

EXAFS Study of U(VI) Adsorption on Calcite

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Introduction

Uptake of U(VI) by sorption onto calcite may influence the mobility of uranium in carbonate-containing soils and aquifer materials. Previous studies have also shown that the structure of surface complexes on calcite controls preferences for incorporation among nonequivalent surface sites. To gain a better understanding of these processes, we characterized the nature of sorbed U(VI) species *in situ* at the calcite-water interface by using extended x-ray absorption fine structure (EXAFS) spectroscopy at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) beamline 12-BM.

Methods and Materials

The calcite sorbent used in the adsorption experiments had an average particle size of 1.8 μm and a N_2 -BET surface area of $\approx 10 \text{ m}^2 \text{ g}^{-1}$. Before reaction with U(VI), calcite-water suspensions containing 0.5 g calcite L^{-1} were equilibrated at atmospheric CO_2 pressure (i.e., in air) for 1 mo. The suspension pH was measured at regular intervals during this period and found to stabilize at a value of 8.3 after about 2 wk. The equilibrated suspensions were spiked with U(VI) concentrations of 50 and 500 μM . Experiments were done with and without the addition of CO_3 upon introduction of U(VI) in the suspension. The samples without additional CO_3 were spiked with appropriate aliquots of a 0.04 M $\text{UO}_2(\text{NO}_3)_2$ stock solution, whereas the samples with additional CO_3 were spiked with aliquots of a stock solution containing 0.04 M $\text{UO}_2(\text{NO}_3)_2$ and 0.1 M Na_2CO_3 . The samples were equilibrated for 2 d and then filtered through 0.22- μm filter paper to collect the calcite solids for EXAFS analysis. The final pH in all samples was approximately 8.3. The wet pastes were loaded into lucite sample holders in the actinide facility at Argonne National Laboratory and sealed with Kapton[®] tape to prevent drying. EXAFS spectra at the U L_3 edge were collected on APS beamline 12-BM (BESSRC-CAT), and the samples were checked after data collection to confirm that they were still moist. Fluorescence spectra were collected by using a multi-element solid-state detector. Data analysis was done with WinXAS2.1 [1] by following standard procedures.

Results

Figure 1 shows the radial structure functions (RSFs) of the U(VI)-calcite adsorption samples, along with the RSF

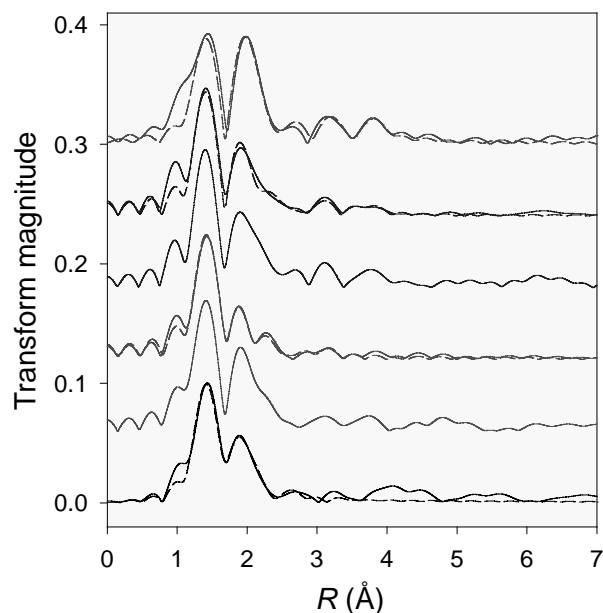


FIG. 1. RSFs of the U(VI)-calcite adsorption samples, aqueous U(VI)-tris-carbonate, and U(VI) incorporated in the calcite structure.

of the aqueous uranyl tris-carbonate complex, which is the dominant U solution species under the reaction conditions studied, and the RSF of U(VI) incorporated in the calcite structure. A split O shell is observed in all samples, with two close axial O atoms at approximately 1.8 \AA and an equatorial shell at a longer radial distance. Except for the sample reacted at 500 μM without added CO_3 , the equatorial O shell of the U-calcite samples could be fitted with six O's at a radial distance of 2.39 \AA . The equatorial shell of the U(VI) tris-carbonate complex was fitted with six O's at 2.43 \AA , which is slightly longer than for the adsorbed samples. The equatorial O shell intensity is, however, reduced for these U-calcite sorption samples relative to the tris-complex, which is reflected in a higher Debye-Waller factor in the fitting results when CN was fixed at 6. In the 500- μM sample where no CO_3 was added with U, there is a distinct splitting of the equatorial shell, with three O's at 2.27 \AA and three O's at 2.48 \AA .

Discussion

Our results may indicate that U adsorbs at the calcite surface as a tris-complex that is, however, (slightly)

distorted in the equatorial shell, probably due to coordination to the surface as a weakly bound inner-sphere complex. The distortion is not strong enough to result in distinct splitting of the equatorial shell. No Ca atoms were needed to obtain good fits, although it was possible to fit a Ca shell at about 3.5 Å. This contribution could, however, also be accounted for by multiple scattering in the dioxo unit (3.6 Å), so it is not possible to make any conclusive statement as to the surface coordination of the inner-sphere U tris-complexes.

The results for the sample reacted at a U(VI) concentration of 500 µM suggest the formation of a U(VI) precipitate in this sample, possibly because of a lack of available CO₃ to stabilize U(VI) in solution as a carbonate

complex. No U-U scattering could be identified for this sample, however, indicating that the precipitate, if present, is amorphous.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. We also acknowledge support from BESSRC-CAT.

Reference

[1] T. Ressler, *J. Physique IV* **7**, C2-269 (1997).