

FINAL REPORT
U.S. DEPARTMENT OF ENERGY

EXPERIMENTAL DETERMINATION OF CONTAMINANT METAL MOBILITY AS
A FUNCTION OF TEMPERATURE, TIME, AND SOLUTION CHEMISTRY

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Executive Summary

Our experimental program on strontium sorption to solid substrates was directed toward producing mechanistic models that can be used in reactive-transport calculations to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment. We are one of the few groups that address the importance of combining molecular characterization methods with laboratory uptake and stability measurements and surface complexation models, because reactions cannot be unambiguously determined from macroscopic measurements alone. This research is very relevant to mobility and attenuation of radioactive contaminants in the vadose zone and in groundwater at many DOE sites. For example, Hanford is developing reactive-transport codes that couple geochemical processes and physical flow to understand the mobility of a number of radionuclides at their site. Unfortunately, these calculations are data limited. Our work adds to the credibility of numerical fate and transport simulations by providing needed geochemical models that have been validated by experiment.

During the FY96-FY99 funding cycle we examined the uptake of aqueous strontium onto goethite, kaolinite, and amorphous silica surfaces as a function of pH, total strontium, and temperature. Our overall goal was to produce a mechanistic sorption model that can be used in reaction-transport calculations to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment. Our approach was to combine structural information derived from EXAFS analysis together with macroscopic uptake data and surface complexation models to clarify the physical and chemical structure of sorbed complexes. In this report we discuss three significant findings from our research.

- Strontium sorbs primarily as a hydrated outer-sphere complexes that are stable for several months over the precipitation of pure strontianite, SrCO₃(s) (with the exception of goethite over a limited pH interval)
- Nucleation of incipient SrCO₃(s) to goethite is tied to carbonate sorption
- Our spectroscopic results allow us to constrain the molecular reactions used in the surface complexation models. For amorphous silica and kaolinite, mechanistic models must describe strontium sorption as outer-sphere complexes that retain their primary hydration sheath. Strontium sorption to goethite is more complicated and may require strontium- carbonate surface precipitates or complexes in addition to outer-sphere complexes.

Our project is a successful University – National Laboratory collaboration.

- We have published the spectroscopic work in two papers in the *Journal of Colloid and Interface Science* [1, 2].
- Carroll presented our work as keynote speaker at the *1999 International Conference of Chemistry and Migration Behavior of Actinides and Mission Products in the Geosphere*.
- We made two presentations at the American Chemical Society in 1999.
- We attended the 1998 and 2000 EMSP workshops.
- This work was the motivation for a symposium that I am organizing at the 2001 Spring American Chemical Society meeting entitled *Surface Complexation Models: A Bridge between Spectroscopy and Fate and Transport*.

Research Objectives

During the FY96-FY99 funding cycle we examined the uptake of aqueous strontium onto goethite, kaolinite, and amorphous silica surfaces as a function of pH, total strontium, and temperature. Our overall goal was to produce a mechanistic sorption model that can be used in reaction-transport calculations to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment. Our approach was to combine structural information derived from synchrotron-based x-ray absorption spectroscopic analysis together with macroscopic uptake data and surface complexation models to clarify the physical and chemical structure of sorbed complexes. We chose to study these solids because of the prevalence of clays and iron hydroxides in natural systems, and because silica colloids probably form beneath leaking tanks at Hanford as caustic waste is neutralized. We have published the spectroscopic work in two papers in the *Journal of Colloid and Interface Science* [1, 2], and will soon submit a third manuscript to *Geochemical Transactions* [3] combining the sorption and spectroscopic data with a mechanistic complexation model.

Methods and Results

As we mentioned above, our approach was to combine structural information derived from synchrotron-based x-ray absorption spectroscopic analysis together with macroscopic uptake data and surface complexation models to clarify the physical and chemical structure of sorbed complexes. Macroscopic sorption studies were conducted over a range of strontium and CO_2 concentrations, pH, and temperature. Early in the study we learned that strontium sorption was independent of temperature (25 to 80°C). All subsequent work was conducted at room temperature. Below, we focus this summary on three important conclusions from our study.

