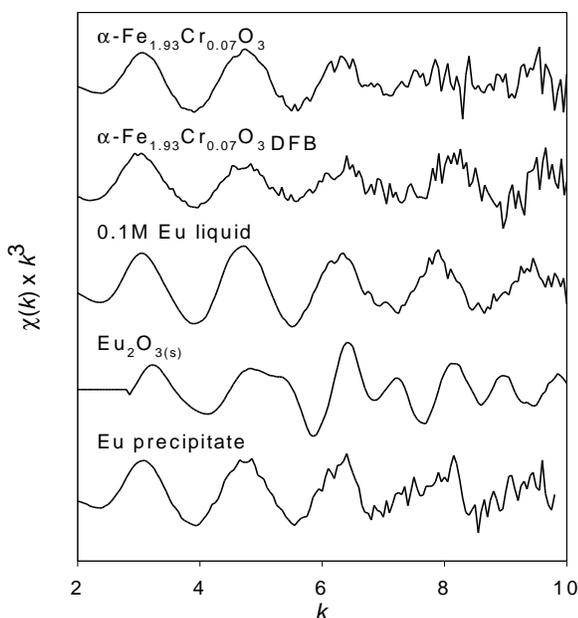
FIG. 1. EXAFS spectra of Eu on 3.5%-Cr-substituted hematite (with and without DFB) and Eu model compounds.
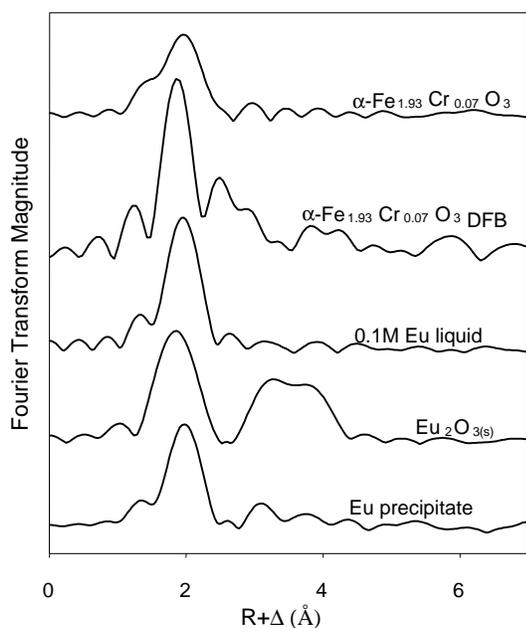
FIG. 2. Radial distribution functions of Eu on 3.5%-Cr-substituted hematite (with and without DFB) and Eu model compounds.

$1.6\,\mu mol/m^2$ for samples with DFB. EXAFS analysis of these samples was based on the structural parameters derived from a FEFF8 [4] theoretical calculation that used a $Eu_3Fe_5O_{12(s)}$ crystalline structure.

XAS analysis showed that the distances between central Eu ions to the first-nearest-neighbor oxygen atoms for sorption samples without DFB are 2.40-2.42 Å, with coordination numbers (CNs) of 8.2-9.5. The second shell can be fitted with a Eu-Fe path at distances of 3.38-3.40 Å with CNs of 0.7-1. For sorption samples with DFB, the spectra can be fitted with Eu-O at 2.33-2.35 Å with CNs of 8.5–9.4 and with Eu-Fe at 3.05–3.08 Å with CNs of 2.1–2.9. Eu liquid had a coordination structure with a Eu-O CN of 11 at a distance of 2.43 Å. For $Eu(OH)_3$ fresh precipitate, the first shell Eu-O distance is 2.44 Å with a CN of 10, and the second shell Eu-Eu distance is 3.51 Å with a CN of 1.6. The Eu_2O_3 model compound has six Eu-O at 2.31 Å and six Eu-Eu at 3.60 Å. The Debye-Waller factors for the first shell Eu-O for the sorption samples are 0.009-0.011, comparable to the factors in the published data [5] for the first shell Eu-O. The Debye-Waller factors for the Eu-Fe path are 0.004-0.005.

EXAFS analysis of the sorption samples suggested that chromium substitution of iron oxide had little effect on the coordination environment of adsorbed Eu. The XANES spectra also showed little differences for these samples. These results were also in accordance with results observed from macroscopic sorption experiments. Sorption samples with and without DFB showed different coordination structures from XAS analysis. While the CNs of first shells are similar among the samples, the atomic distances of Eu-O are shorter for samples with DFB. Shorter Eu-Fe distances are also observed for samples with DFB; the CNs, however, increase from 1 (no DFB) to 2 (with DFB). This structure of adsorbed Eu with DFB is in accordance with that of the formation of a bidentate edge-sharing Eu inner-sphere complex on hematite. The structure of adsorbed Eu without DFB more resembles that of a Eu monodentate inner-sphere complex on hematite. Therefore, we hypothesized that Eu adsorbed onto the iron oxide surface, forming a mixture of monodentate and bidentate inner-sphere complexes. When DFB was introduced into the system, however, only bidentate Eu complexes could be observed on solid surfaces.

Acknowledgments

References

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