Student Abstracts

Speciation of uranium controls its kinetics of reduction by metal-reducing bacteria

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Uranium bioreduction, the microbial reduction of soluble U(VI) to highly insoluble U(IV), is considered one of the most promising in situ bioremediation strategies to immobilize uranium in the subsurface. The ability to predict the success of uranium bioreduction, however, is complicated by the wide range of geochemical conditions at contaminated sites and the strong influence of uranyl speciation on the bioavailability and toxicity of U(VI) to metal-reducing bacteria. To deconvolute the effects of uranyl speciation on uranium bioreduction kinetics, bioreduction incubations and viability assays with Shewanella putrefaciens strain 200 were conducted over a range of pH and DIC, calcium, and magnesium concentrations typically present at uranium-contaminated sites. Results from these incubations were incorporated into a speciation-dependent biogeochemical model able to reproduce the rate of uranium bioreduction across a wide range of geochemical conditions.

The presence of DIC, calcium, and magnesium led to the formation of less bioavailable uranyl carbonate species and decreased rates of uranium bioreduction. The biogeochemical kinetic model described the reduction of uranyl non-carbonate species (e.g. the 'free' uranyl ion, uranyl hydroxide complexes, etc.) with the largest rate constant (1.2E-12 L/cell/day) - orders of magnitude larger than uranyl carbonate (4.5E-14 L/cell/day) and ternary uranyl carbonate species (8.6E-21 L/cell/day) - indicating that non-carbonate species represent the most bioavailable and readily reducible fraction of U(VI) despite being the least abundant species in solution. At high concentrations of bioavailable U(VI), however, bioreduction rates decreased. Viability assays confirmed that the 'free' hydrated uranyl ion is responsible for uranium toxicity to strain 200 and inhibits bioreduction at elevated concentrations. The changes in uranium bioreduction rate across all experimental conditions were successfully predicted by incorporating uranium toxicity into the kinetic model.

Overall, these findings highlight the complex and seemingly counterintuitive influence of uranyl speciation on uranium bioreduction kinetics and identify geochemical conditions that may control uranium bioreduction at contaminated sites. Timely uranium immobilization via bioreduction relies on a delicate balance between maximizing uranium bioavailability and limiting uranium toxicity. These results suggest that efforts to increase uranium bioreduction rates at a given contaminated site by promoting the formation of bioavailable uranyl species will ultimately be constrained by the uranium tolerance of the subsurface microbial community. The new rate law developed in this study may be included in reactive transport models to predict the effect of bioreduction on uranium immobilization over a range of geochemical conditions.