(i) Strontium sorbs primarily as a hydrated outer-sphere complexes that are stable for several months over the precipitation of pure strontianite, $\text{SrCO}_3(\text{s})$

We collected EXAFS spectra on more than 20 amorphous silica, kaolinite, and goethite samples from pH 4 to 10. With the exception of two goethite samples (see below), the EXAFS analyses suggested that the largest fraction of sorbed strontium on these phases was present as hydrated (i.e., water-ligated) complexes (Figures 1 - 3). This interpretation is based on the absence of backscattering atoms beyond the first oxygen shell in the EXAFS spectra. There was no evidence for dehydration of a significant fraction (>50%) of strontium and formation of inner-sphere complexes. We conclusively demonstrated that second-neighbor backscattering would be readily apparent in low-temperature spectra if dehydration occurred based on the analysis of strontium reference compounds [1]. For strontium sorbed to amorphous silica and kaolinite, there was also no evidence in the spectra for backscattering from a carbonate ligand in the presence of dissolved CO_2 . The macroscopic sorption data and equilibrium aqueous speciation are consistent with the EXAFS results. Similar sorption behavior in the presence and absence of dissolved CO_2 .

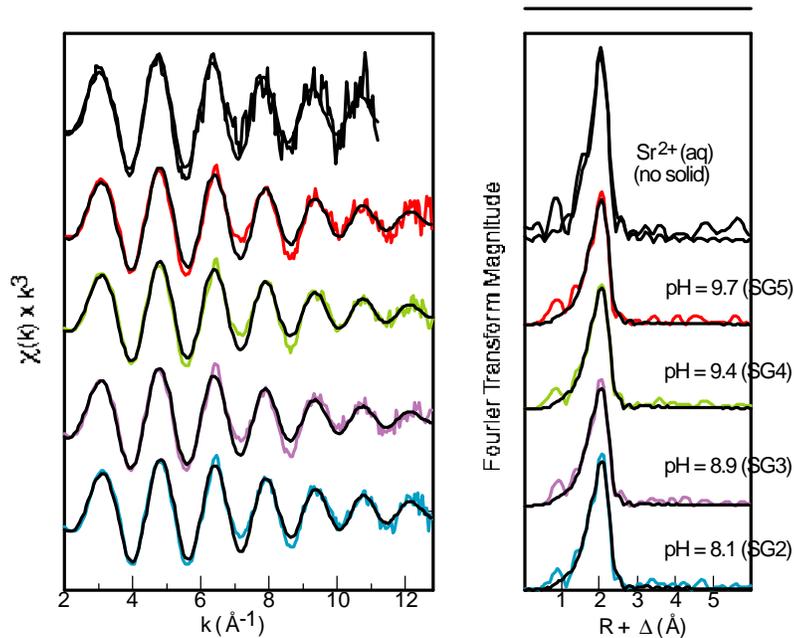


Figure 1. Normalized EXAFS spectra and corresponding radial structure functions for strontium sorbed to amorphous silica (samples SG2-SG5) and for $\text{Sr}^{2+}(\text{aq})$ models. All spectra were collected at 10 K. Data are in solid lines and fits are in dashed lines.

