



## Experiment Report Form



	<b>Experiment title:</b> XAS investigation of adsorbed Eu(III) onto SiO <sub>2</sub>	<b>Experiment number:</b> A20-1 859
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 03.05.23 to: 05.05.23	<b>Date of report:</b> 04.12.23
<b>Shifts:</b> 6	<b>Local contact(s):</b> Kristina O. Kvashnina	<i>Received at ESRF:</i>
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### Report:

The interaction of europium (Eu), a fission product generated during nuclear energy production and a commonly used analogue of trivalent actinides, with quartz (SiO<sub>2</sub>) – an ubiquitous mineral and a model oxide to describe the surface properties of clay minerals – is a matter of concern when assessing the safety of the nuclear waste repository. To understand the immobilization mechanism of Eu(III) and derive realistic surface complexation models able to predict the interaction under given conditions (e.g. pH, ionic strength, [Eu(III)]), it is necessary to know the geometry of Eu(III) adsorbed onto SiO<sub>2</sub>, which still remains unclear. By means of laser-induced luminescence spectroscopy, Stumpf et al. [1] found that Cm(III) was forming a bidentate inner-sphere surface complex onto a siliceous bulk surface, which was subsequently hydrolyzed in a second surface reaction upon raising pH. However, this bidentate coordination was just inferred from former literature data, slope analysis, and surface complexation modeling. Kumar et al. [2], using EXAFS, reported the formation of Eu(III) bidentate corner sharing inner-sphere (IS) complexes at pH ~6 and ~7 onto amorphous silica, whereas bidentate edge sharing complexes were observed at pH ~8. The formation of some small multinuclear atomic clusters consisting of Eu bound in a monodentate manner to many oxygen atoms at the corner of silica polyhedral was also reported between pH 6-8, together with surface precipitation. No information regarding low pH samples was reported by Kumar et al. [2].

Thus, the focus of the measuring campaign was to analyze the molecular environment of europium as a function of pH (3.5-8.0) after being in contact with an amorphous silica. The Fe-poisoning (K edge 7,112.0

eV) of Eu-L<sub>3</sub> spectra is well known and hard to get around with, considering that Fe impurities are present in the Eu chemical itself, in the amorphous silica sorbing phase as well as stray fluorescence (e.g. from the cryostat). Furthermore, the low energy of the Eu L-edges makes it really difficult to get decent EXAFS from low concentration samples. However, the BM20 beamline is equipped with a Johann-type X-ray emission spectrometer that allows measurements of high-energy resolved fluorescence detection – X-ray absorption near-edge structure (HERFD-XANES) and extended X-ray absorption fine structure (EXAFS) data. The use of the HERFD mode is necessary to enhance the sensitivity to spectral changes in the XANES region and should allow to record EXAFS free from the Fe-impurity signal. At the Eu L<sub>3</sub>-Edge (6,976.9 eV), both HERFD-XANES and EXAFS spectra were recorded, in the fluorescence mode. The samples were cooled down to 15 K by using a cryostream. In total, 5 samples were measured, using for the first time at BM20 the XES-5 sample holders. The main results are shown in Figure 1.

