Assessing the Role of Iron Sulfides in the Long Term Sequestration of Uranium by Sulfate Reducing Bacteria (SRB)

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This UM/ASU research seeks to identify the potential for reduced iron sulfide minerals to inhibit the rate of oxidation of reduced U solid phases formed by sulfate reducing bacteria (SRB). Sulfate-reducing bacteria (SRB) utilize sulfate as a terminal electron acceptor and produce sulfide. When iron is also present, iron sulfide solids are produced. At DOE sites contaminated with U, aqueous phase U concentrations can be effectively lowered by reducing dissolved U(VI) species to insoluble U(IV) solids such as uraninite (UO_2(s)). SRB can accomplish this reduction step either directly by enzymatic electron transfer processes, or indirectly, through chemical reduction by the sulfides species produced. ***The working hypothesis of this study is that iron sulfides are preferentially oxidized over U(IV) solids when oxidants such as oxygen, denitrification products, or Fe(III) are introduced present.***

Batch studies were performed to continue the examination of the mechanism and kinetics of FeS protection against UO_2 oxidation under typical groundwater conditions. 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. After FeS is depleted, UO_2 oxidative dissolution occurs at a faster initial rate relative to the control experiments where mackinawite is absent. The kinetic data, along with XRD, Mössbauer, and XAS characterization of reaction products, suggest 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 groundwater conditions (including pH, pCO_2, pO_2) to understand the effects of these geochemical constraints in uranium reoxidation.

Sterile column experiments were performed to observe abiotic UO_2(s) oxidation by oxygen and denitrification products in natural sediments from Rifle CO. Both oxidation studies started with two RABS sediment columns supplemented with (1) chemogenic FeS (0.58g FeS(s)/kg) and UO_2(s) (0.5g UO_2(s)/kg) or (2) UO_2(s) alone (0.5g UO_2(s)/kg), sterilized with 5 Mrad gamma irradiation and by a 0.2 μm cartridge filter. For the oxygen columns, dissolved oxygen was passed through the columns, and for the denitrification products columns, nitrite, nitrous oxide, and dissolved oxygen were passed through sequentially. Effluent concentrations of uranium, sulfate, hydrogen sulfide, in combination with solid phase extractions on uranium, iron, and elemental sulfur show that under abiotic flow-through conditions: (a) iron sulfides protect uraninite from oxidation by dissolved oxygen and oxidizing minerals in RABS, (b) the terminal oxidation state for sulfide is elemental sulfur, (c) nitrite and nitrous oxide are not effective uranium or iron sulfide oxidants, and (d) oxidized RABS has a significant oxidizing capacity for uraninite. Upcoming experiments will further test the oxidizing potential of denitrification products, and will use sterilized bio-reduced sediment columns to better replicate natural systems undergoing oxidative U remobilization.

Biogenic iron sulfide minerals were produced by *Desulfovibrio vulgaris* supplied with various iron sources. Biogenic mackinawite production was demonstrated using either soluble iron or Fe (III) (hydr)oxide minerals in presence of *D. vulgaris*. The biogenic mackinawite derived from soluble Fe^{3+} was less crystallized than the mackinawite derived from soluble Fe^{2+}. By reducing Fe(III) (hydr)oxide solids and sulfate, *D. vulgaris* produced poorly crystalline mackinawite. XRD data further suggested that, in addition to mackinawite, residual Fe(III) (hydr)oxides, elemental sulfur, and vivianite [$Fe_3(PO_4)_2 \cdot 8(H_2O)$] were formed. Soluble iron, however, resulted in spectra containing only mackinawite patterns. The electron donor (lactate or pyruvate) did not have great impact on crystallization of mackinawite, except for soluble Fe^{3+}, where pyruvate led to more crystalline mackinawite. Residual Fe(III) (hydr)oxides and vivanite were present in the final solid products when pyruvate was the electron donor. These results illuminate the impact of the iron source coupled with the electron donor on the biogenic formation of iron sulfide solids that can be used to protect reduced uraninite from reoxidation in natural settings.