Redox dependent interfacial reactivity of hexavalent radionuclides

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Understanding the behavior of radionuclides at mineral-water interfaces is important to make reliable statements for the safety assessments of nuclear waste disposals. Here, the interaction of $U^{VI}O_2^{2+}$ and $Pu^{VI}O_2^{2+}$ with muscovite mica were investigated using a combination of surface X-ray diffraction (crystal truncation rods, CTR, and resonant anomalous X-ray reflectivity, RAXR), alpha spectrometry and Grazing-incidence X-ray adsorption near-edge spectroscopy (GI-XANES). The interfacial behavior highlights the effect of the actinides' different redox properties on their environmental mobility.

The interfacial structures obtained by CTR measurements, on the muscovite (001) basal plane after reaction with PuO_2^{2+} exhibit a large, broadly distributed electron density, which must be related to Pu uptake. This observation could be confirmed by RAXR and alpha spectrometry. In contrast, no significant uptake of UO_2^{2+} is evident by CTR or RAXR.

GI-XANES identifies Pu on the surface as Pu(IV). The oxidation state of Pu in the reaction solution had been adjusted electrochemically, and was controlled by UV/vis spectroscopy, hence a reduction must have occurred during the experiment. In consequence of this reduction, obviously formation of Pu(IV)-oxo-nanoparticles occurred. We attribute the difference in the observed reactivity to the greater stability of low oxidation states for Pu relative to U, in combination with the increased "hardness" of the Pu^{4+} cation, relative to U^{4+}. Once a threshold of $[Pu^{4+}]_{interface}$ is reached, oligomerization may occur, and Pu^{4+} is removed from the redox equilibrium [1]. The reaction then becomes "auto-catalytic". The results demonstrate how redox behavior strongly influences the sorption behavior of hexavalent actinides.

[1] Hellebrandt, S. et al. (2016), *J. Phys. Chem. C.* in preparation.