Effect of background electrolytes composition on the interfacial formation of Th(IV) nanoparticles

J. NEUMANN[1], C. QIU[1], S. HELLEBRANDT[1], P. ENG[2], S. SKANTHAKUMAR[3], M.STEPPERT[4], L. SODERHOLM,[3] M. SCHMIDT[1]

[1] Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, j.neumann@hzdr.de
[2] University of Chicago, Chicago, IL, USA
[3] Argonne National Laboratory, Argonne, IL, USA
[4] Leibniz Universität Hannover, Hannover, Germany

Understanding actinide nanoparticle (NP) formation and its influence on their mobility in ecosystems is essential for the reliable safety assessment of nuclear waste repositories.
Previous surface x-ray diffraction (SXD) results showed a strong and unusual influence of the background electrolyte composition on Th sorption on the mica (001) basal plane. Uptake was shown to be significantly lower (<d.l. ~0.04 Th/A_{UC}; A_{UC} = 46.72 Å², area of mica (001) unit cell) for $NaClO_4$ solution compared to NaCl (0.4 Th/A_{UC}). An exceptionally high coverage was detected for $LiClO_4$ (4.9 Th/A_{UC}), which far exceeds the amount needed for surface charge compensation (0.25 Th/A_{UC}), suggesting the formation of Th-NP.[1] However, it remained unclear, if the reaction occurs at the interface or in solution and if anion and cation effect occur independently.
We applied SXD as well as electrospray-ionization time-of-flight mass spectrometry (ESI-TOF-MS) and *in situ* AFM to address these questions. ESI-TOF-MS measurements show no influence on solution speciation, indicating the processes happen on the mica surface. In all media, only monomers are observed. From Cl^- media higher coverages are found for LiCl (8.8 Th/A_{UC}) and KCl (3.6 Th/A_{UC}) compared to NaCl (0.4 Th/A_{UC}), confirming the trend observed with perchlorates and the occurrence of two independent effects for the electrolyte cation and anion.
In *situ* AFM images show the Th-NP to have variable lateral size and a height of a few nanometers. For higher Th(IV) concentrations the formation of Th-nanochains is observed. In the suggested mechanism the formation of Th-NP occurs on the mica surface. In a first step, Th is adsorbed on the surface, where large local concentrations lead to the formation of Th-NP in some media. These particles move along the surface in a second step to form band-like structures of up to several hundred nanometer length.

References:
[1] M. Schmidt, *Geochim. Et Cosmochim. Acta.* **2015, 165, 280-293.**