



	Experiment title: Determination of Nd uptake mechanisms onto montmorillonite. An X-ray absorption study.	Experiment number: ME-1133
Beamline: BM20	Date of experiment: from: 12.04.2005 to: 18.04.2005	Date of report: 12.09.2005
Shifts: 18	Local contact(s): Sergey NIKITENKO	<i>Received at ESRF:</i>
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Report: Aims of the experiment and scientific background

The underlying goal of the sorption investigations at the Laboratory for Waste Management is to understand the processes controlling the uptake (sorption) and release (desorption) of safety relevant radionuclides on materials and minerals important in the Swiss radioactive waste management programme. The uptake of radionuclides by mineral surfaces is one of the main pillars upon which the performance assessment of radioactive waste repositories rests. The flow of ground water through a repository can potentially result in the release of radionuclides from waste matrices. The released radionuclides can then be transported through engineered barrier systems (cement and clay barriers) and the surrounding geosphere (often clay rich settings) and potentially harm environmental quality. The release of radionuclides can be considerably retarded due to interactions with clay minerals. Thus, a detailed molecular level understanding of sorption mechanisms of radionuclides in clay systems is of fundamental importance for safety assessment for nuclear waste repositories. To this end the work is directed towards investigation of uptake mechanisms and the development of models which can be incorporated into computer codes to predict sorption in real systems. In order to increase our understanding of sorption processes at the atomic/molecular scale, the current wet chemistry investigations are extended to include surface analytical techniques such as time-resolved laser fluorescence spectroscopy (TRLFS) and X-ray absorption fine structure spectroscopy (XAFS). On clay minerals radionuclides and other metal ions can sorb on edge sites and/or interlayer sites. The planar sites result from isomorphous substitution in the octahedral and tetrahedral sheets, and edge sites are due to broken $\equiv\text{Al/Mg-OH}$ and $\equiv\text{Si-OH}$ bonds at the sites of the clay mineral. Montmorillonite is a 2:1 smectite clay mineral with substantial isomorphous substitution. This clay mineral is the major component in bentonite which is almost universally chosen as a backfill material for a high-level waste repository. The aim of this study is to use XAFS to gain molecular-level information on the uptake of Nd onto montmorillonite. Nd(III) is a chemical homologue for trivalent lanthanides and actinides, e.g. Eu(III), Cm(III) or Am(III). Nd(III) is a non-radioactive element and does not interfere with the Fe absorption edge at the L_{III} -edge (montmorillonite contains $>1\%$ Fe). Therefore Nd(III) is among the trivalent lanthanides and actinides the best suited candidate for XAFS measurements.

Experiments + Results

To investigate the competition of metal uptake onto clays an EXAFS study on two series of montmorillonite samples was carried out. In the first series, samples of Ni loaded montmorillonite in the absence of Nd (Ni-A) and the presence of Nd (Ni-B) were prepared (Nd was added as the blocking metal). In the second series, Nd loaded samples prepared in the absence of Ni (Nd-A) and the presence of Ni (Nd-B) as blocking metal was investigated. The experimental conditions are summarized in Table 1.

The EXAFS measurements were performed at the Dutch-Belgium beamline (DUBBLE). The k^3 -weighted K-edge Ni-EXAFS spectra and k^3 -weighted L_{III} -edge Nd-EXAFS spectra of treated

montmorillonite are shown in Fig. 1a and b. The figures reveal that both of the Ni and the Nd EXAFS spectra are very similar. This indicates that the presence of Ni as a blocking metal for the sorption of trace Nd or the presence of Nd as a blocking metal for the sorption of trace Ni, does not have any influence on the surface structural environment of Nd, respectively Ni, taken up on the montmorillonite. This finding confirm the results from wet chemistry measurements in that the Ni and Nd do not compete during uptake onto montmorillonite [1]. It thus appears that the two metals are sorbed to different edge sites on the clay structure.

A previous P-EXAFS study on the uptake of Ni onto montmorillonite revealed that Ni forms inner-sphere mononuclear surface complexes located at the $\equiv\text{Al-OH}$ edge sites of montmorillonite platelets in the continuity of the octahedral sheets [2]. It thus apperas that Nd sorbs to different kind of edge sites, e.g. the $\equiv\text{Si-OH}$ edge sites. In order to determine the reactive edge sites for the Nd uptake a thorough multi-shell data analysis is currently ongoing.

