Novel Imaging Techniques, Integrated with Mineralogical, Geochemical, and Microbiological Characterizations to Determine the Biogeochemical Controls on Technetium Mobility in FRC Sediments

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Technetium-99 is a priority pollutant at numerous DOE sites, due to a combination of its long half-life (2.1×10^5 yr), high mobility as Tc(VII) (TcO_4^-, the pertechnetate anion) in oxic waters, and bioavailability as a sulfate analog. Under anaerobic conditions, however, the radionuclide is far less mobile, forming insoluble Tc(IV) precipitates. As anaerobic microorganisms can reduce soluble Tc(VII) to insoluble Tc(IV), microbial metabolism may have the potential to treat sediments and waters contaminated with Tc. In previous studies we have focused on the fundamental mechanisms of Tc(VII) bioreduction and precipitation, identifying direct enzymatic (hydrogenase-mediated) mechanisms, and a range of potentially important indirect transformations catalyzed by biogenic Fe(II), U(IV), or sulfide. These baseline studies have generally used pure cultures of metal-reducing bacteria, in order to develop conceptual models for the biogeochemical cycling of Tc. There is, however, comparatively little known about interactions of metal-reducing bacteria with environmentally relevant trace concentrations of Tc, against a more complex biogeochemical background provided by mixed microbial communities in the subsurface. This information must be available if in situ remediation of Tc(VII) contamination is to be successful at DOE sites.

The aim of this project is to use a highly multidisciplinary approach to identify the biogeochemical factors that control the mobility of environmentally relevant concentrations of Tc(VII) in FRC sediments, and to assess the effectiveness of strategies proposed to stimulate Tc(VII) reduction and precipitation in the subsurface. Initial experiments have focused on obtaining baseline data from FRC "background" sediments. Progressive microcosms incubated with and without added electron donor (20 mM acetate) have shown that Tc(VII) reduction occurs concomitant with Fe(III)-reduction. The addition of 10 mM nitrate and 20mM acetate had little impact on metal reduction, but 100mM nitrate (with acetate) completely inhibited the reduction of both Tc(VII) and Fe(III). Molecular analyses of the microbial communities present in the sediments confirmed the presence of Fe(III)-reducing bacteria known to reduce both Fe(III) and Tc(VII) in axenic cultures (*Geobacter* and *Geothrix* species), while nitrate-reducing bacteria were also detected (including *Azoarcus* species), and were present at higher concentrations than Fe(III)-reducing bacteria in MPN dilution series. X-ray absorption spectroscopy confirmed that the dominant form of Tc in the post reduction sediments is TcO_2. Reoxidation of immobilized, reduced Tc was also assessed using nitrate and air exposure as oxidants. Addition of nitrate (to 25 mM) had no effect on Tc solubility in reduced sediments, while air exposure resulted in approximately 80% solubilization of reduced technetium, presumably as reoxidized Tc(VII). Current experiments are focusing on the biogeochemical controls on Tc solubility in low pH/nigh nitrate sediments from Area 3 of the FRC, and in developing a sediment column system for analysis using γ-camera imaging techniques, which will allow real-time monitoring of Tc mobility in sediments.