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

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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 are carrying 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 iron(III)/iron(II) couples, we are focusing on mineral phases containing these species. Our approach is to conduct carefully controlled experiments on model, single-crystal iron oxide mineral surfaces grown by molecular beam epitaxy, natural iron oxide single crystals, and synthetic mineral powders. We use the results from the model surfaces, which are very well defined in terms of surface composition, structure, and defect densities, to understand the results obtained on more complex mineral specimens. We are using 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.

Problem Statement

Contamination of subsurface sediments with radionuclides, organic solvents, and Resource Conservation and Recovery Act (RCRA) metals is one of the many challenging environmental problems at DOE weapons sites. Addressing this problem requires 1) an accurate assessment of the risks associated with these subsurface contaminants (in particular, a prediction of transport rates and degradation products in the subsurface) and 2) 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., plutonium, uranium, chromium(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 molecular-level mechanisms of redox reactions at well-defined mineral surfaces.

Research Progress and Implications

Surface Structure of Clean and Hydroxylated Magnetite Surfaces

The first step in gaining a molecular-level understanding of redox-active contaminant interactions with model minerals is to understand the structure of the clean mineral surfaces with which contaminants interact. To this end, we have combined scanning tunneling microscopy (STM) with x-ray photoelectron diffraction (XPD) and molecular dynamics (MD) simulations to understand the surface structure of $\text{Fe}_3\text{O}_4(001)$ (magnetite), one of the most important iron oxide surfaces from the point of view of redox chemistry. The most fundamental surface structural property of materials such as $\text{Fe}_3\text{O}_4(001)$ is surface termination, i.e., which layer is outermost on the stable surface. There are essentially two choices within the inverse spinel structure of $\text{Fe}_3\text{O}_4(001)$: 1) the tetrahedral iron(III) layer (termination A) and 2) the octahedral iron(II,III)/tetrahedral O layer (termination B). A guiding principle that can be used to predict surface termination is that of surface autocompensation, which states that the most stable surface(s) is (are) those for which the cation (anion)-derived dangling bonds are completely empty (full) (Gibson and LaFemina 1996). Both of the aforementioned terminations of $\text{Fe}_3\text{O}_4(001)$ can be made to be autocompensated-model A by removal of every other tetrahedral iron(III) cation (Tarrach et al. 1993) and model B by creation of oxygen vacancies and modification of octahedral iron oxidation states (Voogt 1998). Both surfaces predict a $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction, which is observed (Chambers and Joyce 1999). We have found by STM that both terminations are stable and can be prepared by different surface preparation methods. Termination A (B) is obtained by preparing the surface under more reducing (oxidizing) conditions. We show in Figures 1a and 1b STM images and associated surface structural diagrams for the two terminations A and B, respectively. The bright spots are iron atoms. The different surface symmetries associated with the two terminations are clearly visible. The images in Figures 1a and 1b were obtained at PNNL by Dr. Steve Joyce and at Tulane University by graduate student Barbara Stanka and Professor Ulrike Diebold, respectively.

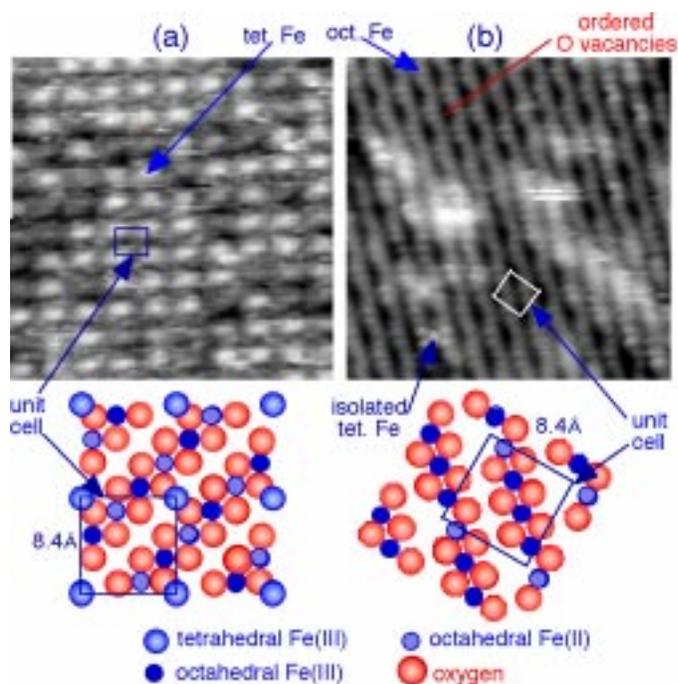


Figure 1. STM Images and Surface Structural Models for $\text{Fe}_3\text{O}_4(001)$ with (a) A and (b) B Terminations

The second most important set of surface structural parameters is the interlayer relaxations that result from creating the surface in the first place. We are currently analyzing XPD data obtained for $\text{Fe}_3\text{O}_4(001)$ to determine these parameters. Although the analysis is still in progress, it appears thus far that the best agreement between theory and experiment for termination A occurs for interlayer relaxations of -38%, -23%, -29%, +67%, and +48% for the first five interlayer spacings, respectively.

