Sorption and surface precipitation as controls on the reactivity and bioavailability of sorbates and sorbents

JANET G. HERING

California Institute of Technology, Environmental Science & Engineering, 1200 E. California Blvd. (138-78), Pasadena, CA 91125, USA (jhering@caltech.edu)

The partitioning of chemical species between solid and dissolved phases determines their mobility in aquatic systems and can strongly influence their reactivity and bioavailability. The interfacial processes of sorption and surface precipitation can affect the reactivity not only of the surface species but also of the underlying solid.

Constraints on the structure of surface species

Insights into the structure of surface species are gained through macroscopic sorption experiments, spectroscopic interrogation, and modeling. These methods provide information that is often complementary and it is critical to examine the level of constraints imposed by each type of information. For example, the protonation level of surface complexes is often inferred from the pH dependence of sorption, but this can be shown to be only a weak constraint. Spectroscopic techniques provide evidence for binuclear surface complexes, but formation of such complexes can be inconsistent with sorption densities observed in macroscopic studies. Further, it is important to consider how the structure of surface species may influence the reactivity of the underlying solid.

Surface reactivity

The effect of surface speciation on the reactivity of the underlying solid is examined in the case of the oxidative dissolution of chromium(III) hydroxide. This reaction exhibits inhibition by the product chromium(VI) at pH 2 but not at pH 9. This pH dependence suggests that the inhibition is due to interaction of chromium(VI) with the surface of the dissolving solid.

The reactivity of both sorbates and sorbents toward microbial reduction will be examined for arsenic(V) sorbed on iron(III) oxyhydroxides. In both field and laboratory studies, reduction of arsenic(V) to arsenic(III) can be observed without any detectable release of arsenic from the iron(III) oxyhydroxide surface into solution. Arsenic(V) reduction is observed to precede reduction of iron(III). Steric, kinetic, and equilibrium constraints to microbial transformations of surface species are considered.

Bacterial adsorption controls on mineral solubility

K.J. JOHNSON AND J.B. FEIN

University of Notre Dame, Civil Engineering and Geological Sciences, 156 Fitzpatrick, Notre Dame, IN 46556, USA (kjohnson@nd.edu, Fein.1@nd.edu)

Bacterial adsorption reactions can dominate the speciation of metal cations under a range of conditions of geologic interest, and hence bacterial adsorption can strongly influence the saturation state of water-rock systems. Although bacterial effects on the rate of mineral dissolution are well-established, the effects of bacteria on mineral solubilities, or the extent of dissolution, have not been studied.

In this study, we measure the effect of the common soil bacteria, *Bacillus subtilis*, on the solubility of the mineral cerrusite ($PbCO_3$). We compare solubility estimates from surface complexation modeling to the observed experimental solubilities, providing a rigorous test of the ability of thermodynamic modeling to account for the observed solubility enhancement.

B. subtilis cells were suspended in 0.1 M $NaClO_4$, and powdered $PbCO_3$ was sealed in dialysis tubing prior to being placed in the bacterial suspension. This approach enabled chemical contact between all components during the experiment, but allowed separation of the mineral from the bacteria after the experiment so that the distribution of released Pb could be determined. Surface complexation models were also developed based on previously determined bacterial site concentrations and stability constants in order to independently estimate the expected effect of bacterial adsorption of Pb on the mineral solubility.

We observed significantly enhanced cerrusite solubility in the bacteria-bearing systems, with Pb-bacterial surface complexes dominating the Pb speciation in the biotic systems. Results from this study suggest that adsorption of mineral-forming cations onto bacterial cell walls can lower the mineral saturation state, causing an increase in mineral dissolution. Surface complexation models can be used successfully to quantitatively estimate the effect of bacterial adsorption on mineral solubilities, thereby providing a better understanding of the role that bacteria play in weathering and porosity evolution in the subsurface.