

 ROBL-CRG	<b>Experiment title:</b> <b>Lutetium L3 and europium L2-edge EXAFS measurements of Lu(III)/Eu(III)-sorbed iron compounds</b>	<b>Experiment number:</b> 20-01-009
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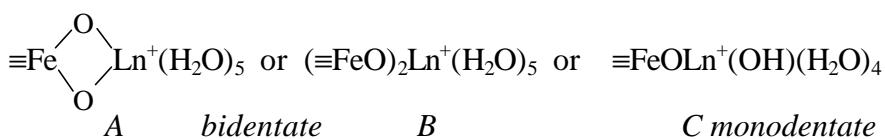
### Report:

#### EXAFS and TRLFS study of lanthanides(III) sorbed onto Hydrous Ferric Oxide (HFO)

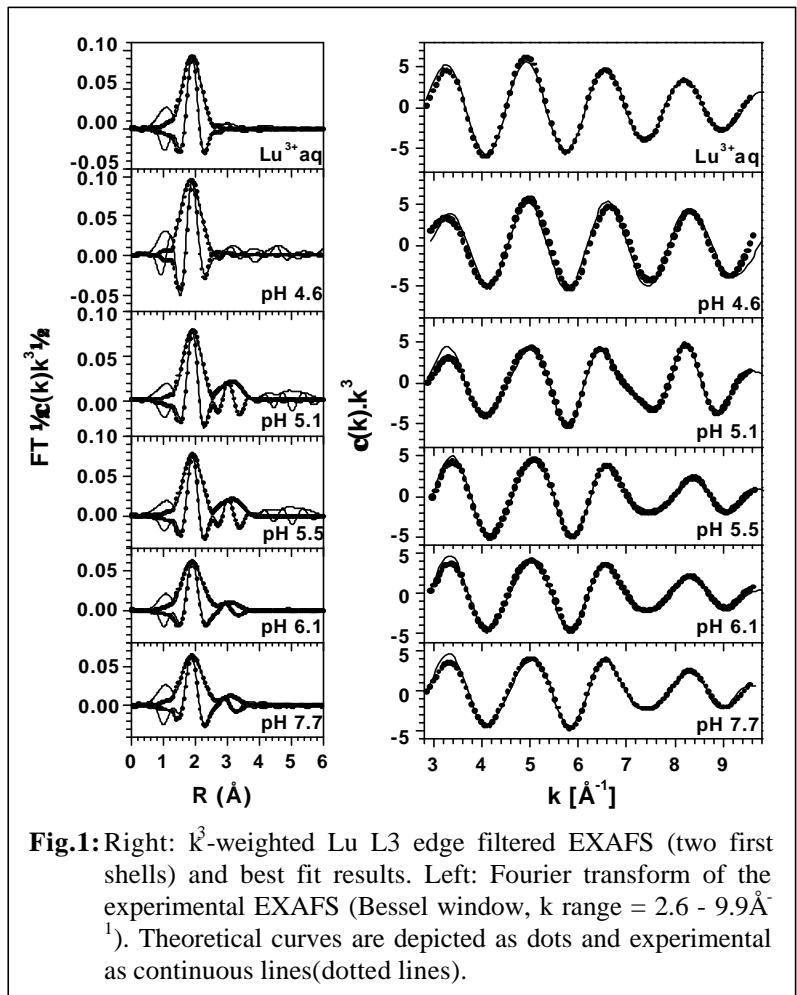
The purpose of this study is to characterize trivalent lanthanide (Ln(III)) species sorbed onto hydrous ferric oxide (HFO) by combining wet-chemical sorption data with spectroscopic investigations. Both extended x-ray absorption spectroscopy (EXAFS) and time resolved-fluorescence spectroscopy (TRLFS) experiments were performed. Eu(III) fluorescence in the visible range  $^5D_0 \rightarrow ^7F_x$  was used for the determination of the number of coordinated water molecules from the fluorescent lifetime. TRLFS is not possible for Lu(III), due to its full 4f shell. EXAFS transmission experiments on HFO:Lu(III) sorbed samples were performed at ROBL and at beamline A1, HASYLAB. Lutetium was used to avoid the spectral interference with the Fe K edge, which is a problem for investigations of HFO:Eu samples at the Eu L3 edge. Using the Eu L2 edge avoids this interference. However, the L2 transition has only one-half the intensity and a high residual Fe absorption, thereby limiting the measureable Eu(III) sample loadings. The transferability of TRLFS results from HFO:Eu(III) to HFO:Lu(III) and EXAFS results on HFO:Lu(III) to HFO:Eu(III) is justified because wet-chemical sorption behavior of both these Ln(III) onto HFO is the same.

A Eu(III)-lifetime of 205  $\mu$ s was obtained from TRLFS on a HFO:Eu solid sample, prepared at pH 5.7. This increase in lifetime over that for the Eu(III) aquo species indicates that five water molecules (and/or hydroxyl groups) are in the first Eu(III) coordination sphere [1].

