ESRF	**Experiment title:** Immoblization mechanisms of heavy metals by Al- and Al13-modified montmorillonite: A polarized EXAFS study	**Experiment number**: ME426
Beamline: BM08	**Date of experiment**: from: 13.3.03 to:16.3.03	**Date of report**: 28.8.03
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Names and affiliations of applicants (* indicates experimentalists):

A. M. Scheidegger*[1,2], G. Furrer*[3], R. Dähn*[1], M. Nachtegaal[3]

[1] Waste Management Laboratory, Paul Scherrer Institute, CH 5232 Villigen, Switzerland.

[2] MicroXAS beamline Project, Swiss Light Source (SLS), Paul Scherrer Institute, CH 5232 Villigen, Switzerland.

[3] Institute for Terrestrial Ecology, Swiss Federal Institute for Technology (ETH), CH 8952, Schlieren, Switzerland.

Report:

Methods of gentle soil remediation, for soils contaminated by heavy metals, have gained a lot of attention in recent years. Many efforts have been made to find or to develop plants that are particularly able to extract heavy metals from soils. However, under field conditions, all available plants exhibit either limited growth or insufficient uptake rates for heavy metals. The time span for remediation by phytoextraction is much too long to be practical. Abiotic techniques of immobilization have been criticized often, because they do not implicate removal of heavy metals from the soil and because the metals can be remobilized if the treated soils become acidified. Our long-term macroscopic sorption studies have shown that the sorption properties of montmorillonite for small cations such as Ni^{2+}, Cu^{2+}, and Zn^{2+} can be strongly improved by modifying the clay mineral with Al species (e.g., Al_{13}-montmorillonite, i.e. montmorillonite intercalated with the Kegin $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}(aq)$ tridecamer aluminum complex) [1, 2]. The application of these Al-modified clay minerals on contaminated sites could potentially lead to a long-term immobilization of the metals from the soil solution, without depriving the soil from essential nutrients [3].

To obtain molecular information on the mechanisms of Ni uptake by Al modified clay minerals, polarized EXAFS (P-EXAFS) was employed to examine Al-modified montmorillonite suspensions that have been in contact with aqueous Ni(II) for five years. These first spectroscopic data allowed us to unequivocally propose a molecular-level picture of the Ni uptake mechanism onto Al-modified clay minerals. Data analysis revealed that Ni "sorbed" onto the intercalated clay material is surrounded by 6 oxygen atoms at ~2.05 Å and 6 aluminum atoms at ~3.02 Å, suggesting that Ni is incorporated into an Al hydroxide-like phase. Furthermore, P-EXAFS data (collected at beamline BM08) showed a pronounced angular dependency, indicating that the Al hydroxide-like phase is highly oriented with respect to the montmorillonite platelets (Figure 1). Consequently, we propose that a Ni^{2+}-doped gibbsite-like monolayer is formed in the interstitial space of the montmorillonite. This *novel* clay mineral uptake mechanism is responsible for the enhanced Ni sorption onto Al-modified montmorillonite (in comparison with untreated montmorillonite) and may lead to a permanent sequestration of Ni in contaminated sites [2].

