Molecular-Level Processes Governing the Interaction of Contaminants with Iron and Manganese Oxides

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Progress Report

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Research Objective

The central tenet of this proposal 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.* Most large-scale, macroscopic models employ global chemical reaction kinetics and thermochemistry. However, such models do not incorporate molecular-level input critical to the detailed prediction of how contaminants interact with minerals in the subsurface. A first step leading to the incorporation of molecular-level processes in large-scale macroscopic models is the ability to understand which molecular-level processes will dominate the chemistry at the microscopic grain level of minerals. To this end, our research focuses on the fundamental mechanisms of redox chemistry at mineral surfaces. As much of this chemistry in sediments involves the Fe(III)/Fe(II) and Mn(IV)/Mn(II) couples, we focus on mineral phases containing these species. Of particular interest is the effect of the local coordination environment of Fe and Mn atoms on their reactivity toward contaminant species. Studies of the impact of local atomic structure on reactivity in combination with knowledge about the types and amounts of various surfaces on natural grain-size minerals provide the data for statistical models. These models in turn form the basis of the larger-scale macroscopic descriptions of reactivity that are needed for reactive transport models. A molecular-level understanding of these mechanisms will enhance the ability to design much greater performance efficiency, cost effectiveness, and remediation strategies that have minimal negative impact on the local environment. For instance, a comprehensive understanding of how minerals that contain Fe(II) reduce oxyanions and chlorinated organics should enable the design of other Fe(II)-containing remediation materials in a way that is synergistic with existing minerals in the subsurface environment.

Research Statement

Contamination of subsurface sediments with radionuclides, organic solvents, and Resource Conservation and Recovery Act (RCRA)-listed metals is one of the many challenging environmental problems at U.S. Department of Energy (DOE) weapons sites. Addressing this problem requires: (i) an accurate assessment of the health and environmental risks associated with these subsurface contaminants (in particular, a prediction of transport rates and degradation products in the subsurface), and (ii) the development of reliable and economical remediation schemes. These two activities, in turn, critically depend on an adequate understanding of the chemistry that occurs when contaminants encounter the solid surfaces (largely minerals) present in the subsurface. In addition to adsorption and precipitation at these surfaces, many of the contaminants (e.g., Pu, U, Cr(VI), CCl_4, TCE, and perchloroethylene) can undergo electron-transfer reactions that can substantially alter the species and, thereby, either help or hinder the remediation process. Predicting the movement of redox-sensitive contaminants through subsurface materials poses a difficult challenge, made more difficult by a lack of fundamental knowledge about the mechanisms and rates of redox reactions with exposed mineral phases. Manipulation of the redox status of aquifers, and the contaminants they contain, by the *in-situ* reduction of iron-bearing minerals, or the addition of elemental iron, are two examples of

proposed remediation techniques that take advantage of redox chemistry at solid surfaces to remove contaminants from groundwater. Although these remediation techniques have shown some success in laboratory-, intermediate-, and field-scale demonstrations, this success has been somewhat fortuitous in that little is actually known about the manner in which they work, and the manner by which they might fail. Clearly, both risk-assessment and remediation activities can benefit from a better understanding of the mechanisms of redox reactions at mineral surfaces.

