Environmental Management Science Program

Project ID Number 54860

Sorption of Heavy Metals and Radionuclides on Mineral Surfaces in the Presence of Organic Co-Contaminants

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June 1, 1998

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Research Objective

This project is designed to determine how organic chelating ligands can influence the partitioning of ionic solutes (heavy metals and radioactive isotopes) between the solution phase and metal-oxide surfaces. Equilibrium states and kinetics of partitioning in these ternary systems will control contaminant transport and bioavailability of the ligands and contaminant metals in groundwater. As a result, this work represents a significant contribution toward efforts to develop predictive modeling for the transport and transformation of groundwater contaminants.

Uranium(VI), strontium(II) and lead(II) have been chosen as representative of high priority pollutants at DOE and non-DOE sites. Strontium in particular has received relatively little detailed attention in the literature. Mineral surfaces chosen for this project include goethite, gibbsite, and kaolinite. The organic chelators - EDTA, NTA, and citric acid - are components of both DOE and industrial wastes. In addition, citric acid is found naturally as a product of metabolic processes in soils and groundwater.

Research Progress and Implications

Project Status as of June 1, 1998:

Uranyl | Citrate | Solid phase systems - Macroscopic equilibrium studies

Results for the batch studies involving uranyl, citrate, and the three mineral phases (goethite, kaolinite, gibbsite) have been summarized and published by Redden, et al. (1997). This part of the project demonstrated that the effect of citrate on uranyl sorption can be dependent on the nature of the solid phase and can be highly variable. A particularly interesting observation concerned the goethite system where citrate dramatically increased uranyl sorption in the low pH range and that the extent of the effect appeared to be dependent on the citrate:surface ratio. The implication is that uranyl is unaffected by citrate until a critical surface concentration is achieved at which point it is possible that the positive surface charge has been significantly reduced (and can be negative even at pH 3.5) and carboxylic acid groups are potentially more available for complexing with uranyl.

Uranyl | Citrate | Goethite system - Phenomenological studies

Biodegradation: It was noted previously that biodegradation of citrate in these experiments can be a problem - or perhaps a useful feature. For longer term experiments where dissolution of the solid phases will be studied, it is necessary to prevent degradation of citric acid. We have been able to reduce or eliminate this risk by taking precautions to maintain sterile conditions (combination of autoclaving and filter sterilization).

Biodegradation of the organic ligand in the presence of heavy metals and solid phases, and the ultimate fate of the metal is an intriguing question in itself. Although this is beyond the primary scope of this study, we have conducted very brief scoping studies to look at the degradation of citric acid in the presence of a sorbing solid phase, and to see if an organism can be isolated that acts on uranyl (redox) in a medium containing citric acid.

Proton Stoichiometry: The proton stoichiometry of citrate sorption on goethite has been described previously. This information will be used to develop a consistent picture of the nature of citrate sorption along with the spectroscopic studies. We are particularly interested in issues of surface charge and available surface-bound carboxylic acid groups.

Ionic strength: Variations in surface partitioning as a function of ionic strength is generally considered to be indicative of the type of surface complex. Strong covalent surface complexes are assumed to be unaffected by changes in ionic strength while weaker outer-sphere complexes are displaced by increasing ionic strength. We have made the unusual observation that increasing ionic strength actually increases uranyl partitioning in the presence of citric acid. The hypothesis is that screening of the net positive surface charge reduces the free energy of the interaction between the uranyl cation and the negative surface-bound citrate groups.

Electrophoretic mobility: We have measured changes in electrophoretic mobility of goethite particles as a function of citrate concentration at pH 3.5, and as a function of pH at a relatively high citrate concentration. The relative changes in mobility have demonstrated that citrate effectively reduces goethite surface charge and can produce a negatively charged surface even at pH 3.5.

Sorption/Desorption: The complexity of the interaction between citric acid and the goethite surface is unknown. It is reasonable to expect that once sorbed, the nature of the complexation can change with time, and that ligand promoted dissolution of the surface can occur. We are conducting studies to determine whether the rate and extent of citric acid desorption varies as a function of pre-equilibration time. We expect the desorption process will become progressively slower as pre-equilibration time increases. The first results have shown this to be the case. We will be particularly interested in whether a complete mass balance for citrate can be verified.

