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Oxidation State, Local Structure, and *Ab-Initio* XAFS Modeling of Chromium in Contaminated Soils and Model Compounds

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Abstract: We have used XAFS spectroscopy, combined with the *ab-initio* multiple scattering code FEFF 7, to model the structures of Cr compounds and Cr sorption complexes and precipitated phases on soils impacted by industrial Cr effluent. We have had success in *ab-initio* modeling of the near-edge structure of Cr model compounds, accurately simulating the Cr pre-edge and edge fine structure which are due to bound-state transitions and multiple scattering among the absorber Cr and its nearest shell of oxygen atoms. We have calibrated the pre-edge feature, a $1s$ to $3d$ electronic transition, and applied this to determining Cr(VI)/Cr(III) ratios in natural, Cr-contaminated soils. The pre-edge feature is particularly useful in following the electron transfer reaction between Cr(VI) and Fe(II) on oxide surfaces such as Fe_3O_4 (magnetite) which, as we have seen in both lab and field studies, results in the reduction of Cr(VI) to Cr(III).

1. INTRODUCTION

Cr in the environment is most hazardous to human health when present in its hexavalent form. Cr(VI) is highly mobile in groundwaters and is known to be carcinogenic. Trivalent Cr, in contrast, is quite insoluble and tends to precipitate from aqueous solution as a solid oxyhydroxide phase, limiting its bioavailability. Electron sources for Cr(VI)-to-Cr(III) reduction in Cr-contaminated soils include Fe(II)-bearing mineral phases which may be naturally present in soils. One such mineral is magnetite ($\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$), which undergoes a topotactic oxidation to maghemite ($\gamma\text{-Fe}_2^{3+}\text{O}_3$) upon exposure to oxidants such as aqueous Cr(VI).

This study presents results of the molecular-level sorption mode and oxidation state of Cr at the magnetite surface as determined by X-ray absorption fine structure (XAFS) spectroscopy, as well as evidence of magnetite-to-maghemite conversion as seen by transmission electron microscopy (TEM). Initial results of long-term oxidation/reduction experiments suggest that a thin layer of maghemite passivates magnetite, and slows the Cr(VI) reduction rate considerably in only a few hours.

XAFS fitting results have demonstrated that partial to full reduction of Cr(VI) to Cr(III) may occur *in situ* at the magnetite surface, whereas mixed Cr(III/VI) oxidation states are stable at most silicate mineral surfaces because these mineral phases lack potential electron sources for Cr(VI) reduction. Theoretical modeling of the Cr K-edge X-ray Absorption Near-Edge Structure (XANES) of model compounds has been used to simulate experimental XANES. Results from such analyses are useful for determining which single- and multiple-scattering paths interact to define the XANES, and are valuable for local structure and oxidation state determinations.

2. EXPERIMENTAL METHODS

Cr K-edge XAFS data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamlines 4-2 and 4-3 using a Si(220) $\phi = 0$ double crystal monochromator. On beamline 4-2, harmonics were eliminated by detuning the X-ray beam by 60%. On beamline 4-3, a Pt-coated mirror was used for harmonics rejection, with the X-ray beam used at full flux. Cr-contaminated soil samples were separated into magnetic and nonmagnetic mineral fractions, ground, and contained in Teflon sample holders with Kapton tape windows. Soils were mounted at 45° to the synchrotron X-ray source, and fluorescent X-rays were collected with a Stern-Heald ion chamber detector [1]. Cr model compounds were mixed with BN to provide approximately one absorption length at 6 keV and pressed into Al sample holders with Kapton tape windows. Their XAFS spectra were measured in transmission using N_2 -filled ion chamber detectors. All spectra were normalized in energy to the edge position (5989.0 eV) of a metallic Cr foil (16% Cr in austen steel). Data analysis of XAFS spectra was performed using EXAFSPAK [2], and theoretical modeling of XAFS spectra was accomplished using FEFF 7 [3]. Electron microprobe data were collected on a Jeol Superprobe 733. High resolution TEM data were collected with a Philips CM20FEG.

3. RESULTS AND DISCUSSION

Building on previous observations of Cr(VI) reduction or partial reduction occurring in the presence of magnetite [4, 5], we have calibrated the Cr XAFS pre-edge peak height to quantify Cr(VI)/total Cr in environmental samples and model compounds. Cr K-edge XANES spectra may be well fit using a sum of pseudo-Voigt peak shapes plus a step function (Fig. 1). Several of the peak amplitudes change progressively as a function of Cr(VI)/total Cr (Fig. 2). The peak with the most marked peak size change is the pre-edge peak, which is attributed to $1s$ to $3d$ bound state transition. The height of the pre-edge peak was

calibrated using model compound mixtures, with an accuracy of $\pm 3\%$ [6], and the calibration was used to determine Cr(VI)/total Cr contents of samples with Cr present in unknown oxidation states.

