ABSTRACT: This UM/ASU research seeks to identify how iron-sulfide minerals can inhibit the oxidation rate of reduced U solids formed by sulfate reducing bacteria (SRB). SRB normally utilize sulfate as a terminal electron acceptor and produce sulfide that precipitates with Fe(II) to form iron-sulfide (FeS) solids. At DOE sites contaminated with U, SRB can also reduce aqueous-phase U(VI) to insoluble U(IV) solids such as uraninite ((UO2(s)). SRB can accomplish U(VI) reduction either directly by enzymatic electron transfer processes or indirectly through chemical reduction by the sulfides species produced. The hypothesis of this study is that iron sulfides inhibit the kinetics of re-oxidation of U(IV) to U(VI) when oxidants such as oxygen, nitrite, or Fe(III) are introduced.

In the past year of this project, we achieved significant progress on all three major tasks: (1) evaluating the impact of a range of iron sources in biogenic FeS production under reducing conditions by Desulfovibrio vulgaris, (2) flow-through reactor studies of the inhibition of the oxidation rates of reduced U(IV) solids by FeS, and (3) packed sediment column studies for assessing the abiotic oxidation dynamics of U(IV) solids in the presence and absence of biogenic FeS under the influence of dissolved oxygen (DO) and nitrite.

Various iron sources were evaluated for biogenic FeS production by D. vulgaris in batch experiments with pyruvate as the electron donor, including soluble Fe(II) and Fe(III) and solid Fe(III) (hydr)oxides. When pyruvate was the electron donor, D. vulgaris produced distinct sulfate- and Fe(III)-reduction patterns and biogenic FeS characteristics. When soluble Fe(II) or Fe(III) was the iron source, simultaneous reduction of sulfate and soluble Fe(III) occurred along with the rapid utilization of pyruvate. Furthermore, the greater proton production during pyruvate fermentation (compared to lactate) lowered the pH, which led to more crystalline FeS formation. With solid-phase Fe(III) as the electron acceptor, complete and more rapid pyruvate consumption (compared to lactate) led to more FeS production and vivianite precipitation due to the greater accumulation of soluble Fe(II).

Continuously stirred tank reactors (CSTRs) were used for examining the inhibition mechanism and kinetics of UO2 oxidation by mackinawite under oxic groundwater conditions. Experiments were conducted as a function of pH, calcium, FeS content, and DO concentrations to assess the impact of geochemical conditions on UO2 oxidation kinetics. Results consistently show that FeS serves as an effective oxygen scavenger to inhibit the oxidation of UO2. The solution pH influences UO2 oxidative dissolution by shifting FeS oxidation mechanism. The presence of Ca2+ in the groundwater leads to the formation of passivation layer on UO2 surfaces, which moderately reduces UO2 dissolution rate. The UO2 dissolution rate is strongly dependent on the concentration of DO and FeS solids in groundwater, with lower rate at lower DO levels and higher FeS content.

Packed column flow-through experiments were used to assess the abiotic oxidation dynamics of uraninite by nitrite and DO in natural sediments in the presence and absence of biogenic FeS. After acetate-induced bioreduction of Rifle sediments in parallel columns, one with sulfate present and one
without, gamma radiation was used to sterilize sediments before the oxidation reaction was initiated. The study shows that abiotic UO₂ oxidation by nitrite is essentially insignificant in comparison to oxidation by DO. Additionally, sediments containing FeS minerals significantly inhibit UO₂ oxidation compared to sediment without FeS present. In both columns, significant amounts of sediment-bound U remained after extensive oxidation, suggesting a U adsorption or other solid-phase incorporation mechanism related to the biologically reduced sediments.