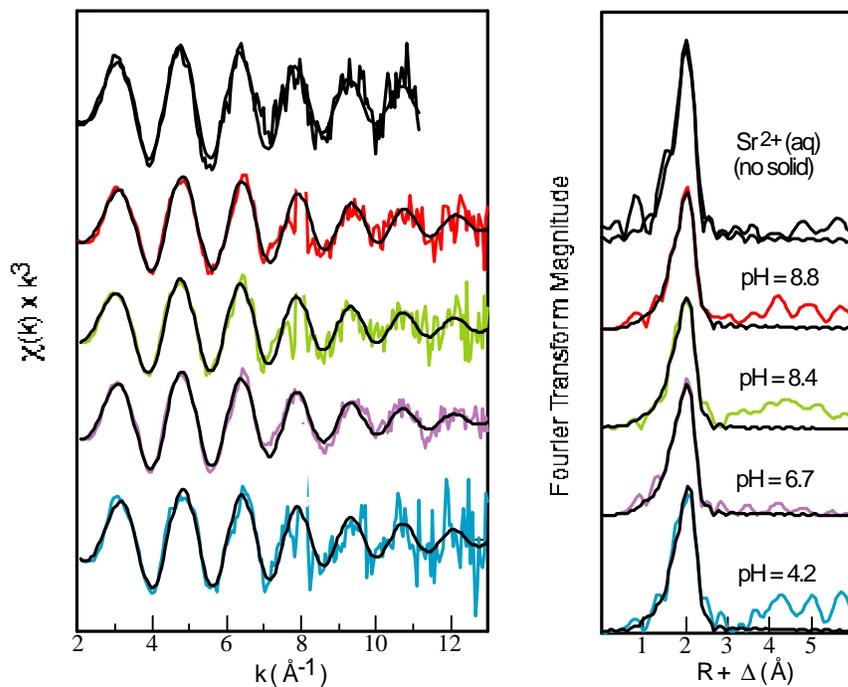


Figure 2. Normalized EXAFS spectra and corresponding radial structure functions for strontium sorbed to kaolinite and for $\text{Sr}^{2+}(\text{aq})$ models. Data are in solid lines and fits are in dashed lines.

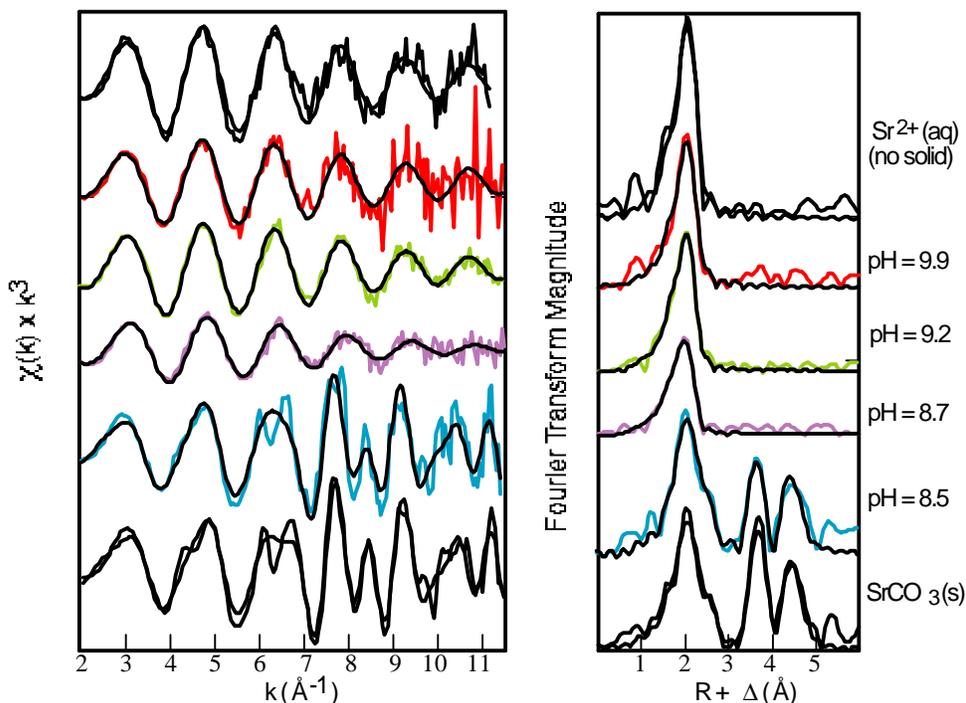


Figure 3. Normalized EXAFS spectra and corresponding radial structure functions for strontium sorbed to goethite and for $\text{Sr}^{2+}(\text{aq})$ and strontianite ($\text{SrCO}_3(\text{s})$) models. Data are in solid lines and fits are in dashed lines.

(ii) Nucleation of incipient $\text{SrCO}_3(\text{s})$ to goethite is tied to carbonate sorption

As mentioned above, limited spectroscopic evidence suggests that the goethite surface may nucleate strontium carbonate precipitation from fairly concentrated solutions ($\text{Sr}_{\text{initial}} = 10^{-3}$ molal). Results to date indicate that nucleation of a precipitate is related to solution pH and to the sorption of carbonate to the goethite surface (which is dependent on pH), rather than on the saturation state of the solution, and to reaction time. Spectra of samples reacted for short times suggested that $\text{SrCO}_3(\text{s})$ nucleation required a critical concentration of carbonate sorbed to the goethite surface, even though reacting solutions for all samples were supersaturated with respect to $\text{SrCO}_3(\text{s})$ (Figure 4). However, kinetic experiments suggested that the strontium carbonate surface precipitate may be a transitory phase (Figure 5). We observed $\text{SrCO}_3(\text{s})$ surface precipitates after four days of reaction, when strontium uptake to goethite was greatest. In a sample aged for 57 days, we observed only outer-sphere complexes and more strontium uptake than for samples aged for shorter times. What is unknown at present is whether or not incipient $\text{SrCO}_3(\text{s})$ surface precipitates form and dissolve with time, and under what conditions of total strontium concentration, surface carbonate concentration, and pH they are stabilized. Because precipitation of carbonate phases may be an important removal mechanism for

strontium from solution under certain conditions, we propose further work to clarify the thermodynamics and kinetics of this process for strontium sorption on goethite.

