



	Probing Eu(III) bound to Fe-containing clay minerals	Experiment number:
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Scientific background and aims

Several countries are currently investigating the safety and reliability of disposing high level nuclear wastes (HLW) in clay-based repositories. The migration out of the repository of the radionuclide (RN) released upon alteration of the waste matrix would be significantly delayed by retention by solids of the multi-barrier system, i.e., the alteration phases, the engineered barriers and ultimately the host rock. Of importance is the reactivity of smectites, such as Mg-smectite forming upon HLW glass alteration [Zwicky, 1989] and Al-smectite, the major component of bentonite, a backfill material used to enhance the retention properties of engineered barriers. Consequently, smectites are foreseen to play a central role in the safe disposal of HLW. However, a thorough molecular scale process understanding of the RN retention mechanism(s) by smectites is necessary to obtain a reliable safety assessment.

The long-term radiotoxicity of HLW is dominated by the actinides. Under the reducing conditions expected to prevail in a HLW repository site, Am, Cm and some fraction of Pu may be in trivalent oxidation state. Because of similar electronic properties related to the presence of *f*-electrons, lanthanides are often used as non-radioactive chemical surrogates for these trivalent actinides. For example, Eu(III) and the long-lived and radiotoxic Am(III) have identical *f*-electronic configuration and similar sizes. Unfortunately, Al- and Mg-smectites contain significant amount of structural iron, and the Fe *K*-edge (7112 eV) severely limits the range of data that can be collected at the Eu *L*₃-edge (6977 eV) for europium adsorbed on smectite. An alternative is to probe the Eu *L*₁-edge (8052 eV).

Experimental part and results

Europium was adsorbed on hectorite, a trioctahedral Mg-smectite, to elucidate the retention mechanism. Low cation concentrations ($[\text{Eu}]_{\text{tot}} = 92 \mu\text{M}$) were considered in order to approach conditions expected for HLW

repositories. Two samples were prepared for different uptake rates: ~ 50 (pH = 6.4(1), sample HEC1) and ~ 95 % (pH = 7.1(1), sample HEC2). Self-standing films were prepared in order to collect polarized EXAFS (pEXAFS) data. Varying the angle ($\alpha = 35, 80^\circ$) between the electric field vector of the X-ray beam and the clay layer plane allows to selectively probe neighboring shells, i.e., in-plane and out-of-plane neighbors. pEXAFS data were collected at the Eu L_1 -edge to avoid the interference of Fe and because the L_1 final states are p -like and more monodirectional in character than the L_3 final states (s and d). Consequently a greater polarization dependency is expected compared to the $L_{3,2}$ -edges. However, the L_1 -edge is much less sensitive than the usually probed L_3 -edge, thus requiring longer acquisition time. For each angle of both samples, 20 to 35 scans were recorded to improve the counting statistics. The spectrum of the Eu aquo ions displays single wave frequency with decreasing amplitude, consistent with a single ordered coordination sphere (Figure 1). In contrast, the spectrum of HEC1 and HEC2 collected at $\alpha = 35^\circ$ (polarized and powder XAS data are identical at this angle) display different features (frequency and amplitude) meaning that Eu is bound to a surface. Unfortunately, the data for HEC1 display a large amplitude frequency at $k \sim 6 \text{ \AA}^{-1}$ that can hardly be attributed to signal from surface bound Eu, but instead from a glitch. Nevertheless, there is no significant polarization effect in the spectra up to $k \sim 6 \text{ \AA}^{-1}$, meaning

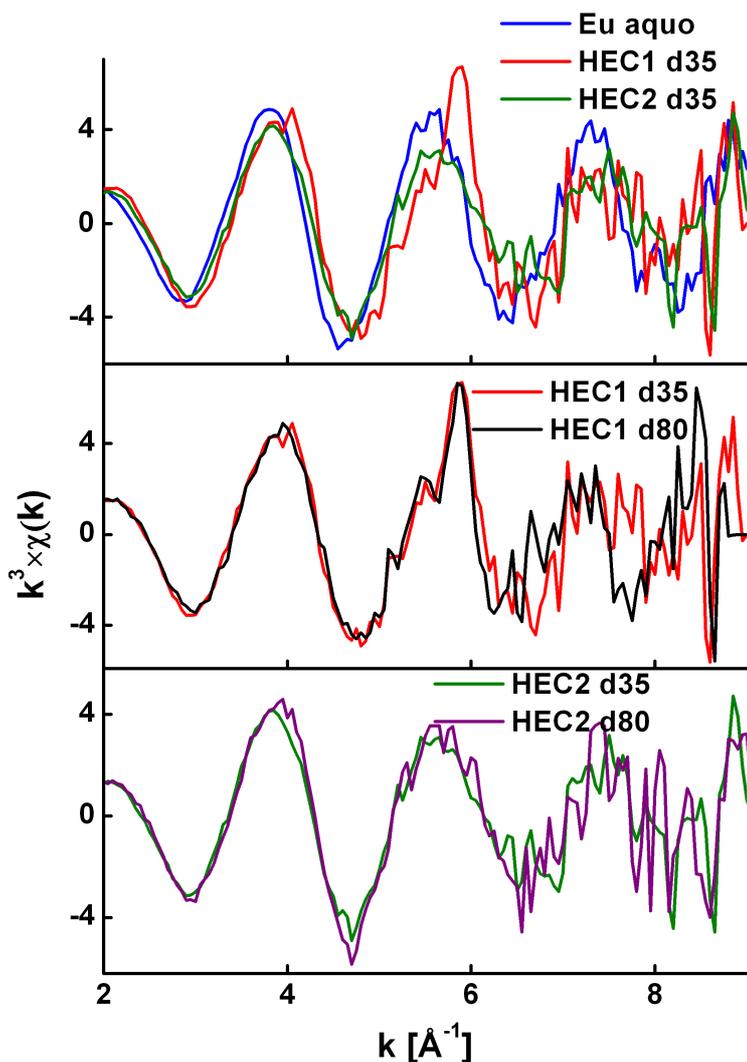


Figure 1. Spectra collected for the Eu(III) aquo ions and for both samples at $\alpha = 35$ and 80° .

that Eu is probably not located in an anisotropic environment. This corroborates the formation of outer-sphere complexes at current pH conditions (6.4(1)), whereby Eu keeps its hydration sphere upon adsorption. In contrast, the pEXAFS data of HEC2 display a slight angular dependence, as seen on the frequency maxima and position at $k \sim 4.0$ and 4.8 \AA^{-1} . This effect indicates that Eu is located in an anisotropic environment and structurally bound to various atomic shells with distinct orientation. This finding corroborates previous results on Lu adsorption on hectorite [Finck, 2009]. For this heavier lanthanide, the chemical environment corroborated with the formation of inner-sphere surface complexes. The same conclusion can be made for Eu, as expected for the pH of sorption (7.1(1)), whereby Eu loses part of its hydration sphere upon binding to the clay platelet.

Acknowledgments

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References

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