MD simulations predict termination B to be lower in energy than termination A. Also, MD predicts that yet another structure is more stable than either A or B (Rustad et al. 1999a). This structure is shown in Figure 2. In this structure, tetrahedrally coordinated iron(III) ions in the top layer of an autocompensated A termination rotate downward to occupy a vacant half-octahedral site in the plane of the second layer. At the same time, half of the tetrahedrally coordinated iron(III) ions in the third layer are pushed upward to occupy an adjacent octahedral vacancy in the second layer. The other half of the third-layer tetrahedral Fe(III) ions remain roughly in their original positions. This surface exhibits the $(\bullet 2 \times \bullet 2)R45^\circ$ surface reconstruction seen experimentally, and is autocompensated. The driving force for the formation of this surface can be thought of as a rearrangement of surface iron ions to achieve the maximum possible coordination number and to keep the Pauling bond order at the surface oxygens close to the bulk value of 2. However, XPD simulations of this surface do not match experiment at all well. This puzzling result is still under investigation.

In addition, MD simulations have been used to predict the structure of the hydroxylated $\text{Fe}_3\text{O}_4(001)$ surface. Hydroxylation represents the next step in understanding the structure of minerals in aqueous environments. The A-terminated surface becomes lower in energy upon hydroxylation, although hydrating the MD-predicted surface (Figure 2) also results in a metastable minimum. Either surface appears to be consistent with temperature programmed desorption (TPD) data for water in that water desorption peaks were observed at three distinct temperatures (225K, 260K, and 325K), corresponding to three distinct iron binding sites on either surface (unpublished results by I Ismagilov and CHF Peden). However, the binding energy of water on tetrahedral Fe(III) sites of termination A (45 kcal/mol) is much closer to that found previously for Fe_2O_3 , which has a large TPD state at 325K (Henderson et al. 1998). In contrast, the binding energy for water on the MD-predicted surface (25 kcal/mol) is about half of that value. Therefore, MD predicts that upon hydroxylation, the surface should revert to termination A if indeed the surface departs from this geometry at all. Hydroxylated structures were also computed for the

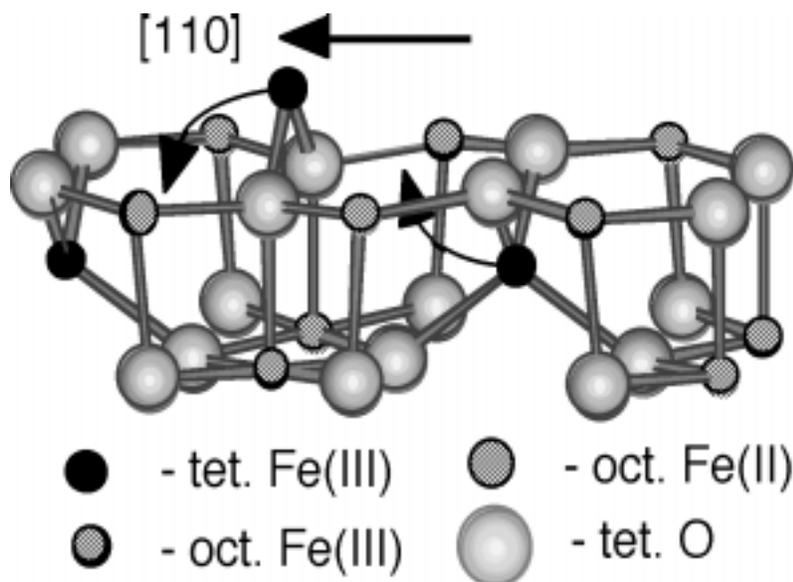


Figure 2. Surface Structure of $\text{Fe}_3\text{O}_4(001)$ Predicted by MD Simulations

B termination. The binding energy for water is nearly the same for each surface, but the A termination has a slightly higher capacity for water than the B termination. Thus, the binding energy of water on a per molecule basis is slightly higher on the B termination. But the effect is relatively small.

