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Nucleation and Precipitation Processes in the Vadose Zone during Contaminant Transport

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Goals and Objectives

To develop better conceptual approaches for treating nucleation and precipitation reactions for ultimate inclusion in reactive-transport models, we conducted a set of experiments to link nucleation processes that occur homogeneously and heterogeneously from supersaturated solutions to their effects on flow in the vadose zone as measured in laboratory column experiments. The overall goal was to delineate the thermodynamics and kinetics of U-silicate phases that control, in part, the mobility of U(VI) in the environment and provide data that can be used in reactive-transport modeling. We focused on the uranyl-silicate system in the presence and absence of quartz and feldspar mineral substrates, and in solutions with controlled compositions including those characteristic of contaminated subsurface sites at Hanford and Oak Ridge. The molecular to nano-scale structure of precipitates was analyzed using high energy X-ray scattering (HEXS), X-ray diffraction (XRD), attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), extended X-ray absorption fine structure (EXAFS) spectroscopy, and high resolution transmission electron microscopy (HRTEM) and solution compositions were characterized for their Si and U concentrations.

Summary: Soderholm L., Skanthakumar S., Gorman-Lewis D., Jensen M.P., Nagy K.L. (2008) Characterizing solution and solid-phase amorphous uranyl silicates. *Geochimica et Cosmochimica Acta* 72:140-150.

We investigated how nucleated solids varied with pH from 2.5 to 11, U:Si ratios of 2:1, 1:1, 1:2, and 1:5, aging times at 25 degrees C of 1, 3, and 10, 90, and 180 days, and effects of moderate temperature increases that accelerated aging. HEXS and XRD data were used to structurally and chemically characterize uranyl-silicate solutions and precipitates formed from a starting solution with U to Si ratio of 1:2 after one day at room temperature from pH 2.2 to 9.1 and after four 4 days at 150 °C from pH 5.1 to 9.1. U-U correlations were observed out to distances of 10 Å or longer in both final solutions

and precipitates. With one exception, all precipitates were amorphous, with no evidence of Bragg diffraction in the XRD data. Room-temperature samples prepared above pH 3.1 all had similar Fourier transforms of their HEXS data, which were obtained from suspended slurries or precipitates. In contrast, hydrothermally-treated precipitates varied in their HEXS correlations at longer distances.

The XRD pattern of the hydrothermal sample with a pH of 5.1 had Bragg reflections that could be indexed as soddyite. While showing no evidence of crystallinity using XRD, the hydrothermal sample at pH 6 showed similar HEXS correlations, which evolved in samples at increasing pH into correlations more consistent with sodium boltwoodite. Results were supported by thermodynamic modeling. The structural correlations seen in the HEXS data to distances of about 4 Å are similar in all samples prepared at pH 4 or higher. We proposed a model for solid formation that includes uranyl silicate building blocks, or synthons, which preorganize in solution and then link into larger structures that vary as a function of pH.

Summary: Gorman-Lewis D., Skanthakumar S., Jensen M.P., Mekki S., Nagy, K.L.. Soderholm L. (2008) FTIR characterization of amorphous uranyl-silicates. *Chemical Geology* 253:136–140.

We precipitated solids from solutions containing 0.05 M uranyl perchlorate and 0.1 M sodium-silicate adjusted to pH values from 4 to 9 and then aged the solids for 6 weeks at 20°C. The chemical composition, XRD patterns, and ATR-FTIR spectra of the precipitates were compared to those of related crystalline phases predicted by thermodynamic modeling. The precipitates were amorphous with U:Si ratios of 0.8 ± 0.1. Their ATR-FTIR spectra revealed changes in the uranyl and silicate vibrations as a function of pH that are consistent with a shift in mid-range structural linkages from those similar to soddyite ($(UO_2)_2SiO_4 \cdot 2H_2O$) to those more like Na-boltwoodite ($Na(UO_2)(SiO_3OH) \cdot 1.5H_2O$). Structural water, hydroxyl, and anionic silica vibrations do not change as a function of pH and are consistent with a mixture of soddyite-like and Na-boltwoodite-like features. Six weeks of aging at ambient temperature was enough time for the precipitate structures to rearrange and adopt mid-range structural linkages characteristic of crystalline phases predicted by thermodynamic modeling.

