

Mechanisms of Slow Lead and Nickel Sorption Kinetics on γ -Al₂O₃ and Pyrophyllite

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Introduction. It is often observed that the kinetics of heavy metal sorption on soil and soil constituents are fast initially and then the reaction rates decrease. The fast reaction is commonly associated with adsorption. For the slow sorption reaction of heavy metals three mechanisms have been proposed: slow diffusion to sorption sites with restricted access (1), precipitation on the surface (1), and sorption to sites of lower reactivity (2). It is possible that in natural systems all three of these reaction mechanisms occur simultaneously. Such slow reactions are often neglected in metal sorption experiments, and could be a cause of the hysteresis observed in many studies. This study compares the slow sorption reactions of Pb and Ni on clays and aluminum oxides. Evidence for the mechanisms responsible for the slow reactions is provided using X-ray absorption fine structure (XAFS) spectroscopy.

Materials and Methods. Well characterized γ -Al₂O₃ and pyrophyllite were used in this study. The initial Pb and Ni solution concentrations were 2 mM and 3 mM, respectively. Both solutions were undersaturated with respect to the thermodynamic solubility product of Ni(OH)₂ or Pb(OH)₂ (ionic strength I = 0.1 M [NaNO₃], pH = 7.0 for Pb suspension and 7.5 for the Ni suspension). The sorption kinetics were determined using a pH-stat batch system that excluded CO₂. Subsamples were taken, separated by filtering and centrifuging, and analyzed for Pb or Ni. The local atomic structure of the Pb and Ni sorbed onto the mineral samples was determined using XAFS analysis. XAFS spectra were recorded at beamline X-11A at NSLS using a Si (111) monochromator crystal. The spectra were recorded in fluorescence mode at 77 K. For data analysis, the programs MacXAFS™ and EXCURVE™ were used.

Results and Discussion. The data for Ni sorption on pyrophyllite (Figure 1) suggest a rapid initial sorption reaction, reaching approximately 25% of the Ni sorbed within the first 30 minutes. After that the reaction slowed considerably, but was continuous for times as long as 72 hours (97% of the Ni is removed from solution). The data for Pb sorption on γ -Al₂O₃ (Figure 2) suggests a similar trend; approximately 80% of the Pb was removed from the solution within the first 24 hours, followed by a slow continuous sorption reaction for up to 190 hours. However, since kinetic experiments represent macroscopic observations, determination of mechanisms responsible for the slow sorption is difficult.

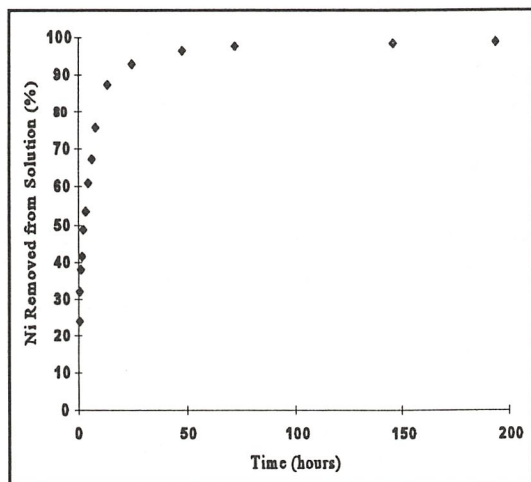


Figure 1. Relationship between sorption and time for Ni on pyrophyllite.

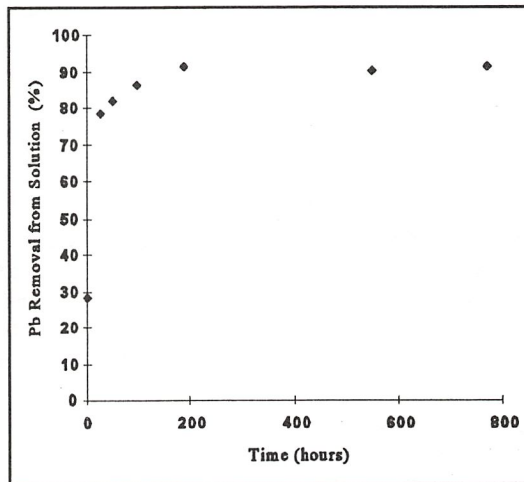


Figure 2. Relationship between sorption and time for Pb on γ -Al₂O₃.

