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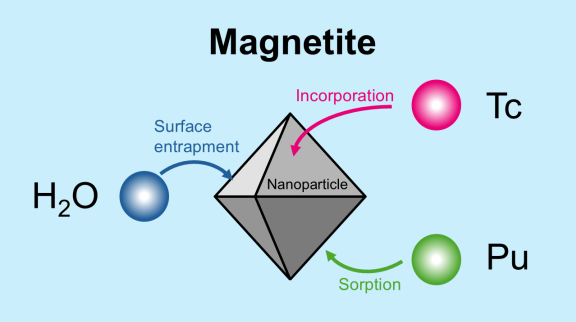

Insights in magnetite-radionuclide interactions: Combining theoretical and experimental techniques

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In many European countries (e.g., France, Switzerland), thick steel casks are foreseen for the containment of high-level radioactive waste in deep geological repositories. In contact with pore-water, steel corrodes forming mixed iron oxides, mainly magnetite (Fe_3O_4). After tens of thousands of years, the casks may breach allowing for leaching of the radionuclides (e.g., Tc and Pu) into pore-water. The radionuclides can be retarded by corrosion products either by adsorption or via structural incorporation [1,2]. The molecular scale mechanisms of these phenomena are investigated by ab initio simulations and X-ray absorption spectroscopy (XAS).

The dominant low-index surfaces of magnetite particles and their termination at the relevant conditions were identified based on density functional theory (DFT). The DFT+U method was employed for the strongly correlated 3d- and 5f- electrons of Fe and Pu, respectively. After benchmarking the model setup, the surface energies of the (111) facet with different surface terminations and water coverage were analysed as a function of redox conditions and pH. The Eh and pH predominance diagram was used to predict the most stable mineral surfaces under real repository conditions [3]. Further, the stability of 2 nm sized nanocrystals was evaluated. Subsequently, ab initio molecular dynamics (MD) were applied to simulate sorption structures of radionuclides on the expected magnetite (111) surfaces based on experimental findings [2,4].

Complementary, wet-chemical batch sorption experiments of magnetite nanocrystals in the presence of Tc or Pu were conducted. The resulting complexes represent the expected incorporation and sorption structures [1,2,4] and were analysed by the XAS techniques (EXAFS, XANES). The synergy of the experimental and theoretical studies contributes to the understanding of the retention mechanism of radionuclides in deep geological repositories.

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