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Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil

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Research Objective

The long-term fate of toxic metals in soils cannot be precisely predicted, and often remediation recommendations and techniques may be ineffective or unnecessary. This work will generate basic knowledge on the kinetics and mechanism(s) of heavy metal retention/release by soil mineral colloids. The information should assist in improving remediation strategies for toxic heavy metal contaminated soils. The objectives are:

1. To determine the effects of residence time on the mechanisms of Cr(VI), Cu(II), Co(II), Cd(II), Pb(II), and Ni(II) sorption/release on Fe and Al oxide and clay mineral surfaces using kinetic studies coupled to extended x-ray absorption fine structure (EXAFS) spectroscopy and fourier transform infrared (FTIR) spectroscopy.
2. To study the effect of temperature, pH, and phosphate on metal sorption by oxides, and derive thermodynamic parameters to describe the sorption process.

Research Progress and Implications

As of June, 16, 1997 several clay minerals were tested for their efficiency of removing Cr from aqueous systems. The materials tested - smectite, vermiculites, illites, and kaolinite - represent the natural clay minerals that are abundant in soils and sediments. The clays were used in either their original or reduced (reduced with sodium dithionite) forms. The experimental result indicate that the reduced clays acted as an efficient remover of Cr(VI) from an aqueous system. The XANES spectra of Cr-treated clays provided evidence that the clays reduced Cr(VI) to Cr(III) and immobilized Cr in the clays at the same time. Sodium dithionite applied directly into aqueous systems reduced Cr(VI) to Cr(III), but could not immobilize Cr even in the presence of the clays. The Cr(VI) removal capacity varied with the clay mineral type and the structural Fe content. For the clays used in this study, the removal capacity follows the orders of smectites>vermiculites and illites>kaolinite. Within the same type of clay minerals, reduction of Cr(VI) is highly related to the ferrous iron content of the clays, which indicates that the reduction of Cr(VI) to Cr(III) results from the oxidation of structural Fe(II) to Fe(III). The results of this study can be used to develop a method for remediation of chromium in waste water.

The mechanisms and conditions for coupled reduction-sorption of chromate in dithionite-reduced smectites was investigated in this study by both equilibrium and spectroscopic methods. The batch study showed that the maximum removal of Cr(VI) by the reduced smectite was highly related to its structural Fe(II) content. The surface cation type and ion strength which affected the expanding of smectite also influenced the electron transfer, and thus the coupled reduction-sorption processes. The pH of the aqueous system was a determining factor for both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqueous and adsorbed species. The environments of chromium in the smectite were studied with various spectroscopies (IR, XRD, XANES, and EXAFS).

Our XANES projects are most heavily concentrated on two areas. The first is a study of chromium redox chemistry on contaminated soils. In this project we began collecting data on coupling between Cr(VI) reduction and Fe(II) oxidation and coupling between Cr(III) oxidation and Mn(IV) reduction in April 1998. The samples we are examining come from an eight-month experiment in incubated soils. A component of this study examines reactions between soil humic substances and Cr(VI), seeking to verify whether humic thiol groups act as reducing agents. Results collected in April confirm this, showing reductions in both thiol and thiophene groups accompanied with increases in sulfate

(as expected) and sulfonate (unexpected). The transfer of electrons between reduced organosulfur groups to oxidized organosulfur groups exceeded the number of electrons needed to completely reduce Cr(VI). One series of proposed experiments will continue this investigation to determine organosulfur reactants and products. The redox chemistry of organosulfur groups in humic substances is part of an expanding program studying the chemistry of humic organosulfur groups. The proposed XANES studies at the S K-edge will allow us to quantify humic thiol ligands, essential data for the study of thiol complexation of chalcophilic (sulfur-loving) metals such as Hg(II) and Ag(I). We recently submitted a paper to Environmental Science & Technology reporting evidence that Hg(II) is coordinated by thiol and disulfide groups from humic substances, a finding of great interest to environmental chemists studying mercury chemistry in the environment. In collaboration with M. B. McBride (Cornell) we plan to study toxic metal chemistry and its relation to organosulfur in soils where municipal sewage sludge was disposed.

Planned Activities

The studies planned for Summer 1998 will examine the coupling of Cr reduction and oxidation to iron and manganese in soil. One series of experiments will study the reduction of soluble Cr(VI) by Fe(II) within the structure of layer silicate minerals. This study will determine changes in solution conditions influencing the reactivity of Fe(II) locked within silicate materials. The second series of experiments will collect Cr, Mn, and Fe K-edge XANES from soils contaminated with Cr(VI) and later treated by additions of soluble Fe(II) to promote reduction and Mn(IV) oxide minerals to promote re-oxidation of Cr(III) back to the toxic Cr(VI) form. The proposed XANES studies for Fall 1998 will concentrate the K-edges of two elements: S and Cr. These studies will examine electron transfer reactions involving organosulfur structures in humic substances and chromium in contaminated soils.

Other Access To Information

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