Experimentally, it is found that exposure of $\text{Fe}_3\text{O}_4(001)$ and (111) to water vapor results in only marginal hydroxylation at pressures up to $\sim 1 \times 10^{-5}$ torr (Kendelewicz et al. 1999a). Increasing the dosing pressure to higher values results in a marked increase in extent of hydroxylation. These results are similar to those obtained earlier on hematite surfaces (Liu et al. 1998) and are interpreted in the same way. The initial hydroxylation occurs at relatively low pressure as dissociative chemisorption of water occurs at steps. Hydroxylation occurs at terraces above a threshold pressure of $\sim 10^{-5}$ torr. Our simulations for hydroxylated A and B terminations for $\text{Fe}_3\text{O}_4(001)$ give 50 to 60% molecular dissociation, less than the 75% dissociation found for $\bullet\text{-Fe}_2\text{O}_3(012)$ (Henderson et al. 1998; Rustad et al. 1999) but greater than the 30% dissociation, mediated by hydrogen bonding within the water adlayer, as predicted by recent total energy calculations on MgO (Giordano et al. 1998).

Interface Structure of Adsorbed Aqueous Chromium on Iron Oxide Surfaces – Comparison with Chromium on Corundum

We have used chromium K-edge grazing-incidence x-ray absorption fine structure (GI-XAFS) spectroscopy to investigate the local structure of surface complexes formed when aqueous chromium(VI) and chromium(III) react with (0001)-oriented $\alpha\text{-Al}_2\text{O}_3$ (corundum), $\alpha\text{-Fe}_2\text{O}_3$ (hematite), and reduced $\alpha\text{-Fe}_2\text{O}_3$ which contains magnetite surface domains in the (111) orientation. The studies of chromium sorption on corundum and unreduced hematite surfaces provide valuable model system data with which data for chromium species on magnetite surface domains can be compared. Our objective is to provide information about the mechanisms of chemical reactions responsible for the speciation and reduction of chromium at the aqueous solution-iron oxide interface.

Samples consisted of $\alpha\text{-Al}_2\text{O}_3(0001)$ substrates and MBE-grown $\alpha\text{-Fe}_2\text{O}_3$ films on synthetic single crystal hematite thin films (~ 350 Å) in the (0001) orientation were grown on $\alpha\text{-Al}_2\text{O}_3(0001)$ substrates. Partially reduced hematite surfaces were produced by annealing thin-film hematite samples at $\sim 500^\circ\text{C}$ in vacuum. These surfaces were exposed to chromium(III) or chromium(VI) containing solutions in a N_2 -filled glovebox and analyzed by GI-XAFS under ambient conditions (i.e., with several monolayers of water present and $T = 23^\circ\text{C}$). Experimental conditions (pH, total chromium concentrations, and background electrolyte) were chosen to avoid the formation of multinuclear chromium complexes or supersaturation of chromium species in solution with respect to known hydroxides, carbonates, or basic salts (Smith and Martell 1976; Baes and Mesmer 1976). X-ray photoelectron spectroscopy (XPS) was used to ensure surface cleanliness prior to the experiment and to estimate surface coverage after reaction.

GI-XAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) (with the SPEAR ring operating at 3 GeV and 60-100 mA) on beamlines 4-2 and 6-2. GI-XAFS data were collected using the SSRL grazing-incidence apparatus in the specular geometry with the incident angle set slightly below the critical angle of the corresponding substrate ($\sim 0.2^\circ$). GI-XAFS data analysis was performed using EXAFSPAK (George and Pickering 1995). Phase and amplitude functions were calculated with FEFF7 (Rehr et al. 1991) and verified by comparison with phases and amplitudes extracted from EXAFS data from model mineral compounds.

The results obtained in this study emphasize the unique capabilities of GI-XAFS for identifying the structure of adsorbed species. An increased surface sensitivity is one advantage of this technique, which

allows one to probe surface coverages well below 0.1 monolayer. In addition, the polarization dependence and the well-defined structure of the single crystal substrate leads to additional constraints that simplify the interpretation of GI-XAFS data compared with conventional XAFS techniques using powdered polycrystalline samples.

Distinct differences in the local structure of the sorbed chromium species were found for the different surfaces as well as for the two different oxidation states of chromium (III and VI) (compare Figures 3 and 4). The reduction of chromium(VI) to chromium(III) by partially reduced hematite surfaces leads to surface species similar to those found after chromium(III) sorption on hematite surfaces (Figure 3). The structural information obtained using GI-XAFS, coupled with the Pauling bond valence principle, was used to rationalize interfacial chromium species and their mode of bonding to the surface (Grolimund et al. 1999).

