Spectroscopic and Structural Investigation of the Lu Incorporation Limit in 2-line Ferrihydrite (2LFh) Transformation Products

K. Dardenne, M.A. Denecke, Th. Schäfer

Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Karlsruhe, Germany

Introduction

Actinide speciation on a molecular scale is prerequisite for understanding actinide (An) mobilization-immobilization processes necessary for reliable model development describing geochemical behavior and transport phenomena of actinides released into the environment. In previous investigations, we demonstrated that, in the case of Lu(III), used as actinide trivalent homologue, ca. 0.5 at% is incorporated into a hematite-like structure during the alteration/transformation of 2-line ferrihydrite, 2LFh, as opposed to being occluded or remaining a sorbed species on the surface [1]. This information is of crucial importance for the actinide mobility in the geosphere. Moreover, it is important to know what amount of An(III) can be incorporated in the transformation product, in order to predict the fate of actinide release from a waste package in a repository. The goal of this study is to determine the incorporation limit of the Lu(III) and the Eu(III) cations in the goethite structure and their environment in that crystal structure.

Methods and Materials

Samples with varying amounts of at% trivalent lanthanide, Lu(III) or Eu(III), were synthesized through co-precipitation of Lu (Eu) with Fe(III) at pH 13 and tempering in air for one week at 70°C. The samples were investigated using x-ray diffraction (XRD) and x-ray absorption near-edge structure (XANES)/extended x-ray absorption fire structure (EXAFS) spectroscopy. The EXAFS measurements (samples with less than 15 at% Lu (Eu) were performed at the BESSRC beamline 12BM using Si(111) crystals in the double-crystal monochromator (DCM), with the APS ring running under top-up mode with a 102 mA current. The EXAFS measurements for the samples with more than 15 at% Lu (Eu) were performed at ANKA (x-ray absorption spectroscopy beamline), with a ring current between 80 and 150 mA, using Si(111) crystals in the DCM. The samples, dispersed in BN, were pressed as pellets and measured in transmission. Two to five scans were averaged, and the EXAFS extracted using standard procedures and the WINXAS software [2]. The Lu L_3 spectra were calibrated by defining the first point of inflection of a Cu foil XANES spectrum as 8979 eV. The Eu L_2 spectra were calibrated in a similar manner using Fe foil and 7112 eV. Theoretical least squares fits of spectra to the EXAFS equation were performed in R space using the feffit software [3] to obtain metric parameters for the different coordination shells. The amplitude reduction factor was fixed at 1. Phase and backscattering amplitude functions for single scattering paths were calculated with FEFF8 [4]. The mean O shell distances were estimated from the XANES using the relation between the distance, R, and the difference in energy between the first XANES resonance and the white line (WL) feature, ΔE; $\Delta E * R^2 = C$ [5]. The value of the constant, C, was obtained by averaging $\Delta E * R^2$ for compounds with known R and was found to be $182 \pm 4 eV.\text{Å}^2$ and $194 \pm 4 eV.\text{Å}^2$ for Lu(III) and Eu(III), respectively.

Results and Discussion

Goethite formation during tempering is evident in the x-ray diffractograms (not shown). For Fe co-precipitated with both Lu or with Eu, an additional Lu-(Eu-) phase, identical to the phase formed for 100 at% Lu (Eu), is observed in samples containing at least 10 at% Lu (2 at% Eu). We interpret this as indicating the incorporation limit in goethite for Lu(III) to lie below 10 at% and below 2 at% for Eu(III). The pure Eu-phase is identified as the hexagonal ($P6_3/m$) $Eu(OH)_3$ phase. Per analogy, the Lu-pure phase is assumed to be an hydroxide, too, but is not listed in the crystallographic database used.

For Fe co-precipitated with Eu, the goethite reflexes are observed in all transformation samples, independent of Eu content. However, for the Lu/Fe co-precipitation samples, the reflexes from the goethite phase disappear when the Lu content exceeds 20 at%. This suggests that 2LFh transformation to goethite is inhibited at these Lu concentrations [6] and/or that the goethite crystals formed are so small that they are XRD amorphous. In order to obtain information on this iron phase, Fe K-edge XANES/EXAFS spectra are recorded. Spectral trends for the transformation samples with increasing Lu content towards a more 2LFh-like XANES are observed. The WL intensity of the Fe K XANES spectra (Fig. 1.) decreases with increasing Lu content, which suggests that the crystallinity of the iron phase decreases with increasing Lu content. In parallel, the multiple scattering (MS) feature around 7178eV decreases in intensity and becomes smeared. The intensity of the pre-peak feature near 7116 eV increases.
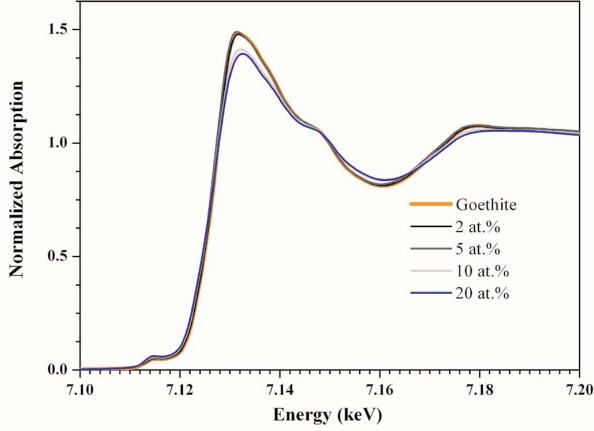
FIG. 1. Comparison of the Fe K-edge XANES of the Lu/Fe co-precipitated, tempered samples for Lu at% less than 30%.

