Reaction of Pu(III) and (V) with magnetite and mackinawite: A XANES/EXAFS investigation

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Plutonium is the major transuranium actinide in nuclear waste and a highly toxic environmental contaminant. As iron (II) minerals are ubiquitous and known to reduce a range of metal (loid)s, including As, Cr, Se, Pu and Np, through surface-mediated redox reactions, we investigated here the reactivity of magnetite (Fe_3O_4) and mackinawite (FeS) towards Pu (III) and (V) using XAFS to analyse the oxidation state and molecular structure of the reaction products.

Mineral syntheses and reactions were carried out under anoxic conditions in N_2 or Ar glove-boxes. Fe_3O_4 and FeS were reacted for 40 days in 0.1 M NaCl with Pu ($1x10^{-5}$M) at approx. pH 8. ^{242}Pu was added as electrolytically prepared Pu (V) to Fe_3O_4 and FeS, and as Pu (III) to Fe_3O_4.

The spectra obtained from tri- and pentavalent Pu reacted with magnetite are nearly identical; shell fitting yielded a Pu-O distance of 2.50 Å, indicative of Pu (III). Using Monte Carlo modeling of the EXAFS spectra (MC) [1], we were able to unequivocally identify a distinct Pu (III) surface complex wherein Pu (III) is connected via three oxygen atoms to three edge-sharing FeO_6-octahedra of the Fe_3O_4 {111} face. This result is in disagreement with [2], where in the absence of spectroscopic evidence Pu (IV) had been proposed as the major oxidation state after reacting Pu (V) with magnetite under anoxic conditions. In the presence of mackinawite, Pu (V) was reduced to Pu (IV) as determined by both XANES and EXAFS shell fitting. The EXAFS spectrum closely resembles that of PuO_2 solids and colloids. Our study demonstrates that under reducing conditions in geological environments both Pu (IV) and Pu (III) species may be relevant and migration as eigencolloids or adsorbed species may play an important role in controlling Pu mobility.

[1] Rossberg *et al.* (2005) *Anal. Bioanal. Chem.* **383**, 56–66.
[2] Powell *et al.* (2004) *Environ. Sci. Technol.* **38**, 6016–6024.

Bioavailability of polymer nanoparticle coatings

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Nanoparticle coatings, whether manufactured or natural, ultimately dictate the fate, transport, reactivity, and toxicicty of the particle [1]. In order to fully understand the behavior of nanomaterials in the environment, it is important to understand the fate of these coatings. An important question is whether or not coatings can be removed by microbial communities. To our knowledge, no one has demonstrated conclusively whether or not surface coatings *attached* to nanoparticles are bioavailable. The objective of this study was to demonstrate whether or not polymers covalently bound to nanoparticles are bioavailable.

Nanoparticle choice was critical for these experiments. We chose to design nanoparticles with covalently bound polymer surface coatings to eliminate coating desorption. We synthesised nanoparticles with a polystyrene-like core and polyethylene glycol (PEG) arms. Polyethylene glycol is biodegradable by certain bacteria whereas the cross-linked hydrophobic particle core is not bioavailable.

We isolated multiple strains of polyethylene glycol degrading bacteria from wastewater treatment sludge, including a *Sphingomonas sp.* and a *Chryseobacterium sp.* We grew these strains in cultures with either PEG or the polymer nanoparticles as the sole carbon source. Growth was comparable in both systems indicating that indeed polymer coatings on nanoparticles are available carbon sources for bacteria. This has significant implications regarding the fate of manufactured nanoparticles in the environment.

[1] Wiesner *et. al.* (2009) *Environ. Sci. Technol* **43**, 6458–6462