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Speciation of uranium sorbed on magnetite/maghemite nanoparticles: HR-XANES and «ab-initio» calculations

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Deep understanding of mobilization/immobilization mechanisms of uranium in the environment is essential for safety assessment of a long-term nuclear waste repository. For example the soluble in groundwater U(VI) can be immobilized by sorption or incorporation into minerals [1]. Iron oxide nanoparticles are abundant in the environment and play a major role in sorption and redox behavior of U. Magnetite (Fe_3O_4) is a ferrous bearing oxide and a corrosion product of steel used in storage containers of nuclear waste.

High-energy resolution X-ray absorption near edge structure (HR-XANES) spectroscopy at the actinide (An) L3 and M4,5 edges is currently developing technique providing new insights into the An electronic and coordination structure [2,3]. We present the U L3/M4 HR-XANES experimental spectra of U sorbed on magnetite or maghemite (U-magnetite, U-maghemite) nanoparticles and U M4 HR-XANES spectra of UO_3 , meta-autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$) and torbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$). The HR-XANES spectra are analyzed on the basis of theoretical simulations to investigate local coordination structure of U in the magnetite/maghemite nanoparticles. Theoretical spectra are calculated by applying a self-consistent field (SCF) full multiple scattering (FMS) method implemented in the FEFF9.6 code [4]. Phase shifts of the photoelectron are calculated in the framework of self-consistent crystal muffin-tin (MT) potential scheme with 15% overlapping MT spheres. Best agreement of energy positions and intensities of spectral features between theoretical and experimental spectra is achieved for spectra calculated with the Hedin-Lundquist potential with non-screened core-hole (final state rule). FMS calculations of U L3-edge HR-XANES spectra of the U-magnetite and U-maghemite nanoparticles is performed for two types of substitution, i.e., uranium replaces iron in octahedral or tetrahedral sites. Comparison of experimental and theoretical spectra suggest that U is incorporated in octahedral magnetite sites for the specific experimental conditions. The FEFF9.6 program is found to be an adequate tool for analysis of U L3-edge and M4,5 edges HR-XANES of U containing compounds.

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