Summary: Uyusur, B. (2010) Transport of aqueous uranium through quartz sediment and applications to the vadose zone. Chapter 5. Ph.D. Dissertation, University of Illinois at Chicago.

We studied the transport of dissolved U(VI), prepared as a $UO_2(ClO_4)_2$ solution, at concentrations of 2×10^{-6} M at pH 6 and 11 experimentally in unsaturated columns of ASTM 20/30 quartz sand (0.591-0.841 mm; Ottawa silica sand, US Silica Company) under steady-state conditions at room temperature. The columns of packed quartz had average water contents of 30 and 24% by volume at pH 6 and 11, respectively, and a linear flow rate of 14.8 mL h^{-1}. Comparison of dissolved U(VI) breakthrough behavior at pH 6 with that of an unreactive tracer (perchlorate ion) indicated that about 52% of the added U(VI) adsorbed to the quartz sand (0.53 µg U/g of sand). Leaching of the columns

using deionized water showed that removal of the U(VI) was negligible. At pH 11 U(VI) breakthrough reached a plateau of about 80% of the initial concentration. The breakthrough curve as well as the Si concentrations in the effluent at this pH indicated possible precipitation of a U(VI) containing solid. Conditions chosen for the initial solutions to precipitate U(VI)-silicates (0.05 M and 0.005 M of U(VI) and 0.025 M of Si) resulted in no enhancement of uranium transport due to the precipitation and deposition of the particles within the pores.

Summary: EXAFS measurements of U uptake on feldspar (Rouff et al., unpublished).

A set of experiments designed to precipitate U-silicate phases on labradorite feldspar (An60) substrates and characterize the precipitates using EXAFS spectroscopy was carried out. Solution compositions were designed to simulate the Hanford subsurface: 0.1 M sodium nitrate solutions adjusted to pH 6.5 or 9.0 and reacted with 0.00001 to 0.001 M uranyl-nitrate. Some pH 6.5 samples were treated with 0.001 M dissolved Si to simulate the higher concentrations that might be expected in confined pores and cracks in the vadose zone feldspars prior to contact with contaminant U solutions. Samples were prepared in the presence of atmospheric $P_{CO2(g)}$ with the exception of selected pH 9.0 samples. EXAFS data collected at the U-L3 edge indicate show differences that vary with initial [U], and suggest increased precipitation with increasing [U]. These data are in the process of being analyzed.

Summary: Uranium-silicate solid formation at ambient temperatures from pH 3 to 11 (Nagy et al., ms. in preparation).

A large matrix of uranium(VI)-silicate solutions between pH 3 and 11 at a U concentration of 0.05 M and varying U:Si ratios was prepared(Table 1). The solutions were allowed to age at 1, 3, and 10 days and the precipitated solids were characterized using HEXS (at beamline 11ID-B of the Advanced Photon Source) and ATF-FTIR. Selected solids were imaged using high resolution transmission electron microscopy (HRTEM). Solutions were analyzed for Si and Na concentration using ICP-OES, U concentration using alpha-counting, and pH with a glass or solid-state electrode. Initial and final solution saturation states were calculated using the aqueous geochemical modeling code PHREEQC with a modified database that included current thermodynamic data for aqueous and solid U(VI) species.

All solutions were made from stock uranyl-perchlorate and sodium metasilicate solutions using analytical grade perchloric acid and sodium metasilicate (Fisher Scientific), uranium(VI)-oxide (99.8 %, Strem Chemicals) and 18 mΩ deionized water. The uranyl-perchlorate solution was prepared by adding $UO_3(H_2O)_{0.8}$ to 14 M $HClO_4$ and deionized water and stirring for 2 h to obtain a final concentration of 0.5 M U in 2.5 M $HClO_4$. Uranium stock solution concentration was confirmed by alpha-counting (α Alpha Analyst, Canberra). The sodium metasilicate stock solution was prepared by adding $Na_2SiO_4 \cdot 0.9\ H_2O$ to deionized water to reach a concentration of 0.4 M. Silica concentration of the stock solution was determined by ICP-OES (PerkinElmer, Optima

4300 DV) analysis and the pH was 12.4. Four primary solutions were prepared by mixing the two stock solutions and deionized water while stirring in proportions needed to produce a constant U concentration of 0.05 M and Si/U concentration ratios of 1:2, 1:1, 2:1, and 5:1 (solutions SA, SB, SC and SD respectively, Table 1). All primary solutions had a final volume of 7 mL.