Figure 2 compares the envelope function of the Fourier transform (FT) EXAFS spectra of the samples with Lu content below 30 at%. The double second-shell FT peak (maxima at ~2.6 Å and ~3Å), corresponding to Fe-Fe distances characteristic of the goethite structure, changes in intensity and shape with increasing Lu content. The intensity of the FT peak decreases, and the component around 3 Å is reduced to a shoulder on the 2.6 Å peak. This shape is characteristic for the 2LFh [7].
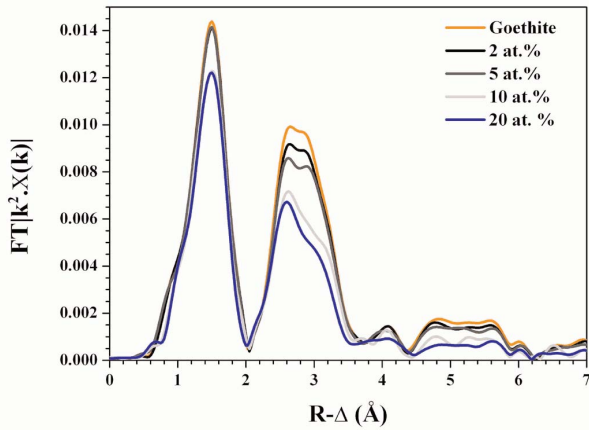

FIG. 2. Fourier transforms of k^2-weighted EXAFS at the Fe K edge for the Lu/Fe co-precipitated, tempered samples.

To characterize the Lu(Eu) species in the samples, Lu L_3 (Eu L_2) XANES spectra are measured. The XANES WLs are centered at 9247.7eV (7622.0eV) for Lu (Eu). The Lu L_3 XANES in the range between 9255 and 9299 eV are shown in Fig. 3. The intensity of the first major XANES feature above the WL progressively
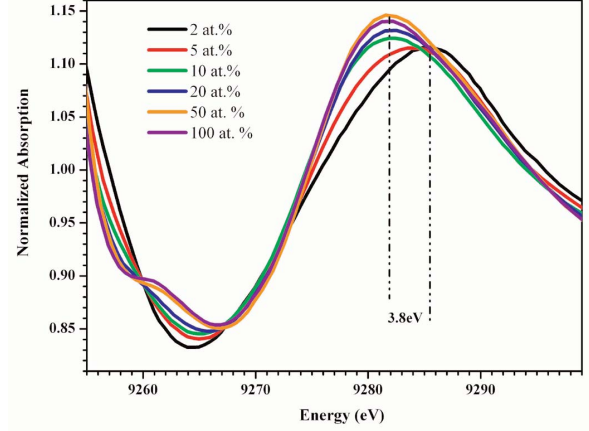

FIG. 3. Zoom of the Lu L_3 XANES features. All WLs are aligned at 9247.7 eV. The shift maximum (3.8 eV) of the major XANES feature is indicated.

increases and shifts 3.8 eV (from 9285.6 to 9281.8 eV) with an increase of Lu content from 2 at% to 15 at.%. At the same time, the minor XANES MS feature at ~9262 eV gradually appears. The shift of the major XANES feature to lower energies can be correlated to an increase in the mean Lu-O bond length.

The Lu-O distances extracted from the XANES are given in Table 1. At low Lu content, the Lu-O distances are short (~ 2.19 Å), which indicates a six-fold coordination [8] as would be expected for Lu incorporated in the goethite structure.

Results show that above a Lu content of 20 at%, Lu is mainly found in a separate, Fe-free phase, as opposed to being incorporated into the goethite. The XANES spectra of the samples above 20 at% Lu are the same as that for the pure, 100 at% Lu phase. The XANES features also do not significantly vary, indicating that bond distances remain constant. Comparison to results from analysis of EXAFS spectra of these samples confirms this result.

TABLE 1: Mean Lu/Eu-O distance obtained from the XANES spectra.

