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Experimental Determination of Contaminant Metal Mobility as a Function of Temperature Time and Solution Chemistry

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Research Objective

The objective of this work is to determine the fundamental data needed to predict the behavior of ^{90}Sr at temperature and time scales appropriate to thermal remediation. Our approach combines macroscopic sorption/precipitation and desorption/dissolution kinetic experiments which track changes in solution composition with direct molecular characterization of Sr in the solid phase using x-ray absorption spectroscopy. These experiments will be used to identify mechanistic geochemical reactions and their thermochemical properties that will be incorporated into geochemical computer codes.

Research Progress and Implications

As of May 1998, we have completed most of our static sorption experiments as a function of temperature (25, 60, and 80°C), solution pH (4 to 10), initial Sr concentrations (10⁻⁷ to 10⁻³ M), and partial pressure of CO₂ (100% N₂ or atmospheric CO₂). We chose to study goethite, kaolinite, gibbsite, and amorphous silica because iron and aluminum (oxy)hydroxides, aluminosilicate clays, and quartz are key components in soils, sediments, and aquifers. We have completed x-ray absorption analysis of Sr sorption to kaolinite and goethite at 25°C, initial Sr of 10⁻³ M, and pH 9.

Strontium sorption to goethite, kaolinite, and amorphous silica is dependent on solution pH, with little or no sorption between pH 4 and 7, and increasing sorption from pH 8 to 10. No sorption occurred at the gibbsite-water interface from pH 4 to 10. Strontium removal from solution is catalyzed by reactions at the goethite, kaolinite, and amorphous silica surfaces, because minimal amounts of Sr were removed from solution without these solids in waters supersaturated with respect to strontianite (SrCO₃). Strontium sorption from 10⁻³ M Sr solutions at pH 10 and atmospheric CO₂ was greater to amorphous silica (100%), than goethite (50%) and kaolinite (20%). Strontium sorption to kaolinite and goethite is not dependent on temperature from 25 to 80°C.

The dominant surface complexes, as determined by x-ray absorption spectroscopy (XAS), are outersphere hydrated-Sr complexes at the kaolinite-water interface and both outersphere hydrated-Sr complexes and reactive multinuclear Sr-carbonate complexes. For all of the kaolinite samples identical x-ray absorption spectra were obtained, yielding 6 to 9 first neighbor O atoms at an average distance of 2.60 Å. If innersphere or multinuclear complexes form we would expect to see second neighbor Al, Si, or Sr atoms in the x-ray absorption spectra. Outersphere hydrate-Sr complexes at the kaolinite-water interface appear to be very stable. Spectra from sorption experiments aged for two months showed only outersphere hydrated-Sr complexes. In solutions supersaturated with respect to strontianite, we had expected multinuclear Sr-carbonate surface complexes to form as the samples aged.

Strontium complex formation at the goethite-water interface consists of disordered multinuclear Sr-carbonate complexes in atmospheric CO₂ experiments and outersphere hydrated-Sr complexes in CO₂ free experiments. The multinuclear Sr-carbonate complex consists 6 to 9 first neighbor O atoms at 2.60 Å, 1 second neighbor Fe atom at 2.04 Å, and 7 to 8 second neighbor Sr atoms at 4.1 Å and 2 second neighbor Sr atoms at 4.88 Å. Interestingly, aging the goethite experiments with initial

atmospheric CO₂, yielded outersphere hydrated-Sr surface complexes identical to those observed in CO₂ free sorption experiments and the kaolinite sorption experiments. During aging, it is possible that dissolved carbonate diffused into channels in the goethite structure, lowering the degree of solution supersaturation with respect to strontianite, dissolving the Sr-carbonate surface complex and forming outersphere hydrated-Sr complexes.

Our results to date agree with field observations of ⁹⁰Sr mobility at Hanford, and show that Sr is a highly mobile element with minimal retardation at mineral-water interfaces. Furthermore, transport of Sr sorbed to Fe and Si colloids in pH 8 to 10 waters is likely. These colloids may form from iron and silica rich alkaline waste streams as the pH decreases due to dissolution reactions with the aquifer geology. Our results also suggest that a closely monitored amorphous silica reactive barrier buffered at pH 10 to 11 may effectively trap Sr at a contaminant plume front.

Planned Activities

For the remainder of this project (1.5 years) we will combine the solution chemistry and solid phase speciation to model strontium sorption as a function of temperature (25, 60, and 80°C), solution pH (4 to 10), initial Sr concentrations (10⁻⁷ to 10⁻³ M), and partial pressure of CO₂ (100% N₂ or atmospheric CO₂). Our model will be based on the mechanistic geochemical reactions and thermochemical properties identified in our experiments, such that this information can be used to predict ⁹⁰Sr mobility at Hanford and potential radioactive waste repositories, and to optimize any clean-up programs.

Additional experiments include flow-through Sr sorption/desorption experiments to goethite and amorphous silica at pH 9 in solutions open to atmospheric CO₂. These experiments will be complimented with x-ray absorption spectroscopy experiments to determine solid phase speciation, including Sr speciation at the amorphous silica-water interface from the static sorption experiments.