Table 1: Matrix description of primary uranium-silicate solutions.

Solutions	[Si] mol L⁻¹	[U] mol L⁻¹	pH	Si:U mol ratio	Physical Aspect
SA	0.025	0.05	1.1	1:2	clear yellow solution
SB	0.05	0.05	1.1	1:1	clear yellow solution
SC	0.1	0.05	3.2	2:1	clear yellow solution
SD	0.25	0.05	11.5	5:1	yellowish precipitates[*]

[*] Solid-like, pale yellow precipitates were formed immediately after mixing the two stock solutions. The precipitates did not settle upon pH adjustment.

Small amounts (< 120 µL) of 14 M $HClO_4$ or 10 M NaOH were added to each primary solution (within 3 minutes after preparation) to adjust the pH to 3.5, 5, 7, 9, and 11. Each primary solution matrix was thus reproduced five times for pH adjustment purpose with a final volume of each pH-adjusted solution of 7 mL + ΔV [1.5 % max]. The resulting matrix of 20 samples was reproduced twice more for the purpose of aging separate samples of the same composition for three different time periods. Aging was considered to start immediately after the pH adjustments. Aging occurred in Nalgene® vials sealed with screw caps on the benchtop at room temperature periods of 24, 48, and 240 hours.

Multiple systematic trends were observed in the evolution of both solution compositions and solids as a function of solution composition. More subtle trends, abrupt changes, or no changes were observed in solid characteristics as a function of time, except at pH 11. Precipitates formed in all experiments except the pH 3 samples at the two lower U:Si ratios. At pH ≤ 9, the syntheses produced mixtures of solids with structural features characteristic of crystalline uranyl-silicates. At pH = 11, the dominant features are like those in boltwoodite and possibly amorphous silica. At all pH values < 11, the kinetics involved in the structural reorganization (polymerization of uranyl-silicate synthons, Na structural incorporation, etc.) required to produce larger particles were too slow to observe changes over 10 days. For the pH = 11 series, the rates were more rapid as seen in obvious changes in the IR spectra, the XRD patterns, and the HEXS pair distribution functions. XRD patterns (Figures 1a and 1b) of 1-day and 10-day samples at pH 11 show similar variability in number and intensity of peaks as a function of U:Si ratio. The Fourier Transform (pair distribution function or pdf) of HEXS data for the SC (U:Si = 1:2) series samples shows an evolution of correlations with time (Figure 1c); whereas, the pdf analysis of HEXS data for the SB (U:Si = 1:1) series samples are a function of pH (Figure 1d). A distinct difference in the correlations occurs between syntheses at pH 9 and 11 that indicates the formation of nanoparticles at the higher pH.

