



	Experiment title: Determination of uptake mechanisms of metal ions onto clay minerals using XAFS	Experiment number: 01-01-614
Beamline: BM1b	Date of experiment: from: 6.11.03 to: 11.11.03	Date of report: 15.3.04
Shifts: 15	Local contact(s): Hermann EMERICH	<i>Received at ESRF:</i>
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Report:

The bioavailability and migration of trace metals in the environment is governed by reactions taking place at soil solution-particle interfaces. Thus, determining the kinetics and mechanisms of the interfacial reactions is of utmost importance to insure the implementation of sound remediation strategies, to predict metal stability in soils over time, and to successfully model the fate of trace metals in the environment.

Recent research has shown that the sorption properties of montmorillonite, a highly reactive 2:1 clay mineral, for divalent cations such as Ni²⁺, Cu²⁺, and Zn²⁺ can be strongly improved by intercalating the clay mineral with Al species (e.g., Al₁₃-montmorillonite, i.e. montmorillonite intercalated with the Keggin AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁷⁺(aq) tridecamer aluminum complex) [1, 2]. Therefore, Al-modified clay minerals offer a great potential for gentle and cost effective soil remediation and environmental engineering, including the use of the material as a liner for waste deposits and a sorbent in waste water treatment systems [2].

The goal of the present study was to obtain molecular information on the mechanisms of Ni²⁺ and Cu²⁺ uptake by Al modified clay minerals. Large amounts of ⁵⁹Ni and ⁶³Ni occur as fission products in nuclear waste and Cu is one of the most prevalent contaminants in waste deposits. Al-modified montmorillonite was reacted with Ni and Cu under various reaction conditions (pH-range: 5-8, metal loadings: 250 – 3000 ppm, reaction times up to 9 yrs). Thereafter, self-supporting films for polarized EXAFS (P-EXAFS) experiments were prepared from the metal treated clay suspension.

In P-EXAFS, neighboring atoms along the polarization direction of the X-ray beam are preferentially probed, whereas atoms located in a plane perpendicular to this direction are attenuated. Polarized-EXAFS spectra were consequently measured of the oriented clay films at various incident angles ($\alpha=10^\circ$, $\alpha=35^\circ$, $\alpha=55^\circ$ and $\alpha=80^\circ$), to determine the in-plane ($\alpha=10^\circ$) and out-of-plane ($\alpha=80^\circ$) EXAFS contributions.

Our initial EXAFS results showed that Ni is surrounded on average by 6 oxygen atoms at ~2.05 Å and 6 Al at ~3.01 Å, suggesting the incorporation of Ni into a Ni²⁺-doped aluminum hydroxide, which resembles the structure of gibbsite [3]. The polarized EXAFS experiments now performed at BM01b showed changes in spectral intensity with increasing α angle (Figure 1), indicating that the coordination chemistry of Ni is anisotropic and more specifically, that the Ni atoms are oriented with respect to the layering of the clay mineral. The finding that a Ni doped Al phase is formed in the interstitial phase of the clay minerals represents a novel mechanism for Ni uptake onto Al modified clay minerals and explains the enhanced Ni sorption onto Al-modified montmorillonite (in comparison with untreated montmorillonite) observed in batch experiments. One might suspect that the novel uptake mechanism may lead to a permanent sequestration of Ni in contaminated sites [2]. Our results at BM01b also helped to confine the reaction conditions under which this Ni doped Al phase formed, i.e., pH 5-7 and Ni loadings not exceeding 3000 ppm.

