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Molecular Characterization of Cr Phases in Contaminated Soils by Cr and Fe EXAFS: A Tool for Evaluating Chemical Remediation Strategies

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Abstract. The successful remediation of Cr contaminated soils via chemical reduction and stabilization of soluble, toxic Cr(VI) species to insoluble Cr(III) species relies on the long term leachability and reoxidation of reduced Cr compounds. Information of Cr chemical environments is invaluable for evaluating the efficiency of proposed stabilization technologies. We describe a matrix of Fe and Cr K-edge EXAFS data on synthetic model compounds that have been used to identify different Fe and Cr local environments of two soil samples.

1. Introduction

Contamination of soils and groundwater by Cr(VI) is of increasing concern because of its high mobility in the environment and its high toxicity to humans, plants and animals. Chemical reduction of Cr(VI) by Fe(II) can immobilize Cr(III) in insoluble (Fe,Cr)oxides, thus limiting the possibility of reoxidation and leaching.[1] Mechanisms under which Cr(III) could be remobilized are dependent upon the solid phase speciation and coassociation of Cr with other soil constituents following implementation of the in situ reduction technology which are dependent on the geochemical conditions in the system, (*i.e.* mineralogy, pH, solution chemistry and organic material present).[2] Thus, information of Cr chemical environments is invaluable for evaluating the efficiency of proposed stabilization technologies. Previous XAFS studies have illustrated the usefulness of the technique for identifying different (Cr,Fe)oxide solid-phases.[3] To date, however, the XAFS technique has rarely been used to analyze environmental soil samples from Cr-contaminated sites and evaluate the effectiveness of the different real-life remediation strategies. Utilizing a filter/Soller slit assembly, transmission and fluorescence Cr and Fe K-edge XAFS experiments were conducted on two Cr-contaminated soils and many different synthetic model compounds of mixed Cr/Fe oxides, salts and humic acids.

2. Sample Preparation

To enable solid-phase identification and to evaluate stability, a matrix of samples was prepared. In one dimension of the matrix, oxide samples were prepared using modified batch precipitation methods[4] under conditions which may be expected in natural and engineered systems. Crystalline (goethite) and non-crystalline (ferrihydrite) (Fe, Cr) oxides, similar to the phases typically found in the Southeastern part of the United States, were synthesized using a range of Cr/Fe ratios, allowing for surface adsorption of Cr to iron oxide and co-precipitation of Cr with Fe. To investigate the effect of pH on the synthesis process of these samples, different families of the crystalline and non-crystalline samples, just described, were prepared with pH values of 3.5, 6 and 11. NO₃⁻, Cl⁻ and SO₄²⁻ counterions were used to also investigate their effect on the resulting (Cr,Fe) oxides. Finally, humic acids samples with varying Fe/Cr ratios were also prepared.

3. Data collection and Analysis

XAFS experiments at the Fe and Cr K-edges were performed on the previously described synthetic model compounds as well as on two soil samples from a Cr-contaminated site in the Southeastern part of the U.S. Simultaneous fluorescence and transmission measurements were made at room temperature, utilizing a filter/Soller slit combination. Measurements were made at the Naval Research Lab beamline X23B [5] at the National Synchrotron Light Source. This fixed-exit, focused beamline has a Si (111) monochromator. All data were normalized and converted to photoelectron wavenumber following previously described methods.[6] The Cr K-edge $\chi(k)^*$ data, resulting from the merging of six consecutive $\chi(k)$ scans, from the two soil samples are shown in Fig. 1a (sample 1) and Fig. 1b (sample 2). All Cr K-edge data were Fourier transformed with k-ranges of 2.6-9.8 Å⁻¹, modified

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Hanning functions of $0.5 \text{ \AA}^{-1}$ to reduce truncation ripple, and a k -weighting of 1. Fig. 2a shows a comparison of the Cr K-edge Fourier transformed data for sample 1 and Cr_2O_3 , and Fig. 2b shows a comparison of the Cr K-edge Fourier transformed data for sample 2 and 1% Cr coprecipitated with an amorphous Fe oxide. Fe K-edge data were analyzed in the same manner as the Cr K-edge data.

Fig. 1 (a,b) See text.

Fig. 2 (a,b) See text.

4. Discussion

Comparison of the Fourier transformed data in Fig. 2a shows the average Cr local environment in unknown sample 1 to be very similar to that of Cr_2O_3 and Cr adsorbed on Fe oxide. (See Ref. 3) Comparison of the Fourier transformed data in Fig. 2b shows the average Cr local environment in unknown sample 2 to be very similar to coprecipitated dilute Cr in Fe oxide, possibly with an undetermined amount of surface adsorption. (See Ref. 3) Qualitative comparison of the Fe Fourier transforms with previously published data [3] indicates the average Fe local environment in sample 1 to be similar to a hematite phase while the average Fe local environment in sample 2 seems to be more similar to a poorly crystalline goethite phase with less than the 4 double corner bonds (see reference 3) typical of the goethite structure. These results illustrate the capability of the XAFS technique to provide the valuable information required to analyze environmental soil samples from Cr-contaminated sites and evaluate the effectiveness of real-life remediation strategies. In future studies, we intend to repeat these measurements at low temperature and to use the FEFF6 codes to simulate the basic oxide structures. Then, the effect of slight modifications/distortions of these and other basic oxide structures on the multiple scattering contribution to the XAFS signal can be investigated. These results will hopefully enable a more definitive identification of the variations of the different oxide phases, and help make XAFS a preferred technique for evaluating Cr-contaminated sites.

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