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## Effect of background electrolyte composition on the sorption behavior of Th(IV) and Zr(IV) on the muscovite (001) basal plane

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Reliable long-term predictions about the safety of a potential nuclear waste repository must be based on a sound, molecular-level comprehension of the geochemical behavior of the radionuclides. Especially, their reactivity at the water/mineral interface will control their mobility and thus hazard potential.[1] A recent study has found a surprising dependency of the uptake of Th(IV) on the muscovite (001) basal plane on the composition of the background electrolyte.[2]

Two effects were observed a sorption reducing effect of perchlorate relative to chloride and a sorption increasing effect of Li relative to Na. Thus, a simple change from NaClO<sub>4</sub> medium to LiClO<sub>4</sub> led to an increase in surface occupancy by more than two orders of magnitude, which subsequently leads to the formation of Th(IV)-(hydr)oxo-nanoparticles. A mechanistic interpretation is hitherto not available, so it remains unknown whether cation and anion effects occur independently and whether the background electrolyte's cation affects the formation of nanoparticles in solution or increases sorption at the water/mineral interface.

To probe whether anion and cation effects occur independently, Th(IV) sorption was studied in the presence of LiCl and KCl ([Th] = 0.1 mM, pH = 3.3, I = 0.1 M) using the surface X-ray diffraction techniques crystal truncation rod (CTR) diffraction and resonant anomalous X-ray reflectivity (RAXR). The findings show strong uptake at the muscovite basal plane in both cases, exceeding the surface occupancy previously described in NaCl media,[3] thus confirming that the cation effect is indeed independent of the background electrolyte's anion.

To elucidate whether the observed differences occur, when oligomers are present before introduction of the mineral surface, we studied the uptake behavior of Zr(IV). Zr(IV) has a much more pronounced hydrolysis, and similar subsequent formation of oligomers and nanoparticles compared to Th(IV). The interfacial structure of muscovite was characterized in contact with Zr(IV) in solutions of various background electrolytes MCl (M = Li–Cs, [Zr] = 0.1 mM; pH 2.5, I = 0.1 M). In parallel, we performed AFM to characterize the morphology of any particles found on the mineral surface. The results clearly show that only small differences are induced by the electrolyte composition, which are generally well explained by the alkali cations sorption affinity and speciation at the muscovite (001) basal plane. Apparently, the background electrolyte effect is suppressed (or not effective at all) when the initial speciation of the metal is as small oligomers, indicating that the effects observed for Th(IV) occur at the water/mineral interface, and not in solution.

(1) Geckeis, H.; Lützenkirchen, J.; Polly, R.; Rabung, T.; Schmidt, M., *Chem. Rev.* 2013, 113, 1016-1062.

(2) Schmidt, M.; Hellebrandt, S.; Knope, K. E.; Lee, S. S.; Stubbs, J. E.; Eng, P. J.; Soderholm, L.; Fenter, P., *Geochim. Cosmochim. Acta* 2015, 165, 280-293.

(3) Schmidt, M.; Lee, S. S.; Wilson, R. E.; Soderholm, L.; Fenter, P., *Geochim. Cosmochim. Acta* 2012, 88, 66-76.

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