The peaks in the pdf extend to approximately 30 nm, a size dimension confirmed by TEM images of the particles in this sample.
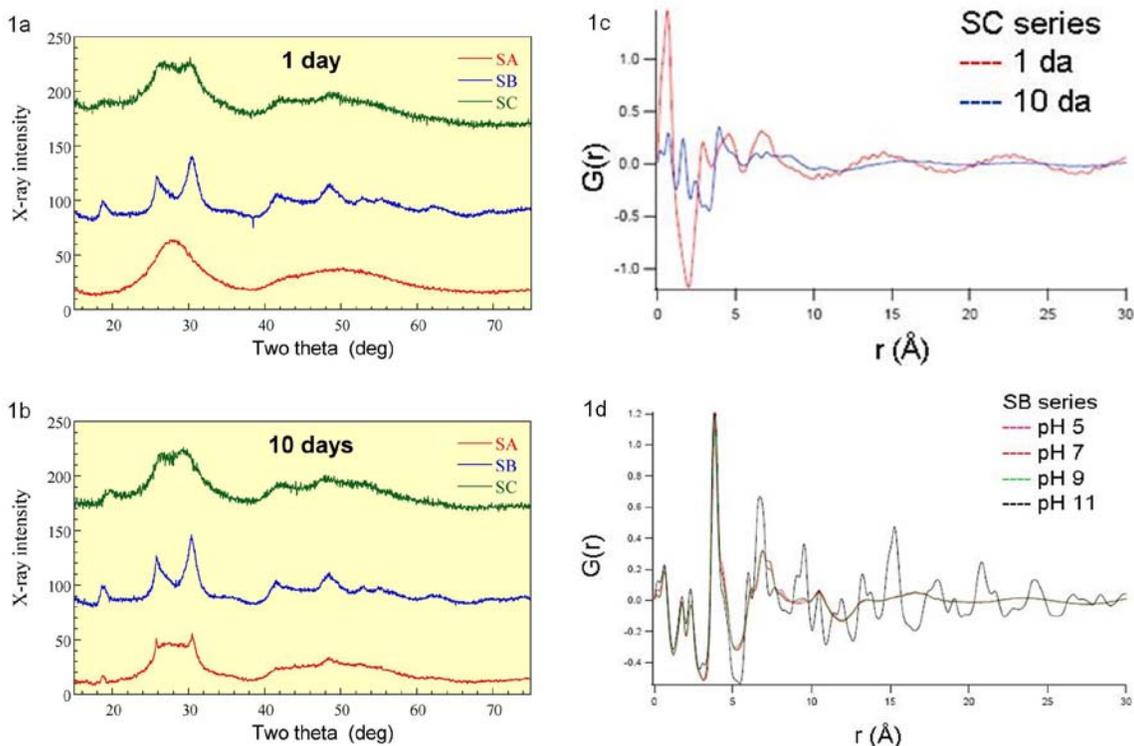

Figure 1. (a) and (b) XRD patterns of precipitates at pH 11 from solutions of different initial U:Si ratio (see Table 1) show differences with composition, but virtually no change after aging from 1 to 10 days. (c) HEXS pdf of SC series samples changes with time. (d) HEXS pdf of samples are similar from pH 5 to 9 as shown previously in Soderholm et al. (2008), but the pdf for the pH 11 sample is dramatically different, indicating a higher degee of crystallinity for this precipitate.

In the ATR-FTIR spectra, small but systematic shifts, appearances of peaks, and disappearances of peaks characteristic of U(VI) and Si bonding configurations occur as a function of Si:U ratio and pH (Figure 2a,b). Aging has little effect on peak positions or
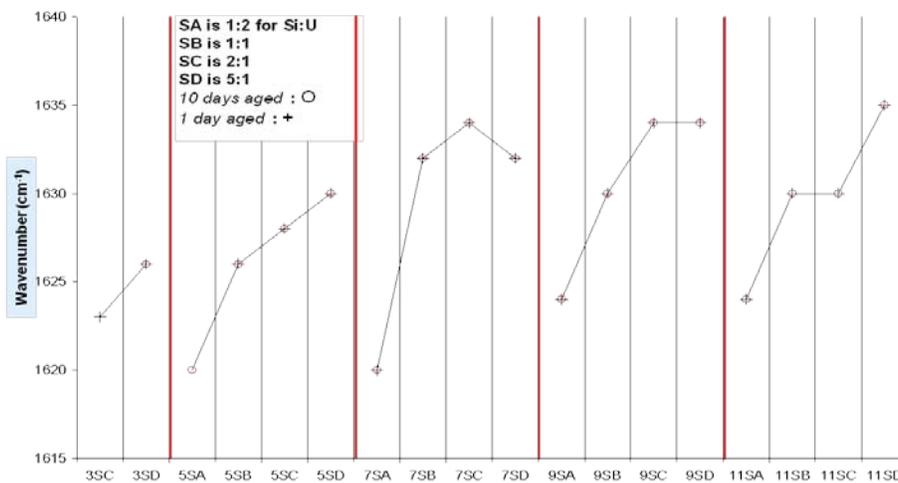