Experiment	Trace metal loading ($\mu\text{mol g}^{-1}$)	Blocking metal concentration (mol L^{-1})	S:L ratio (g L^{-1})	pH
Ni-A	3.9	-	2.06	7.1
Ni-B	2.5	5×10^{-5} (Nd)	2.06	6.7
Nd-A	7.5	-	2.06	6.7
Nd-B	7.8	5×10^{-4} (Ni)	2.06	6.7

Table 1: Summary of experimental conditions for the sorption of Ni and Nd on Na-STx-1 (0.3 M NaClO_4) at trace concentrations in the absence and presence of Nd, respectively Ni, as blocking metal.

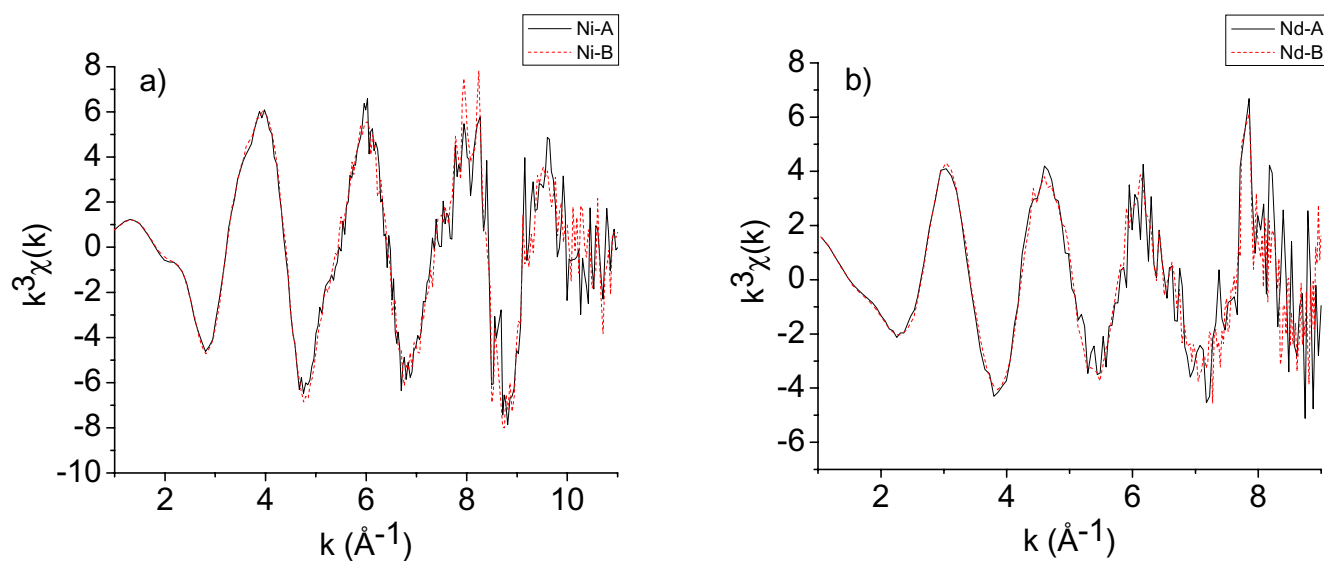


Fig. 1. (a) k^3 -weighted Ni K-edge EXAFS spectra of Ni loaded montmorillonite in the absence of Nd (Ni-A, solid line) and the presence of Nd (Ni-B, red dotted line). (b) k^3 -weighted Nd L_{III} -edge EXAFS spectra of Nd loaded montmorillonite in the absence of Ni (Nd-A, solid line) and the presence of Ni (Nd-B, red dotted line).

References:

1. Bradbury, M.H. and Baeyens, B., *Experimental measurements and modelling of sorption competition on montmorillonite*. Geochim. Cosmochim. Acta, 2005. **69**(17): p. 4187-4197.
2. Dähn, R., Scheidegger, A.M., Manceau, A., Schlegel, M.L., Baeyens, B., Bradbury, M.H., and Chateigner, D., *Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals. A polarized X-ray absorption fine structure study*. Geochim. Cosmochim. Acta, 2003. **67**(1): p. 1-15.