Introduction

The surfaces of steel and iron structures that are used in Department of Energy (DOE) facilities usually develop passivity layers in which contaminants may reside. These layers are complex mixtures comprised mainly of iron oxides and foreign-ion-substituted iron oxides (e.g., Cr-substituted iron oxides). The incorporation of contaminants into these passivity layers increases the complexity of decontamination processes that are required in DOE facilities. One proposed method of decontamination is the use of siderophores to dissolve the surface oxide passivity layers, releasing associated 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. The principle objectives of this study are to investigate the effects of chromium Cr-substitution into iron oxide on metal ion sorption and the local structural environment of sorbed europium (Eu) or neodymium (Nd) on different oxide surfaces.

Methods and Materials

Europium and Nd were used as the representative lanthanides and as the analogs of actinides, americium and curium. The pure forms of iron oxides (i.e., hematite, Fe₂O₃) were synthesized based on the methods from Schwertmann. Cr substituted iron oxides and eskolaite (Cr₂O₃) were prepared according to the procedures proposed by Busca et al. Europium and Nd XAS spectra were collected at L₂-edge and L₃-edge, respectively, at the GSECARS, secton 13 at the 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 conducted elsewhere in the United States due to the high Fe/Cr contents in the samples, with their K-edge energy close to the L-edge energy of Eu and Nd.

Results and Discussion

Figure 1 shows the XAS spectra and radial distribution functions (RDFs) of selected Eu sorption samples and model compounds. The results derived from XAS (Table 1.) were used to determine the local structures of adsorbed metals on solid surfaces (e.g., coordination numbers and atomic distances) in situ. The results indicated that sorbed Eu or Nd formed inner-sphere complexes at solid/water interfaces with similar local structures regardless of the different characteristics of adsorbents. Because of the similarities of the structures, it suggested that Eu/Nd sorption processes mainly occurred at the surface-hydroxyl sites on the solid surfaces, possibly on the iron sites, and the bulk structure of the solid had little effect on the sorption process under the experimental conditions used in this study. The XAS results also strongly supported what was observed from the sorption experiment: that Eu/Nd sorption behavior was independent of the adsorbent characteristics under investigation (data not shown). Furthermore, XAS data of Eu sorption samples reacted for 6 months was similar to that of samples with 24 hours of reaction time. Thus, it suggested that aging had little impact on Eu sorption under the conditions used in this study.

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References


Table 1. Summarized results from XAS analysis on Eu/Nd sorption samples

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>first shell (Me-O)</th>
<th>second shell (Me-Fe/Cr)</th>
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<tbody>
<tr>
<td></td>
<td>CN</td>
<td>R</td>
</tr>
<tr>
<td>Eu</td>
<td>7.4-9.4</td>
<td>2.39-2.43</td>
</tr>
<tr>
<td>Nd</td>
<td>7.7-10.0</td>
<td>2.47-2.50</td>
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