

# XAS investigation of Eu sorption at iron-chromium oxide/water interfaces

C.-C. Chen, S. Traina, and D. Beak  
The Ohio State University, Columbus, OH 43210 USA

## Introduction

The Department of Energy (DOE) must decontaminate a large number of surplus facilities with approximately 180,000 metric tons of metal. Previous studies have confirmed that radioactivity is incorporated in a passivity layer that is a complex structure of a mixture of oxides [1]. To decontaminate these iron and steel surfaces, it is necessary to dissolve the surface oxide layers to release the contaminants. As a result, it is important to identify the local structure and coordination chemistry of sorbed species at the mineral-water interface in order to develop molecular scale predictions of the efficacy of organic ligands for the removal of contaminant metals. This direct structural information can only be obtained from the results by microscopic studies such as x-ray absorption spectroscopy (XAS) analysis.

The objective of this XAS project is to probe the surface structure of sorbed contaminants on different synthetic oxides that resemble the oxide layers observed from the steel and iron in most of the DOE facilities. Europium (Eu) is selected as the sorbate because it is a common fission product in the DOE facilities and because of the similarity of its chemical characteristics to that of americium. The results from this study will provide valuable information on the chemical structures of the contaminants at the oxide-water interfaces, and thus be a significant step toward successful decontamination.

## Methods and Materials

The pure forms of iron oxides (i.e., hematite and maghemite) were synthesized based on the methods from Schwertmann [2]. Chromium (Cr)-substituted iron oxides were prepared according to the procedures proposed by Busca *et al.* [3]. These oxides included 10% and 25% Cr-substituted hematite and 25% Cr-substituted maghemite. Eskolaite, a pure form of chromium oxide ( $\text{Cr}_2\text{O}_3$ ), was also synthesized using the Busca method. The Eu sorption samples were prepared in a glove box under argon gas with 0.01 M sodium nitrate as the background electrolyte. These samples were then put in a shaker to equilibrate for 24 hours at room temperature before centrifuging. The Eu sorption samples were then stored in bottles in a paste form under argon and loaded into the sample cells prior to XAS data collection. The Eu precipitate sample was prepared by raising the solution pH of a 0.1 M  $\text{Eu}(\text{NO}_3)_3$  solution in a glove box. Eu XAS spectra were collected at  $L_{II}$ -edge at the GESCARS sector 13 at the Advanced Photon Source (APS) using a wavelength dispersive spectrometer (WDS). The WDS was selected because of its ability to differentiate energy within a close range. This work could not be accomplished without using WDS because of the high iron (Fe) contents in the samples with Fe K-edge only 500 eV apart from Eu  $L_{II}$ -edge.

## Results

Eu XAS data of sorption samples were collected at pH = 7 or 9 using different sorbents. The extended x-ray absorption fine structure (EXAFS) spectra and radial structure functions (RSFs) are shown in Figures 1 and 2, respectively. The surface coverages of Eu on solids are within the same order of magnitude, which ranges from 1.3 to 3.3  $\mu\text{mol}/\text{m}^2$ , except for that on eskaolite, which is 10.2  $\mu\text{mol}/\text{m}^2$ . EXAFS analysis of these samples was based on the structural parameters derived from a FEFF 8 [4] theoretical calculation using an  $\text{Eu}_2\text{O}_{3(s)}$  crystalline structure. The coordination numbers (CNs) for all sorption samples are between six and seven. The distances between central Eu ion to the first-nearest-neighbor oxygen atoms for sorption samples using hematite, maghemite, and eskolaite as substrates are 2.39, 2.42, and 2.40 Å, respectively. For sorption samples with chromium-substituted iron oxides, the Eu-O distance is 2.42 Å. The first-shell Eu-O distances for the Eu liquid sample, Eu precipitate, and  $\text{Eu}_2\text{O}_3$  model compound are 2.39, 2.44, and 2.31 Å, respectively.

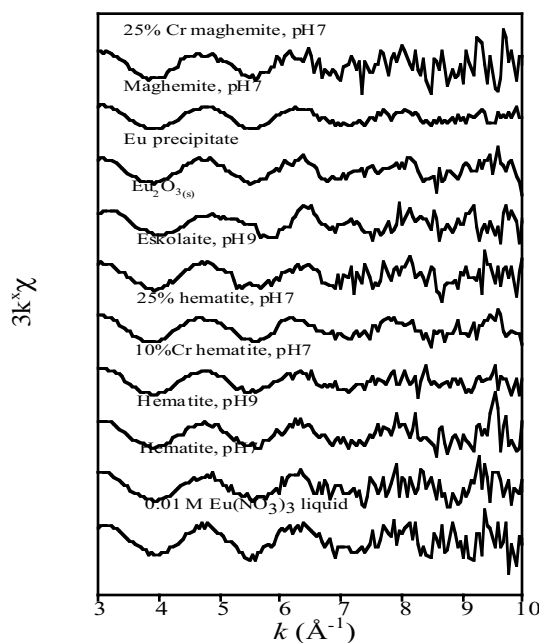


Figure 1: EXAFS spectra for the Eu sorption samples, Eu liquid sample, Eu precipitate, and  $\text{Eu}_2\text{O}_{3(s)}$  model compound.

