Atomistic simulations of uranium in the environment: Diffusion, adsorption, and incorporation

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Uranium is the most common radionuclide contaminant in subsurface systems associated with the U.S. Department of Energy (DOE) sites where nuclear materials were processed and stored. We have used a suite of atomistic simulation techniques to provide an atomic-level characterization of U properties in model systems relevant to DOE sites.

U preferentially associates with intra-grain domains in U-contaminated sediments collected from the DOE Hanford site and diffusion is expected to control the future mobility of U in these sediments. Therefore, we present molecular dynamics simulations of the diffusion and adsorption of uranyl carbonate species in intra-grain micropores, using feldspar-water fractures as a model system. Uranyl carbonate species dominate U(VI) aqueous speciation in Hanford groundwater conditions. The simulations show the effects of confinment and of the presence of the mineral surface on the diffusion of water and several uranyl carbonate species [1-3].

Uranium sorption by Fe-(hydr)oxides, which are common minerals in soil systems, has been conceptualized as a surface process; however, sorption is not necessarily reversible. The potential for incorporation into the mineral structure is supported by EXAFS studies; however, the evidence for incorporation rests on distances that do not match distances claimed for simple adsorption. Therefore, independent data are needed to confirm the structural incorporation hypothesis.

In this paper, we present atomistic modeling performed to evaluate the coordination of U incorporation in three Fe-(hydr)oxides [4]. The simulations provided information on U-O and U-Fe distances, coordination numbers, and lattice distortion for U in different sites and oxidation states. Comparison of the simulations with available experimental data provides further evidence to support the structural incorporation hypothesis.

[1] Kerisit S. Ilton E.S. & Liu C. (2008) *Geochim. Cosmochim. Acta* **72**, 1481–1497. [2] Kerisit S. & Liu C. (2009) *Environ. Sci. Technol.* **43**, 777–782. [3] Kerisit S. & Liu C. (2010) *Geochim. Cosmochim. Acta* **74**, 4937–49521. [4] Kerisit S. Felmy A.R. & Ilton E.S. (2011) *Environ. Sci. Technol.* **45**, 2770–2776.

Probing mineral-water interfaces with computer simulation

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The atomic-level structure of water at mineral sufaces is an important controlling factor in interfacial reactions. Therefore, differences in interfacial water structures could contribute to variations in surface reactivity between different surfaces of a single mineral. In this presentation, the water interfacial structure of three hematite surfaces, namely, the (012), (110), and (001) surfaces, will be contrasted [1]. An extensive comparison with X-ray scattering data provides further evidence that MD models can be used to reliably predict the structure of mineral-water interfaces. In addition, the MD trajectories were analyzed to gain insight into the surface structural controls on the interfacial water structure.

Mineral-water interactions also play an important role in carbonation reactions, which are one of the principal families of chemical interactions relevant to geological CO_2 capture and storage (CCS). Although carbonation of minerals in contact with a CO_2-containing aqueous phase has been extensively studied, carbonation reactions involving water-bearing supercritical CO_2 fluids (WBSF) have received comperatively little attention. However, the limited number of studies published to date all highlighted the dependence of the extent and rate of reaction on the water content of the WBSF. Therefore, a detailed understanding of the structure of the WBSF-mineral interface as a function of water content is critical to elucidating the mechanisms of carbonation reactions in conditions relevant to CCS.

MD simulations of a model forsterite surface in contact with WBSF of varying water content were performed to determine the partition of water between the WBSF and the mineral surface and the nature of CO_2 and H_2O bonding at the interface. The simulations show that water readily displaces CO_2 at the surface and that the formation of a water film at least three-monolayer thick can be exothermic even for water contents below saturation. The density, diffusion, and degree of hydration of CO_2 as well as the extent of CO_2/H_2O mixing at the interface were all predicted to depend strongly on the water content of the WBSF.

[1] Kerisit S. (2011) *Geochim. Cosmochim. Acta* **75**, 2043–2061.