Sorption studies indicate a change in the sorbed species with increasing pH. At low pH, formation of a monodentate species according to the reaction  $\equiv\text{Fe}-\text{OH} + \text{Lu}^{3+}(\text{H}_2\text{O})_{8-9} \rightarrow \equiv\text{Fe}-\text{O}-\text{Ln}^{2+}(\text{H}_2\text{O})_5$  is proposed, where  $\equiv\text{Fe}$  represents an iron atom on the HFO surface. At pH values above ~5.5, a change in the surface species formed is observed. The following three structures for the sorbed species are possible:



EXAFS structural parameters for the Lu coordination in HFO:Lu(III) samples prepared at varying pH allow characterization of the monodentate species formed at low pH and differentiation between species at higher pH, the monodentate deprotonated species (*C*) and the two possible bidentate species: *A*, with Lu(III) bonding via iron oxide polyhedral edges, and *B*, with geminal corner-sharing bonding.



**Fig.1:** Right:  $k^3$ -weighted Lu L3 edge filtered EXAFS (two first shells) and best fit results. Left: Fourier transform of the experimental EXAFS (Bessel window,  $k$  range =  $2.6 - 9.9 \text{ \AA}^{-1}$ ). Theoretical curves are depicted as dots and experimental as continuous lines(dotted lines).

shell of  $7 \pm 1$  oxygen atoms around Lu atoms at a distance of  $2.30 (\pm 0.01) \text{ \AA}$ . The coordination number of Lu sorbed onto HFO is lower than that of the aquo species ( $9 \pm 1$ ), but the Lu-O bond lengths are comparable, without evidence of any splitting of the first coordination shell into more than one distance.

The presence of a second peak above pH 5 at  $\sim 3.1 \text{ \AA}$  (not corrected from phase shift) is attributed to a Lu-Fe distance observed for sorption samples at pH  $\geq 5.5$ , at  $3.38 (\pm 0.01) \text{ \AA}$ . This distance is associated with the formation of a bidentate complex with bonding *via* edge sharing (species A) to  $\text{FeO}_6$ -octahedra. The samples prepared at pH  $< 5.1$  show no Fe shell, as expected for monodentate coordination. No evidence for surface precipitation and no noticeable difference between wet paste and dried powder samples is found.

**Table 1:** Average structural parameters N,R and their statistical error obtained from fits in  $k$  and  $R$  scale for different extraction procedures.  $S_0^2$  was held constant at 1.

Sample	pH	Lu - O				Lu - Fe			
		N	R [ $\text{\AA}$ ]	$s^2$ $10^{-3} [\text{\AA}^2]$	$\Delta E_o$ [eV]	N	R [ $\text{\AA}$ ]	$s^2$ $10^{-3} [\text{\AA}^2]$	$\Delta E_o$ [eV]
Lu(III):HFO	4.6	$6.2 \pm 0.8$	2.28	$2.5 \pm 0.5$	3.9			-	
Lu(III):HFO	5.1	$6.5 \pm 0.5$	2.31	$6.1 \pm 0.5$	5.6	$1.7 \pm 0.3$	3.48	$6.3 \pm 1.7$	4.6
Lu(III):HFO	5.5	$7.7 \pm 1.0$	2.30	$10.3 \pm 1.3$	7.0	$2.7 \pm 0.8$	3.38	$15 \pm 3$	3.9
Lu(III):HFO	6.1	$7.6 \pm 0.6$	2.30	$10.5 \pm 1.0$	6.5	$3.2 \pm 0.8$	3.38	$21.5 \pm 3$	3.4
<sup>a</sup> Lu(III):HFO	6.1	$7.3 \pm 0.4$	2.30	$7.7 \pm 0.6$	6.5 <sup>b</sup>	$2.7 \pm 0.4$	3.38	$17 \pm 2$	3.4*
Lu(III):HFO	7.7	$7.0 \pm 0.5$	2.30	$9.2 \pm 0.7$	6.1	$3.3 \pm 0.3$	3.38	$20.5 \pm 0.4$	3.2
Lu(III) aquo		$9.1 \pm 0.3$	2.31	$7.8 \pm 0.5$	4.9				

<sup>a</sup> wet paste sample - \* fixed to the value of the dried sample

<sup>b</sup> held constant at the value obtained for the dried sample, pH 6.1.

[1] W. De W. Horrocks and D.R. Sudnick, J. Am. Chem. Soc. 101, 334 (1979)

[2] A.L. Ankudinov, B. Ravel, J.J. Rehr and S.D. Conradson, Phys. Rev. B, 7565 (1998)

[3] K. Dardenne, T. Schäfer, M.A. Denecke, J. Rothe, and J.I. Kim, Radiochim. Acta (2001, accepted)

The  $k^3$ -weighted Lu L3 edge EXAFS spectra for air-dried Lu(III): HFO sorption samples and their corresponding FT's are shown Fig. 1. From visual comparison of the spectra, it is evident that the sample prepared at pH 4.6 shows a larger oscillatory amplitude than the other samples. Furthermore, this sample shows no evidence for further distant coordination shells, whereas the other four samples all exhibit a FT peak at  $\sim 3.1 \text{ \AA}$ . Although the intensity of this peak is small, its presence corresponds to the perturbation of the main oscillation frequency in the EXAFS spectra at around  $7 \text{ \AA}^{-1}$ . Metrical parameters obtained from fits to these spectra using a model of one Lu-O coordination shell are summarized in Table 1. Also included are results for the Lu(III) aquo species,  $\text{Lu}^{3+}(\text{H}_2\text{O})_{8-9}$ , used as a reference. Phase and amplitude functions generated by FEFF8 [2] for a single scattering Lu-O and Lu-Fe paths were used in the fits.

EXAFS results for Lu(III):HFO sorption samples prepared in the pH range 4.6 to 7.7 [3] show that their EXAFS spectra exhibit a single first