SLAC-SFA: Biogeochemical processes and diffusive transport limitations affecting the stability of biogenic U(IV)

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Fundamental knowledge about the molecular-scale speciation and reactivity of U(IV) products of microbial U(VI) reduction is crucial for the success of *in-situ* bioremediation strategies in uranium-contaminated sites and can provide information about the fate of uranium present in naturally reducing zones. Recent studies have shown that U(IV) products of microbial reduction of U(VI) include uraninite (UO_2) and U(IV) bound to biomass (i.e., monomeric U(IV)). UO_2 is the most desirable product of *in-situ* bioremediation because it is orders of magnitude less soluble than other U species. Biogeochemical processes, molecular structure and composition, and diffusive transport limitations can affect the stability of U(IV) species in subsurface environments. The focus of this portion of the SLAC SFA project was to assess the reactivity of uraninite under carefully controlled conditions.

The relative lability of different forms of U(IV) have been probed in a series of chemical extractions that target U(IV) fractions that are water soluble, ion exchangeable, amenable to complexation by a ligand, and oxidizable. Biogenic UO_2 and molecular U(IV) had similar low degrees of mobilization to chemogenic UO_2 in all of the extractions except for the oxidizing one (oxygen or persulfate) in which the biogenic U(IV) species were more easily extracted.

Laboratory experiments were performed to evaluate adsorption and precipitation reactions occurring in the presence of groundwater cations that can affect UO_2 dissolution. Oxidative UO_2 dissolution rates were 1450 times lower in the presence of Zn^{2+} and 7 times lower in the presence of Ca^{2+} than in water free of divalent cations. Electron microscopy and x-ray absorption spectroscopy analyses of UO_2 solids recovered from the experiments suggest that adsorbed or precipitated phases of calcium and zinc can block the surface of UO_2 and inhibit its oxidative dissolution. We posit that the UO_2 solid may facilitate the formation of a Ca-U(VI) phase through adsorption of Ca^{2+} and subsequent surface precipitation. A Zn carbonate phase precipitated on the UO_2 solids recovered from experiments performed in the presence of Zn. Interactions with divalent groundwater cations have implications for the longevity of UO_2 and the mobilization of U(VI) from these solids in remediated subsurface environments.

The effects of diffusive transport limitations on the dissolution of UO_2 were investigated using a synthetic groundwater prepared to simulate the conditions at the Old Rifle site. The dissolution of UO_2 was measured in the absence and presence of diffusive limitations exerted by permeable sample cells. Dissolution rates of UO_2 at diffusion-limited conditions were two orders of magnitude lower than those measured in well-mixed systems, suggesting that transport processes could affect the fate of U immobilized during *in-situ* bioremediation. Characterization of unreacted and reacted UO_2 solids suggest that oxidative dissolution was more evident in the absence of diffusive limitations. A 1-D transport model successfully simulated diffusion-limited UO_2 dissolution with the dominant rate-limiting process being the transport of U(VI) out of the permeable sample cells. These findings advance our overall understanding of the coupling of geochemical and transport processes that can lead to differences in dissolution rates measured in the field and in laboratory experiments.