 ROBL-CRG	Experiment title: Hydration, Hydrolysis and Sorption of Sm ³⁺ and Eu ³⁺ in the Interlayer Space of the Clay Mineral	Experiment number: CH 2544
Beamline: BM 20	Date of experiment: from: 20.02.2008 to: 23.02.2008	Date of report: 14.11.2008
Shifts: 9	Local contact(s): Dr. Andreas SCHEINOST	<i>Received at ROBL:</i>
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The clay minerals consist of negatively charged alumino-silicate layers held together by cations to give a stacked (crystalline) structure. Under humid conditions the interlayer cations and the internal clay surfaces hydrate. Clay materials have been selected as the most suitable buffer material for high level radioactive waste repositories in order to retard the migration of radionuclides in case the waste containers corrode. For our investigation we have chosen Eu³⁺ and Sm³⁺ cations because of their chemical similarity to Pu³⁺ and Am³⁺. In our previous neutron diffraction experiment [1,2] we studied the structural parameters of the coordination of Sm³⁺, adsorbed in the interlayer space of the montmorillonite. It was found that the number of hydrogen atoms (5.5 ± 2.0) in the first coordination shell of Sm³⁺ is equal or even slightly smaller than those of oxygen atoms (7.5 ± 1.0). It was supposed that the Sm³⁺ ion binds to the clay surface via oxygen siloxane atoms, and it is probably partially hydrolyzed.

The aims of this experiment

- 1) To determine the number of oxygen atoms nearest to Eu and Sm and to distinguish between the oxygen atoms belonging to the montmorillonite layers and the oxygen atoms of water molecules.

- 2) To determine the oxidation state of Eu in Fe(II) doped montmorillonite. Fe(II) contained in natural montmorillonite can affect the sorption ability of the redox sensitive radionuclides in the interlayer space through the redox reaction $Mn^{+} \rightarrow Mn^{(n-1)+}$, $Fe(II) \rightarrow Fe(III)$.

The measured samples

- Eu –Fe(II) doped montmorillonite
- Sm aqueous solution (0.05M)
- Sm-montmorillonite samples with different concentration of Sm

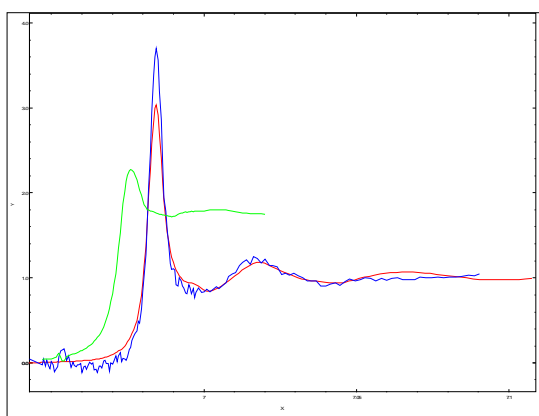


Fig. 1 Eu LIII-edge XANES of Eu – Fe(II) doped montmorillonite (blue) in comparison to $EuCl_3$ (red, $E=6982.2$ eV) and $EuCl_2$ ($E=6972.6$ eV, green).

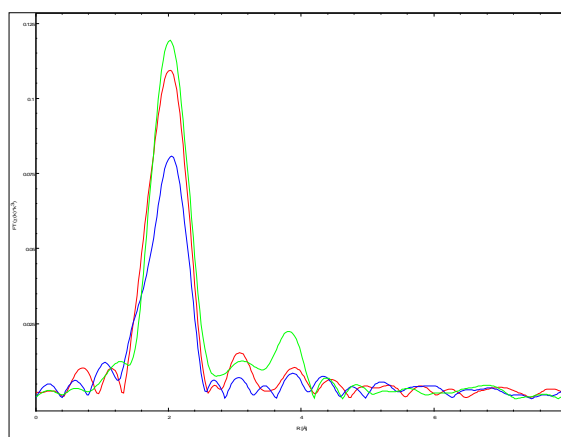


Fig. 2 Sm LIII-edge EXAFS. Sm-1 (high concentration, red), Sm-2 (low concentration, blue), Sm^{3+} aqua 0.05 M in nitric acid (green)

Results

- An experiment with Eu –Fe(II) doped montmorillonite (Fig. 1) did not show reduction of Eu^{3+} . Therefore there is no electronic transfer between the structural iron and the interlayer Eu^{3+} .

Analysis of the experiments with Sm aqueous solutions and Sm-montmorillonite samples is still in progress. However, preliminary results do not reveal any indications of the contacts of the Sm^{3+} cations with the clay surface. Thus we can suppose that the Sm^{3+} cation is sorbed as an outer sphere complex with water molecules.

References

- [1] ILL Experimental Report No: 6-02-365
 [2] O. Sobolev, L. Charlet, G. J. Cuello, A. Gehin, J. Brendle, N. Geoffroy, *J. Phys.: Cond. Matt.* 2008, 20 104207