

Defining and calibrating surface complexation models for predictive simulations of reactive transport in field applications

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It is widely understood that surface complexation models (SCM's) provide the approach to describing metal- and metalloid-ion adsorption most compatible with scientific understanding of solid-liquid interfacial reactions. In systems where solutes adsorb on materials whose surface functional groups are known, SCM's written in terms of reactions between specific surface moieties and adsorbing species to form surface complexes identified spectroscopically provide a complete thermodynamic description of adsorption over a wide range of chemical conditions. However, this level of sophistication is generally not achievable in field applications, such as contaminant transport in groundwater, because of the difficulty in identifying dominant surface complexes. Surface complexation models have been successfully applied in predictive simulations of contaminant transport by identifying the minimum number of reactions required to quantify adsorption over the field-relevant range of chemical conditions.

The structure and calibration of SCM's for reactive transport applications are examined using field experiments conducted in an aquifer with variable chemical conditions. Adsorption properties are controlled by mineral-grain coatings dominated by aluminum-substituted goethite and illite/chlorite clays of variable composition. SCM's are defined and calibrated using laboratory experiments conducted with site-specific materials and applied to predict results of field experiments and field-scale plume characterization studies. Accounting for variable pH and dissolved salt concentrations on adsorption is examined using a series of experiments conducted with nickel, zinc, and lead. Accounting for competitive adsorption is examined in experiments with phosphate and arsenate. Incorporating surface complexation models into complex reaction networks is examined in experiments involving denitrification coupled to iron oxidation and its impact on fate and transport of arsenic and other solutes. These and studies conducted elsewhere demonstrate that surface complexation models provide a practical approach to quantifying the impact of adsorption on transport under variable chemical conditions, as typically observed in field applications.

Dynamics of interfacial electron transfer: Implications for biogeochemical reactions

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The redox chemistry of microbe-mineral interfaces is central to many biogeochemical processes such as microbial iron respiration. Indeed, dissimilatory metal reducing bacteria (DIRB) can use insoluble metal oxides as terminal electron acceptors for anaerobic growth. DIRB possess an electron transport chain, mostly composed of multi-heme cytochromes, which forms a pathway for transporting electrons across the cell membrane and allows for interfacial electron transfer (ET) to extracellular metal oxide minerals.

Throughout this presentation, we will use hematite ($\alpha\text{-Fe}_2\text{O}_3$) as a model iron (III) oxide mineral. Computational techniques were applied to explore the molecular interactions between a well-defined model cytochrome and hematite surfaces and to determine the rate of elementary ET reactions. The simulations indicate that interfacial ET distances of 1 nm or less can be achieved for the purpose of oxide reduction. Moreover, the calculations strongly suggest that, although feasible, the interfacial ET step is a potential kinetic bottleneck.

One of the main outcomes of microbial iron respiration is the release of iron (II) into solution. In turn, iron (II) can interact with the iron oxide surface and undergo oxidative adsorption. Therefore, the rates of iron (II) adsorption and ET reactions between adsorbed iron (II) and surface sites were computed to shed light on the mechanisms of iron (II) oxidative adsorption. Interestingly, these calculations reveal that iron (II) oxidation from an outersphere position is a possible pathway, despite the slower kinetics of the ET step, because iron (II) adsorption as an innersphere complex requires overcoming a large energy barrier.

Finally, the injection of electrons, via either microbial respiration or iron (II) oxidative adsorption, results in the net dissolution of the iron oxide mineral. Previous computational work in our group showed that injected electrons can move through iron oxide lattices via a polaron hopping mechanism. Therefore, a kinetic Monte Carlo model was designed and implemented to explore the catalytic effect of electron injection on iron oxide dissolution. The simulations indicate that dissolution rates are enhanced due to roughening of the surface, which, in turn, is a direct consequence of the ability of electrons to move away from their initial injection point.