Combined ab initio and XAFS spectroscopy study on the characteristics of metal uptake by clay minerals

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The high sorption capability of clay minerals is extensively used in various concepts for the geological disposal of high level radioactive wastes (HLW). In the Swiss concept for HLW disposal sites, the vitrified HLW will be encapsulated into thick walled steel disposal casks surrounded by compacted bentonite. Due to the corrosion of the steel container in the post-closure period, large quantities of Fe will be dissolved. After the fail of the disposal casks, groundwater will reach the HLW and radionuclides (e.g. U) will begin to slowly dissolve. Radionuclides will be released into the engineered barrier system then subsequently into the host rock. It has experimentally been shown that the presence of Fe(II) reduces the uptake of other radionuclides (e.g. uranium) at clay minerals due to sorption competition [1]. Additionally, the sorption of Fe at the edge sites of clay minerals can substantially be enhanced by structural Fe(III) due to redox processes. It has been demonstrated that the combination of X-ray absorption fine structure (XAFS) spectroscopy and atomistic simulations is the most promising approach to investigate such a highly heterogeneous environmental systems on the molecular level [2,3]. Molecular simulations based on density functional theory (DFT) are suitable to ascertain the preferential occupation sites of the clay particles and to serve as the basis for the XAFS data analysis [2,3]. The data analysis of the XAFS spectra allow in the best cases determining the nature of the surface complexes formed at clay mineral edge sites. In this study, the U and Fe sorption mechanisms on clay minerals were investigated. The results suggested that Fe(II)/Fe(III) valence interchange occurs between the Fe atoms absorbed on the surface and incorporated structurally into the bulk [3].

[1] Soltermann et al., *ES&T.*, 48(1), 190-198
[2] Churakov, Dähn, *ES&T.*, 46(11), 5713-5719
[3] Kéri et al., *ES&T.*, 51(18), 10585-10594