

X-ray absorption characterization of the sorption mechanism of divalent and trivalent cations by pillared clays.

M. L. Schlegel ; CEA de Saclay

Alain Manceau, Université Joseph Fourier and CNRS, Grenoble

Scientific background and Interest of the experiment

The design of safe repositories for toxic and radioactive waste requires the setup of geochemical and engineering barriers that would efficiently confine pollutants. Montmorillonites exchanged with Al cations and Al_13 polymers have been considered as possible candidates for such barriers [1, 2], because the intercalation of Al compounds increases their retention capacity [3, 4]. However, so far little was known on the molecular aspects of these retention reactions. In principle, all sorption reactions observed for pure smectite clays, that is, cation exchange on permanent charge sites located on smectite basal planes, and pH-dependent sorption on the edges of clay platelets, ought to exist on pillared clays (Figure 1). Other mechanisms may occur as well: metal cations may adsorb on the interlayer pillars, and they may react with Al or Si released by the dissolution of interlayer polymers, or smectite clays, to form mixed precipitates (Fig. 1). The goal of our experiment was to identify the actual molecular mechanism of cation retention on these Al-clay phases by polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy. The angular information collected by using this technique was deemed necessary to discriminate between several sorption mechanisms resulting all in Zn binding to ‘light’ (Al, Si) atoms at comparable distances, but with distinct orientations.

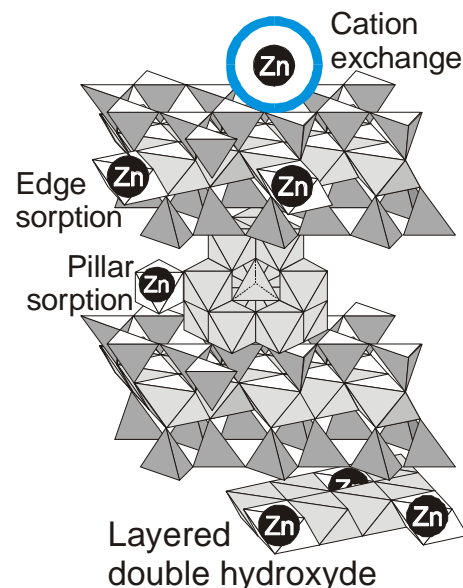


Figure 1. Visualization of the pillared clay structure, and possible mechanisms of cation sorption on these solid phases.

Scientific and technical outcome.

We successfully recorded polarized and powder EXAFS spectra on several self-supporting films of Zn-sorbed, Al-exchanged montmorillonite (Al-mont) reacted under distinct conditions of pH (pH 6, 7), sorbate to sorbent ration (25 to 100 $\mu\text{M Zn g}^{-1}$ Al-mont), and reaction time (24 h to 64 days). Figure 2a gives an example of the strong angular dependence observed for the EXAFS spectra collected on self-supporting films of Zn sorbed on Al-montmorillonite. This dependence demonstrates a structural association between Zn and the montmorillonite platelets. The Fourier Transforms (FTs) of these spectra display several peaks indicating the presence of several atomic shells surrounding sorbed Zn (Figure 2b). Of special importance is the peak observed at a distance (uncorrected for phase shift) of $\sim 2.6 \text{ \AA}$, corresponding to the contribution of nearest cationic shells. The maxima of the peak amplitude and imaginary part coincide in position, showing that this peak predominantly results from the contribution of ‘light’ (Al, Si) cations [5, 6]. Furthermore, the amplitude of this EXAFS contribution decreases with increasing angle α between the electric film vector and the montmorillonite self-supporting film. This angular dependence is typical for backscattering shells oriented along the plane of the montmorillonite particles [7, 8], and suggests that Zn was surrounded by in-plane Al at $\sim 3 \text{ \AA}$. These results were interpreted by assuming that Zn sits in the vacant octahedral sites of gibbsite-like $(Al(OH)_3)$ sheets parallel to the basal plane of montmorillonite platelets. We are now in the process of fitting these data to support these qualitative assessments.