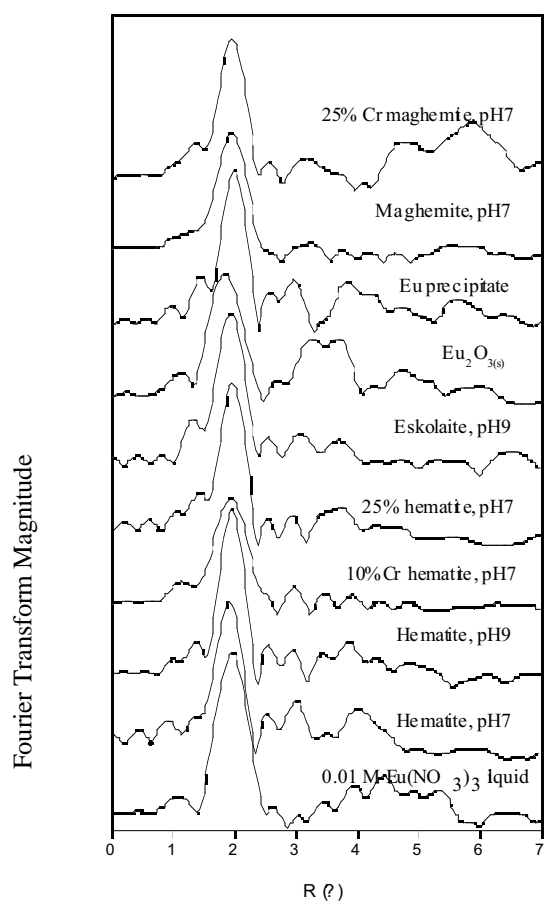


Figure 2: RSFs for Eu sorption samples.

## Discussion

The EXAFS spectra become quite noisy at  $k$  larger than eight (Figure 1); thus, it is difficult to derive a reliable structural coordination for the second shell and above. Nevertheless, as shown on the RSFs (Figure 2), the structural information provided by the first shell alone should be sufficient to evaluate the effects of Cr substitution on Eu sorption. The Debye-Waller factors for the sorption samples range between 0.008 to 0.011. These values are comparable to that of the published data [5] for the first Eu-O shell, indicating a reasonable fit of these samples. Judged by the fact that Eu precipitate has different structural parameters from all sorption samples, there is little possibility that Eu was precipitated out from the aqueous phase under the experimental conditions used in this study.

The first-shell structural parameters for Eu sorption on pure hematite and eskolaite are similar to each other, as expected, since both solids have similar crystal structure and atomic radius. For the Cr-substituted hematite samples, their first-shell structural coordination is similar, but their Eu-O interatomic distances are about 0.02 Å longer than that of the pure oxide samples. This observation is in agreement with the result from x-ray absorption near-edge structure (XANES) analysis (data not shown). The peak position of absorption jump shifts about 2 eV to the lower energy for those Cr-substituted samples comparing to that of the pure

end-member oxides. It was reported for a sample with mixtures of Eu(III) and Eu(II), a distinctive shoulder on the absorption edge corresponding to Eu(II) at about 6 to 7 eV below the Eu(III) peak was observed [6]. Thus, the edge shift observed between these samples did not result from the different Eu oxidation states, but from the different molecular structure on the solid surfaces. These results suggest that Eu is more loosely bonded to the surface of Cr-substituted hematite compared to that of pure hematite or eskolaite.

The EXAFS and XANES for Eu sorption on maghemite and Cr-substituted maghemite samples, on the other hand, show little differences. The XAS spectrum for Cr-substituted maghemite sample, however, is quite noisy, which may affect the results of EXAFS analysis.

Furthermore, the fact that both the XANES and EXAFS spectra of the Eu liquid sample are different from that of other sorption samples excludes the possibility that Eu forms outer-sphere complexes on the oxide surface under these experimental conditions.

The results from this work are significant in terms of assessing the surface coordination structures of sorbed Eu. This work also demonstrates the ability of using the WDS at GSECARS-13 to collect XAS data for samples containing elements of interest with close absorption energy (e.g., Eu  $L_{II}$ -edge and Fe K-edge in this study). It would be very difficult, if not impossible, to collect these data at other beamlines.

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