

The Role of Bioligands in Microbe-Metal Interactions Emphasis on subsurface bacteria and actinides

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Metallic contaminants are continuously being introduced by various processes into environments such as the terrestrial subsurface. One important group of metallic contaminants is the radioactive actinides, which can cause damage to living organisms by their radioactive decay. To be capable of causing damage the metal needs to reach the living organism - it needs to be mobile. Microorganisms can influence metal mobility. This thesis compiles studies on how microorganisms from the terrestrial subsurface can influence the mobility primarily of actinides by means of producing and consuming bioligands.

Three species of bacteria isolated from subsurface environments, *P. fluorescens*, *P. stutzeri* and *S. putrefaciens*, were shown to excrete siderophore-type bioligands under aerobic conditions. In addition, *P. stutzeri* and *S. putrefaciens* excreted bioligands under anaerobic conditions. The potential of these bioligands, as well as that of the siderophore deferoxamine mesylate (DFAM), to affect the solid-aqueous phase partitioning of metals was tested. *P. fluorescens* efficiently mobilized U from uranium ore. This mobilization was attributed to the complexation of U to pyoverdine secreted by *P. fluorescens*, since the pyoverdine was found capable of forming a pyoverdine - UO_2^{2+} complex with a log β_{112} of 30.5 ± 0.4 and a log β_{111} of 26.6 ± 0.4 . The other two species did not mobilize U but instead mobilized V, Cr and Mo from the uranium ore. Furthermore, the solid-aqueous partitioning of Fe, Pm, Th and Am was studied in the presence of quartz sand or TiO_2 powder and secretions from aerobically cultured *P. fluorescens*, *P. stutzeri* and *S. putrefaciens* and anaerobically cultured *P. stutzeri* and *S. putrefaciens*. In the quartz set-up, siderophore-containing supernatants from aerobic cultures partitioned more than 50% of the total added amount not only of Fe but also of the actinides Th and Am to the aqueous phase. The anaerobic supernatants were most efficient at maintaining Am in solution with 40% of the total amount left in solution. In samples with the more fine-grained TiO_2 , the overall amounts of metal in solution were lower; however, again aerobic supernatants were capable of maintaining Fe and also Th in solution. Anaerobic supernatants maintained Fe and Th in solution as well, albeit to a much lesser extent. In another study, the dissolution behaviour of spent nuclear fuel pellet fragments in the presence of DFAM and the pyoverdine of *P. fluorescens* was observed. The pyoverdine maintained significantly higher concentrations of Np and Pu in solution than the control. In addition, both the pyoverdine and the DFAM leached Ru from the fuel pellet fragments.

Included in the thesis is a study on the degradation of the actinide-mobilizing ligand isosaccharinic acid by anaerobic subsurface microorganisms. There were several indications that the tested metabolic groups did not degrade the isosaccharinic acid. This result is in accordance with other studies, indicating the low biodegradability of isosaccharinic acid.

Microorganisms can affect the mobility of metallic contaminants in the environment by affecting the pool of bioligands that can form metal-complexes. In this thesis it was shown that some subsurface microorganisms are capable of excreting bioligands under both aerobic and anaerobic conditions. These bioligands were capable of affecting the solid-aqueous phase partitioning of various metals including actinides. Processes like these may impact the mobility of these elements in a variety of environments.

Key words: Actinide, bioligand, subsurface, microorganisms, pyoverdine, DFAM, isosaccharinic acid.