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Project ID: **55014**

Project Title: **Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil**

DOE Report Number: de-fg07-96er14718

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PUBLICATION DATE: 07/19/99

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RESEARCH OBJECTIVES

The effective remediation of DOE superfund sites contaminated by toxic heavy metals has been hampered by the paucity of knowledge about the kinetics and mechanism(s) of heavy metal retention/release by site media particles. Thus remediation strategies have been costly and ineffective.

The information acquired in this project should assist in improving remediation strategies for toxic heavy metals contaminated soils. The objectives are:

1. To determine the effects of residence time on the mechanisms of heavy metals [i.e., Cr(IV), Cu(II), Co(II), and Pb(II)] sorption/release on soil 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 clay minerals and derive thermodynamic parameters to describe the sorption process.

RESEARCH PROGRESS AND IMPLICATIONS

As of June, 1998 lead sorption in a common soil clay mineral in its pure form (smectite), was investigated by equilibrium sorption studies, coupled with spectroscopic methods. The isotherm and pH edge of lead sorption in the smectite were measured in batch experiments. The sorption isotherms under controlled pH were best-fitted to the Langmuir equation, while those with a fixed pH of 5.5 were best-fitted with the Freundlich equation. The pH-edge of lead sorption shifted to a higher pH as the lead concentration increased. The ionic strength only affected lead sorption in the low pH range. The effects of associated nitrate and perchlorate anions were significant only for lead sorption at high lead concentration (>2 mM). FTIR and XRD spectroscopies were performed with oriented clay samples. In the infrared spectra, a peak with a maximum near 1398 cm^{-1} and a shoulder centered near 1470 cm^{-1} was significant for the samples treated with >1mM lead at pH >5.6. This peak may be composed of several IR bands, including an OH bending band from lead hydroxides and CO_3^{2-} stretching bands from lead carbonates. The basal spacing of lead-treated smectite increased with increasing lead content in the clay and correlated well with the intensity of OH bending band (around 1621 cm^{-1}) of adsorbed water. The increase of basal spacing at low pH (pH <3.3) was poorly correlated with the intensity of water OH bending band.

The effect of pH and phosphate on adsorption of lead and cobalt by the clay mineral kaolin was also studied. Batch equilibrium studies for kaolin and phosphate treated kaolin in contact with metal solutions at pH ranging from 3 to 8 were performed. The sorption of metals from $\text{Pb}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ solutions by kaolin was found to be pH dependent. For both metals, little sorption occurred below pH 6.0; increased sorption was observed around pH 6-7 with maximum sorption at pH 8. However, lead and cobalt control solutions (without clay) indicate that above pH 7, some of the lead and cobalt ions were removed from solution by precipitation.

The pH of maximum sorption was chosen and kinetic studies performed for periods ranging from 5 minutes to 3 months. The results indicated that reaction equilibrium was attained within 10 minutes. Furthermore investigations on effect of lead sorption on phosphate treated (phosphate adsorbed on clay first then lead adsorbed to clay surface) revealed that lead sorption significantly increased with phosphate already present on the surface (compared to phosphate free surface); with maximum sorption in pH 6-8 range. Kinetics of lead sorption on kaolin-phosphate surfaces indicated a very fast reaction which reached equilibrium within 10 minutes over a 3 month study period (i.e., there was no change in the quantity of lead sorbed after 10 minutes). On the other hand, cobalt sorption decreased on the kaolin-phosphate surface compared to the phosphate free kaolin surface. In our future studies these results will be further investigated. We conclude that these reactions require fast kinetics methodology (i.e., pressure jump technique) to elucidate their mechanisms.

The lead and cobalt sorption phenomena is further being investigated using EXAFS spectroscopy. EXAFS spectra for lead and cobalt sorbed to phosphate free kaolin as well as kaolin-phosphate surfaces were recently collected from Brookhaven's National Synchrotron Light Source. The next step is to resolve the spectra in an attempt to discern the type of sorption (i.e., surface complexes) formed between lead and the kaolin surfaces investigated.

Using Cr K-edge x-ray absorption fine-structure (XAFS) spectra, we investigated Cr sorption on oxide surfaces, we found no evidence for Al or Fe atoms in the second atomic shell surrounding Cr adsorbed to oxide minerals. The absence of Al or Fe in the second atomic shell demonstrates that chromate adsorbs by a weak outer-sphere mechanism.

We also examined the reductive capacity of thiol (-SH) groups in soil humic substances. We used S K-edge x-ray absorption near structure (XANES) spectra to quantify the various oxidation states of sulfur in soil humic substances, including thiol sulfur. The reaction between Cr(VI) and humic substances, followed using both Cr K-edge and S K-edge XANES, revealed humic substances reduce Cr(VI) to Cr(III) using thiol instead of quinone groups, the reducing agent most soil chemists believe to be important in redox reactions.

We also studied sorption of Cu(II) by oxide and hydroxy-interlayer layer silicates. The tendency of Cu(II) ions to form surface precipitates depends on the oxide surface they are adsorbed to. Using both x-ray absorption spectroscopy and electron paramagnetic resonance, we found that Cu(II) forms hydroxide precipitates on silica surfaces at loadings as low as 5% of a monolayer while no Cu(II) precipitates form on alumina surfaces at 20% monolayer coverages. We also found that Cu(II) binds to the interlayer hydroxide in adsorption experiments using hydroxy-interlayer clay minerals. Hydroxy-interlayer clay minerals are common in the B-horizon of Altisol and Ultisols found in humid climate along the East Coast of the U.S.

PLANNED ACTIVITIES

We will request a 6 months no cost extension of the project. During that time we intend to further investigate the sorption of lead and cobalt on kaolin surface with and without phosphate already sorbed. EXAFS and FTIR spectroscopies will be used to acquire surface chemical information. Also equilibrium isothermic experiments will be performed at different temperature, pH and ionic strengths to acquire thermodynamic data and further elucidate the sorption phenomena between lead and cobalt on kaolin surface with and without phosphate already sorbed.

OTHER ACCESS TO INFORMATION

PRESENTATIONS

Shen, S., Taylor, R. W., Bleam, W. F., Tu, S. I., 1998. Coupled reduction-sorption of chromate in dithionite-reduced smectites, *Agronomy Abstracts*, Baltimore, MD, p. 189.

Bleam, W. F., Helmke, P. A., Szulczewski, M. D., Bloom, P. R., Taylor, R. W., Weesner, F. J., Xia, K., 1998, Recent advances in understanding the chemistry of Cr(VI), Pb(II) and Hg(II) in soils, *Agronomy Abstracts*, Baltimore, MD, p. 36.

Szulczewski, M. D., Xia, K., Helmke, P. A., Bleam, W. F., Taylor, R. W., 1998, Evaluating the reductive capacity of humic substances: Reactions between thiol/thio groups and chromate, *Agronomy Abstracts*, Baltimore, MD, p. 38.

Taylor, R. W., Shen, S., Bleam, W. F., Tu, S. 1999. Chromate removal by dithionite-reduced clays. 5th International Conference on the Biogeochemistry of Trace Elements, Vienna Austria, July 11-15, 1999.

REFEREED PUBLICATIONS

Shen, S., Taylor, R. W., Bart, H., Tu, S. 1999. Equilibrium and spectroscopic studies of lead retention in smectite. *Commun. Soil Sci. Plant Analysis* (in press).