

The Interaction of Uranyl with the Calcite Surface: Batch Sorption and Synchrotron X-ray Standing Wave Studies

S. Rihs,^{1,2} N. C. Sturchio,^{1,3} K. A. Orlandini,¹ L. Cheng,¹ P. Fenter,¹ M. J. Bedzyk^{1,4}

¹Argonne National Laboratory, Argonne, IL, U.S.A.

²Université Louis Pasteur, Strasbourg, France

³University of Illinois at Chicago, Chicago, IL, U.S.A.

⁴Northwestern University, Evanston, IL, U.S.A.

Introduction

Characterization of radionuclide mobility in the environment is a major goal of applied geochemistry. Uranium (VI) mobility in oxic surface water and groundwater is strongly enhanced by the formation of stable complexes with carbonates. The formation of these uranyl-carbonate complexes is controlled by the pH of the water and the CO₂ partial pressure, and, in most bicarbonate groundwater, the dominant species of U(VI) are UO₂(CO₃)⁰, UO₂(CO₃)₂²⁻, and/or UO₂(CO₃)₃⁴⁻.

An abundance of literature is now available on adsorption of U(VI) by various solids (quartz, α -alumina, clinoptilolite, amorphous silica, hydrous Fe-oxides, clays, gels). The pH dependencies of U(VI) sorption on these minerals is generally similar, suggesting that U(VI) sorption is not as sensitive to the surface charge characteristics of the sorbent as it is to the effective surface area [1]. In natural CO₂-rich groundwater systems, it has been shown that up to 90% of the initial U(VI) can remain in the water, despite the precipitation of iron hydroxides and calcite [2]. Predictions of U(VI) interaction with mineral surfaces are complicated by the fact that U(VI) does not exist as a free metal ion in aqueous environments but develops strong covalent bonds with two oxygen atoms, forming the linear uranyl moiety UO₂²⁺.

Few studies have addressed the sorptive and coprecipitative behavior of U(VI) with respect to carbonate minerals [3-6]. Calcite is a ubiquitous component of sediments in both fresh water and marine environments, in which uranium can be efficiently trapped for, at the least, several hundreds of thousands years. However, a comprehensive atomic-scale view of the U(VI) binding mechanism with the calcite surface is still lacking. Because of advances in analytical methods, *in situ* synchrotron techniques are now suitable for this purpose. For instance, recent work of Reeder et al. [5, 6] addressed mechanisms of U(VI) uptake during calcite growth by using x-ray absorption fine structure (XAFS) and luminescence spectroscopy. Geipel et al. [7] used XAFS and time-resolved laser induction fluorescence spectroscopy to investigate the interaction of uranyl solutions with calcite. Sturchio et al. [8] used XAFS and

x-ray fluorescence to demonstrate that tetravalent U substitutes for Ca in a 35-million-year-old calcite.

We report on an investigation of U(VI) sorption onto the calcite surface that used batch sorption experiments and x-ray standing wave (XSW) spectroscopy of the sorbed U on the calcite (104) cleavage surface. The objectives throughout these experiments were to define the mode of sorption as well as the molecular structure and the reaction stoichiometry of uranyl species on calcite.

Methods and Materials

Batch sorption experiments were conducted at room temperature by reacting various U(VI) solutions with two sorbents: reagent calcite powder and freshly cleaved crystals of natural spar calcite. Uranium (VI) stock solution was obtained by dissolution of a uranium-236 nitrate salt [UO₂(NO₃)₂ · 6H₂O] in a disodium ethylenediaminetetraacetic acid (EDTA) aqueous solution. The EDTA complexing ligand was used to maintain undersaturation with U solid phases. Lower-concentration solutions were prepared by dilution. No additional background electrolyte or pH buffer was used. The ionic strength in all solutions was lower than 1 mM.

Adsorption on single calcite crystals was also investigated. The calcite samples were cut from large natural spar crystals from Russia and freshly cleaved on the (104) cleavage plane immediately before reaction with U(VI) solutions. Adsorption was controlled by allowing the solution to react with the crystal surface for 90 s, after which the surface was rinsed with methanol. Activities of uranium-236 sorbed onto the crystal surfaces were determined by direct α -counting of the cleavage surface, with an Al foil slit controlling the exposed surface area. For each sorption experiment, replicates on two or three crystals were measured. Because of the low surface area (unlike powder experiments), a small total number of U atoms was sorbed, resulting in larger 1-s counting errors (from 10 to 20%) for these samples. However, coverages measured in single-crystal adsorption experiments agreed fairly well with those from powder adsorption experiments.