Uranyl | Citrate | Goethite system - Spectroscopic Studies

FTIR: The first part of an FTIR study of citrate surface complexation was conducted at the beginning of this project with colleagues at the Umeå University in Sweden. In that study, it was possible to demonstrate that a covalent surface complex was formed and that uranyl was at least partially associated with surface-bound citrate, however this first study was constrained by sensitivity limitations. A second and concluding study is planned for this summer. An advanced ATR cell (attenuated total reflectance), and anticipated improvements in instrument performance should make it possible to obtain more complete spectroscopic information about the nature of the citrate-surface bonding, the state of uncomplexed carboxylic groups, and whether uranyl is associated with the citric acid.

EXAFS: An EXAFS study (Extended X-ray Absorption Fine Structure spectroscopy) of the uranyl-citrate-goethite system was started in May of this year at the DOE supported Stanford Synchrotron Radiation Laboratory. This study is intended to compliment the FTIR study by providing information about that local environment of uranyl in the presence of citric acid. Results from the first of three planned experimental sessions were considered very good from the standpoint of data quality and sensitivity. Preliminary evaluation of the spectra shows distinct qualitative differences between model systems (e.g., uranyl, uranyl-citrate, and uranyl-goethite systems) and the uranyl-citrate-goethite system in several pH regimes. Although our original working hypothesis has been that citrate is involved in a goethite-citrate-uranyl ternary complex, the EXAFS results suggest that, at least under the conditions under which the samples were prepared, the system may be better represented by multiple uranyl surface complexes and that uranyl may act as a bridge between goethite and citrate.

These results along with the demonstration of good sensitivity for lower uranyl concentrations are now being used to design systems for the second set of EXAFS analyses.

Lead | EDTA, citrate | Goethite system - Macroscopic equilibrium studies

Based on the relatively extensive scrutiny of the goethite-citrate-uranyl system, the analogous system with lead EDTA, and citrate are now being studied. Batch sorption experiments are being run

to determine whether a corresponding behavior for lead can be observed, and to extend the system with a chelating ligand that is significantly different from citrate. Based on past work we expect that biodegradation of EDTA will be less of a problem although the same precautions will be exercised to ensure sterility of the systems.

Lead | Carbonate | Goethite system - Macroscopic and Spectroscopic studies

Most relevant natural systems will have carbonate as a significant solution component due to mineral, atmospheric and biological sources. It is very likely, given the chemical similarities between carbonate and organic carboxylic groups, that carbonate solution species will influence the degree to which organic ligands affect metal partitioning. An extensive study of carbonate sorption on goethite is nearing completion. This is now being extended to a study of the effect of carbonate on lead sorption using batch sorption experiments and ATR-FTIR analysis of the surface bound complexes.

Strontium | Ligand | Solid phase systems - Preliminary modeling studies

System involving strontium have received little attention to date. Sorption of strontium in the presence of citrate and EDTA, and in systems with goethite, gibbsite, and kaolinite, are being initiated using the methodologies developed for the goethite-citrate-uranyl system.

Planned Activities

Planned Activities and approximate timetable:

Macroscopic sorption studies (following protocols developed for the uranyl-citrate-goethite system):

- Citrate desorption kinetics => present through August, 1998.
- Lead-citrate-goethite system => present through March, 1999.
- Lead-EDTA-goethite system => present through June, 1999.
- Lead-ligand-gibbsite, kaolinite systems => November, 1998 through June, 1999.
- Strontium-ligand-solid systems => July, 1998 through June, 1999.
- Lead-carbonate-goethite system => present through November, 1998.

Spectroscopic studies:

- EXAFS study of the Uranyl-citrate-goethite system => July, October 1998
- FTIR study of the Uranyl-citrate-goethite system => November, 1998
- FTIR study of the lead-carbonate-goethite system => present through September, 1998.

Additional selective FTIR and EXAFS studies are anticipated depending on results from macroscopic experiments.