Certain results of the present spectroscopic investigation are inconsistent with assumptions commonly used in surface complexation modeling, where different coordination environments of *isolated* surface species are postulated without direct molecular-level knowledge of the types of surface complexes present (Dzombak and Morel 1990). We found, for example, strong evidence for *multinuclear* chromium surface complexes on the hematite (0001) surface in contact with aqueous solution (Figure 3). Such multinuclear chromium species were observed even at extremely low surface coverages and

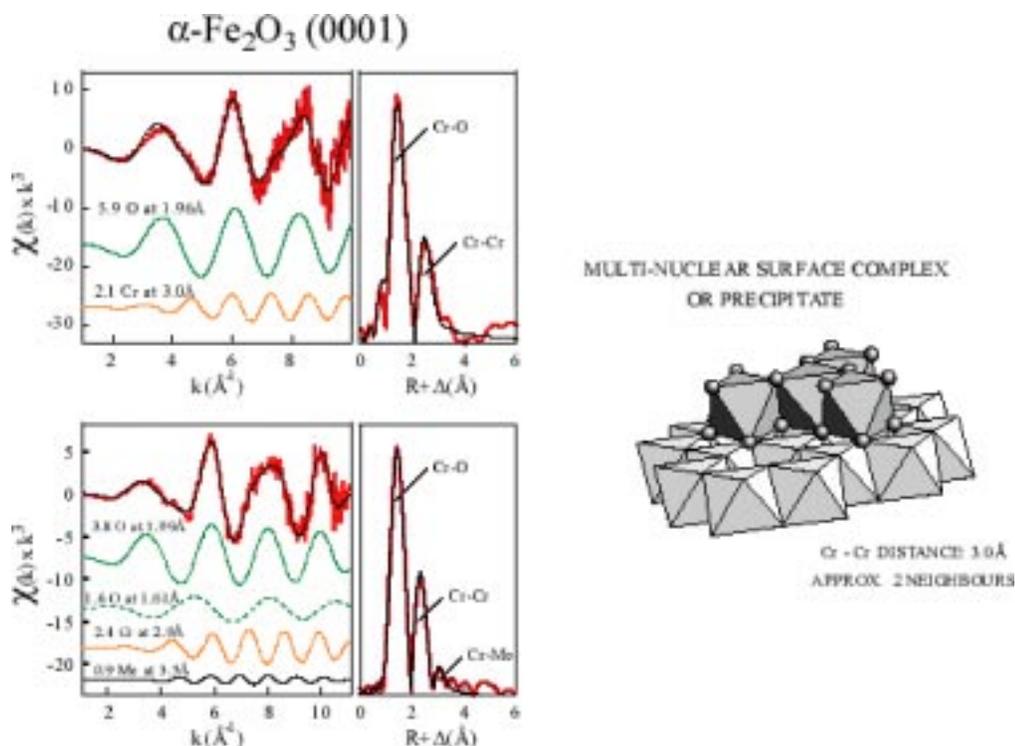


Figure 3. Chromium- K-Edge GI-XAFS Data for Chromium Sorbed on an α - $\text{Fe}_2\text{O}_3(0001)$ Single Crystal Surface (left) and Corresponding Visualization of the Proposed Interfacial Complex (right). The spectrum shown on the top-left corresponds to unreduced hematite reacted with chromium(III), while the spectrum shown on the bottom-left represents partially reduced hematite exposed to chromium(VI). Least-squares fits of the EXAFS including shell-by-shell deconvolution and Fourier transforms uncorrected for phase shift are shown.

