ESRF	Experiment title: Determination of Ni Sorption Mechanisms on Montmorillonite Using Polarized EXAFS	Experiment number: CH-778
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Shifts: 18	Local contact(s): Pierre Emanuel Petit	*Received at ESRF:*

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Report:

Aims of the experiment and scientific background

The aim of this study is to use P-EXAFS to determine sorption mechanisms of Ni(II) on montmorillonite, an important smectitic mineral responsible for the retention of metals in the geosphere. Furthermore, the clay is used as a backfill material in the Swiss concept for a high level radioactive waste repository and thus, metal sorption on montmorillonite has been investigated in our laboratory in great details. On smectitic clay minerals Ni(II) can sorb as surface complex on edge sites and/or interlayer sites, or precipitate as a Ni-hydroxide-like phase. Differentiating these sorption modes by powder EXAFS is often ambiguous. In P-EXAFS, however, the contribution of cations from the tetrahedral sheets of the 2:1 clay mineral is minimised by orienting the layer plane parallel to the electric field vector $\vec{\varepsilon}$. Conversely, the contribution of cations from the octahedral sheet is extinguished in the perpendicular orientation of $\vec{\varepsilon}$. Thus, based on the angular dependence we anticipate to gain a detailed molecular level understanding on the sorption mechanisms of Ni onto montmorillonite.

Experiments + Results

The samples were prepared by adding Ni to a montmorillonite suspension (pH 8 and pH 7.2, high ionic strength of 0.3 M $NaClO_4$ to block cation exchange processes). After 14 days of reaction time the suspensions were filtrated and highly oriented self supporting films were prepared. Ni K-edge fluorescence P-EXAFS spectra were recorded for incident beam angles of 10, 35, 55 and 80 degrees with respect to the film normal using Si[220] monochromator crystals and a PIN photodiode.

Figure 1. shows the angular dependence of 1.98 µmol/g Ni (110 ppm) sorbed onto montmorillonite at pH 8. With increasing angle a characteristic shoulder at 5.3 $Å^{-1}$ appears.

The corresponding radial distribution function (RDF) (Δk-range of 3.2-9 $Å^{-1}$) is shown in Fig. 2. Figures 3 and 4 show the EXAFS and the RDF for a sample having 10 times more sorbed Ni (19.1 µmol/g Ni=1100 ppm, pH 7.2). A comparison between Fig. 1 and 3 reveals that the shoulder at 5.3 $Å^{-1}$ is less distinct than in the dilute sample. Data analysis indicates that the first peak in the RDFs represents an oxygen shell for both samples. The structural assignment of the second shell peaks as a function of the experimental angle is under way. Preliminary analysis suggests that in the dilute sample there are no Ni-Ni contributions and we rather hypothese specific sorption of Ni onto edge sites of the clay. In the more concentrated sample, however, a fraction of Ni is present as a Ni-hydoxide-like phase.

ID26 is well suited for this kind of experiment. The high flux together with the use of photodiodes allows stringent P-EXAFS measurements to be performed on diluted samples. Unfortunately, owing to instabilities in the I_0 signal, EXAFS spectra could not be treated above 9 $Å^{-1}$. The change of the undulator from U35 to U42 did not solve this problem.

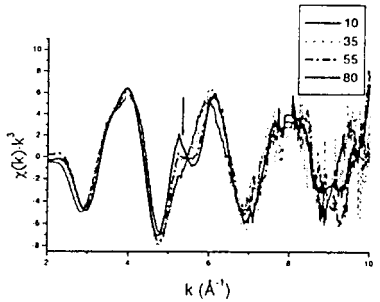

Figure 1: k^3-weighed Ni K-edge EXAFS spectra at beam angles of 10, 35, 55 and 80 degrees for 1.98 µmol/g Ni sorbed onto montmorillonite at pH 7.2

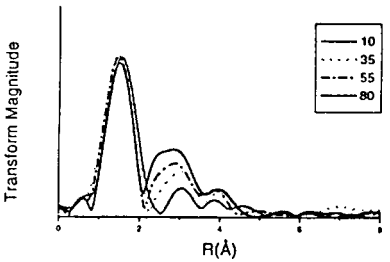

Figure 2: Polarisation dependence of the Ni K-edge RDF of 1.98 µmol/g Ni sorbed onto montmorillonite at beam angles of 10, 35, 55 and 80 degrees at pH 7.2

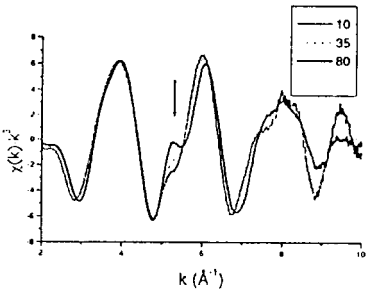

Figure 1: k^3-weighed Ni K-edge EXAFS spectra at beam angles of 10, 35 and 80 degrees for 19.1 µmol/g Ni sorbed onto montmorillonite at pH 8

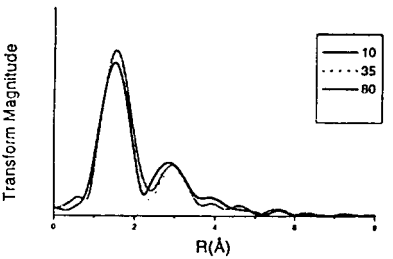

Figure 4: Polarisation dependence of the Ni K-edge RDF of 19.1 µmol/g Ni sorbed onto montmorillonite at incident angles of 10, 35 and 80 degrees at pH 8