I. Oxidation and Solubilization of Bioreduced U(VI) under Reducing Conditions

Part of our current work examines effects of varying OC concentrations on U mobility under reducing conditions. Through a long-term laboratory column experiment using FRC Area 2 soils, under continuous infusion of lactate. The steady decline in effluent U(VI) aq concentrations (contrary to conventional expectation), high inorganic C concentrations, thermodynamic calculations, and direct measurements using laser fluorescence spectroscopy. This hypothesis was further supported by Phase II tests, where high Fe(II) concentrations in influent U(VI) aq were reduced. Highest Fe(II) production from mineralization of high OC influxes utilized highest concentrations of Fe(III) in effluents. At very low times ~700 days, Fe(II) concentrations were reduced, while influent OC concentrations decline and a new Fe(II) influx occurred. More recent experiments are in progress to determine if Fe(III) is a TEA for U(VI) oxidation, and that its in-situ depletion is very slow.

II. II. Available terminal electron acceptors for U reduction under sustained reducing conditions

Several factors point to a residual reactive Fe(III) fraction in sediments as the likely TEA for U reoxidation, and we are currently conducting experiments to further test this hypothesis. These include even longer column incubations targeted at completely reducing the reactive Fe(III) fraction in sediments. Micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy for determining distributions of Mn(II) and Fe(III) and U oxidation states in sediments at various stages of OC-stimulated bioreduction, and chemical methods for determining concentrations of Fe(III) and Fe(II). Results to date (100 days) continue to support the presence of a residual reactive Fe(III) fraction that can require years of sustained reduction to deplete.

III. 16S PhyloChip analysis

High-density 16S rRNA microarrays (PhyloChips) were used to monitor changes in bacterial community composition (16S PCR amplicons) and prokaryotic community activity (direct 16S rRNA hybridization).

Overall Summary

- Influent OC is largely mineralized to dissolved (bi)carbonate, including U(VI)-carbonate complexes.
- Thus, U(VI) concentrations become proportional to influent OC concentrations while TEAs for U reoxidation remain available, even under reduced conditions.
- Depletion of TEAs for U reoxidation can require years of sustained reduction, after which U(VI) concentrations decline slowly.
- A μ-XANES spectra show rapid reduction of Mn(II), and very slow reduction of Mn(IV), indicating that residual Mn(II) can persist over many hundreds of days under reducing conditions.
- PCR-independent direct RNA analysis demonstrated the activity of U reducing bacteria despite observed reoxidation and uncoupled potential synergistic interactions.
- Long-term experiments are needed to evaluate remediation strategies that rely on precipitating actinides and metals.

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Discussion

1. Oxidation and Solubilization of Bioreduced U(VI) under Reducing Conditions

Our long-term laboratory studies involved sustained reduction of U(VI) by microorganisms. The steady decline in effluent U(VI) aq concentrations (contrary to conventional expectation), high inorganic C concentrations, thermodynamic calculations, and direct measurements using laser fluorescence spectroscopy. This hypothesis was further supported by Phase II tests, where high Fe(II) concentrations in influent U(VI) aq were reduced. Highest Fe(II) production from mineralization of high OC influxes utilized highest concentrations of Fe(III) in effluents. At very low times ~700 days, Fe(II) concentrations were reduced, while influent OC concentrations decline and a new Fe(II) influx occurred. More recent experiments are in progress to determine if Fe(III) is a TEA for U(VI) oxidation, and that its in-situ depletion is very slow.

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