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Modelling uranyl adsorption to quartz – application of the CD-MUSIC concept

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Within the NEA-adsorption forum one test case concerned uranyl adsorption to quartz (MINUSIL). This contribution presents a refinement of previous modelling attempts on this test case. The refinements are done with a coupling of FITEQL2.1 as speciation code with the fitting program UCODE. The data were modelled using a charge distribution multisite complexation approach. First, the quartz acid-base properties were modelled with a one-site basic Stern model using a stability constant for the deprotonated silanol groups (site density 4.6 sites/nm²) as predicted by the bond valence principle. The Stern layer capacity and one electrolyte binding constant were fitted. These parameters were fixed for the modelling of the uranyl adsorption data. Data covered different carbon dioxide partial pressures and the presence of fluoride. It was assumed that in the pH-range of uranyl adsorption neither carbonate nor fluoride adsorbed to quartz in the absence of uranyl, although they might adsorb in terms of ternary silanol-uranyl-anion surface complexes.

The structure of possible uranyl surface complexes was based on literature on molecular scale information. Thus a bidentate inner-sphere surface complex was involved, which had been observed *via* surface spectroscopy. Additionally, outer-sphere complexes found in molecular modelling were tested and found to improve the model compared to the absence of such complexes. Preliminary tests applied ideal charge distribution for the uranyl surface complexes based on the bond valence principle. Further refinement was possible using charge distribution coefficients as adjustable parameters as optimised by UCODE.

The modelling attempts show that it is possible to involve molecular scale information in modelling macroscopic adsorption data within a comprehensive surface complexation model and obtain a good description of those data.

Furthermore, the use of UCODE as a fitting routine shell combined with a flexible speciation code provides new possibilities in surface complexation modelling compared to FITEQL: Thus, it is possible to optimise on any parameter and to define relations between parameters. However, it is stressed that this combination neither should be used as a black box nor that important information such as parameter correlations should be neglected in the interpretation of the results.

Future, options of UCODE may encompass uncertainty analysis and relatively easy access to sensitivity analyses.

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Interactions of actinides with hydroxyaluminosilicate colloids in “*statu nascendi*”

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The formation of hydroxyaluminosilicate (HAS) colloids under near natural aquifer conditions and the incorporation of trivalent actinides in their oxo-bridged structure are studied. Colloid-borne actinides undergo migration in natural aquifer systems with little geo-chemical hindrance increasing the mobility of actinides. Hydroxyaluminosilicate (HAS) colloids are generated by heterogeneous nucleation in presence of trace amounts of trivalent actinides (Cm(III) and Am(III)). Two sets of experiments are presented using monomeric or oligomeric Si species and various Al concentrations for coprecipitation. The colloids are characterized by laser-induced breakdown detection (LIBD), AFM, EDX, and XPS. The particle size of colloids is in the range of 10 nm – 50 nm with a mass concentration of 10 – 50 ppb and a Si/Al ratio of 0.7-1.0.

For speciation of the colloid-borne Cm(III), the nucleation process is investigated by time-resolved laser fluorescence spectroscopy (TRLFS) with the assistance of radiometry. Spectroscopic speciation shows that coprecipitation with monomeric silicate leads to the formation of two colloid-borne Cm species, Cm-HAS(I) with a peak maxima at 598.5 nm and Cm-HAS(II) at 601.8 nm. Using oligomeric Si-species, a third Cm(III) species with a peak maximum of 606.8 nm (Cm-HAS(III)) is formed for pH > 6.3. The long fluorescence lifetime ($\tau = 518.5 \mu\text{s}$) of the latter species proves that the Cm(III) has lost its primary hydration sphere and is imbedded into the molecular structure of the aluminosilicate colloids. Aging and tempering of the colloids formed by coprecipitation with monomeric silicate also result in a complete dehydration of Cm(III) and incorporation into HAS colloids. The stability of the colloids was studied by 2-D LIBD and TRLFS. Long-term measurements confirm the stability of the actinide containing HAS colloids under natural aquifer conditions (pH > 6). The present work gives new insights into the generation of colloid-borne actinide(III) in the near and/or far field of a given nuclear waste repository, which thus facilitates the actinide(III) migration.