Strontium Sorption on Amorphous Silica, Goethite and Kaolinite. I. Spectroscopy and Surface Complexation Models

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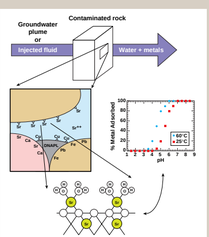
Introduction

➡ **Our experimental program on strontium sorption to solid substrates is directed toward producing mechanistic, reaction-based models that can be used in reaction-transport codes to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment.**

➡ **Radioactive strontium is a somewhat unique fission product of nuclear weapons manufacture because it is an alkaline earth element. Strontium salts and carbonates are quite soluble and strontium forms relatively weak sorption complexes, making it very mobile compared to other actinides such as uranium, neptunium, and plutonium. This is of concern at Hanford, because strontium could be released into the environment during sluicing of waste storage tanks.**

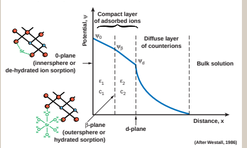
➡ **This work is motivated by the lack of fundamental data needed to assess long-term hazards from metal pollution and the need for technologies to remediate subsurface metal pollution. Understanding and quantifying the sorption characteristics of strontium are critical to the accurate prediction of its mobility in the environment. Geochemical factors that may contribute to Sr mobility in natural waters are the solubilities of phases such as strontianite ($SrCO_3$) and formation of aqueous and surface complexes.**

➡ **Our objective is to determine the processes controlling Sr mobility by combining macroscopic experiments, molecular analysis**



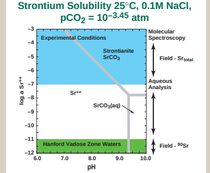
Experimental & Theoretical Approach

Triple-layer surface complexation model



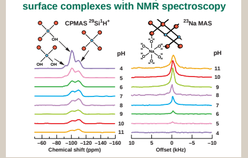
Strontium Batch Sorption Experiments:	Molecular Spectroscopy — X-ray Absorption Fine Structure (XAFS)	Molecular Spectroscopy — Nuclear Magnetic Resonance (NMR)
Temperature: 25°C	Batch Sorption Experiments:	Na and Cs pH-stat Experiments:
Solution: [Sr], 10^{-3} or 10^{-4}M; pH 4 to 10; 0.1 N NaCl	[Sr], 10^{-3}M; 25°C; pH 5 to 9	0.1 N NaCl or CsCl; 25°C; pH 4 to 11
pCO2: open to atm & 100% N	Time: 48 hours and 2 months	Time: 24 hours
Solids: Goethite, Kaolinite, Silica Gel	Spectra Collection: SSRL on beam line 4-3 Si(220) monochromator crystal detuned to reject 13-element Ge array detector 10, 70, and 298 K ~40 scans per sample EXAFSPAK and FEFF	Spectra Collection: ^{27}Na and ^{133}Cs Static and Magic-Angle-Spinning; ^{29}Si Cross-polarization Magic-Angle-Spinning
Time: 48 hours to 14 days		

Strontium Solubility 25°C, 0.1M NaCl, $pCO_2 = 10^{-3.45}$ atm

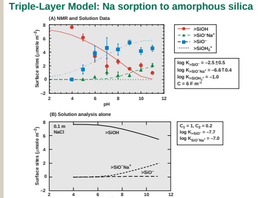


Amorphous Silica

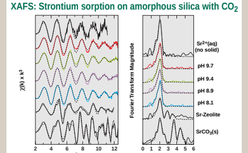
Evidence of >SiOH, >SiO⁻, & >SiO⁻Na⁺ surface complexes with NMR spectroscopy



Triple-Layer Model: Na sorption to amorphous silica



XAFS: Strontium sorption on amorphous silica with CO_2



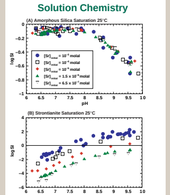
Triple-Layer Model: Sr and Na sorption to amorphous silica with and without $CO_2(g)$

Surface Complexes: n_s, 4.6 sites nm^{-2}, $C_1 = C_2 = 6.0$ F m^{-2}

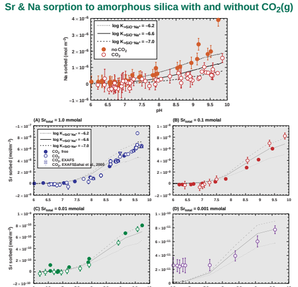
		Log K
1. >SiOH + H⁺ = >SiOH₂⁺		–1.0
2. >SiOH = >SiO⁻ + H⁺		–2.5
3. >SiOH + Na⁺ = >SiO⁻Na⁺ + H⁺	Outersphere	FITEQL 4.0 (Herbelin and Westall, 1999)
4. >SiOH + Sr²⁺ = >SiO⁻Sr²⁺ + H⁺		FITEQL 4.0

Aqueous Species: CO_3^{2-}, $SrCO_{3(aq)}$, $SrCl^+$, $NaHCO_{3(aq)}$, $NaCl_{(aq)}$