Figure 1: Cr K-edge XANES data and peak deconvolution for Cr(III) and Cr(VI) model compounds (A) Cr_2O_3 and (B) $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$. An edge step function was fit to the Cr(VI) edge and held constant in fitting mixtures of Cr(III) and Cr(VI) model compounds.

Cr-contaminated soils from two field sites were examined: (1) a chemical waste disposal facility at Sandia National Laboratory, Albuquerque, NM; and (2) a chromium plating facility near Keyport, WA which had experienced Cr effluent seepage into the surrounding soil from a corroded disposal pipe. The Cr contents at Sandia were as high as 2 wt.%, with highly variable Cr(VI)/total Cr contents: 2 to 67% of the Cr was present as Cr(VI) in the Sandia soils. Trace quantities of Fe(II)-bearing minerals were present, but no difference in Cr oxidation state was noted on the Fe(II)-rich mineral fraction. In contrast, soils from the Keyport site showed no measurable Cr(VI) on the Fe(II)-rich mineral fraction (predominantly magnetite). All the Cr present associated with magnetite was present as Cr(III) whereas the Cr associated with the silicate mineral fraction contained up to 6.4% Cr(VI)/total Cr. Total Cr contents of this soil were much lower, ≤ 0.1 wt.%, which may have allowed the electron transfer from Fe^{2+} in magnetite to occur without significant passivation of the magnetite surface.

Figure 2: Trends in peak height with Cr(VI)/total Cr content for the Cr model compounds of Fig. 1. The model-calibrated pre-edge peak height was used to determine Cr(VI)/total Cr content of natural soil samples.

FEFF fits of the Sandia and Keyport soils were used to determine that the local structures about Cr in these soils are consistent with several Cr(III) and Cr(VI) phases, including CrOOH , Cr_2O_3 , CrPbO_4 , and CaCrO_4 . The presence of these phases in the soils was confirmed by electron microprobe analysis. *Ab-initio* FEFF 7 models of the XANES of Cr(III) and Cr(VI) compounds provide a quantitative understanding of the main contributions to the Cr K-edge structure. For Cr(VI), Cr-O single- and multiple-scattering in the CrO_4 tetrahedra alone simulates the XANES spectra quite well, and our results are similar to theoretical modeling of CrO_4^{2-} done by others [7, 8]. In contrast, FEFF models of Cr(III) compounds require single-multiple-scattering paths out to $> 5 \text{ \AA}$ from the central Cr to closely simulate the XANES.

Passivation of the magnetite surface by maghemite was investigated through long-term Cr(VI) reduction experiments using synthetic magnetite in anoxic 50 mM Cr(VI) solution at pH 7. The heterogeneous oxidation/reduction proceeds by a reaction such as

or

The exact stoichiometry of the reaction depends on the final Cr phase which forms, as well as the degree to which the initial magnetite converts to maghemite. TEM evidence (Fig. 3a) reveals an alteration rim on magnetite grains which had been reacted at pH 7 in anoxic Cr(VI) solution for 5 weeks. In contrast, magnetite which had not been exposed to Cr(VI) shows no such surface alteration (Fig. 3b).

Figure 3: A synthetic magnetite grain oriented along the $\langle 110 \rangle$ zone axis shows (A) development of an altered surface region after reaction with 50 mM Cr(VI) solution, whereas an unreacted magnetite grain in the same orientation (B) shows bulk structure out to the edge. Scale is the same for both photos.

4. CONCLUSIONS

Mitigation of chromium contamination in the environment requires knowledge of the Cr oxidation state(s) and phase(s) present. XAFS spectroscopy on natural soils can be used to quantify Cr(VI)/total Cr and to identify the Cr-bearing mineral and precipitate phases associated with soil minerals. XANES analysis of mineral separates demonstrated that Cr(VI) may be reduced to Cr(III) by naturally occurring magnetite, whereas Cr(VI) is not reduced on non Fe(II)-bearing minerals. XAFS spectroscopy, in conjunction with TEM and other techniques, has been used to describe the surface structure and oxidation states of the sorbed or precipitated Cr contaminant and to show the surface alteration of the magnetite substrate. Theoretical modeling of Cr XANES indicates that single- and multiple-scattering among Cr(VI) and its first shell of oxygens dominates in the Cr(VI) XANES, whereas the Cr(III) XANES contains contributions from many more shells of atoms $> 5 \text{ \AA}$ distant from the central Cr.

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