Analysis of the radial structure function (RSF) from the Ni sorption kinetic samples illustrates the development of a second shell with time (Figure 3). The second shell results from backscattering among multi- or polynuclear Ni complexes.

Subsequent data analysis has shown that the multinuclear species is a mixed Ni/Al phase (3). Therefore, the XAFS data imply that the formation of surface precipitates growing in size with increasing reaction time is the predominant mechanism responsible for the slow kinetics in the Ni/pyrophyllite system.

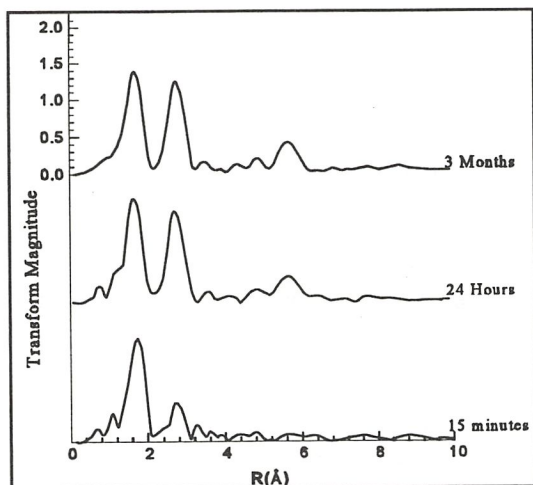


Figure 3. RSF for Ni sorption on pyrophyllite, uncorrected for phase shift.

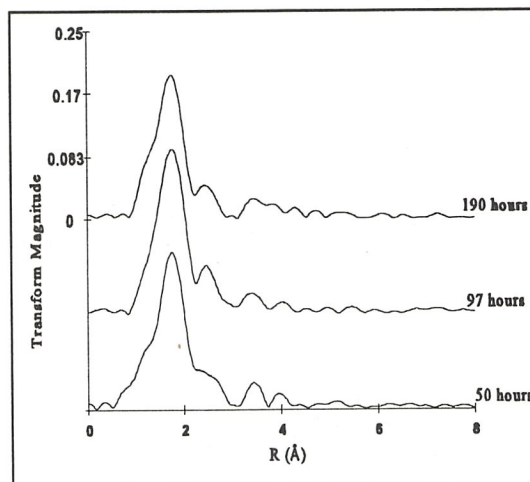


Figure 4. RS for Pb on g-Al₂O₃, uncorrected for phase shift.

The lack of a second peak in the RSF from the Pb sorption kinetic samples (Figure 4) suggests that a multinuclear Pb-complex is not forming. This means that either diffusion and/or sorption to sites of lower reactivity is probably responsible for the slow kinetics in the Pb/ γ -Al₂O₃ system. A separate experiment conducted on the Pb system at pH = 5.5 showed similar slow kinetics, indicating that the slow sorption step is pH-independent. This behavior further supports the hypothesis that diffusion is the mechanism responsible for the slow kinetics because adsorption and precipitation are both strongly pH-dependent reactions.

In spite of the fact that the two minerals have distinctive properties, we suspect that the reason for the presence or absence of a mixed Ni/Pb-Al phase is the difference in the ionic radius (1.20 Å for Pb and 0.69 Å for Ni [5]), rather than the minerals. XAFS analysis of Pb sorption on pyrophyllite also revealed the absence of a second peak in the RSF. Ainsworth et. al. (1994) observed that the extent of sorption/desorption reversibility was positively correlated to the ionic radius of the sorbing metals. Coughlin and Stone (1995) also observed that coprecipitation of metal ions with Fe was directly dependent on ionic radius. These observations agree well with our data, which suggest that Ni (the smaller ion) forms a mixed precipitate, while Pb does not.

In conclusion, it appears that the formation of a mixed cation phase depends on the ionic radii of the ions present in solution. In the Ni system, dissolved Al from the pyrophyllite is a source of ions in solution, has a similar ionic radius, and will cause the formation of mixed Ni/Al precipitates. In contrast, in the Pb system the formation of a mixed precipitate phase is not favorable because of a lack of an ion of similar radius to Pb. Thus, the conclusion that diffusion is responsible for the slow Pb sorption, and precipitation is responsible for the slow Ni sorption, is reasonable for our systems.

Literature Cited.

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