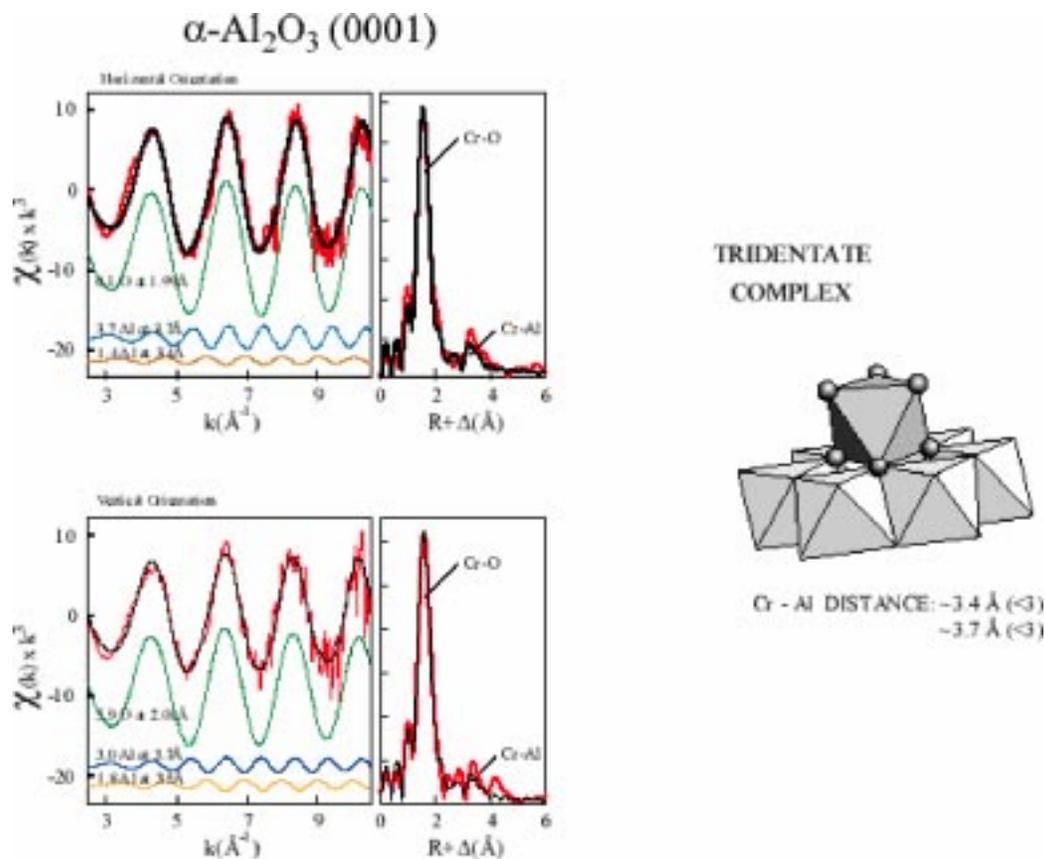


Figure 4. Chromium- K-Edge GI-XAFS Data of Chromium Sorbed on an $\alpha\text{-Al}_2\text{O}_3$ (0001) Single Crystal Surface (left) and Corresponding Visualization of the Proposed Interfacial Complex (right). The spectrum at the top left was taken with the electric field vector of the x-ray beam parallel to the surface plane. The spectrum at the bottom left was taken with the electric field vector of the x-ray beam perpendicular to the surface plane. Least-square fits of the EXAFS including shell-by-shell deconvolution and Fourier transforms uncorrected for phase shift are shown.

solution conditions undersaturated with respect to precipitates. These hydroxo-bridged chromium-polymers were either limited in size and predominately “two-dimensional” or correspond to more extended clusters with a considerable degree of structural disorder. The existence of chromium at the oxide-water interface in the form of multinuclear complexes even at a surface coverage of <0.1 monolayer was not anticipated based on the findings of earlier EXAFS studies of metal ion surface complexation as a function of metal loading. For example, earlier EXAFS studies (Chisholm-Brause et al. 1996; O’Day et al. 1996; Towle et al. 1999) report evidence for mononuclear complexes of cobalt(II) at the lowest surface coverages examined ($\sim 0.05 \mu\text{M}/\text{m}^2$), with multinuclear complexes or precipitates forming at higher surface coverages. Nevertheless, our finding of multinuclear chromium surface complexes is consistent with observations presented in a previous study investigating chromium(III) sorption on iron oxides using STM (Eggleston and Stumm 1993). Such multinuclear complexes can be expected to have a distinctively different reactivity than isolated monomeric species, including a higher threshold for desorption.

In contrast to the multinuclear species present in the chromium/hematite sorption samples, mono-nuclear chromium(III) complexes were found at the aqueous solution-corundum interface. The observed two shells of aluminum backscatterers at 3.5 and 3.7 Å (Figure 4) is consistent with the presence of isolated, uniform tridentate chromium(III) complexes on the α -Al₂O₃ single crystal surface as the dominant surface species. Significant levels of other potential interfacial species can be ruled out based on crystallographic arguments or the incompatibility of various sorption complex geometries with the observed polarization dependence (Figure 4).

The observed differences in surface complex type for the (0001) surfaces of α -Al₂O₃ and α -Fe₂O₃ suggest fundamental differences in the structures and reactivities of these two surfaces in contact with aqueous solutions. The finding of multinuclear surface complexes emphasizes the need for an improved, molecular-level conceptualization of reactions occurring at the solid-aqueous solution interface.

