

Mineral-water interface reactions of actinides – all mechanisms understood?

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Behavior of actinides in aquifer systems is significantly influenced by mineral-water interface reactions. Central to sorption modeling approaches to describe such reactions is the assumption of molecular entities of well defined structure forming at mineral surfaces.

Over the last years our insight into actual surface speciation and sorption processes has significantly widened by combining batch sorption experiments and geochemical modeling with state-of-the-art spectroscopic and quantum chemistry approaches [1]. Respective studies reveal that even at well defined mineral surfaces, inner-sphere sorbed actinide ions very often cannot be attributed to just one single well defined molecular structure. Spectroscopic and theoretical studies reveal that the actinide ion is rather located in various slightly variable ligand field environments (see e.g.[2]).

Reduction of redox sensitive actinide ions (U, Pu, Np) to poorly soluble species is well known at the reducing conditions of subsurface aquifers. Recent experimental studies show that reduction of Np(V) can also be thermodynamically favoured in solutions at relatively high Eh. Fe(II) fixed in the structure of e.g. clay minerals apparently accelerates reactions by surface induced reduction [3].

Beside formation of pure surface species, incorporation into mineral structures appears to be a common reaction for radionuclides with a variety of minerals (e.g. calcite, calcium silicate hydrates etc.). While spectroscopic evidences for such type of reactions (surface solid-solution formation, entrapment) are available, the exact quantification for given geochemical conditions remains a challenge. This, however, is a prerequisite to assess the relevance of such reactions.

The talk will describe recent achievements in elucidating sorption reactions and discuss open questions.

[1] Geckeis, H., Lützenkirchen, J., Polly, R., Rabung, Th., Schmidt, M. (2013), *Chem. Rev.* **113**, 1016-1062 [2] Polly, R., Schimmelpfennig, B., Rabung, T., Flörsheimer, M., Klenze, R., Geckeis, H. (2010), *Radiochim. Acta*, **98**, 627-634 [3] Marsac, R., Banik, N., *et al* (2014), in preparation