

Immobilisation of hexavalent actinides in cementitious materials: Evidence for structural incorporation in calcium-silicate-hydrates

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Abstract

Cementitious materials are an important component of the multi-barrier concepts developed in many countries for the safe disposal of low and intermediate level radioactive waste in deep geological repositories. Studies of the retention of radionuclides by cementitious materials have focused predominantly on adsorption as the relevant uptake process. However, other immobilization processes, such as incorporation in the solid matrix, may take place and, thus, exert a beneficial effect on radionuclide retardation. Calcium silicate hydrates (C-S-H), the major cement constituent, are characterized by high recrystallisation rates making them an ideal system for the incorporation of radionuclides present in cement-based repositories.

In the present study, wet chemistry and luminescence spectroscopy experiments have been performed under high pH conditions, with the aim of determining the speciation of hexavalent actinides (An(VI)), U(VI) and Np(VI), in C-S-H. Batch sorption experiments have been carried out with C-S-H and titanium dioxide, a solid phase stable under high pH conditions and often used as a model material for surface complexation studies. Comparison of the sorption of U(VI) and Np(VI) on both solids allows the influence of incorporation processes on the immobilisation of hexavalent actinides by C-S-H to be determined.

The An(VI) sorption behaviour on TiO₂ and on C-S-H phases appeared to be nearly identical; R_d values were found to decrease with the increasing predominance of negatively charged species in the aqueous phase suggesting the weaker sorption of these actinyl anions. Uranyl-doped C-S-H exhibited inhomogeneously broadened luminescence bands following non-selective laser excitation at liquid helium temperature (4K). Luminescence spectra following selective resonant laser excitation showed these broad band structures to consist of a superposition of many overlapping narrower bands associated with slightly different non-interacting uranyl luminescence centers in a disordered environment indicating incorporation in the amorphous C-S-H structure. The characteristics of the luminescence spectra provided information on the local coordination geometry of the incorporated uranyl moiety leading to the conclusion that it is incorporated in the C-S-H interlayers. The study shows that, under high pH conditions, the wet chemical behaviour (pH dependence and effect of aqueous Ca concentration) is similar for An(VI) incorporated in the interlayers of C-S-H and uranyl bound on the surface of TiO₂.