Studies on abiotic mechanisms and kinetics of chemogenic uraninite oxidation in the presence of mackinawite and its implication in uranium remediation

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This research seeks to identify the potential of iron sulfides (primarily mackinawite) in inhibiting the reoxidation of U(IV) solids and evaluate the protective nature of mackinawite for long-term sequestration of uranium at DOE contaminated sites. Over the past three years, abiotic studies have been extensively conducted and thoroughly examined to 1) identify and quantify dominant geochemical mechanisms that protect uranium against mobilization in the presence of mackinawite under moderate oxic conditions; 2) evaluate the influence of a range of groundwater conditions on the ability of iron sulfides to inhibit reoxidation and remobilization of uranium; 3) assess the impact of post oxidation products of iron sulfides on uranium stability and mobility.

For this study, a continuously mixed batch reactor system has been developed and utilized along with an array of analytical methodologies to examine the mechanism and kinetics of FeS protection against UO_2 oxidation. Experimental results show that mackinawite serves as an effective oxygen scavenger to inhibit the fast oxidation of chemogenic uraninite under simulated groundwater conditions. The kinetic profiles of dissolved uranium indicate that 5 g/L mackinawite inhibits UO_2 oxidative dissolution for about 60 hr under pH = 7, P_{O2} = 0.02 atm, and P_{CO2} = 0.05 atm. During the lag time, oxidation of structural Fe(II) and S(-II) of mackinawite control the DO levels, leading to the formation of iron hydroxides and elemental sulfur, respectively, as determined by X-ray diffraction (XRD), Mössbauer and X-ray absorption spectroscopy (XAS). The redox potential of the reaction system appears to accurately track the stages of mackinawite oxidation. After FeS is depleted, DO levels increase and UO_2 oxidative dissolution occurs at a faster initial rate relative to the control experiments where mackinawite is absent. Oxidized U(VI) formed stable ternary Ca-UO_2-CO_3 complexes and dominates aqueous U(VI) species based on thermodynamic simulations. Approximately 20% - 40% of soluble U(VI) products are adsorbed by iron hydroxides (i.e. nanogoethite and ferrihydrite) formed from FeS oxidation depending on Fe:U molar ratio and calcium concentration. The kinetic data, along with XRD and XAS characterization of reaction products, suggests that the rapid uptake of U(VI) by FeS oxidation products during the initial stages of UO_2 oxidation is responsible for the accelerated rate of UO_2 oxidative dissolution compared to the control in absence of FeS. Ongoing research is testing other groundwater conditions (including pH, pCO_2, pO_2) to understand the effects of these geochemical constraints in uranium reoxidation.

A completely mixed flow reactor (CMFR) is currently under development to study the rate of UO_2 oxidative dissolution in the presence of FeS under various experimental conditions. Dissolution reactions in flow-through systems are kept far from equilibrium by constantly refreshing reactant solutions and preventing accumulation of U(VI) products. The newly designed reactor system has advantages of better pH control and flexibility of varying influent compositions, and of providing accurate UO_2 dissolution rates more efficiently in comparison to the batch studies.

This research has benefited from active collaborations with multiple institutions, including Arizona State University, Synchrotron Radiation Lightsource and Pacific Northwest National Laboratory. The collective effort has resulted in the production of joint publications and constructive intellectual exchange. This work, while providing the mechanistic basis for the role of FeS in the long-term uranium sequestration, also facilitates the identification of the controlling redox reactions when natural systems comprised of iron sulfides and reduced uranium are subjected to oxidants in the subsurface.