

Sorption of Np, Pu, Tc, and I to saltstone and cement formulations under oxidizing and reducing conditions

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Plutonium, neptunium, technetium, and iodine present appreciable risks at sites around the world due to their potential mobility. Sorption of each of these radionuclides is profoundly influenced by oxidation/reduction reactions. Therefore, the mobility of each radionuclide may be greatly influenced by redox speciation. The primary focus of this study was to determine distribution coefficients (K_d) for each radionuclide for engineered saltstone systems with varying amounts of reducing slag. Sorption experiments were performed under oxidizing and reducing conditions using Np(V), Pu(IV), Tc(VII), and I(I). Np and Pu both exhibited strong affinity for concrete and saltstones under both oxidizing and reducing conditions. Distribution coefficient (K_d) values of $>10^5$ were calculated for all Np and Pu systems under oxidizing and reduction conditions. Experimental conditions had a far greater effect on Tc sorption. Under oxidizing conditions, Tc showed similar affinity for concrete and saltstone despite the presence of reducing slag and K_d values remained around 10. However, under reducing conditions, Tc sorption increased relative to the oxidizing conditions and the K_d values increased with increasing reducing slag concentration in the solid. This behavior is consistent with reduction of Tc(VII) to Tc(IV). Similar reduction of Tc(VII) in the presence of saltstone was observed by Lukens *et al.* [1]. The rate of Tc sorption, from which reduction was inferred, increased with increasing reducing slag content. It was determined there is a second order dependence on slag concentration and a steady state is reached around 3 weeks. Under oxidizing conditions, the iodide exhibited similar behavior to Tc and had K_d values significantly lower than Np and Pu. However, unlike the Tc systems, increased sorption was not observed under reducing conditions thus indicating that the majority of iodine remains as the initially amended iodide in both systems.

[1] Lukens *et al.* (2005) *Environmental Science & Technology* **39**, 8064–8070.

Reduction of Hg(II) to Hg(0) by nitrate enrichment cultures derived from subsurface sediments

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Although microbial mercury (Hg) reduction has been well documented in aerobic resistant prokaryotes carrying *mer* operons that are capable of reducing Hg(II) to Hg(0), little work has been undertaken to investigate *mer* activities among anaerobes and in anoxic zones. In this study, we conducted laboratory experiments to explore the mechanisms of Hg(II) transformation by denitrifying enrichments, as nitrate is often present as a co-pollutant in many heavy metal contaminated sites.

Enrichments were established with subsurface sediments from Oak Ridge, TN, and an oligotrophic growth medium that simulated *in situ* groundwater chemistry. Ten (or 20) mM acetate and 5 (or 10) mM nitrate were chosen as the electron donor and terminal electron acceptor, respectively. Data from Hg toxicity experiments showed that Hg inhibited denitrifying activities at concentrations higher than 10 μ M. Under this threshold, the enrichments detoxified Hg by reducing Hg(II) to Hg(0), as indicated by the formation of Hg(0) trapped in a solution consisting of strong acids (i.e. nitric acid and sulfuric acid) and oxidants (i.e. permanganate and persulfate). Surprisingly, denitrification and an increase in cell biomass did not follow Hg(II) reduction; rather, Hg(0) was oxidized to Hg(II) upon onset of growth in the enrichments. The nature of these interesting observations is currently investigated.

Two bacterial strains isolated from the enrichments and identified as *Ralstonia* sp. and *Bradyrhizobium* sp. (99% identity, based on 16S rRNA gene sequencing) reduced Hg(II). Using degenerate PCR primers, *merA*, the gene encoding for mercuric reductase, was detected in both isolates. Taken together, these results suggest that Hg redox cycling, including detoxifying processes that result from the activity of Hg-resistant denitrifiers, could affect Hg speciation and hence Hg mobility in anoxic environments. A better understanding of the processes mediated by anaerobic microbial consortia that control the mobility of Hg in groundwater aquifers is crucial for future environmental management and remediation efforts.