

Sorption and incorporation of radionuclides at mineral surfaces studied with quantum chemical methods

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The reliable long-term prediction of actinide migration in geological formations requires understanding of the adsorption/desorption and incorporation mechanism at the molecular level. The sorption and incorporation of metal ions at mineral surfaces is a very important process which leads to the retention/retardation of radionuclides such as actinide ions and fission products.

We present three different investigations in this talk: (1) the interaction of trivalent lanthanides and actinides with the solvated corundum (110) surface, (2) interaction of selenite with the hydrated calcite surface and (3) the incorporation of trivalent lanthanides and actinides in calcite. Study (1) is carried out with orbital based ab initio and DFT methods using TURBOMOLE, whereas (2) and (3) with plane-wave DFT, as implemented in the Vienna Ab initio Simulation Package (VASP).

The corundum (110) surface is a challenging task for a theoretical investigation because singly, doubly and triply coordinated aluminol groups are present simultaneously. We used the $\text{Al}_{27}\text{O}_{75}\text{H}_{67}$ cluster in this study as a model system for the corundum (110) surface. In a first step, we determined the structure and deprotonation properties of this cluster and calculated the vibrational frequencies of the surface aluminol groups. These results are compared with experimental data to validate our cluster model. In a second step we determined the structure of the inner-sphere complexes of the trivalent lanthanides and actinides at the surface. Various multidentate surface bound inner-sphere complexes are found to predominate. They are characterized and compared with experimental results.

Se-79 is a fission product of U-235 with a long radioactive half life of 1.1×10^6 years. Selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) interact only weakly with common mineral surfaces. Therefore they have been identified as crucial radio nuclides for long term safety assessments of nuclear waste disposal. We determined the structure of the water/calcite interface and identified surface sorbed and incorporated selenite species at the calcite/solution interface.

The last point tackles the incorporation of trivalent lanthanides and actinides into calcite. Earlier spectroscopic investigations suggest incorporation of lanthanide/actinide ions occupying Ca-sites in the calcite lattice. Charge compensation is achieved by the substitution of two Ca atoms by one trivalent lanthanide/actinide and one Na ion. Here, we studied modifications of the calcite structure induced by the substitution.