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Micro-scale investigations of U(VI) immobilization by cementitious materials

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Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of low- and intermediate-level radioactive waste. Cement is used to condition the waste materials and for the construction of the engineered barrier system (container, backfill and liner materials) in deep geological repositories. The cementitious near field is subject to chemical alteration processes due to the interaction of cement with groundwater infiltrating from the host rock. A molecular-level understanding of the interaction of radionuclides with cement improves long-term predictions of radionuclide retention in cement-based repositories with regards to influences of the heterogeneity of the cement matrix and the chemical evolution of the cementitious near field with time caused by cement degradation.

In this study the speciation of U(VI), which is the dominant oxidation state under oxidizing and slightly reducing conditions in cementitious environments, was investigated by a combination of wet chemistry and synchrotron-based (micro-)spectroscopic and micro-diffraction techniques. Wet chemistry experiments were carried out to quantify U(VI) uptake by cement. Sorption isotherm measurements enabled us to distinguish U(VI) retention by sorption from solubility-controlled effects. Complementary to wet chemistry experiments, we carried out synchrotron-based X-ray absorption spectroscopy (XAS) studies on U(VI) doped crushed cementitious materials (bulk-XAS) and micro-X-ray fluorescence (micro-XRF), micro-XAS and micro-diffraction studies (micro-XRD) on U(VI) doped compact hardened cement pastes (HCP) to obtain information on the U(VI) speciation on the molecular level. Micro-scale studies provided structural information on U(VI) binding mechanisms which are essential for the development of thermodynamic models of U(VI) uptake by cementitious materials. To the best of our knowledge, the combined use of bulk-XAS, micro-XAS and micro-XRD techniques for speciation studies on U(VI) doped HCP materials is novel.

The synchrotron-based studies showed that in the cement samples with low U(VI) concentration, i.e., in the linear range of U(VI) sorption, U(VI) was predominantly bound onto calcium silicate hydrates (C-S-H). The latter phases are among the most important cement phases governing immobilization processes. The coordination environment of U(VI) was found to resemble that of U(VI) in uranyl silicate minerals under these conditions. At high U(VI) loadings, however, where U(VI) immobilization is controlled by a solubility-limiting process, a second U(VI) species was observed in addition to uranyl-silicate-like U(VI) coordination. The coordination environment of this species was similar to that of U(VI) in Ca-uranate.

This study demonstrates that C-S-H are the uptake-controlling phase for U(VI) in HCP. This finding, in combination with the observed long-term existence of C-S-H phases in an evolving cementitious near field, implies that safe disposal of U(VI) in a cement-based repository should be possible over a very long period of time.

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