Speciation of actinides in environmentally relevant systems by advanced synchrotron techniques

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The disposal in deep geological repositories is a widely considered option for the management of spent nuclear fuel (SNF). SNF consists mainly of actinides (An): uranium (U), minor An and fission products which are potentially released from the SNF and may migrate then into the geologic environment. Such scenario depends on the stability of the SNF matrix and engineered geological barriers, as well as from the groundwater conditions at the disposal site. The versatile chemistry of An with their complex interaction and their low content in the natural environments require highly sensitive and non-destructive techniques for speciation and structural characterization.

We report a systematic application of X-ray absorption spectroscopies (XAS) measured at U L_3 and M_4 edges in the high-energy resolution flurloresce detected (HERFD) mode for the investigation of complex U systems. Here reported systems include U interaction with magnetite nanoparticles in laboratory systems and U speciation in the granite fracture coating from 86 m depth profile of the Forsmark investigation site. U M_4 HERFD-XAS clearly distinguishes U(IV), U(V) and U(VI) existing simultaneously in the same sample. U(V) is the main species formed and stabilized in the structure of magnetite at environmentally relevant U concentrations even when exposed on air for several hundred days. U L_3 HERFD-XAS analysis of the granite shows that a mixed U oxide with composition close to U_4O_9 is formed on the surface of material. This finding agrees with reducing conditions for the investigated depth profile. U_4O_9 may have varying content of U(IV), U(V) and U(VI) depending on chemical conditions and spectra analysis. XAS shows that up to 28% of total U can be present in U_4O_9 as U(VI). Sequential leaching of granite results in 24% of soluble U, preferably as U(VI), supporting preliminary XAS results. Based on the spectroscopic analysis and available chemical data structural and redox transformation pathways are proposed.