Research Progress

Growth of Model Fe-Oxide Surfaces by Molecular Beam Epitaxy

Successfully developed, for the first time, is a comprehensive methodology for growing very well defined surfaces of the oxides of iron by molecular beam epitaxy (MBE). Such surfaces are essential for gaining a detailed, molecular-level understanding of sorption and redox chemistry of contaminants on iron-bearing minerals; naturally occurring iron oxides are, in general, too heterogeneous and ill-defined to be useful for this kind of research. Our approach allows us to span the full range of stoichiometry and surface orientation. In particular, we can now routinely prepare $Fe_{1-x}O$ (wustite) (001) and (01l), where x = 0 to ~0.2, Fe_2O_4 (magnetite) (001) and (01l), γ-Fe_2O_3 (maghemite) (001) and (01l), and a-Fe_2O_3 (hematite) (0001), $(11\bar{2}0)$ and $(10\bar{1}2)$ surfaces. Al1 surfaces are phase-pure and possess negligible densities of point defects. With the exception of (011)-oriented FeO, Fe_3O_4, and γ-Fe_2O_3, these surfaces are quite flat, with mean roughnesses of a few Ä, as measured by x-ray reflectivity. The (011)-oriented FeO, Fe_3O_4, and γ-Fe_2O_3 are rough only because the MgO(011) substrates upon which they are grown facet while being thermally cleaned prior to MBE growth. The key parameters that determine the characteristics of the as-grown surfaces are substrate temperature, iron flux, oxygen flux, and growth rate. We have developed a phase diagram for the formation of MBE-grown films of the four iron oxides mentioned above, and can now produce these surfaces with very high yields for the other investigators in this program.

Scanning Probe Microscopy Images of Model Iron Oxide Surfaces

Two epitaxially grown Fe_3O_4(100) surfaces have been examined with scanning tunneling microscopy. One sample was 50 nm thick, the other 250 nm. Both were cleaned in ultrahigh vacuum by repeated annealing in oxygen. The thinner sample was heated to 300°C, while the thicker film was generally annealed at 380°C. A small amount of magnesium out-diffusion from the MgO substrate was observed for the thinner sample after ~30 hours of cumulative annealing. No such out-diffusion was observed for the thicker sample, even though it was heated to higher temperatures, consistent with standard diffusion models, which predict a time-squared rate dependence on thickness. In general, both surfaces are found to be relatively flat. Over length scales of a few hundred nanometers, roughly 4 to 5 exposed layers are typically observed.
For the 50 nm film, the uppermost layer comprises dispersed, oriented square islands a few nanometers in size. These islands are on successively larger islands, which ultimately coalesce. A preferred orientation of the edges of the islands is observed. Based on preliminary low-energy electron diffraction experiments, the orientation is tentatively assigned to the <100 > direction.

For the 250 nm film, the islands are larger, the edges more irregular, and they show a pronounced anisotropy (i.e., the islands are longer in one direction than the other). Low-energy electron diffraction experiments are planned to determine the relevant crystallographic directions of this anisotropy. Based on these observations, it appears that the films grew via an island-nucleation mechanism, as opposed to either step flow or ballistic deposition. Step-flow growth is characterized by large, flat terraces with little or no island density. Ballistic or random growth is characterized by statistically rough surfaces. For example, the 50-nm-thick film would have, on average, 16 exposed layers if ballistic growth occurred, as opposed to 5 layers observed. The island edges represent surface sites that are under-coordinated with respect to the ideal terrace sites and as such may have different chemistries. A detailed analysis of the edge densities is currently underway. Initial estimates suggest that the densities are only of the order of 10% for the 50 nm film and lower yet at 5% for the 250 nm film. For comparison, single crystals of "high quality" samples, such as commercially available semiconductors or metals, still have defect densities of 2-3%. Comparison of the heterogeneous chemistry on samples with differing defect densities will allow for an assignment of the importance of defects in influencing sorption and redox of contaminants.

Synchrotron Radiation Studies of Aqueous/Fe-Oxide Interfaces

Grazing-incidence x-ray absorption fine structure spectroscopy (GI-XAFS) studies of aqueous Pb(II) sorbed on single-crystal MBE-grown films of α -F_2O_3(000l), $(11\bar{2}0)$ and $(10\bar{1}2)$ were carried out at Stanford Synchrotron Radiation Laboratory (SSRL). The XAFS results show that Pb(II) is chemi-sorbed on α -Fe_2O_3($10\bar{1}2$) in an inner-sphere fashion, which is the sorption mode of aqueous Pb(II) on α -Al_2O_3(1 $0\bar{1}2$). Pb(II) also appears to chemi-sorb on α -Fe_2O_3(0001) in an inner-sphere fashion, initially, but apparently undergoes some type of coupled photocatalytic oxidation-reduction reaction in which a gas is liberated in the sample cell; the Pb-XAFS spectrum changes significantly after an hour of exposure of the sample to the synchrotron x-ray beam. We plan to repeat this experiment to more fully document and understand these changes.