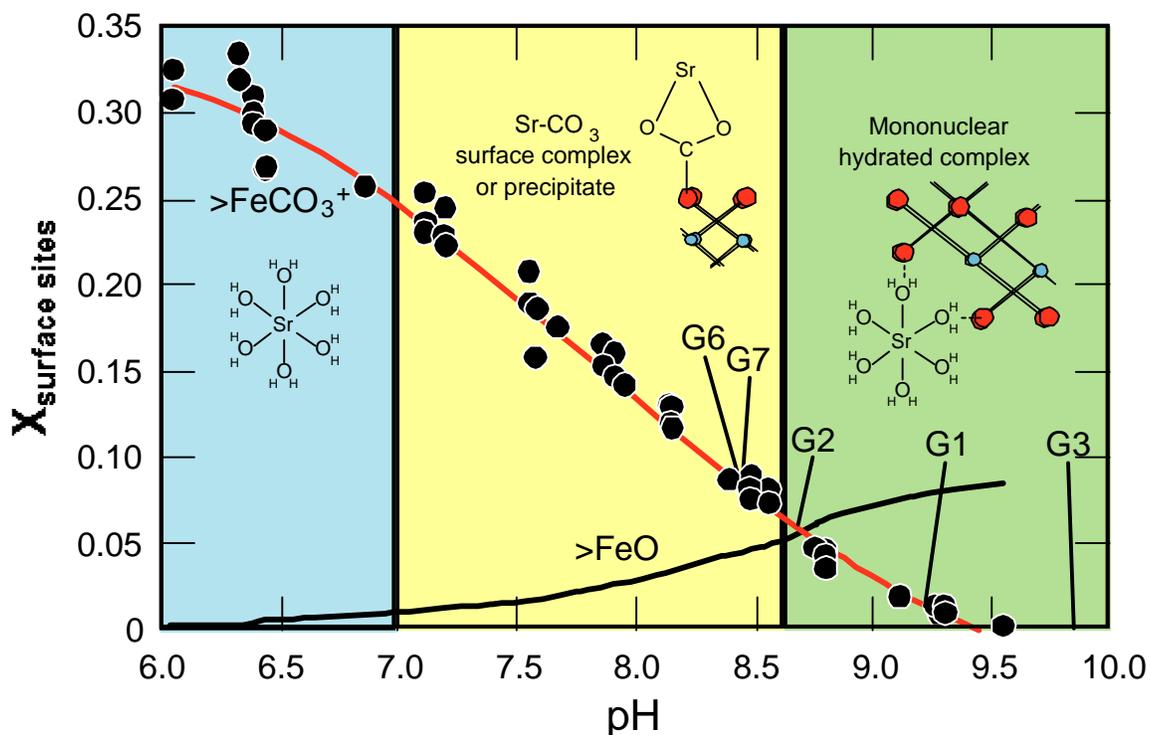


Figure 4. Calculated mole fraction of carbonate (solid circles) and $>FeO^-$ and $>FeOH_2^+$ surface sites for goethite experiments prepared in atmospheric CO_2 as a function of final pH and measured dissolved CO_2 using Van Geen et al.'s sorption constants [4] and Dzombak and Morel's [5] Diffuse Double Layer surface complexation model. The schematic representation of strontium surface precipitate or hydrated strontium surface complex identified by EXAFS are correlated to the calculated mole fractions of carbonate sorbed to goethite by the pH of the EXAFS samples. Strontium carbonate surface complexes may form between pH 7 and 10 but were not detected in the bulk EXAFS spectra.

