

Surface complexation modeling of U(VI) and Np(V) adsorption onto the bacterial cell wall of *Bacillus subtilis*

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Adsorption of radionuclides onto mineral and bacterial surfaces can control the speciation, and hence the mobility, of these elements in the subsurface. Considerable attention has been paid to mineral surface adsorption. However, relatively little research has focused on radionuclide adsorption onto bacteria. In this talk, we present results from recent studies of Np(V) and U(VI) adsorption onto a common Gram-positive soil bacterium, *Bacillus subtilis*. In the Np study, we performed batch adsorption experiments as functions of pH, total Np concentration, and ionic strength. Under most pH conditions, Np adsorption is reversible and exhibits an inverse relationship with ionic strength, with adsorption increasing with increasing pH. At low pH in the 0.1 M ionic strength systems, we observed irreversible adsorption which is consistent with reduction of Np(V) to Np(IV). We model the adsorption reaction using a non-electrostatic surface complexation approach to yield ionic strength dependent NpO_2^+ -bacterial surface stability constants.

In oxygenated, CO_2 -rich systems, negatively charged uranyl complexes dominate the aqueous uranium speciation, and it is commonly assumed that these complexes exhibit negligible adsorption onto negatively charged surfaces such as bacteria. We measured aqueous uranium adsorption onto *Bacillus subtilis* as functions of pH, solid:solute ratio, and dissolved CO_2 and Ca concentrations. We observed extensive uranium adsorption onto the bacterial surface under all conditions, results that could dramatically alter predictions of uranium mobility in near-surface environments. Thermodynamic modeling of the data suggests that uranyl-hydroxide, uranyl-carbonate and calcium-uranyl-carbonate species each can form stable surface complexes on the bacterial cell wall.

The influence of metal reducing bacteria on plutonium speciation

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Dissimilatory metal-reducing bacteria (DMRB), which derive energy by using oxidized metals as terminal electron acceptors (ie. respiration), may play an important role in plutonium speciation and mobility in anoxic environments. Plutonium redox chemistry is complicated and under environmental conditions its III, IV, V, and VI oxidation states can each be stable and co-exist. Pu(V) and Pu(VI) are the most soluble Pu species found under environmental conditions, and the redox potentials of Pu(V) and Pu(VI) species are situated within the range accessible to metal-reducing bacteria.

We are investigating the ability of DMRB, *Shewanella oneidensis* MR1 and *Geobacter metallireducens* GS15 to use plutonyl ($\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ and $\text{Pu}^{\text{V}}\text{O}_2^+$) species as terminal electron acceptors. During cell suspension experiments we have observed that *G. metallireducens* GS15 and *S. oneidensis* MR1 rapidly reduce plutonyl (V and VI) species. For example, with an approximate cell density of 5×10^8 cells/mL, *S. oneidensis* removed from solution ~99% of the added Pu within 4 hours and *G. metallireducens* removed from solution ~97% of the added Pu within 24 hours. The corresponding abiotic controls showed no reduction in plutonyl concentration during the course of the experiment. Diffuse reflectance analysis of the solid precipitate from these experiments was consistent with a Pu(IV) (hydr)oxide solid, indicating that the added plutonyl was enzymatically reduced to Pu(IV) by these bacteria. Additionally, preliminary experiments indicate plutonyl may also support growth of these bacteria.