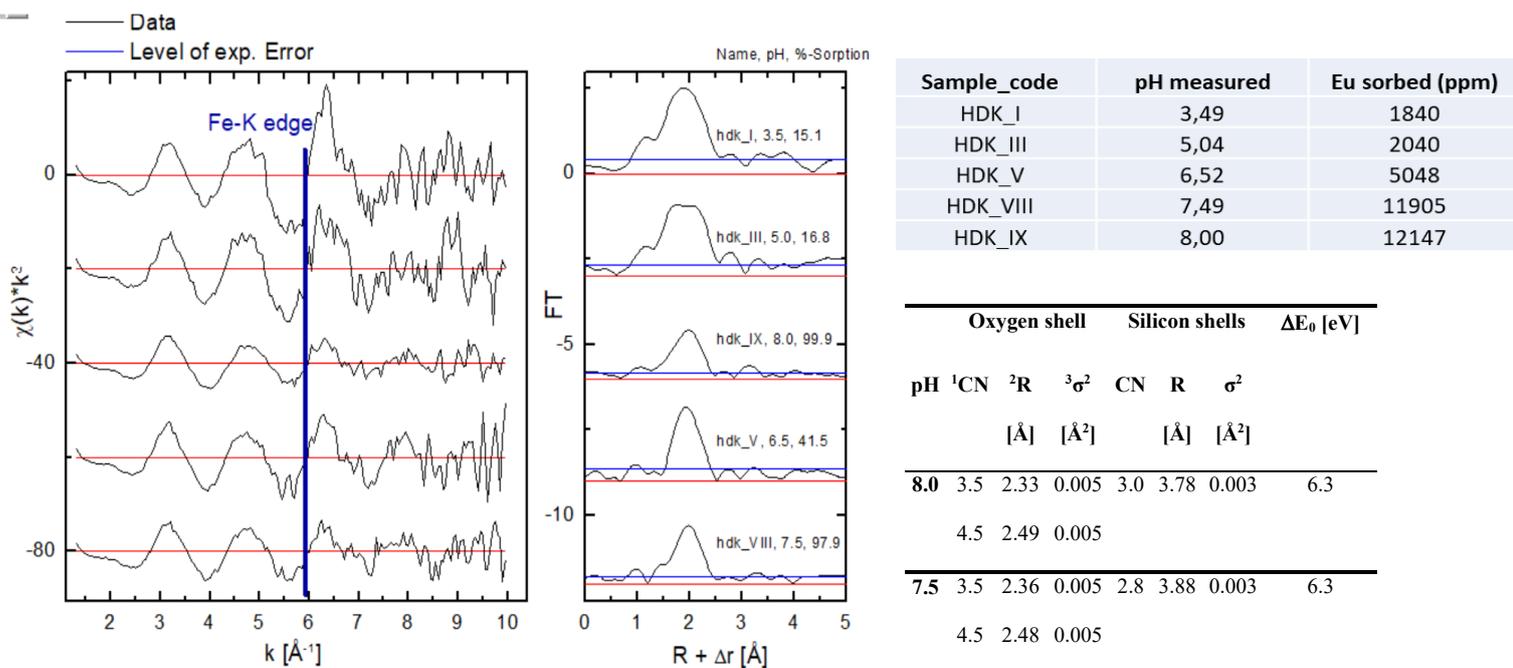


Figure 1. Fourier transforms (FT) of the Eu L<sub>III</sub>-edge EXAFS spectra of Eu retained on amorphous silica for different Eu loadings and pH values and EXAFS fit results. <sup>1</sup> CN: coordination number, error  $\pm 25\%$ , <sup>2</sup> R: radial distance, error  $\pm 0.02$  Å, <sup>3</sup>  $\sigma^2$ : Debye-Waller factor, error  $\pm 0.0005$  Å<sup>2</sup>.

It can be observed that the shape of the EXAFS spectra of Eu interaction with amorphous silica strongly depends on the pH (Figure 1). Samples at acidic and circumneutral pH (hdk\_I, hdk\_III, hdk\_V) all show a strong residual when fitting first shell O atoms and the residual contains strong influence of Fe-K edge, despite the use of the Johann-type spectrometer and a sufficiently high loading of europium. Hence hdk\_I, hdk\_III, and hdk\_V cannot be considered at this stage, unfortunately. However, for pH 7.5 and 8.5, we observed a splitted first O shell with 3 - 4 O atoms at 2.33 Å - 2.48 Å and three Si atoms at 3.78 Å - 3.88 Å pointing to the presence of surface coordinated Eu-species.

To resolve the issue at low pH, further measurements of the sorbing phase without europium will be performed under the same chemical and measuring conditions. The idea behind is to subtract the Fe contribution from the low pH samples. If this approach would not be successful, then measurements with yttrium (K edge 17,038.4 eV) will be performed, there no interferences from Fe impurities are to be expected.

## References

1. S. Stumpf et al., *Journal of Colloid and Interface Science*, **2008**, 318, 5-14.
2. S. Kumar et al., *Polyhedron*, **2012**, 33, 33-40.