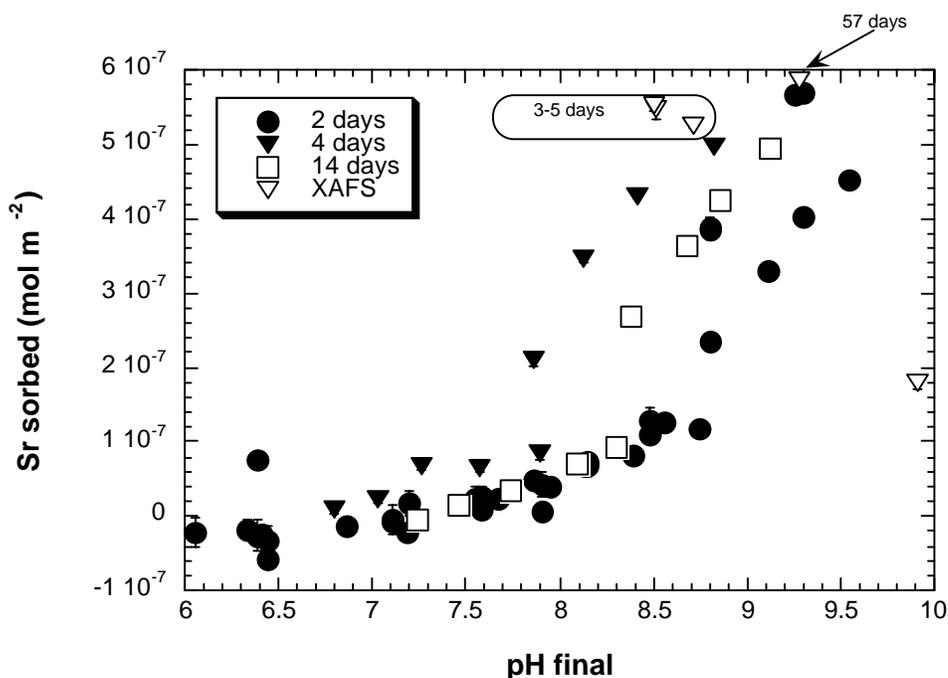


Figure 5. Strontium sorbed to goethite as a function of solution pH and reaction time. $\text{SrCO}_3(\text{s})$ was identified by EXAFS in samples aged for 3 to 5 days. These samples correspond to the highest amount of strontium uptake. An outer-sphere complex was identified by EXAFS analysis in a sample aged for 57 days.

(iii) Surface Complexation Model

Our spectroscopic results allow us to constrain the molecular reactions used in the surface complexation models. For amorphous silica and kaolinite, mechanistic models must describe strontium sorption as outer-sphere complexes that retain their primary hydration sheath. Strontium sorption to goethite is more complicated and may require strontium-carbonate surface precipitates or complexes in addition to outer-sphere complexes.

We successfully modeled the uptake of strontium to amorphous silica as an outer-sphere complex over a range of initial strontium concentrations ($[\text{Sr}]_{\text{initial}} = 7 \times 10^{-6}$ to 10^{-3} molal) and pH (6 to 10) at constant ionic strength (Figure 6). We used deprotonation and surface capacitance constants ($\log K_{>\text{SiO}^-} = -2.5$ and $C_1 = C_2 = 6 \text{ Fm}^{-2}$) determined by the direct observation of the pH-dependence of $>\text{SiOH}$ and $>\text{SiO}^-\text{Na}^+$ amorphous silica surface sites using nuclear magnetic resonance spectroscopy [6]. From these values and our experimental uptake data, we have determined outer-sphere sorption constants for strontium, $\log K_{>\text{SiO}^- \text{Sr}^{2+}} = -9.5$, and for sodium, $\log K_{>\text{SiO}^- \text{Na}^+} = -6.6$.

