

Surface-mediated formation of Pu(IV) nanoparticles on muscovite

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Nanoparticles have long been recognized as an important factor in actinide chemistry,[1] as well as reactive transport.[2, 3] The formation of Pu(IV) nanoparticles can be enhanced by the presence of a mineral surface[4], even if Pu is not initially present as Pu(IV).[5] Redox activity of the mineral surface is not a prerequisite for this oxidation/ polymerization reaction.[6]

Upon reaction of a solution of Pu(III) with muscovite mica the formation of Pu(IV)-oxo-nanoparticles was observed by surface x-ray scattering [crystal truncation rods (CTR) and resonant anomalous x-ray reflectivity (RAXR)] and atomic force microscopy (AFM).[6] The surface-mediated polymerization has been related to the enhanced concentration of mobile plutonium near the interface, as well as the redox equilibrium of Pu(III) and Pu(IV) under atmospheric conditions.

Here we present our recent findings demonstrating that the same mechanism is also found when Pu is initially present in its hexavalent state PuO_2^{2+} , thus requiring reduction instead of oxidation to reach the tetravalent state. Surface x-ray scattering in combination with x-ray absorption near-edge spectroscopy (XANES) reveal the presence of Pu(IV) nanoparticles after 12 hours reaction time. Grazing incidence XANES shows only Pu(IV) at the interface, within the detection limits. The interfacial structure revealed by CTR and RAXR will be discussed and compared to the structures formed upon sorption of preformed Pu(IV) nanoparticles[7], as well as after surface-mediated formation of nanoparticles from trivalent plutonium.[6]

[1] Knope, K.E., *et al Chem. Rev.*, 2012. 113(2): 944; [2] Kersting, A.B., *et al Nature*, 1999. **397**: 56; [3] Novikov, A.P., *et al Science*, 2006. **314**: 638; [4] Powell, B.A., *et al ES&T*, 2011. **45** (7): 2698; [5] Kirsch, R., *et al ES&T*, 2011. **45** (17): 7267; [6] Schmidt, M., *et al ES&T*, 2013. **47** (24): 14178; [7] Schmidt, M., *et al Langmuir*, 2012. **28**: 2620.