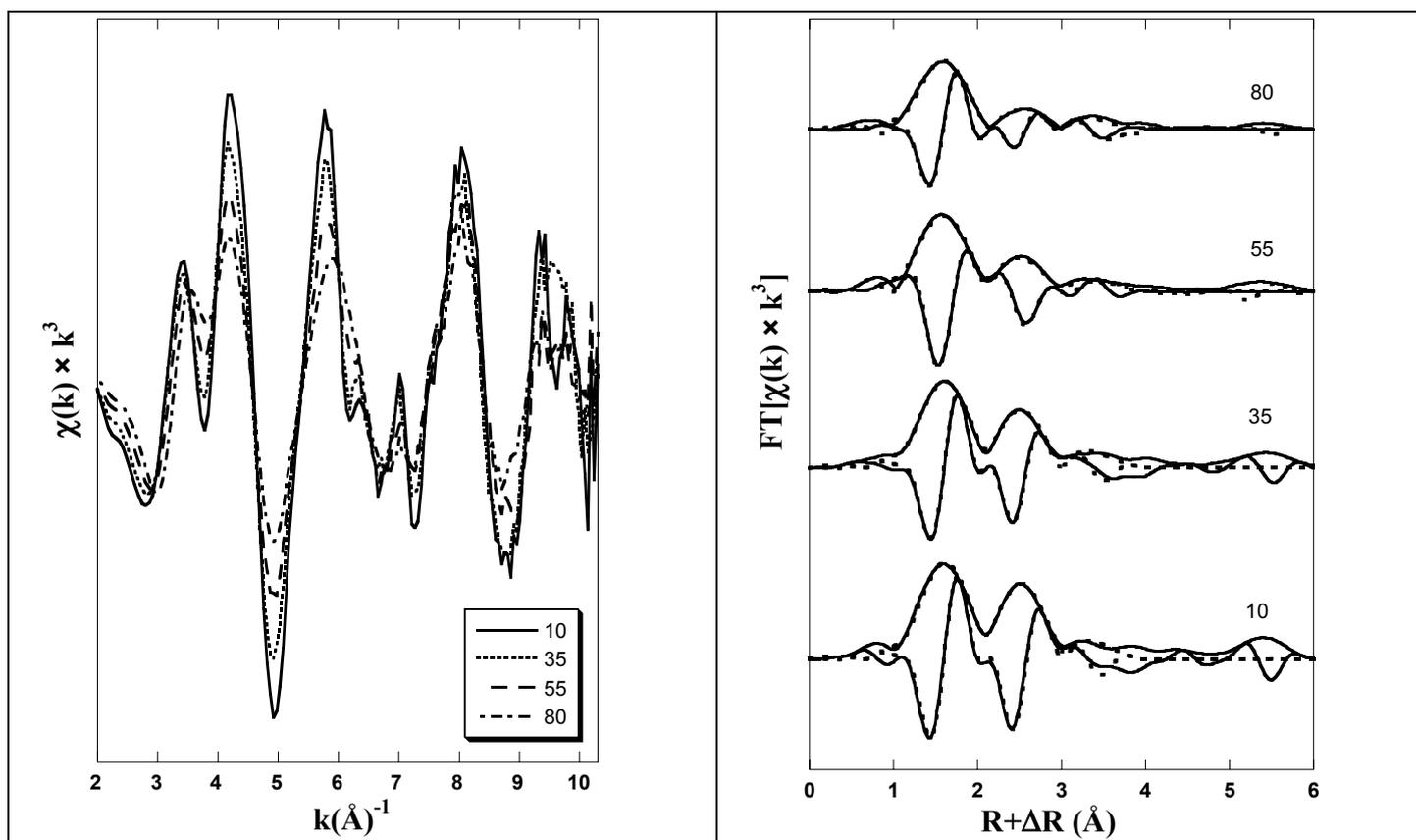


Figure 1: Polarization dependence of the k^3 -weighted (left) and the RSFs (right) Ni K-edge P-EXAFS spectra of a Al-modified montmorillonite film at α angles of 10° (for in-plane contribution), 35° (for reference powder EXAFS), 55° and 80° (for out-of-plane contribution).

The EXAFS studies with Cu treated Al modified montmorillonite revealed a completely different uptake mechanism of Cu by Al modified montmorillonite. Copper was found to be surrounded only by 6 oxygen atoms when sorbed to the Al doped montmorillonite at pH 5, suggesting that Cu forms predominantly outer-sphere complexes, that can easily be desorbed. At pH 7, Cu was found to be coordinated by six O atoms and two Al atoms, suggesting the formation of a bidentate inner-sphere complex with either the Al edge sites of the clay mineral or the Al_{13} keggin complex. In both cases, the incorporation of Cu into the interstitial gibbsite monolayer, as in the case of Ni, could be excluded. These findings have large implications for the stability of Cu in the environment and the use of Al modified montmorillonite as liner material.

References:

- [1] Lothenbach, B., Furrer, G. and Schulin, R. 1997. *Environ. Sci. Technol.*, 31:1452
- [2] Lothenbach, B., Furrer, G. and Schulin, R. 1999. *Environ. Sci. Technol.*, 33:2945
- [3] Immobilization of Ni by Al-Modified Montmorillonite: A Novel Uptake Mechanism. Nachtegaal, M., Scheidegger, A., Dähn, R., Chateigner, D., Furrer, G. 2004. *Geochimica Cosmochimica Acta*. *In Preparation*