Biotransformations of Plutonium and Uranium by Naturally Occurring Bacteria

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This project will characterize and quantify specific biotransformation mechanisms that control the environmental distribution of actinides (Pu and U) and may be used for in situ biostabilization. Radionuclide contaminants may generally follow the pathways of the redox-active major elements, Fe and Mn. For example, Fe^{III} forms discrete complexes with polydentate chelators, such as co-contaminant EDTA and bacterial siderophores, that have 1:1 ligand to metal stoichiometry and low molecular charge. Pu^{IV} forms similar complexes; however, as a consequence of its larger coordination sphere and higher charge, it also forms additional species, including $Pu^{IV}(EDTA)_2$ and $Pu^{IV}EDTA(CO_3)_2$. These similarities and differences have direct consequences on biogeochemical behavior, as demonstrated by the dissimilar biodegradation of Fe- and Pu-EDTA and bioaccumulation of Fe- and Pu-siderophore complexes.

Microbacterium flavescens (JG-9), which utilizes a FhuD-type siderophore receptor, takes up Fe^{III}-desferrioxamine more rapidly and approximately five times more effectively than Pu^{IV}-desferrioxamine. When desferrioxamine complexes of both metals are simultaneously added to the bacteria, the rate of uptake of each is reduced by a factor of two, indicating comparable recognition by the same receptor sites. Towards determining if Pu-siderophore uptake is general, we isolated and purified the pyoverdin siderophore of *Pseudomonas putida*. Under conditions where Fe^{III}-pyoverdin is accumulated by metabolically active cells of *P. putida*, the corresponding Pu^{IV} complex is not. Interestingly, NTA complexes of both metal ions are taken up at the same rate ($k = 6.3 \times 10^{-2}$ min^{-1}) and in the same amount, indicating that pyoverdin is preorganized for metal binding in the receptor and metal uptake is via a ligand exchange mechanism (NTA to pyoverdin-receptor). Further voltametric and spectrophotometric studies showed that, unlike Fe^{III}, Pu^{IV} can form bis-pyoverdin complexes. When Pu^{IV}-pyoverdin/*P. putida* studies were repeated under conditions of lower siderophore-to-metal ratios that would favor the mono-pyoverdin complex (the direct Fe^{III}-pyoverdin analog), then the same amounts of Fe and Pu were taken up at the same rate. These studies indicate that under environmental conditions Pu^{IV} will be accumulated by bacteria via siderophore receptors and may be stabilized with respect to long-range transport.

In addition to forming different species, Fe^{III} and Pu^{IV} also differ in their redox properties, with Pu^{IV} having a much broader potential electrochemical range and more readily accessible oxidation states. These properties suggest that bacteria-mediated redox processes could transform plutonium to either less mobile or more mobile forms. Unlike uranyl, which is reduced to relatively stable $U^{IV}O_2$, plutonyl ($Pu^{VI}O_2^{2+}$ and $Pu^{V}O_2^{+}$) could be reduced beyond Pu^{IV} to Pu^{III}, which is not preferred. We have shown that plutonyl species are reduced by *Geobacter metallireducens* GS15 and *Shewanella putrefaciens* CN32. We are now assessing the ability of these bacteria to respire Pu and comparing their growth rates during Pu and U reduction.