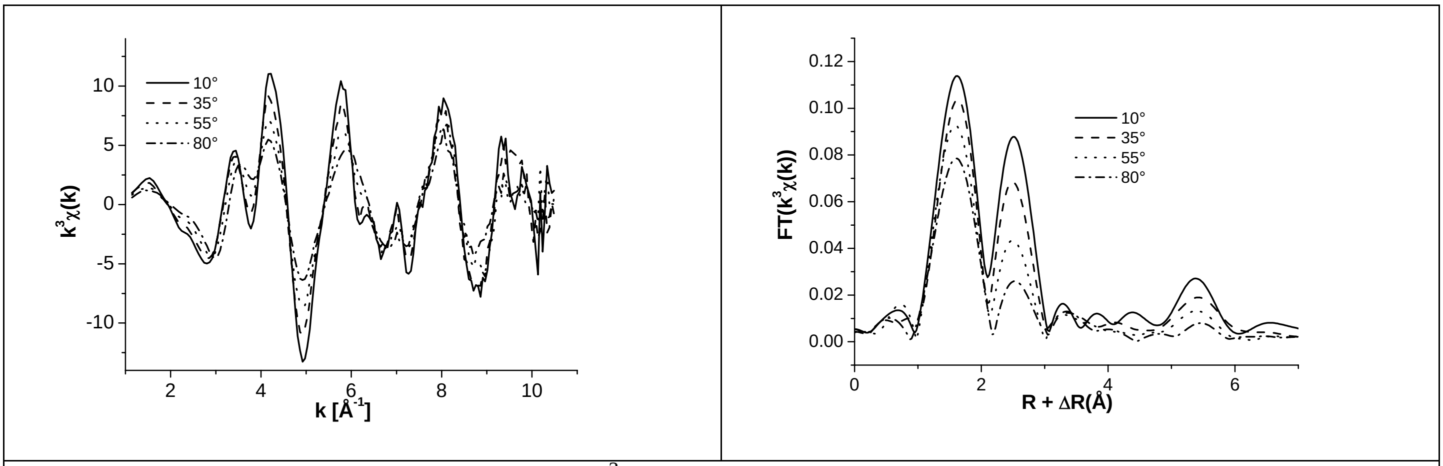

Figure 1: Polarization dependence of the k^3-weighted (left) and the PRSFs (right) Ni K-edge P-EXAFS spectra of a Al-modified montmorillonite film at α angles of 10° (for in-plane contribution), 35 (for reference powder EXAFS), 55° and 80° (for out-of-plane contribution).

The EXAFS experiments at BM08 also showed that the process of Ni incorporation could be significantly speed up by elevating the reaction temperature (Figure 2). Figure 2 shows an increase in intensity of the second peak (corresponding to Al) in the pseudo radial structure function (PRSF) at $R + \Delta R \approx 2.5$ Å, when the experiment was conducted at 80°C instead of room temperature (RT) and a reaction time of 3 months (a reasonable time span for applying gentle soil remediation techniques). This intensity increase suggests that the formation of a gibbsite-like monolayer in the interstitial space of the montmorillonite clay minerals is enhanced at elevated temperatures. This finding is also supported by the fact that the spectrum collected at 80°C represents an intermediate between the spectra of the samples treated with Ni at RT for 3 months and 5 years, respectively. Thus, our P-EXAFS experiments on the aged samples provided a plausible explanation for the observed increase in hindrance of Ni release from the Ni treaded Al-modified clay material with increasing time, as observed in the macroscopic desorption experiments [3].

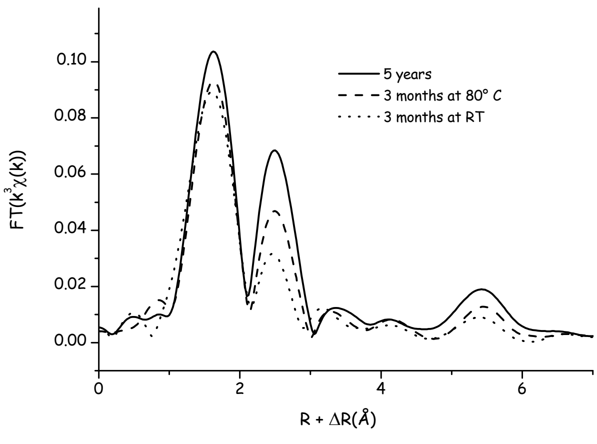

Figure 2: PRSFs of Al-modified montmorillonite treated with Ni, of the 5 year old sample (RT), 3 months (reacted at 80 °C) and 3 months (RT) (bulk EXAFS)

References:

[1] Harsh, J.B. and Doner, H. E.. 1984. *Soil Sci. Soc. Am. J.*, 48; 1034.
[2] Lothenbach, B., Furrer, G. and Schulin, R. 1997. *Environ. Sci. Technol.*, 31:1452.
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