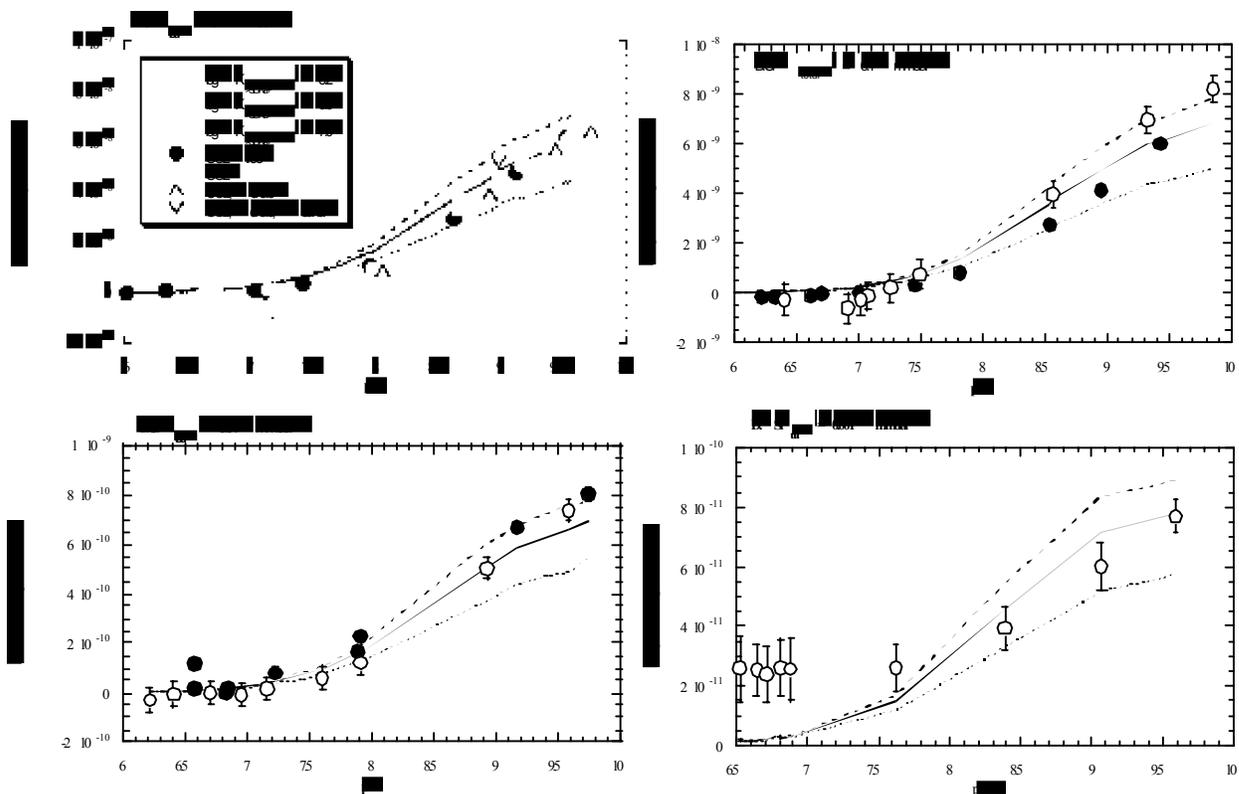
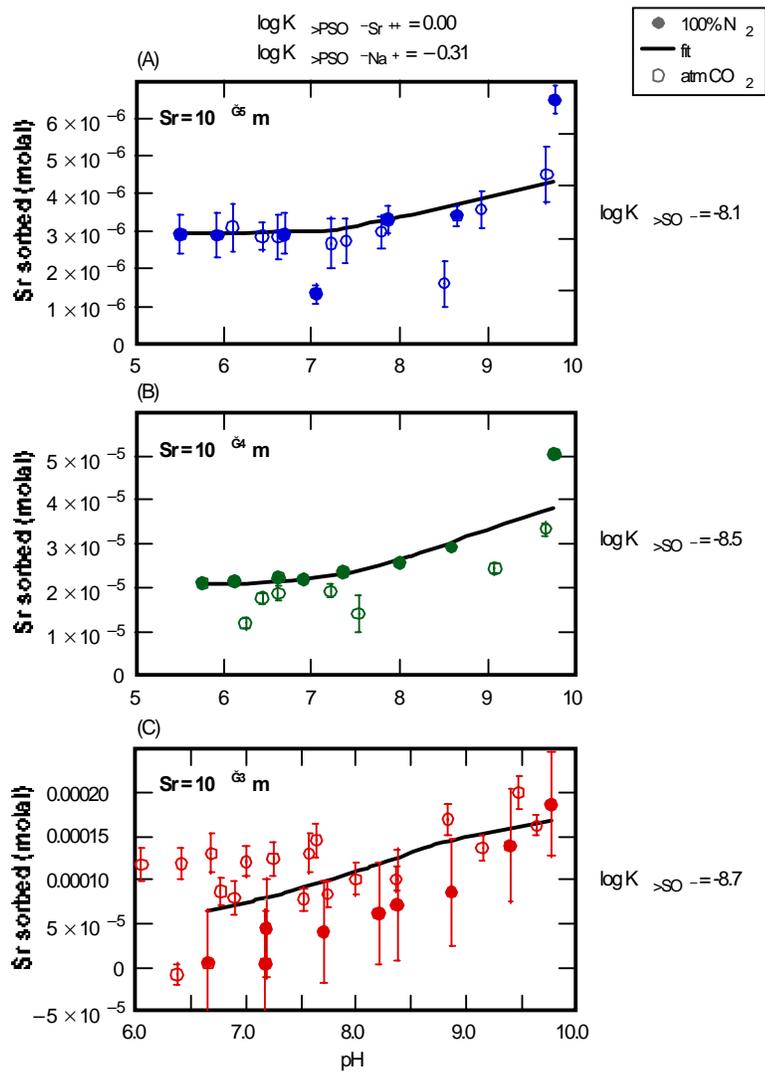