Solution Chemistry

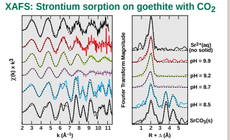


Sr & Na sorption to amorphous silica with and without $CO_2(g)$



Goethite

XAFS: Strontium sorption on goethite with CO_2



Triple Layer Model: Sr sorption to goethite with CO_2

Surface Species

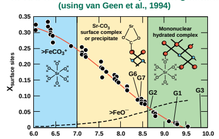
n_s, 16.4 sites nm^{-2}, $C_1 = C_2 = 6.0$ F m^{-2}

		Log K
1. >FeOH + H⁺ = >FeOH₂⁺	outersphere	FITEQL 4.0
2. >FeOH = >FeO⁻ + H⁺		–6.6
3. >FeOH + Na⁺ = >FeO⁻Na⁺ + H⁺		–9.5
4. >FeOH + Sr²⁺ = >FeO⁻Sr²⁺ + H⁺		
5. >FeOH + HCO₃⁻ = >FeCO₃⁻ + H₂O		8.5 (van Geen et al, 1994)
6. >FeOH + HCO₃⁻ + Sr²⁺ = >FeOHSrCO₃⁻ + H⁺		FITEQL 4.0

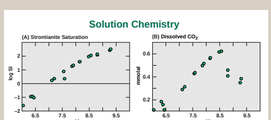
Solids

1. $Sr^{2+} + HCO_3^- = SrCO_{3(strontianite)} + H^+$

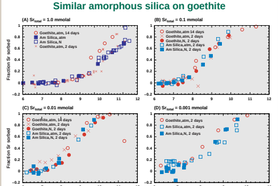
Sr XAFS and carbonate sorption on goethite (using van Geen et al., 1994)



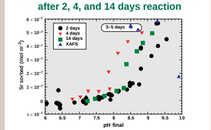
Solution Chemistry



Similar amorphous silica on goethite

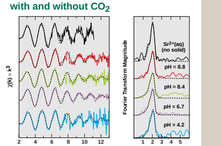


Strontium (10^{-3} m) sorption to goethite after 2, 4, and 14 days reaction



Kaolinite

XAFS: Strontium sorption on kaolinite with and without CO_2



Triple Layer Model: Sr sorption to kaolinite

Surface Complexes: n_s, 8.3 sites nm^{-2} (Schroth and Sposito, 1998)

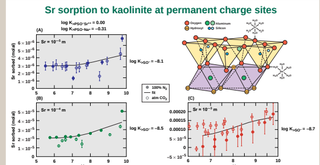
		Log K
1. >SOH + H⁺ = >SOH₂⁺	outersphere	–1.1
2. >SOH = >SO⁻ + H⁺		FITEQL 4.0
3. >SOH + Na⁺ = >SO⁻Na⁺ + H⁺		–6.6
4. >SOH + Sr²⁺ = >SO⁻Sr²⁺ + H⁺		–9.5

Cation exchange complexes: n_s, 8.3 sites nm^{-2} (Schroth and Sposito, 1998)

1. >PSO⁻ + Na⁺ = >PSO⁻ Na⁺	outersphere	FITEQL 4.0
2. >PSO⁻ + Sr²⁺ = >PSO⁻Sr²⁺		

Aqueous Species: CO_3^{2-}, $SrCO_{3(aq)}$, $SrCl^+$, $NaHCO_{3(aq)}$, $NaCl_{(aq)}$

Sr sorption to kaolinite at permanent charge sites



Results and Conclusions

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. 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, $SrCO_3(s)$

We collected EXAFS spectra on more than 20 amorphous silica, kaolinite, and goethite samples from pH 4 to 10, including comparison of low- and ambient-temperature spectra. With the exception of two goethite samples (discussed below), the EXAFS analyses suggested that the largest fraction of sorbed strontium on these phases was present as hydrated (i.e., water-ligated) complexes. 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. 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, or from a phosphate ligand in the presence of dissolved phosphate. 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 or phosphate suggests that strontium coordination is the same in both systems and that sorption involving dissolved anion ligands is minimal for amorphous silica and kaolinite.

(ii) Surface Complexation Models

Our spectroscopic results allowed 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 ($[Sr]_{initial} = 7x10^{-4}$ to 10^{-3} molal) and pH (6 to 10) at constant ionic strength. We used deprotonation and surface capacitance constants (log $K_{>SiO^-H^+} = -2.5$and $C_1 = C_2 = 6$ Fm^{-2}) determined by the direct observation of the pH-dependence of >SiOH and >SiO⁻Na⁺ amorphous silica surface sites using nuclear magnetic resonance spectroscopy (NMR). From these values and our experimental uptake data, we have determined outer-sphere sorption constants for strontium, log $K_{>SiO^-Sr^{2+}} = -9.5$–$0.2$and for sodium, log $K_{>SiO^-Na^+} = -6.6$–0.4. It is important to note that we needed the capacitance and deprotonation constants determined in the NMR spectroscopic study to develop a surface complexation model that fit both the macroscopic uptake data and the EXAFS results. It is important to note, that the protonation and deprotonation constants yield very high surface charge. One possibility is the total site density is lower than 4.6 site nm^{-2}. We are currently exploring this possibility and its impact on strontium sorption to amorphous silica.

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 ($[Sr]_{initial} = 10^{-3}$ to 10^{-7} molal) and pH (5 to 10) at constant ionic strength. The negative sites on the kaolinite basal plane are due to the isomorphic 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.