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## Effect of background electrolyte composition on the formation of Th(IV) nanoparticles on the muscovite (001) basal plane

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Actinides are known to form nanoparticles (NP), which were shown to enhance radionuclide transport in the environment. Understanding these processes on the molecular level is therefore of particular interest.

Previous results showed a strong and unusual influence of the background electrolyte on Th sorption on the mica (001) basal plane based on surface x-ray diffraction (SXD) data. Uptake was shown to be below the detection limit for NaClO<sub>4</sub> solution but not NaCl (0.4 Th/AUC). Additionally an exceptional high coverage was detected for LiClO<sub>4</sub> (4.9 Th/AUC) and surprisingly intermediate sorption occurs for KClO<sub>4</sub> (~0.1 Th/AUC) under otherwise identical solution conditions.

We combined Surface X-ray Diffraction (SXRD) and in situ AFM to investigate this previously reported unusual electrolyte effects on Th uptake on mica for a broader range of electrolytes and two different Th concentrations. At low [Th] (0.1 mM), interfacial structures show a broad Th electron density (~50 Å). A linear decrease of Th uptake with decreasing hydration enthalpy of the electrolyte cation (Li<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cs<sup>+</sup>) indicates a competitive effect between Th and the electrolyte cation. Na<sup>+</sup> is a clear outlier from this trend, with significantly lower Th uptake. In situ AFM imaging confirms the results. Particles show a vertical size of ~1–2 nm and larger lateral dimensions of ~10–20 nm, which is typical for particles formed at interfaces by a heterogeneous nucleation mechanism.

At high [Th] = 1 and 3 mM, all investigated electrolytes (ACl, A = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) show similar Th uptake, indicating a much smaller impact of electrolyte composition. The interfacial structures are dominated by a high Th loading at a distinct distance (~6.5 Å) from the surface. Therefore, the main retention mechanism at high [Th] is suggested to be the sorption of Th NPs aggregated from Th oligomers present in solution via homogeneous nucleation.

Preliminary investigations suggest a connection of the observed behavior to the complexation behavior of nitrate, which was present in our solutions in low concentrations due to the use of Th(NO<sub>3</sub>)<sub>4</sub> as a starting material.

**Primary authors:** Dr NEUMANN, Julia (Helmholtz-Zentrum Dresden-Rossendorf); Dr QIU, Canrong (Helmholtz-Zentrum Dresden-Rossendorf); Dr ENG, Peter (Center for Advanced Radiation Sources, University of Chicago); Dr SKANTHAKUMAR, Suntharalingam (Argonne National Laboratory); Dr SODERHOLM, Lynne; Prof. STUMPF, Thorsten; SCHMIDT, Moritz (HZDR)

**Presenter:** SCHMIDT, Moritz (HZDR)

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