Reduction and reoxidation of uranium: Mechanisms, species, and implications for dispersal

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The use of uranium(U) for energy generation and military purposes has created stockpiles of spent nuclear fuel, mine tailings, and waste material from the enrichment process. Modern extraction technologies, such as *in situ* recovery or hydraulic fracturing also carry a risk of dispersing uranium via the mining fluids. Predicting the spread of contamination and developing remediation approaches requires a better understanding of the coupled biological, chemical, and physical processes that control uranium transport, from the atomic to the field scale.

A signigficant control on U mobility is its valence state, with U^{VI} species being more soluble than the U^{IV} species produced in reducing environments. However, the mobility for a particular U valence can depend on speciation, which in many cases cannot be predicted for U^{IV} from current thermodynamic data. In particular, we have shown that when aqueous U^{VI} ions encounter biological or abiotic reductants under envrironmentally-relevant conditions the resulting species are often different from the least soluble U^{IV} mineral, uraninite (UO_2). We will disciss the atomic structure and the factors leading to several distinct but relatively uncharacterized forms of U^{IV}, such as phosphate-bound or surface-adsorbed species, in which the U^{IV} ions remain separated due to complexation (a.k.a. monomeric U^{IV}).

We have also characterized the oxidation kinetics of such non-uraninite U^{IV} phases to evaluate the relative risk of U mobilization during influx of oxidized groundwater. Using XANES and EXAFS to track U speciation, the oxidation rate of amorphous U^{IV}-Ca-PO_4 was found to be similar to that of nanoparticulate uraninite in solutions equilibrated with atmospheric O_2 and CO_2 at pH 7.0 ($k_{SA,UIVPO4} = 1.04 – 2.7 \times 10^{-8}$ m s^{-1} vs. $k_{SA,UO2} = 1.40 \times 10^{-8}$ m s^{-1}). The rates and oxidized products depended on the presence of Na, Ca, and PO_4. Our results suggest that Ca and PO_4 can slow down the rate of U^{IV} oxidation by up to an order of magnitude, but that the rates are still fast enough to cause complete oxidation of U^{IV} to U^{VI} within days under fully oxygenated conditions.