Molecular-Level Processes Governing the Interaction of Contaminants with Iron and Manganese Oxides Project (ID Number: 54635)

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Research Objective:
The central tenet of this program is that a fundamental understanding of specific mineral surface-site reactivities will substantially improve reactive transport models of contaminants in geologic systems, and will allow more effective remediation schemes to be devised. To this end, we carried out a program of research that focuses on the fundamental mechanisms of redox chemistry of contaminants on mineral surfaces. As much of this chemistry in sediments involves the Fe(III)/Fe(II) couples, we focussed on mineral phases containing these species. Our approach was to conduct carefully controlled experiments on model, single-crystal Fe oxide mineral surfaces grown by molecular beam epitaxy, natural Fe oxide single crystals, and synthetic mineral powders. We used the results from the model surfaces, which were very well defined in terms of surface composition, structure, and defect densities, to understand the results obtained on more complex mineral specimens. We used a variety of experimental probes, along with molecular modeling theory, to determine clean mineral surface structure, details of the chemisorption and decomposition of water, and the interface structure and redox chemistry of important contaminants such as CrO$_4^{2-}$ on these surfaces.

Research Progress and Implications (summary of the entire three years):
- Studies on Single Crystal Iron Oxide Surfaces
  We have studied the interaction of aqueous chromate (CrO$_4^{2-}$) with the iron oxides hematite ($\alpha$-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$). Model surfaces of hematite and magnetite were grown by oxygen-plasma-assisted molecular beam epitaxy on single crystal substrates of $\alpha$-Al$_2$O$_3$ and MgO, respectively. Natural specimens were also used for water and chromate chemistry experiments. Clean surface composition, geometric structure and morphology were investigated experimentally using a combination of x-ray photoelectron spectroscopy and diffraction, and scanning tunneling microscopy. Theoretical surface structure predictions were also made using molecular dynamics (MD) simulations. It was found that a simple surface autocompensation model is adequate to predict the stable terminations(s) of these surfaces. The interlayer relaxations were experimentally determined and found to compare favorably with MD simulations for hematite, but not magnetite. These surfaces were then exposed to the pure solvent (H$_2$O) in a controlled fashion from the vapor phase to investigate surface hydroxylation. Using
x-ray photoelectron spectroscopy, it was found that both surfaces exhibit a threshold pressure for hydroxylation of $\sim 10^{-3} - 10^{-4}$ torr which appears to be dictated by thermodynamic driving forces, rather than kinetics. The kinetics of reduction of Cr(VI) in $\text{CrO}_4^{2-}$ to Cr(III), and the structure of adsorbed Cr(III) on surfaces initially containing Fe(II), were then determined using x-ray photoemission, x-ray absorption spectroscopy, and extended x-ray absorption fine structure. The reduction kinetics were found to be highly pH dependent, with the fastest rates occurring at pH values below the point of zero charge of magnetite (i.e. those pH values for which the surface is positively charged). At the highest rate, the surface redox reaction is $\sim 90\%$ complete within 5 minutes, leaving behind a thin (15±5Å) layer of mixed, insulating Cr oxyhydroxide that shuts down the electron transfer process. The reduction product, Cr(III), is bound as an inner-sphere (i.e. no mediating waters) edge-sharing, bidentate complex on the oxidized surface. The $\text{CrO}_4^{2-}$ reduction kinetics on magnetite single crystals were found to be almost identical to those measured earlier on “zero-valent iron” powders. This fact strongly suggests that it is the magnetite native oxide on the surface of such particles that interacts chemically with sorbed $\text{CrO}_4^{2-}$ rather than Fe(0). In addition, the fact that the process ceases after just a few minutes, with the formation of an ultrathin, insulating oxyhydroxide layer, establishes that the latter quenches charge transfer above a critical thickness of $\sim 15\text{Å}$. Thus, deployment of such a remediation process will be “surface limited” and high surface area materials will be required to reduce a significant amount of $\text{CrO}_4^{2-}$.

• Studies on Hematite Powder

Powdered hematites present several crystalline faces for surface reactions and thus represent a system that is intermediate in complexity between the single-crystal surfaces described above and the heterogeneous mixture of surfaces found in soils and sediments. We conducted several experiments with hematite powder to understand the thermodynamics and kinetics of $\text{CrO}_4^{2-}$ sorption, with particular emphasis placed on competitive sorption by chromate, phosphate and sulfate oxyanions by laser photoacoustic spectroscopy (LPAS). Sorption of $\text{CrO}_4^{2-}$ and phosphate species to hematite is dominated by divalent anions even at low pHs where monovalent anions predominate in solution. As a consequence, aqueous speciation (i.e. the fraction of the total species in solution available in the form of a divalent anion) is a more important determinant of the relative amount of $\text{CrO}_4^{2-}$ or phosphate sorbed than the intrinsic selectivity of the anions for the surface. In mixed-anion systems typical of groundwater, significantly different sorption affinities may be observed than predicted solely on the basis of relative single-anion sorption constants.

An important outcome of this work is the development of a powerful new tool with which competitive adsorption of anions on minerals in suspension can be investigated in real time. We have demonstrated that nontoxic anions present in the subsurface environment, such as phosphate, may compete with toxic anions, such as $\text{CrO}_4^{2-}$, for sorption sites on redox-active minerals to an extent that is highly pH dependent. Significantly, LPAS can be used for studies of pure mineral phases, such as hematite in the present experiments, as well as for multi-component soil mixtures. Thus, controlled and “real-world” experiments can be carried out to determine the extent to which competing nontoxic anions can prevent adsorption and reduction of toxic anions by minerals or redox-active remediation agents, such as zero-valent iron.