



	Experiment title: Determination of Ni Sorption Mechanisms on Montmorillonite Using Polarized EXAFS (P-EXAFS).	Experiment number: CH-994
Beamline: ID26	Date of experiment: from: 18.04.2001 to: 23.04.2001	Date of report: 25.02.2002
Shifts: 18	Local contact(s): Pierre Emmanuel Petit	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): R. Dähn, Paul Scherrer Institut, CH-5232 Villigen PSI A. M. Scheidegger, Paul Scherrer Institut, CH-5232 Villigen PSI I. Bonhoure, Paul Scherrer Institut, CH-5232 Villigen PSI D. Grolimund, Paul Scherrer Institut, CH-5232 Villigen PSI		

Report:

Abstract

The nature of surface complexes formed upon Ni uptake onto montmorillonite (a dioctahedral smectite) has been investigated over an extended time period by polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy. Self-supporting films of Ni-sorbed montmorillonite were prepared by contacting Ni and montmorillonite at pH 7.2, high ionic strength (0.3 M NaClO₄) and low Ni concentration ($[\text{Ni}]_{\text{initial}} = 19.9 \mu\text{M}$) for 14 and 360 days reaction time. The resulting Ni concentration on the clay varied from 4 - 7 $\mu\text{mol/g}$. Quantitative texture analysis indicates that the montmorillonite particles were well orientated with respect to the plane of the film. The full-width at half maximum (FWHM) of the orientation distribution of the c^* axes of individual clay platelets about the normal to the film plane was 44.3° (14 days reaction time) and 47.1° (360 days reaction time). These values were used to correct the coordination numbers determined by P-EXAFS for texture effects.

Ni K-edge P-EXAFS spectra were recorded at angles between the incident beam and the film normal equal to 10°, 35°, 55°, and 80°. Spectral analysis led to the identification of three nearest cationic subshells containing 2.0 ± 0.5 Al at 3.0 Å and 2.0 ± 0.5 Si at 3.12 Å and 4.0 ± 0.5 Si at 3.26 Å. These distances are characteristic of edge-sharing linkages between Al and Ni octahedra and of corner-sharing linkages between Ni octahedra and Si tetrahedra, as in clay structures. The angular dependence of the Ni-Al and Ni-Si contributions indicates that Ni-Al pairs are oriented parallel to the film plane, whereas Ni-Si pairs are not. The study reveals the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets and thus, that heavy metals binding to edge sites is a possible sorption mechanism for dioctahedral smectites. Data analysis further suggests that the number of neighboring Al atoms remains constant and that the structural order of the observed surface complexes increases with increasing reaction time. Thus, it appears that over an extended reaction time period of one year the uptake mechanism of Ni onto montmorillonite remained unchanged, and especially the diffusion of Ni in the octahedral layer was not observed.

Dähn R., Scheidegger A. M., Manceau A., Schlegel M. L., Baeyens B., Bradbury M. H., and Chateigner D. (2002) “Structural evidence for the sorption of metal ion on the edges of montmorillonite layers. A polarized EXAFS study.” *Geochim. Cosmochim. Acta*, in press.