



Contribution ID: 41

Type: Poster

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

Tuesday 20 May 2014 17:30 (4h 30m)

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.

Acknowledgments

This work is supported by the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DADD)(Project P-2014a-1).

References

- [1] Riley, R. G.; Zachara, J. M. Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research; U.S. Department of Energy, Office of Energy Research: Washington, DC, 1992.
- [2] Vitova T et al. 2010 PRB 82 235118
- [3] Kvashnina K O, Butorin S M and Glatzel P 2011 J. Anal. At. Spectrom. 26 1265
- [4] JRehr J J, Kas J J, Prange M P, Sorini A P, Takimoto Y and Vila F 2009 C. R. Physique 10 548 59

Primary author: PODKOVYRINA, Yulia (Southern Federal University)

Co-authors: Prof. SOLDATOV, Alexander (Southern Federal University); Mr PIDCHENKO, Ivan (Institute for Nuclear Waste Disposal); Dr KVASHNINA, Kristina (European Synchrotron Radiation Facility); Mr PRUESS-MANN, Tim (Karlsruhe Institute of Technology); Dr VITOVA, Tonya (Karlsruhe Institute of Technology)

Presenter: PODKOVYRINA, Yulia (Southern Federal University)

Session Classification: Poster

Track Classification: Theoretical and Modeling Tools