Lu/Eu content (at%)	Mean Lu-O distance (Å)	Mean Eu-O distance (Å)
2	2.19	2.36
5	2.23	2.40
7	2.28	2.42
10	2.30	2.42
15	2.33	2.44
20	2.30	2.44
30 -100	2.31	2.44

The EXAFS data for the sample with 2 at% Lu is well-fit using the goethite structure cluster as model, i.e., keeping Fe shells coordination numbers fixed to values expected for the goethite structure and a total of 6 oxygen atoms for the first coordination shell. One ΔE_0 per atom type is refined in the fit, ΔE_0 for both O shells and ΔE_0^* for the three Fe shells. The results are shown Fig. 4. The fit yields a distribution of 6 O atoms into two shells, 4 O at a short 2.19 Å distance and 2 O at 2.32 Å, with Debye-Waller factor values, σ^2, of 7.3×10^{-3} Å^2 and 3×10^{-3} Å^2, respectively and ΔE_0 6.0eV. The next Fe neighbours are distributed into three shells. Two Fe at 3.04 Å, 2 Fe at 3.24 Å and 4 Fe at 3.45 Å, with σ^2 values of 7.9×10^{-3} Å^2, 1.4×10^{-3} Å^2 and 8.0×10^{-3} Å^2, respectively, and a ΔE_0^* of 0.2eV. These Lu-Fe distances are in agreement with those expected for Fe-Fe in goethite (3.02 Å, 3.31 Å, 3.45Å).
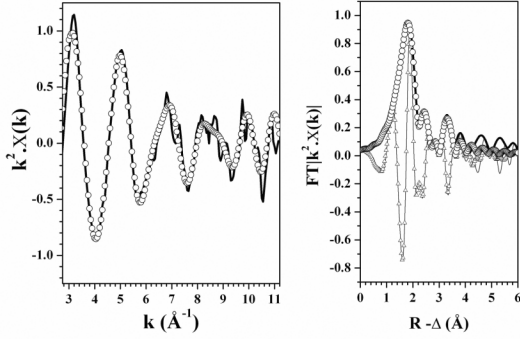

FIG. 4. *k^2-weighted EXAFS at the Lu L_3 edge (left) and corresponding Fourier transforms (right). Experimental data (2 at% Lu) are depicted as lines and fit results as open circles.*

The longer 2.31± .01Å Lu-O distance (see Table 1) observed in the pure Lu phase matches an eight-fold coordination. The intermediate distances result from a mixing of the two hexa- and octa- coordinate species, as the progressive character of the XANES, EXAFS and XRD changes suggests. That means that in the 5 at% Lu sample, where the Lu-O mean distance Lu-O is already longer than for the 2 at% sample, only a fraction of the Lu cation is incorporated into goethite and a minor part, not detectable with XRD, stays in the Lu Fe-free phase.

A similar trend is observed for the Eu samples, with the 2 at% Eu sample being significantly different than the other samples. The Eu L_2 XANES features are shown in Fig. 5. The intensity of the major XANES feature progressively increases and shifts 2.8 eV with increasing Eu content. Above 5 at% Eu, a MS feature at ~7636 eV appears. Comparison to XRD results implies that the appearance of this feature indicates the onset of Eu being mainly incorporated in a separate, Fe-free
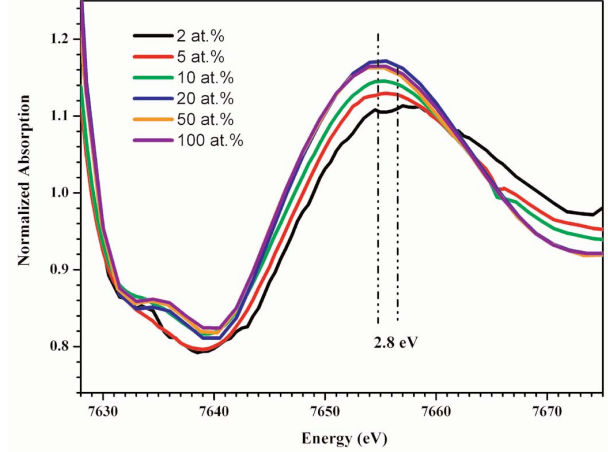

FIG. 4. *k^2-weighted EXAFS at the Lu L_3 edge (left) and corresponding Fourier transforms (right). Experimental data (2 at% Lu) are depicted as lines and fit results as open circles.*

phase. The quality of the 2 at% Eu EXAFS is not sufficient to fit to the data. The 3.44 Å Eu-O distance extracted from the XANES spectrum for the 100 at% Eu sample, identified by XRD as $Eu(OH)_3$, is in agreement with the crystallographic data (9 O at 3.465± .01Å [9]).

In summary, XANES, EXAFS and XRD results indicate that a content of 2 at% Lu results in complete Lu incorporation into the goethite structure for Lu/Fe co-precipitated, tempered transformation products. Iron K XANES of the 5 at% Lu sample shows significant changes in the mean Lu-O distance compared to the 2 at% Lu sample, suggesting Lu to be only partially incorporated into goethite. The remaining Lu forms a Lu Fe-free phase. We conclude that the Lu incorporation limit in goethite lies below 5 at%.

The significantly shorter 2.36Å Eu-O distance of the 2 at% Eu sample compared to the Eu-O in the $Eu(OH)_3$ phase (3.44 Å) suggests that a significant amount of Eu is incorporated in the goethite. However, the XRD pattern of the 2 at% Eu sample shows reflexes belonging to the $Eu(OH)_3$ phase. Therefore, the incorporation limit of Eu into goethite lies below 2 at% Eu.

Acknowledgments

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