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ABSTRACT TITLE: Manganese redox mediation of UO2 stability and U fate in the subsurface: Molecular and meter scale dynamics

ABSTRACT: Injection of electron donors into the subsurface to stimulate soluble U(VI) reduction to less soluble U(IV) species is being tested as an approach for in situ remediation of U contamination. The success of this approach depends on the long-term stability of U(IV). The reduction of Fe and Mn oxides during U(VI) reduction produces reduced metals which may later be oxidized forming strong oxidants such as MnO_2 after the addition of electron donor has ceased and oxidizing conditions return. The primary focus of our project has been on the interactions between Mn and U and with groundwater constituents and their effects on U(IV) stability.

The effect of Mn(II) on the UO_2 dissolution rate under reducing and oxidizing conditions was investigated. Under reducing conditions, a strong inhibitory effect was observed. Solid characterization suggested that precipitation of $MnCO_3$ may limit the exposure of U(IV) surface sites on UO_2 to trace level oxidants. In contrast, a promotional effect was observed under oxic conditions. It is hypothesized that Mn(II) adsorbed to UO_2 can be oxidized by dissolved O_2. The oxidation of Mn(II) could form reactive Mn(III) or Mn(IV) species, which could serve as additional oxidants for UO_2 that accelerate UO_2 dissolution. As an intermediate in Mn biogeochemical cycling, soluble Mn(III) has recently been found as an important environmental oxidant in oxic-anoxic interfaces. The kinetics of oxidative UO_2 dissolution by soluble Mn(III) stabilized by pyrophosphate was quantified. Soluble Mn(III) induced rapid UO_2 dissolution at a rate higher than by a comparable concentration of dissolved O_2. Self-consistent kinetic models were derived with excellent fits of the experimental results. The quantification of the reaction kinetics of oxidative UO_2 dissolution by soluble Mn(III) may help interpret the enhanced UO_2 oxidation mediated by Mn redox cycling and inferred from field measurements at Rifle, CO.

Our previous work in diffusion-limited agarose gels has shown that microbial Mn(II) oxidation did not enhance U(IV) oxidation by oxygen but that U(VI) produced was less mobile due to its sorption onto newly formed MnO_2. This past year we probed more complex sediment systems and evaluated whether the same outcome would be observed. Duplicate columns packed with Old Rifle sediments were run in the laboratory with an influent simulating Rifle groundwater, amended with U(VI) and either containing or devoid of sulfate. After U(VI) reduction and the accumulation of U(IV) over ~75 days, replicate columns were switched to an effluent containing 50 µM Mn(II) and 5% O_2 or only 5% O_2 to simulate oxidizing conditions. While microbial Mn(II) oxidation had been reported for unaltered sediments, the presence of U(IV) or the reducing conditions prevalent in the columns precluded significant Mn oxidation in the columns. However, the oxidation of U(IV) by O_2 was evident and led to the release of U(VI) in the effluent. We examined the microscopic distribution of U, Fe, S and Ca for columns before and after O_2 oxidation. In reduced sediments U was often associated with Ca but not directly with Fe or S. This suggests Ca adsorption to the surface of UO_2 as well as the association of Ca with non-crystalline U(IV). In the oxidized sediments, U was found primarily in association with S^0, iron sulfide minerals or $CaSO_4$, suggesting that the oxidation of S^{2-} by O_2 produces either S^0 or SO_4^{2-}. The implications of this work are that microbially mediated Mn(II) oxidation may be limited in reduced sediments despite the availability of O_2 and that the mechanism of redox buffering in sulfate-reducing sediments include the formation of S^0 and $CaSO_4$.