A total of five calcite single crystals were cleaved and reacted with U(VI) solutions. Dissolved U(VI)

concentrations were 5.0×10^{-5} , 9.8×10^{-5} , and 1.3×10^{-4} mol/L. Higher U concentrations led to random distribution of uranium at the crystal surface, and lower concentrations led to a signal-to-noise ratio too low for monitoring. By means of vacuum grease, the crystals were gently held on a Kel-F cell mounted on a four-circle diffractometer, inside a thin Kapton® bag flushed with high-purity He gas for the duration of the XSW measurements. Measurements were made by scanning the sample through the (104) Bragg reflection of the calcite lattice. No measurements of the (006) Bragg reflection could be achieved because of the extremely low U fluorescence signal in the (006) geometry. The full width at half maximum (FWHM) rocking curves of the calcite (104) Bragg reflection ranged from 0.0007° to 0.0009° , close to the theoretical value predicted by the dynamical diffraction theory for a perfect calcite crystal.

Results

Five XSW measurements of sorbed U(VI) on the calcite surface were performed with respect to the (104) lattice plane. An XSW scan for a typical sample is shown in Fig. 1, along with the best-fit curve model. The coherent position values range from 0.80 to 0.88, with a mean value of 0.84 ± 0.02 . These results show that the coherent position of the sorbed U atoms does not exhibit dependence on the solution composition (total U concentration or aqueous U species distribution) within the range of experimental conditions. The coherent fraction ranges from 0.15 to 0.65, and the total U coverage ranges from 0.05 to 0.43 monolayer.

From the mean coherent position, it is possible to calculate the projected height h_H of the U atoms in the [104] direction with the following relation: $h_H = P_H \times d_H$, where d_H = the lattice spacing of the (104) diffraction plane, which is 3.04 Å in this case. The mean h_H of U(VI) normal to the (104) lattice plane is therefore 2.55 ± 0.06 Å.

Discussion

XSW results show that the amount of dissolved U(VI) does not influence the coherent position of the sorbed atoms, indicating that U(VI) sorption at the calcite surface is surface-controlled. The linear sorption isotherm and the rapid kinetics observed during batch sorption experiments also suggest that the dominant process governing the uptake of the uranyl ions is a specific surface adsorption process rather than a surface precipitation or cation exchange reaction. Owing to its configuration and size, the linear UO_2^{2+} ion is not expected to substitute readily into the calcite lattice. The significant deviation of the U coherent position from the Ca coherent position confirms that a substitution of Ca_2^+ by UO_2^{2+} is not the main mechanism probed here. Further, the calculated U(VI) (104) plane distance (2.55 ± 0.06 Å) is sufficiently short to

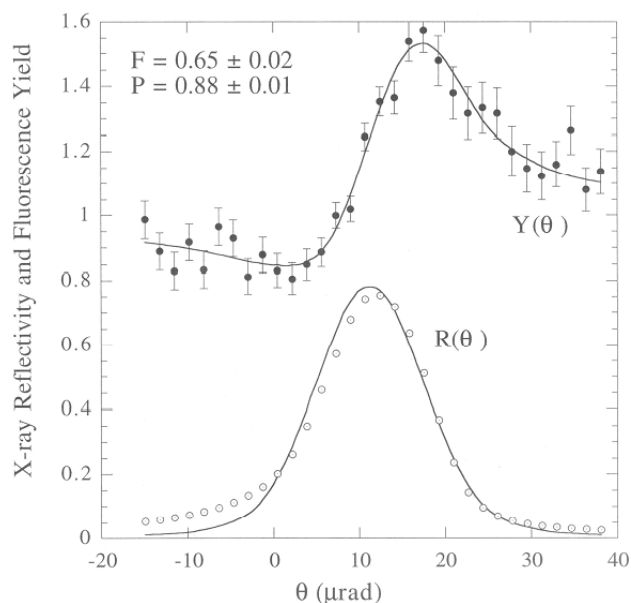


FIG. 1. Angular dependence of the experimental U-L3 fluorescent yield $Y(\mathbf{q})$ (normalized to unity for off-Bragg angles, closed circles), and the x-ray reflectivity $R(\mathbf{q})$ (open circles). Best fits to the reflectivity (from using dynamical diffraction theory) and the fluorescence yield are shown by smooth lines.

rule out an outer-sphere sorption. Sorption of U(VI) onto the calcite (104) surface can thus be explained only by a surface complexation of uranyl species via inner-sphere interaction with at least one carbonate group. However, we do not have definitive evidence to elucidate the nature of the uranyl species complexing this surface. Since the dominant dissolved uranyl species is the uranyl triscarbonato complex, sorption of this onto the calcite surface represents the most probable hypothesis. The measured distance of the U(VI) atoms above the (104) plane thus indicates a monodentate coordination of the sorbed uranyl species, in agreement with the conclusions of previous studies.

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