Redox Chemistry of Chromate on Magnetite

Having gained some understanding of the interaction of water with magnetite surfaces, we now turn to the interaction of aqueous chromate with Fe₃O₄(001) and (111). The speciation of chromate was investigated using core-level x-ray photoemission (XPS) and chromium L-edge, iron L-edge, and oxygen K-edge x-ray absorption spectroscopy using synchrotron radiation at the SSRL (Kendelewicz et al. 1999b). The adsorbed layer, which is deposited by dipping the magnetite surface in chromate solution and drying in a N₂-filled glovebox, consists mostly of chromate with negligible iron oxide. The chromate layer thickness increases to a maximum value of ~15 Å with increasing chromate concentration in solution and exposure time. Oxygen 1s XPS reveals the presence of OH⁻ ligands surrounding chromium and the small amount of iron present. Chromium(VI) is reduced to chromium(III) upon adsorption on the magnetite surface. For Fe₃O₄(111) reacted with 5 mM chromate solutions for 10 minutes or longer, a significant amount of chromium(VI) remained in the outermost portion of the adlayer, indicating incomplete chromium(VI) reduction. Complete chromium(VI) reduction was found on surfaces exposed to 50 • M chromate solution for 1 minute or longer, indicating rapid reaction kinetics. These results are summarized in Figure 5. As seen in the figure, all chromium(VI) is converted to chromium(III) for • M concentrations.

However, mM concentrations result in incomplete reduction, presumably due to the complete consumption of iron(II) on the surface. Longer exposures at mM concentrations result in the accumulation of even more chromium(VI). In contrast, chromate adsorbed on well-defined surfaces of hematite (Fe₂O₃) remain unreduced, *unless* small amounts of iron(II) left over from surface preparation processes remain. In this case, limited reduction by an amount commensurate with the amount of iron(II) present initially is seen to occur.

An important implication of the above findings for reductive sorption of chromate on iron bearing minerals and “zero-valent” iron in the subsurface is that the process is very much self limiting as iron(II) is consumed on the surface. Zero valent iron is actually coated with a thin oxide skin consisting mostly of magnetite. The redox process converts magnetite and zero-valent iron, which are conductive and facilitate electron-transfer processes, to an insulating oxyhydroxide containing only iron(III). Chromium(III) oxyhydroxide builds up on of this layer. The insulating nature of these layers prevents electron transfer from deeper layers, thus bringing the redox process to a halt. *Therefore, high-surface area iron(II) bearing remediation agents and/or natural minerals are required for high reductive capacity of chromate.*