Figure 2a. Trends in one selected ATR-FTIR peak (~1620-1635 cm^{-1}) as a function of solution Si:U ratio.
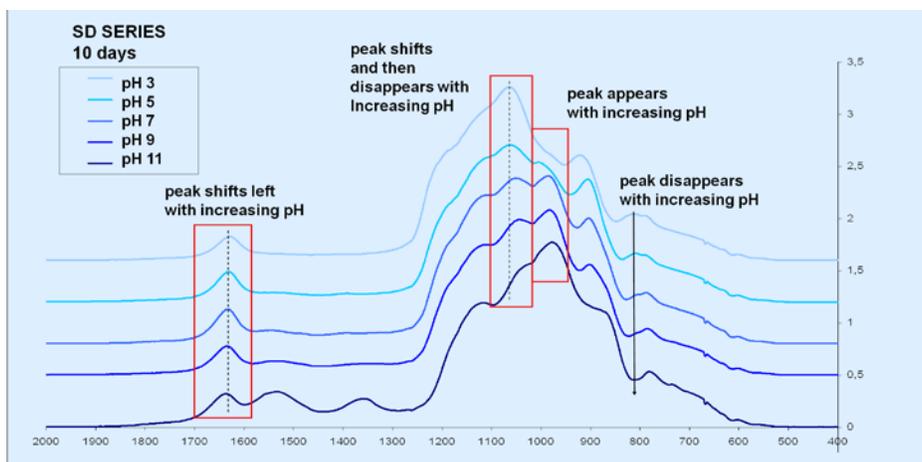
Figure 2b. Trends in ATR-FTIR spectra in samples aged for 10 days as a function of solution pH.
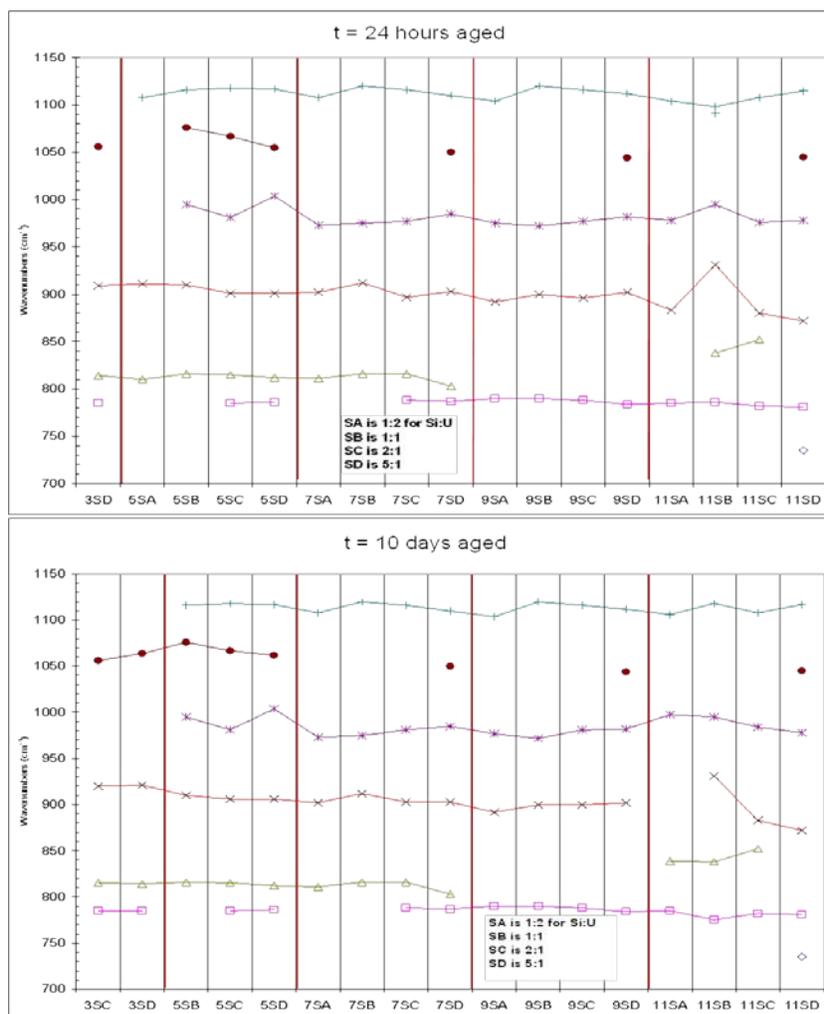
their presence or absence (Figure 3).

Figure 3. Either no trend or the appearance and disappearance of peaks was observed in ATR-FTIR spectra as a function of initial solution composition.