Figure 6. Strontium sorption to amorphous silica as hydrated outer-sphere strontium complexes.

We modeled the uptake of strontium to negatively charged sites on the kaolinite basal plane as an outer-sphere complex ($\log K_{>PO-Sr^{2+}} = 0.0$) over a range of initial strontium concentrations ($[Sr]_{\text{initial}} = 10^{-5}$ to 10^{-3} molal) and pH (5 to 10) at constant ionic strength. The negative sites on the kaolinite basal plane are due to the isomorphous substitution of Al^{3+} for Si^{4+} in the silica layer. In our model we assumed that the protonation of this site is dependent on pH (Figure 7).

Our efforts to model strontium sorption to goethite as a combination of strontium-carbonate surface precipitates or complexes and to outer-sphere complexes was unsuccessful. We suspect that the protonation and deprotonation constants are poorly constrained for goethite because we observed similar strontium uptake to goethite and amorphous silica as a function of pH, even though each mineral has distinct surface properties (Figure 8). General knowledge of mineral surface charge has been derived from the differences in measured and calculated solution pH from acid-base titration. These experiments are problematic because the measured pH is not a unique measurement of the uptake or release of protons from the mineral surface. Other reactions, such as change in the distribution of carbonate species, mineral dissolution, and electrolyte sorption, can also effect solution pH. Unfortunately for goethite, it is not possible to measure the pH dependence of $>FeOH_2^+$, $>FeOH$, and $>FeO^-$ directly using current spectroscopic techniques. Sorption constants of fundamental protonation-deprotonation reactions must be well constrained before both carbonate and strontium

uptake can be modeled accurately within evidence imposed by spectroscopic observation.



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Figure 7. Strontium sorption to kaolinite as hydrated outer-sphere strontium complexes sorbed to permanent charges at the surface.

