Biogeochemistry of Uranium under Reducing and Re-oxidizing Conditions: An Integrated Laboratory and Field Study

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This project builds on our prior research to integrate laboratory and field studies focused on microbial U reduction at hematite surfaces. In the field, sampling for characterization of subsurface microbial communities is restricted by drilling costs, contaminated groundwater disposal, and difficulty with aseptic techniques. As an alternative, Biofilm Coupons (stainless-steel mesh cylinders loaded with mineral particles) were placed in the FRC-contaminated aquifer. A microbial community that attached to hematite surfaces was dominated by putatively metal-tolerant *Alcaligenes* spp. and acidophilic *Frateuria* spp., reflective of the high level of dissolved metals and low pH at the site. These populations were not a significant part of the community in nearby pristine groundwater. Current work is focused on understanding the influence of mineral type on attached community structure, and on the relationship between mineral coupon communities and those in the surrounding groundwater and sediments.

We are evaluating specific physiological activities of subsurface communities that develop on the coupons, and have focused on hydrogenase enzyme activities, as this enzyme is likely involved in electron transfer between metal-respiring bacteria and metal electron acceptors in the subsurface. To date, we have identified the DNA sequence of a 420 bp fragment of the [NiFe] hydrogenase gene from the sulfate-reducing bacterium *Desulfovibrio alaskensis,* and have shown successful in situ PCR amplification of the [NiFe] hydrogenase gene and 16S rDNA.

In the lab, in the presence of hematite and quartz, U(VI) was reduced to nanometer-sized uraninite particles by *Desulfovibrio desulfuricans* G20. Observations made at EMSL using HR-TEM, selected area electron diffraction, and energy-dispersive x-ray spectroscopic analysis confirmed that precipitated U associated with cells was uraninite with particle diameters of 2.6–3.6 nm. However, under electron donor–limited conditions, bioreduced U was partially reoxidized, likely by Fe(III) present in hematite. Using the same techniques, cell-free precipitates were found to be iron sulfides of varying Fe:S ratios. The *d*-spacings of randomly selected Fe-rich precipitates were most closely related to greigite. With G20 in column reactors containing hematite, dolomite, and calcite, over a period of two months of operation, columns with dolomite and calcite showed more than 99% U(VI) removal, while approximately 60% of U(VI) was removed from columns in the presence of hematite and a 10 mM bicarbonate buffer.

Comparison of the abiotic rates of reduction of uranyl ions by sulfide and sorbed Fe(II) (separately and together) is under investigation using an anoxic groundwater that closely simulates conditions found at the NABIR FRC (pH 6.4, high carbonate). Solid sorbents in these studies include hematite and quartz sand. Work has focused on sorption of Fe(II), which is low under these conditions, and on uranyl ions in the presence and absence of aqueous carbonate.