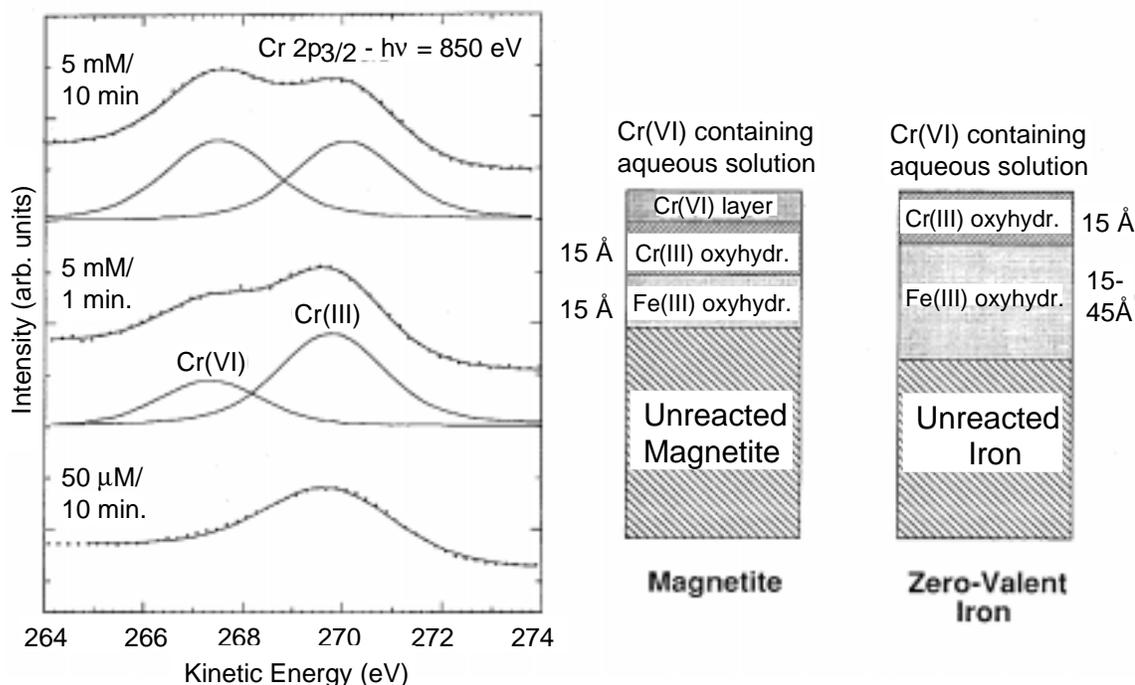


Figure 5. Chromium $2p_{3/2}$ Photoemission Spectra of Chromate on $Fe_3O_4(111)$ for Various Chromate Concentrations and Exposure Times (left) and Structural Diagrams of the Aqueous Chromate/Magnetite and Chromate/Zero-Valent Iron Interfaces after the Redox Reaction Has Come to a Self-Limiting Halt

Chromate Sorption on Hematite Surfaces

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 chromium(VI) sorption, with particular emphasis placed on competitive sorption by chromate, phosphate, and sulfate oxyanions. Although our focus here is on the thermodynamic results, we note that improvements were made to our kinetic flow cell that decreased the experimental volume to 3 mL and shortened the mixing time to about 10 seconds, while retaining the ability to nondestructively analyze changes in trace-level chromate concentrations by laser photoacoustic spectroscopy (LPAS).

Batch sorption experiments with 20 mg of hematite powder (specific surface of $9.7 \text{ m}^2 \text{ g}^{-1}$ by BET- N_2) in a 15 mL solution were conducted at room temperature with initial chromate, phosphate, or sulfate concentrations ranging from 2.7 to $54 \cdot M$ (i.e., 140 ppb to 2.8 ppm). Preliminary experiments established that equilibration times of one hour were sufficient, and the concentrations of the anions remaining in solution after this time were determined by ion chromatography. The solutions were not buffered for pH to eliminate interferences from the anions associated with buffering agents, and as a consequence, final sorption pHs ranged from 6.0 to 6.8. Despite the range in final pH, the results of these sorption experiments (Figure 6a) could be described well by the linearized Langmuir isotherm equation:

$$C_{\text{final}}/C_{\text{sorbed}} = (1/C_{\text{max}})C_{\text{final}} + b$$

where C_{final} and C_{sorbed} are the equilibrium concentrations in solution and on the hematite surface, respectively, C_{max} is the maximum sorption capacity of the mineral under the conditions of the experiment, and b is a constant. Maximum sorption capacities of the hematite for sulfate, chromium(VI), and phosphate, were 3.5 , 8.3 , and $9.3 \cdot \text{M g}^{-1}$, respectively, indicating that chromium(VI) and phosphate were sorbed more strongly than sulfate. In fact, C_{max} , which is an estimate of the relative sorption affinity of each of the three anions, is strongly correlated with pK_2 , the negative log of the second acid dissociation constant for each anion (Figure 6b). Such a relationship would be expected because the protons are the charge-determining ions on the hematite surface and larger pK_2 values indicate greater proton affinities on the part of the anions.

