Nano-FeS control of uraninite reoxidation in oxic groundwater

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Redox conditions are critical in governing the mobility and accumulation of uranium (U) in subsurface soils and groundwater. Mackinawite (FeS), produced during *in situ* bioremediation of U, can serve as an electron source or an oxygen scavenger and inhibit UO_2 reoxidation upon oxygen intrusion once active bioreduction is halted [1, 2]. However, if FeS becomes completely oxidized, dissolved oxygen (DO) levels may rise, leading to oxidation and remobilization of U. The rate controlling redox reactions of Fe and U species during an anoxic to oxic transition will dictate the fate and transport of U in the subsurface, yet these have not been sufficiently characterized. The present study investigated the kinetics and mechanisms of UO_2 reoxidation and U(VI) transport in the presence of oxygen and nanoparticulate FeS using batch and flow-through reactors as a function of pH, FeS content, DO and calcium concentrations. FeS and UO_2 oxidation products were characterized by transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS). FeS reaction products, i.e., Fe(III) hydroxides and aqueous Fe(II), were isolated and examined for their influence on UO_2 oxidative dissolution rate. This study illustrates that FeS serves as an effective oxygen scavenger to maintain UO_2 stability until it drops below a threshold concentration. The dissolution rate of UO_2 in the presence of FeS is over an order of magnitude lower than those in the absence of FeS. After FeS depletion, however, UO_2 dissolution rate is accelerated at neutral pH and low calcium concentration as compared to the control. The passivation layer on UO_2 surfaces may be distrupted during the period of inhibited oxidation, which allows for rapid oxidation of U(IV) after DO breakthrough. This study shows the critical role of geochemical conditions in controlling FeS transformation, which in turn strongly influences U remobilization in the subsurface environment. These findings have direct implications for our understanding of uranium redox transition and long-term stability in the subsurface.

[1] Bi et al. (2013), *Geochim. Cosmochim. Acta* **102**,175-190
[2] Bi & Hayes. (2013), *Environ. Sci. Technol* **48**, 632-640