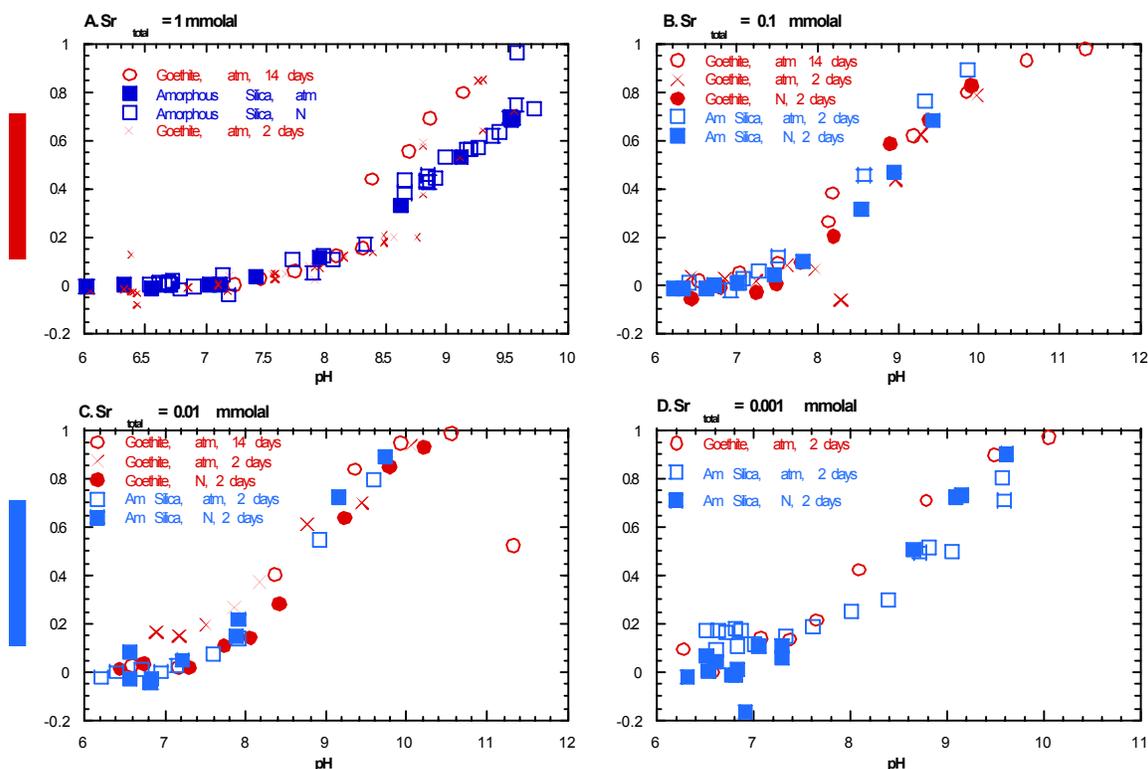


Figure 8. Identical amounts of strontium sorb to amorphous silica and goethite.

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Relevance, Impact, and Technology Transfer

- a. Our experimental program on strontium sorption to solid substrates was directed toward producing mechanistic models that can be used in reactive-transport calculations

to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment. We are one of the few groups that address the importance of combining molecular characterization methods with laboratory uptake and stability measurements and surface complexation models, because reactions cannot be unambiguously determined from macroscopic measurements alone. This research is very relevant to mobility and attenuation of radioactive contaminants in the vadose zone and in groundwater at many DOE sites.

b. This work will enhance our predictive capabilities for strontium mobility in the subsurface. It will also aid in the design of remediation processes of tank waste and soils. Although it is important to note that additional experimental work is needed to build a more robust model that includes the effect of strontium sorption as a function of ionic strength. This is very important for the Hanford site, because past leaks to the subsurface have very high ionic strengths, but rain water and tank sluicing waters do not. Because strontium forms primarily outer-sphere complexes its uptake will be dependent on ionic strength.

c. Our work is an important piece of the information gap needed to accurately predict contaminant mobility in the subsurface using reactive-transport codes. For example, Hanford is developing reactive-transport codes that couple geochemical processes and physical flow to understand the mobility of a number of radionuclides at their site. Unfortunately, these calculations are data limited. Our work adds to the credibility of numerical fate and transport simulations by providing needed geochemical models that have been validated by experiment.

d. This research supported the partial salaries of two LLNL scientists and summer salary for one professor for three years and one post-doc for one year. The post-doc is now a university professor. The work utilized DOE synchrotron facilities. Our published results are already in use by other EMSP and NSF investigators. Within the next couple of years we will publish our modeling results, so they will be made available to the scientific community.

e. It is important to note that additional experimental work is needed to build a more robust model that includes the effect of strontium sorption as a function of ionic strength and to conduct reactive-transport experiments on DOE sediments. This is very important for the Hanford site, because past leaks to the subsurface have very high ionic strengths, but rain water and tank sluicing waters do not. Because strontium forms primarily outer-sphere complexes its uptake will be dependent on ionic strength. This was part of our renewal proposal which was not awarded because of a limit pool of EMSP funds.

f. I am currently working directly with John Zachara at PNNL and Carl Steefel at LLNL conducting Cs reactive transport experiments to validate Zachara's Cs ion exchange model. This work is funded by the Hanford site. I think our EMSP funded research help establish this collaboration.

g. Before this work was conducted very little was known about strontium sorption. We now have a good understanding of its chemistry and how to model it mechanistically. This data can be used in reactive-transport calculations.

h. We need more experimental data as a function of ionic strength. Reactive-transport experiments, that test the resulting model is needed, as is a better understanding of the importance of the strontium-carbonate precipitate that forms the goethite surface.

i. Most of the interest in this project has been from other EMSP investigators interested in strontium chemistry.