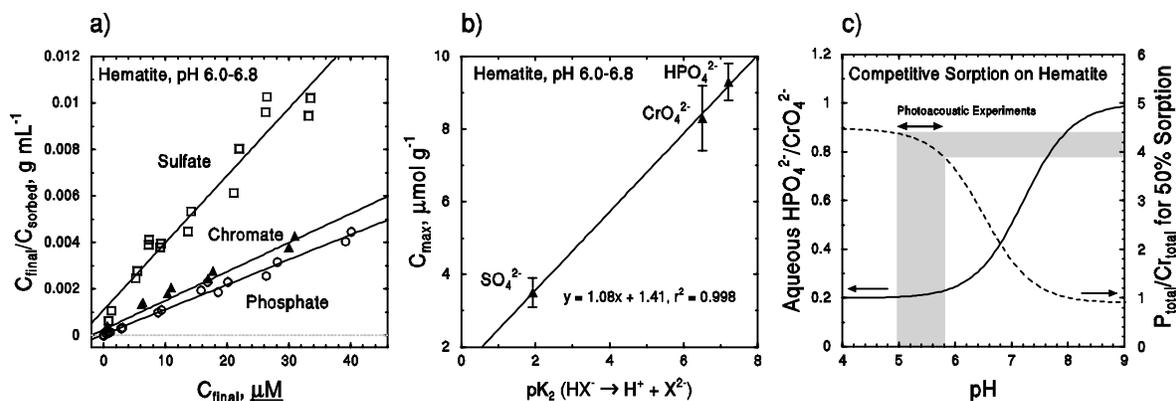


Figure 6. Results of Hematite Sorption Studies with Sulfate, Chromate, and Phosphate: a) linearized Langmuir isotherm plots of sorption of mono-anionic solutions; b) correlation between observed C_{max} values for mono-anionic solutions and the acidities of the anions; c) influence of pH on aqueous speciation of phosphate and chromate (solid line-left axis) and the ratio of total phosphate to chromium(VI) needed to achieve equal sorption (dashed line-right axis).

The correlation of C_{max} with pK_2 values suggests that only the divalent anion species (i.e., SO_4^{2-} , CrO_4^{2-} , and HPO_4^{2-}) contribute significantly to sorption. This premise can be tested by competitive sorption experiments because the amounts of divalent anion available for sorption will vary differently for each anion when pHs close to the pK_2 values are selected. Although experiments at pHs near the pK_2 of sulfate are impractical, such experiments with chromium(VI) and phosphate are both practical and directly relevant to groundwater chemistry because the pK_2 values for these anions are near 7. The expectation is that the relative sorption of chromium(VI) and phosphate would be directly proportional to the aqueous concentrations of CrO_4^{2-} and HPO_4^{2-} . Speciation calculations show the ratio of these two species in solution (i.e., $\text{HPO}_4^{2-}/\text{CrO}_4^{2-}$) varies from about 0.2 to 1 in going from pH 4 to 9 (Figure 6c, solid curve) and suggest that sorption of chromium(VI) would be favored over phosphate over much of this range. We can estimate the relative amount of total phosphate needed to achieve 50% sorption [i.e., equivalent sorption with chromium(VI)] by

$$[\text{P}_{\text{total}}/\text{Cr(VI)}_{\text{total}}]_{50\%} = [C_{\text{max(Cr(VI))}}/C_{\text{max(P)}}][\text{CrO}_4^{2-}/\text{HPO}_4^{2-}]$$

and this result is also plotted in Figure 6c (dotted curve, right axis). On this basis, we would predict that about 4.5 times as much phosphate as chromium(VI) would be needed at pH 5 for equal sorption by the two anions on hematite, whereas equal sorption would occur at pH 8 with equal concentrations of

chromium(VI) and phosphate. In fact, the prediction at pH 5 is in excellent agreement with the results of competitive sorption experiments carried out using LPAS and reported in last year's report (shown by the shaded portion of the graph).

Based on these results, we can draw the following conclusions. Sorption of chromium(VI) 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 chromium(VI) 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 chromium(VI), 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.

Summary

This project involves the coordinated efforts of a multidisciplinary team of scientists using state-of-the-art experimental and computational methods to attack complex and important problems in heterogeneous contaminant/mineral chemistry. Our approach is reductionist by design. Activities range from determining and understanding the structure of well-defined, clean, redox-active mineral surfaces, such as $\text{Fe}_3\text{O}_4(001)$, to investigating the interaction of such surfaces with water (the universal solvent), to determining the rates and extents of redox chemistry of important aqueous contaminants, such as chromate, with these surfaces. While we have made significant progress toward our stated goal of understanding the interaction of chromate with iron oxide surfaces, we have only scratched the surface of what could be learned, given the opportunity. It is with considerable regret that this outstanding team will be disbanded in September without renewal of the 1996 EMSP projects.

Planned Activities

Between now and the end of the project, our activities will include the following tasks:

1. Complete the surface structure determination by XPD of $\text{Fe}_3\text{O}_4(001)$.
2. Resolve some uncertainties related to determining the conditions under which the A and B terminations of $\text{Fe}_3\text{O}_4(001)$ are formed.
3. Determine the nature of the (1x3) reconstruction of $\text{Fe}_3\text{O}_4(001)$ that forms after extensive annealing in ultrahigh vacuum.

4. Complete theoretical analysis of the solvated $\text{Fe}_3\text{O}_4(001)$ surface.
5. Compute structures of chromate surface complexes on $\text{Fe}_3\text{O}_4(001)$.
6. Conduct water and aqueous chromium sorption experiments on a variety of natural and MBE grown manganese-oxide surfaces.
7. Conduct competitive sorption experiments on hematite powder for chromium(VI) with carbonate and with sulfate.
8. Conduct competitive sorption experiments for chromium(VI) with phosphate on single-crystal MBE-synthesized hematite.

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