Soft x-ray XAFS studies of the interaction of aqueous PO, with natural hematite surfaces were also carried out. A natural α -Fe_2O_3(0001) surface was prepared by cleaving and polishing for these experiments. The sample was placed in our main vacuum chamber on SSRL beam line 3-3 for LEED and surface EXAFS studies. The clean surface was found to give a good LEED pattern characteristic of the (0001) surface. Photoemission experiments also showed the surface to be relatively free of contaminants, with only minor amounts of C, Si, and Al detected. This sample was then reacted with an aqueous solution containing 30 µg of KH_2PO_4 for ten minutes in a nitrogen-filled glove bag that was connected to the preparation chamber of the UHV system. P K-XAFS spectra were collected out to an energy of 250 eV above the P K-edge. A similar experiment also was carried out on PO, deposited on a reduced hematite surface, which is similar to magnetite. The EXAFS spectra and Fourier transforms of these two samples show significant differences that suggest a different sorption mode for PO, on the two surfaces. The data are currently being fit to derive detailed models of the sorption geometry of PO, surface complexes.

A study was initiated of the interaction of water with MBE-grown hematite and magnetite as a necessary step before reacting them with aqueous solutions containing **chromium** and chlorocarbons. These experiments were carried out on SSRL beamline 10^{-1}. Photoemission (O 1s) and Fe L-edge and O K-edge XAFS data were collected on α-Fe_2O_3(0001) and $(10\bar{1}2)$, and on Fe_2O_3(110) magnetite model surfaces. These measurements were also made on natural hematite (0001) and magnetite (110) surfaces, and on natural polycrystalline samples of goethite and limonite. The goethite and limonite data show clear signatures of OH groups coordinating iron, which serve as fingerprints for the dissociative chemi-sorption of water on water-exposed hematite and magnetite surfaces. The photoemission data show that the threshold water pressure required for extensive reaction on Fe_2O_3(0001) is a 2 x 10^{-4} torr exposure for three minutes. In contrast, the same orientation of α-Fe_2O_3(0001) required a threshold water pressure of 2-4 torr for three minutes before significant interaction occurred.

Plans are underway to continue studies of the interaction of water on other orientations of MBE-grown hematite and magnetite surfaces. This work should lead to an estimate of defect levels on these surfaces, which is critical for understanding reactivity on iron oxide surfaces in general. This work will have direct bearing on planned studies of the reaction of chromium on these surfaces, which will be a major focus of the work during the remainder of year 1. In addition, GI-XAFS studies of Cr deposited from aqueous solutions onto MBE-grown hematite and magnetite surfaces will be initiated. These studies will reveal the geometric details of the sorption products, which are necessary for defining reaction mechanisms. The uptake of Cr(VI) and Cr(III) on high-surface-area hematite and magnetite powders using powder XAFS methods will also be investigated.

Chromate Adsorption Kinetics Using Photoacoustic Spectroscopy

The ability to detect very low concentrations of chromate in solution in real-time using pulsed-laser photoacoustic spectroscopy has been developed. This technique relies on absorption of light at a specific wavelength by the analyte and the generation of an acoustic wave from heat released as the atom or molecule returns to the ground state. The amplitude of the acoustic wave is proportional to the concentration of the analyte and is detected using a pressure transducer in acoustic contact with the solution. Because 90-100% of the light energy absorbed by molecules is typically released as heat, rather than as fluorescence, photoacoustic detection has an inherent sensitivity up to two orders of magnitude greater than fluorescence spectroscopy and several orders of magnitude greater than conventional absorption spectroscopy.

