

Potential formation of secondary hydrotalcite-like precipitates during Zn and Cu sorption to pyrophyllite

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The long term fate and mobility of metals in the environment are influenced by reactions at the soil mineral-water interface. Recent research has shown that secondary precipitates with hydrotalcite-like structures form during sorption of Ni and Co to aluminum oxide and aluminosilicate surfaces (Scheidegger *et al.*, 1997; Scheidegger *et al.*, 1998; Towle *et al.*, 1997). Formation of these 'surface' precipitates occurs at less than theoretical monolayer surface coverages and circumneutral pH values. The aluminum incorporated into the hydrotalcite-like (or mixed metal-Al hydroxide) structure is apparently derived from the sorbent lattice. Enhanced release of Si concurrent with metal sorption suggests that a dissolution-reprecipitation process is involved during the evolution to a 'surface' precipitate (Scheidegger *et al.*, 1998).

A review of the earth science and catalysis literature suggests that most of the first row transition metals may be incorporated into either hydrotalcite- or pyroaurite-like structures (Taylor, 1984; Cavani *et al.*, 1991). We hypothesize that the formation of a mixed-metal 'surface' precipitate will depend, in

part, on the initial formation of a critical concentration of an innersphere surface complex. To test this hypothesis, we have characterized the sorption behaviour of Cu and Zn onto the pyrophyllite surface as a function of reaction pH.

Materials and methods

Copper or Zn sorption onto pyrophyllite was monitored as a function of reaction time for systems maintained at pH 6 or 7.5. Pyrophyllite suspensions (5 g/L) were preequilibrated at the reaction pH and 0.1 M NaNO₃ for at least one month. The pH of experimental systems was held constant through addition of the following buffers: 0.05 M MES (pK_a = 6.0) and 0.05 M HEPES (pK_a = 7.5) for pH 6 and 7.5 systems, respectively. Dissolved concentrations of Cu, Zn and Si were measured by inductively coupled plasma atomic emission spectroscopy. In all cases, total Zn or Cu concentrations were undersaturated with respect to a pure metal hydroxide or carbonate. The structure of the sorption complex was characterized by X-ray

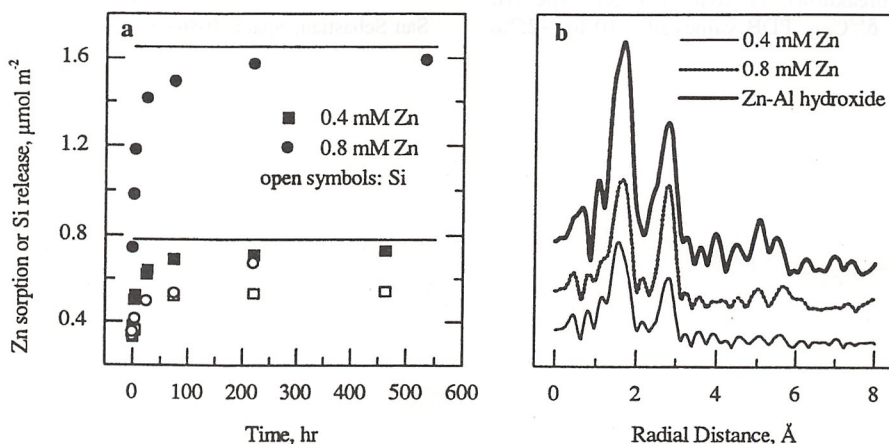


FIG. 1. A) Zn sorption and concurrent Si release as a function of time at pH 7.5. B) XAFS radial structure functions (uncorrected for phase shift) for a mixed Zn-Al hydroxide and Zn reacted with pyrophyllite.

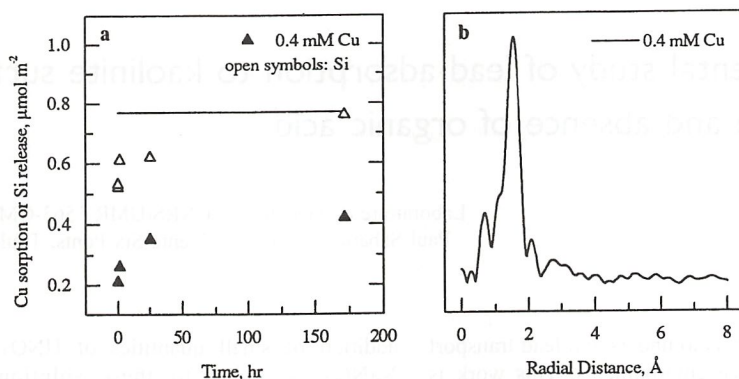


FIG. 2. A) Cu sorption and concurrent Si release as a function of time at pH 6. B) XAFS radial structure functions (uncorrected for phase shift) for Cu reacted with pyrophyllite.

absorption fine structure (XAFS) spectroscopy. Details for XAFS data collection are provided in Scheidegger *et al.* (1997).

Results and discussion

Results for Zn sorption and characterization of the local sorption environment for an aged sample are shown in Fig. 1. The macroscopic data indicates an initial rapid uptake of Zn within the first 50 hours followed by a slower rate of sorption (Fig. 1a). The solid lines plotted in Fig. 1a indicate the 100% sorption level at the two respective total Zn concentrations. This value was rapidly approached within approximately 200 hours in both systems. Concurrent with Zn uptake, Si was released into solution. This behaviour has been observed previously for Ni-pyrophyllite systems, and appears consistent with an enhanced dissolution of surface Si during metal sorption (Scheidegger *et al.*, 1997). The levels of Si released were similar at both Zn loadings indicating that it was not a congruent process, i.e. at least some of the Si may have been coprecipitated during formation of a secondary Zn precipitation product.

Results of XAFS characterization of aged Zn-pyrophyllite samples and a mixed Zn-Al hydroxide precipitate are shown in Fig. 1b. The radial structure functions for all samples indicate two well-defined peaks at approximately 1.6 and 2.8 \AA (uncorrected for phase shift). The first peak is due to backscattering from oxygen nearest neighbours while the second peak is most likely attributed to backscattering from Zn next-nearest neighbours. Comparison of these spectra suggests the formation

of a mixed Zn-Al hydroxide 'surface' precipitate. Thermogravimetric analysis of the 0.8 mM Zn sorption sample confirmed the formation of a hydrotalcite-like phase (data not shown).

The macroscopic sorption behaviour for Cu at pH 6 was similar to that observed for Zn at pH 7.5. There was an initial rapid uptake of Cu within 50 hours followed by a slower continuous sorption process. However, only 50% of the Cu had been sorbed within 200 hours, suggesting either that the sorption process was much slower than observed for Zn at pH 7.5 or a different mechanism was involved. Similar to the Zn systems, there was a net release of Si into solution. The radial structure function for Cu in an aged sample (uncorrected for phase shift) revealed only significant backscattering from the first shell, indicating insignificant levels of Cu in the second shell. The absence of significant quantities of a 'surface' precipitate suggests there were either kinetic limitations to the formation of a mixed precipitate phase at pH 6 or that Cu was less readily incorporated into a hydrotalcite-like structure under these reaction conditions. It should be noted that negligible Zn sorption occurred at pH 6, thus limiting formation of a mixed Zn-Al 'surface' precipitate (data not shown).

The contrasting behaviour for Zn and Cu under these experimental conditions suggests that reaction parameters such as pH as well as the physicochemical characteristics of the sorbing metal play an important role in the ultimate evolution of 'surface' precipitation products. Future research in our laboratory will address the relative role of these factors in an effort to better define the reaction mechanism leading to the formation of secondary hydrotalcite-like precipitates.