

## Uranium dioxide oxidation and behavior under hydrothermal conditions

Kalmykov Stepan<sup>1</sup>, Batuk Olga<sup>1</sup>, Zakharova Elena<sup>2</sup>

<sup>1</sup>Chemistry department of Lomonosov Moscow State University, Moscow, Russia

<sup>2</sup>Frumkin Institute of Physical and Electrochemistry RAS, Moscow, Russia

*The oxidation behavior of UO<sub>2</sub> in hydrothermal conditions and changes in its local structure were studied by various spectroscopic and microscopic techniques. It was established that two competitive processes occur in hydrothermal conditions – bulk UO<sub>2</sub> oxidation and formation of secondary phases.*

*Keywords – uranium dioxide, oxidation, XAFS, neutron diffraction, TEM-SAED*

The study of UO<sub>2</sub> behavior in aqueous solutions under oxidizing conditions is important to predict and model its behavior under reactor and repository conditions. Earlier the mechanism of UO<sub>2</sub> oxidation to U<sub>4</sub>O<sub>9</sub> was studied by various methods but controversial results were obtained from comparison of XAFS and neutron diffraction data [1-3]. Short U-O bond at 1.7-1.8 Å typical for uranyl moiety was found in EXAFS spectrum while it contradicts with neutron diffraction data that indicate the formation of oxygen superstructure in fluorite lattice of UO<sub>2+x</sub>. In this paper we study wet hydrothermal oxidation of UO<sub>2+x</sub> under 70 °C and 150 °C in oxidizing conditions. The obtained samples collected in the course of the experiment were analyzed by various techniques including XAFS, neutron diffraction, Raman spectroscopy, HR-TEM and SAED.

The difference in kinetics of oxidation of uranium dioxide at 70 °C and 150 °C was established. For the sample leached at 70 °C rather fast bulk oxidation up to UO<sub>2.25</sub> (U<sub>4</sub>O<sub>9</sub>) occurred within 1.5 months with almost no secondary phase formation as demonstrated by XRD and scanning electron microscopy. At 150°C the intensive secondary phase formation occurred while the bulk oxidation was slowed down – the UO<sub>2.25</sub> composition was reached within 4 months. Secondary uranium phases were needle-shape crystals and did not contain Na, K and Ca from background electrolyte as determined by EDX. The surface of both samples was characterized at the nano-scale by HR-TEM and SAED. The uranium dioxide sample leached at 70 °C kept its cubic structure, while for sample leached at 150 °C the surface was completely covered by nanoparticles of secondary phases that were identified as schoepite nano-crystals according to SAED. Formation of such nanoparticles prevents subsequent bulk oxidation of uranium dioxide due to significant difference in diffusion coefficients of oxygen for different crystalline structure types.

The local structure of actinides in samples was studied by X-ray absorption spectroscopy (XANES/EXAFS) at U L<sub>III</sub> edge was performed in Novosibirsk Centre of Synchrotron Radiation. No significant changes in XANES spectra of

leached samples were observed compare to the initial sample. The EXAFS regime is more sensitive for speciation of tetravalent actinide - actinyl ion mixtures from the short axial oxygen distance than is identification using the XANES resonance feature corresponding to multiple scattering along the axial oxygen atoms. The increase of axial U-O interactions was observed with increasing of leaching duration. The Debye-Waller factor also increased that indicates increasing of disorder in uranium dioxide upon leaching. Leaching time dependency of Debye-Waller factor was in a good agreement with changes of lattice parameter determined by XRD.

Samples collected in the course of sample oxidation at 70 °C (in the range UO<sub>2.002</sub> to UO<sub>2.25</sub>) were used to study local structure of UO<sub>2+x</sub>. The calculated lattice parameter from XRD examination decreased with increasing of oxygen content in the samples that well agreed with previously published data.

The examination of UO<sub>2+x</sub> samples by neutron diffraction method is sensitive to the light oxygen sublattice. The intensities of reflexes in neutron diffraction spectra of more oxidized samples are decreased, that could be interpreted by the formation of oxygen superstructure and also by the disorder of oxygen lattice.

No significant differences in the XANES spectra for studied UO<sub>2+x</sub> samples were found. No multiple scattering resonance typical for uranyl moiety (appearing as a shoulder around 10-15 eV above the white line absorption maximum) was observed in the spectra, even for rather oxidized samples with U(VI) content of about 25%. However, the Fourier transformed EXAFS spectra that are more sensitive to the mixture of valence states indicate the presence of two metal-oxygen distances. Such split in oxygen coordination is characteristic for axial and equatorial oxygen atoms comprising uranyl cation coordination polyhedra. The short distance in EXAFS spectra can be modeled using a typical uranyl distance and physically reasonable values for coordination number and the Debye-Waller factor. This may indicate that the interstitial oxygen atoms introduced into the lattice upon UO<sub>2</sub> oxidation lie closer to the uranium atoms than the shortest U-O distance in non-stoichiometric phases.

The work was supported by ISTC (project 3720) and Russian Federal Agency for Science and Innovation (project 02.516.11.6138).

[1] N. Masaki and K. Doi, Acta Cryst., B28, 728, 1972

[2] R.I. Cooper and B.T.M. Willis, Acta Cryst., A60, 322, 2004

[3] S.D. Conradson, Inorg. Chem., 43, 6922, 2004