Manganese redox mediation of UO_2 stability and U fate in the subsurface: Molecular and meter scale dynamics

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Successful bioremediation of U in the subsurface depends on the long-term stability of U(IV). As a strategy to immobilize U, injection of electron donors to the subsurface to stimulate U(VI) reduction is being tested. During the process, Mn and Fe oxides sequentially undergo reductive dissolution. Once the injection of electron donor is ceased, however, zones where U(IV) precipitated may return to oxidizing conditions and the stability of U(IV) affected by the formation of strong oxidants such as MnO_2. The focus of our project is 1) to determine how certain groundwater constituents affect the coupled Mn(II)/U(IV) oxidation process, 2) to examine the fate of U once it is oxidized by MnO_2 in both lab and field settings, and 3) to quantify the effects of physical and chemical parameters on MnO_2/UO_2 interaction.

The oxidation of U(IV) by Mn(II)-oxidizing bacteria and Mn oxides has been shown in laboratory experiments to occur very rapidly. To assess the effect of groundwater constituents typical of the Rifle field site and the form of U(IV) on coupled Mn(II)/U(IV) oxidation, we investigated the effect of O_2 and common groundwater chemical species (Ca^{2+}, Mg^{2+}, and HCO_3^-) on Mn(II) and U(IV) oxidation by a model Mn(II)-oxidizing organism, *Bacillus* sp. SG-1 spores. Increasing O_2 resulted in increased levels of U(IV) oxidation which were attributable to both direct oxidation of U(IV) by O_2 and to the formation of biogenic MnO_2 which subsequently oxidized U(IV). Interestingly, Ca^{2+}, Mg^{2+}, and HCO_3^- showed varying effects on coupled Mn(II)/U(IV) oxidation by exerting its impact on either Mn(II) or U(IV) oxidation.

To understand the reaction between U(IV) and MnO_2, biogenic UO_2 or monomeric U(IV) were embedded in agarose gels with SG-1 spores. 65% and 74% of the total U was oxidized in gels containing UO_2 and monomeric U(IV) respectively. Additionally, more loss of U was observed from gels incubated with O_2 in the absence of Mn(II), suggesting that the impact of Mn oxidation is U(IV) immobilization. Bulk XAS results showed that the majority of U after Mn(II) oxidation was in the U(VI) form. MicroXAS analyses showed, two main particle types associated with U(VI), single particles or aggregates of U(IV) and Mn oxide particles.

In order to gain a field-relevant understanding of U(IV) oxidation by Mn oxides, several columns were deployed in the Rifle field site, under Mn-oxidizing conditions. These columns contained sediment from the Rifle site that had been pre-loaded (*in situ*) with U(IV). Total digestion of the sediments carried out prior to deployment and after 2 months showed a large decrease (from 40-65%) in the amount of U present in sediments that received higher levels of Mn(II), indicating that Mn(II) oxidation may play a role in the oxidation of U(IV) species.

Finally, laboratory experiments have been performed to understand the physical and chemical factors controlling the interaction of MnO_2-UO_2. Experiments with a multi-chamber reactor with a permeable membrane that prevented direct contact between MnO_2-UO_2 indicated that physical contact or close proximity is required for effective oxidation of UO_2 by MnO_2. When contact was allowed, an increase in the MnO_2:UO_2 ratio significantly increased the UO_2 dissolution rate. The product of MnO_2-UO_2 interaction, U(VI), was substantially adsorbed to MnO_2 and the release of Mn was less than expected based on the stoichiometry of the reaction.