Initially, we used light at 355 nm from a Nd-YAG laser to excite chromate in a pH-3 HCl solution in a standard l-cm path-length quartz cuvette. The maximum absorbance of chromate is at about 372 nm, and the relative absorbance at 355 nm is -50% of the maximum. Thus, the detection limits we are able to obtain thus far are at least twice as large as those achievable with light of the appropriate wavelength. The appropriate laser capability will become available in June 1997 with the final acceptance of an Alexandrite tunable laser. Detection was accomplished using a Pb-Zr-titanate (PZT) pressure transducer attached to the outside of

the cuvette. The transducer signal was amplified 500 times and the area under the initial photoacoustic signal was integrated using a boxcar integrator.

Preliminary experiments consisted of measurements of the photoacoustic signal with 1.5 ml of stock solution in the cuvette in the presence and absence of chromate and of an 8-mm diameter α-Al_2O_3(0001) disk of the type used as substrates for MBE synthesis of hematite surfaces. The solution was spiked with 30 ng of Cr(VI); it was then possible to establish a detection limit of 2-4 ng Cr(VI). The sapphire disk, which had been equilibrated with pH-3 HCl for a minimum of 30 minutes, was then immersed in the solution and rested at the bottom of the cuvette below the light path. The decrease in concentration of Cr(VI) to 0 ng could then be followed over a period that ranged from 90 minutes to 210 minutes, depending on whether chromate adsorbed to the disk had been cleaned off prior to a specific run. Adsorption of Cr(VI) to the quartz cuvette was negligible in tests conducted without sapphire present.

It is believed that this technique represents a major step forward in real-time analysis of Cr(VI) in solution in that no other technique can nondestructively analyze Cr(VI) at these low levels during an actual kinetics run. The performance of a series of experiments are planned at different pHs with sapphire, after which we will move to the hematite and magnetite surfaces prepared by MBE to measure adsorption and reduction kinetics of Cr(VI) by these materials. A special flow-through cell will also be designed to allow adsorption testing on the MBE surfaces without contributions from the substrates.

Theoretical Modeling of Electron Transfer Rates

Theoretical modeling efforts thus far have been directed at producing an empirical potential for Fe(II)-O-OH-H_2O interactions, consistent with the current model for Fe(III)-O-OH-H_2O interactions. The goal is to predict relative electron affinities of surface species within a framework that allows both surface solvation and variable proton stoichiometry. The latter has been shown to be crucial in homogeneous electron transfer reactions in solution where the rates are strongly dependent on pH. Benchmarks for success were the successful prediction of: (i) the Fe(II)-Oÿÿdistance in hexaaqua Fe(II) (213 pm), (ii) the a_{1g} *octahedral* stretch (380 wavenumbers) and, (iii) the heat of solution of Fe(II). Moreover, to simulate electron transfer reactions, the model must also reproduce analogous quantities involving Fe(III) without a change in any parameter other than the change in charge (+2e to +3e). Experimental and calculated quantities differ systematically because the former are measured in condensed phases and calculations are performed on gas-phase quantities. The extent of this variation was assessed with quantum mechanical DFT and *ab initio* calculations. It was found that Fe(II)-O and Fe(III)-O bond lengths are overestimated by approximately 3% and a_{1g} stretching frequencies were underestimated by approximately 50 wavenumbers. Taking into account this systematic variation, this final model predicts bond lengths and energies to better than 2% for all Fe(II) and Fe(III) species. Because of constraints imposed by the model for water, however, a consistent overestimate was made of the a_{1g} stretching frequencies by 100 wavenumbers. The heats of solution are accurate to within 5%. Hydrolysis constants for both Fe(II) and Fe(III) correlate

well with gas-phase acidities, except for the third hydrolysis constant for Fe(II). A paper is in progress that describes these findings and applies them to the calculation of electron affinities of octahedral sites on hematite (0 12).