

Assessment of Ni sorption mechanisms on soil mineral surfaces using time-resolved X-ray absorption fine structure (XAFS) spectroscopy

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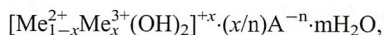
Many kinetic studies have shown that sorption of metal cations onto soil, clay mineral and metal (hydr)oxide surfaces is described by a two step process comprising a rapid stage and a slow stage (Ainsworth *et al.*, 1994). The rapid initial stage, occurring on time scales of seconds, minutes or hours, has been interpreted as an adsorption phenomenon (Sparks, 1995). However, the slow reaction stage, associated with time scales on the order of days, weeks or months is not clearly understood. Three possible mechanisms have been attributed to the slow sorption stage including: 1) adsorption onto sites of lower reactivity (Dzombak and Morel, 1986), 2) diffusion of the adsorbate into the adsorbent via micropores and/or directly in the solid material (absorption) (Pignatello and Xing, 1995), and 3) surface precipitation formation (Scheidegger *et al.*, 1996). However, until recently, the proposed mechanisms for slow metal sorption were based strictly on macroscopic measurements via sorption isotherms and kinetic studies. To definitively prove sorption mechanisms one must employ molecular approaches. With the advent of in-situ spectroscopic and microscopic techniques, it is possible to identify the cause of slow metal sorption mechanisms.

While adsorption is characterized as a two-dimensional surface feature, surface precipitation is depicted as three-dimensional growth. Precipitation is the formation of a solid mixture either by inclusion or by coprecipitation or on the surface of a pre-existing solid phase (surface precipitate). Precipitation is initiated by either homogeneous or heterogeneous nucleation. Surface precipitation follows a process which involves 1) adsorption of the metal onto the surface, 2) surface nucleation, and 3) crystalline growth outward from the surface. Site saturation is manifested in pH edges by a plateauing of the curve at some level below 100 percent sorption. However, it is difficult to detect site saturation for metal cations because of the formation

of hydroxide precipitates either in solution or on the surface, occurring at both high- and low-affinity binding sites, prior to bulk solution precipitation. Contribution of surface precipitates to overall sorption increases as sorbate/sorbent ratios increase and may become the dominant sorption mechanism at very high ratios. However, recent studies on the formation of surface precipitates indicate that high sorbate/sorbent ratios are not necessary and that site saturation is not achieved (Scheidegger *et al.*, 1996).

Scheidegger *et al.* (1996) investigated Ni sorption onto pyrophyllite using X-ray absorption fine structure (XAFS) spectroscopy. They observed the formation of a Ni surface precipitate on the pyrophyllite surface and noted that the product was not Ni(OH)_{2(s)}. The nucleation of the heterogeneous solid at the surface interface is a mixed Ni-Al hydroxide phase which is similar to takovite (Ni₆Al₂(OH)₁₆CO₃·H₂O). This finding suggests that Ni sorption may have caused dissolution of the mineral surface, releasing Al³⁺ into solution which was incorporated into a precipitate.

The formation of polynuclear hydroxide complexes in solution has been noted in the literature (Taylor, 1984). The common chemical formula for the mixed-cation compounds is



where Me²⁺ could be Co(II), Fe(II), Mg(II), Mn(II), Ni(II), or Zn(II), and Me³⁺ is Al(III), Cr(III), or Fe(III). Interlayer anions, A⁻ⁿ, can be represented as Br⁻, Cl⁻, ClO₄⁻, I⁻, NO₃⁻, or OH⁻. The net positive charge, x, is counterbalanced by an equal negative charge, n. The remaining interlayer space is occupied by water molecules, m.

Precipitation kinetics of heavy metals (e.g. Ni and Co) on natural surfaces has recently become an area of great interest. Spectroscopic studies have shown that formation of mixed metal phases can occur within a matter of minutes, even at surface loadings less than monolayer coverage. This study investi-

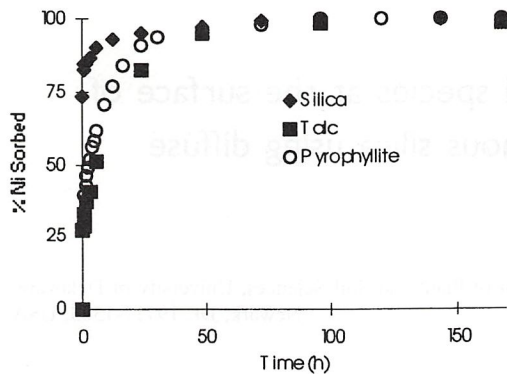


FIG. 1. Batch Ni sorption kinetics.

gated the kinetics of Ni sorption on amorphous silica, pyrophyllite, and talc at a low solution concentration (3 mM), short time scales and at a pH (7.5) lower

than one would expect the production of Ni(OH)₂ (s), according to its solubility product (Fig. 1). Time-resolved XAFS studies were conducted to assess how the local chemical environment of Ni on the mineral surfaces changed over a range of time scales.

References

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