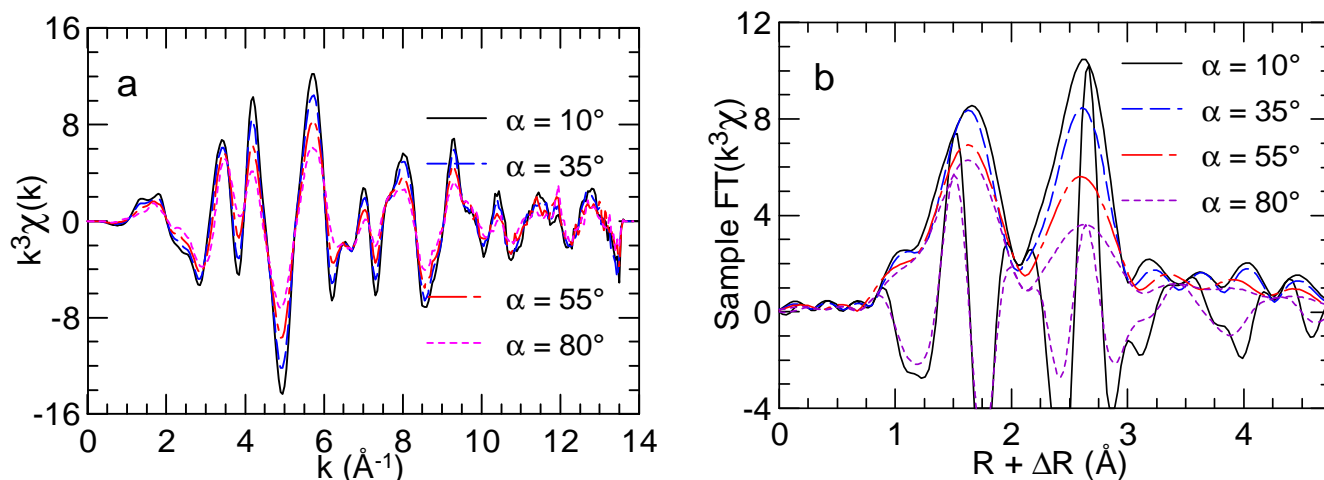


Figure 2. Angular dependence of the polarized EXAFS spectra (a) and Fourier transforms (FT) (b) with the angle α between the electric field vector of the X-ray beam and the plane of the self supporting film of Zn-sorbed Al-mont. Imaginary parts of the FTs are given for $\alpha = 10^\circ$ and 80° only. Note the strong decrease in amplitude of all FT peaks with increasing α .

Future expectations

The expectations resulting from the success of our experiment are threefold.^s

- The data collected on about 9 samples with varying preparation conditions should allow us to write a publication on the mechanism of Zn retention and immobilization by Al-modified montmorillonite.
- These results will also allow to critically discuss the choice of materials for the setup of engineering barriers for disposal of nuclear and chemical waste. Specifically, the choice of the material will rely on the specific role of Al and Al₁₃ polymers on the retention of clay minerals. The impact of reaction time on the Zn environment will also be discussed, specifically for the Al₁₃-exchanged montmorillonite, for which a great disparity between the short-term and long-term Zn environments was observed.
- Finally, the EXAFS and polarized EXAFS spectra recorded in this study will be implemented in general databases used for the geochemical speciation of Zn in heterogeneous environments, such as landfills, soils, and sediments. This information in turn will help to trace the possible mechanism of element retention by natural solids in the field, from our knowledge of the preparation conditions of laboratory samples.

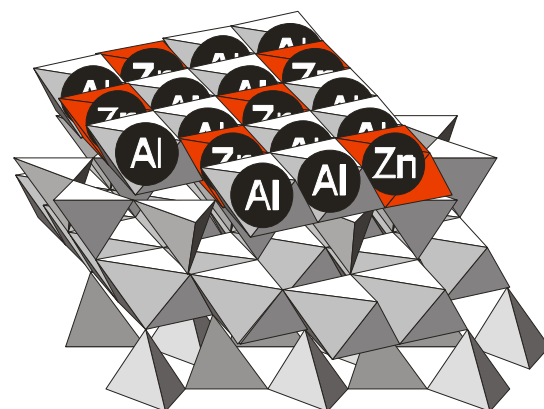


Figure 3. Proposed crystallochemical environment for Zn uptake on Al-mont, as inferred from EXAFS results.

Bibliography

- [1]. B. Lothenbach, G. Furrer, et al. *Environ. Sci. Technol.* **33**, 2945-2952 (1999).
- [2]. B. Lothenbach, G. Furrer, et al. *Environ. Sci. Technol.* **31**, 1452-1462 (1997).
- [3]. A. Manceau, M.A. Marcus, et al. *Geochim. Cosmochim. Acta* **68**, 2467-2483 (2004).
- [4]. A.C. Scheinost, R. Kretzschmar, et al. *Environ. Sci. Technol.* **36**, 5021-5028 (2002).
- [5]. A. Manceau, D. Chateigner, et al. *Phys. Chem. Minerals* **25**, 347-365 (1998).
- [6]. M.L. Schlegel, A. Manceau, et al. *Geochim. Cosmochim. Acta* **65**, 4155-4170 (2001).
- [7]. M.L. Schlegel and A. Manceau. *Geochim. Cosmochim. Acta*, in press (2006).
- [8]. M.L. Schlegel, A. Manceau, et al. *Am. J. Sci.* **301**, 798-830 (2001).