Sequestration of Uranium in Iron-Rich Sediments under Sequential Reduction-Oxidation Conditions

University-led Research

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Integrated field and laboratory studies indicate that iron species play a critical role in the sequestration of uranium at DOE sites with the relatively high iron content of sediments (up to 5-6% as w/w). In a long-term study conducted in Area 3 of the ORIFRC site, intermittent addition of ethanol stimulated sulfate and Fe(III) reduction with a concomitant decrease in soluble U to low levels. Re-oxidation with oxygen and nitrate led to a rebound in soluble U. Solid phase analyses revealed the formation of Fe(III)-U(IV) solids.

Well-defined solutions of dissolved Fe(II) reduced soluble U(VI) (50 mg/L) to U(IV) precipitates when pH was increased to values that were favorable for U(VI) reduction (pH>5.5 for these systems). When solutions containing U(IV) were then exposed to oxygen, U(IV) species were oxidized, as confirmed by XANES analysis, but almost all the oxidized U(IV) was bound to Fe(III) solids. Aqueous phase U(VI) levels were low (<0.01 mg/L) at pH > 5.5. This result establishes that U can be sequestrated in the presence of Fe(III) solids. A long-term (1210-day) microcosm experiment was performed to monitor the effects of dissolved oxygen (DO) on the sequestration of bioreduced U. Two bottles containing sediment from the bioreduced zone (1404 mgU/kg) were allowed to oxidize through long-term exposure to headspace air. As oxygen penetrated the sediment, aqueous uranium initially increased from <0.03 mg/L to a peak concentration of 0.1 mg/L at 400 days, but then decreased to <0.03 mg/L. Aqueous U concentrations remained at < 0.03 mg/L, at pH 7.0-7.2, despite the presence of 5-6 mg DO/L, 0.5 mM Ca and 2 mM HCO_3. This indicates that the uranium was strongly attached to the solid phase. To evaluate the impact of nitrate on U sequestration, nitrate (1.2 mM) was added to one of these bottles. A change in sediment color from black to brown indicated that the sediment was oxidized, but aqueous U concentrations did not increase. The U remained sequestered under the conditions of this incubation. Long-term field testing at ORIFRC Area 3 (over 1,000 days) has continued to examine the effects of exposure of bioreduced sediments to nitrate. Nitrate-contaminated groundwater was allowed to invade the bioreduced area via natural groundwater inflow. The geochemical response was variable depending on the proximity to the influx of contaminated groundwater from the highly contaminated source zone located up gradient. In general, the nitrate concentrations in the previously bioreduced area increased gradually from near zero to ~50-300 mM and then stabilized. The pH declined from post manipulation levels of 6.2-6.7 to below 5.0 as the site was recontaminated. Uranium concentrations rebounded in all monitoring wells but were well below upgradient contaminated groundwater levels for two years or more after active bioreduction stopped. In several monitoring wells uranium levels rebounded, declined, then a slowly rebounded as contaminated groundwater reentered the bioreduced zone. The results indicates significant sequestration of U when nitrate was a allowed to re-enter the bioreduced zone. The change in microbial communities in the subsurface was monitored in relation to the reduction and oxidation processes and functional microorganisms for iron and U reduction and oxidation were identified. The results suggest that reduction followed by re-oxidation could be an effective in situ U sequestration strategy for iron-rich sediments.