

An XAFS Study of Zn Sorption Mechanisms on Montmorillonite over Extended Reaction Times

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Introduction

Highly contaminated metals in soils and sediments can have a toxic effect on soil organisms, plants, animals, and ultimately people. Understanding of metal speciation and sorption products is important to select appropriate management options and clean-up strategies for the contaminated soil environment. Because the form of the metal influences all aspects of its geochemistry, including its mobility, bioavailability, and ultimately its toxicity in the environment, the final form of sorption products plays a critical role.

Clay minerals and oxides have high surface areas and influence the mobility of metal ions in the environment. Sorption of metal ions on surfaces of clay minerals and oxides is a main factor in controlling their fate in soil, sediment, and aquatic systems.^{1,2}

Adsorption isotherms, empirical and semi-empirical equations, and surface complex models have been developed and used by many researchers to describe sorption phenomena. Macroscopic studies used to develop these models provide useful information about sorption phenomena, but they contain no information on actual mechanism or molecular processes.³ *In situ* spectroscopic measurements are necessary to probe molecular-level information about surface speciation and sorption mechanisms with macroscopic experiments.⁴ X-ray absorption spectroscopy (XAS) is an element-specific *in situ* technique. It can be used to determine the local structure — bond distance, number, and type of near neighbors — around a sorbing element.

The goal of this research is to understand sorption mechanisms and identify sorption species and the local chemical environment of metal sorbed on clay mineral and oxide surfaces over an extended reaction timespan. Findings from this research will provide fundamental understandings of metal sorption reactions and mechanisms in soil environmental systems and ultimately help in choosing environmentally sound planning, management, assessment, and strategy in cleanup processes.

Materials and Methods

Batch sorption experiments of Zn onto montmorillonite were conducted at room temperature with fixed pH of 7.0 in 0.1 M NaNO₃. Tests were conducted both in a system open to atmospheric CO₂ (the reactor suspension was mixed by a stirrer and purged by air) and in a CO₂-free system (high-purity N₂ gas was purged and mixed by a stirrer inside of a N₂ chamber). Na-montmorillonite (Swy-2, obtained from the Clay Minerals Society) was used as received without any pretreatment. For the XAFS sample preparation, 50 or 100 mL of suspensions equilibrated up to 6 months were collected periodically and centrifuged at 12,900 rpm for 30 min to separate the solid and liquid phase. Supernatants were filtered again using a 0.2-mm pore membrane filter to meas-

ure the concentration. The solid part (wet paste or freeze dried) was saved for the XAFS measurement. Zn XAFS spectra were collected at K-edge at the Materials Research Collaborative Access Team (MRCAT) sector 10-ID at the Advanced Photon Source (APS).

Results and Discussion

For samples exposed to atmospheric CO₂ over contact times of 1 day, 1 month, and 6 months, the observed Zn loadings were 2.83, 5.29, and 6.03 mg/g, respectively. Radial structure functions (RSF) changed over time (Fig. 1). Qualitative analysis of the RSF shows that there are no significant changes for the first coordination shell of Zn with increasing reaction time. However, the structure of the second shell and even higher shells increased with time. These structural differences of Zn sorbed onto mont-

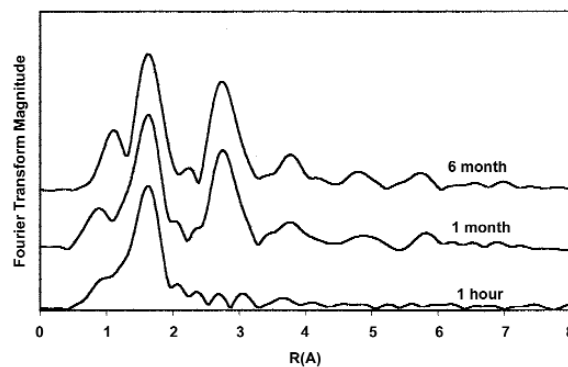


FIG. 1. RSF of Zn sorbed onto montmorillonite obtained by Fourier transformation.

morillonite may come from Zn-Zn scattering by the formation of Zn surface precipitate or more ordered structures as aging occurs. Full analysis of XAFS is required to interpret the sorption reaction and to gain molecular level information.

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