

	<b>Experiment title:</b> High energy resolution X-ray absorption valence state and electronic structure investigation of uranyl magnetite nanoparticles	<b>Experiment number:</b> <b>EC-743</b>
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 2.02.2011 to: 8.02.2011	<b>Date of report:</b> 11.04.2011
<b>Shifts:</b> 18	<b>Local contact(s):</b> Kristina Kvashnina	<i>Received at ESRF:</i>
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### Report:

Heterogeneous reduction of  $U^{6+}$  to  $U^{4+}$  by ferrous iron is believed to be a key process influencing the fate and transport of U in the environment. The reactivity of both sorbed and structural  $Fe^{2+}$  has been studied for numerous substrates, including magnetite. Varying results have been published for experiments with  $U^{6+}$ -magnetite (regular crystal size) and  $U^{6+}$ -magnetite nanoparticles [1], ranging from partial reduction [2] to formation of a ~3nm thick  $UO_2$  surface layer [3]. More recently, Ilton and co-workers [4] found evidence for  $U^{6+}$  reduction to  $U^{5+}$ , with no evidence of  $U^{4+}$ , which is in contradiction to thermodynamic calculations. This implies that the system was not in redox equilibrium so that sorbed  $U^{5+}$  was stable for at least up to 56 days and points to the potential influence of redox kinetics.

The main motivation for our work on uranyl magnetite nanoparticle interaction presented here is to answer the following: 1) Is U(V) really formed and will it be transformed to U(IV), i.e., can we continue to employ thermodynamic calculations based on the independently measured pe/pH conditions presently in use or do we need new thermodynamic data? 2) Can we describe the kinetics involved? We employ U L3 edge high energy resolution X-ray absorption near edge structure (HR-XANES), also called partial fluorescence yield XANES (PFY-XANES), to clarify these questions.

### Experimental details:

The U L3 PFY-XANES for six samples of U sorbed onto magnetite and maghemite nanoparticles, freshly prepared under anoxic conditions at different pH conditions (5, 8 and 11 in 0.01 M NaCl), and for tetra-, penta- and hexavalent U reference materials  $\{U^{4+} (UO_2); U^{5+} ([UO_2Py_5][KI_2Py_2]); U^{6+} (\text{autunite: } Ca(UO_2)_2(PO_4)_2 \cdot 10-12(H_2O), \text{ weeksite: } K_2(UO_2)_2(Si_6O_{15}) \cdot 4H_2O \text{ and schroeckingerite: } NaCa_3(UO_2)(CO_3)_3(SO_4)F \cdot 10H_2O)\}$  were recorded at the ID26 beamline at the ESRF, Grenoble. During the experiment, the synchrotron radiation was monochromatized by a Si(311) double crystal monochromator. The experimental energy resolution was about 1.8 eV, which is the width of the quasi-elastic peak scattered by a Si wafer. The energy of the primary monochromator was scanned from 17155 to 17180 eV with 0.1 eV

step width over the U L3 edge (17166 eV). For each excitation energy, the emitted photons from the sample were monochromatized by three spherically bent Ge(777) analyzer crystals and focused on an avalanche photodiode as detector. The sample, crystal and detector were positioned on a circle (Rowland geometry) with 1m diameter, equal to the bending radius of the crystals.

## Results and discussion:

Results from a standard U L3 edge XANES comparative study of references with different U oxidation states and U magnetite nanoparticles previously performed at the INE-Beamline at ANKA, Germany, were inconclusive [5]. The large core-hole lifetime broadening of the U 2p state (>7 eV), yielding broad spectral features, prevented unambiguously distinguishing between the different oxidation states in the XANES of the U-magnetite nanoparticles. In the present investigation, we suppressed the core-hole lifetime broadening by measuring PFY-XANES, thereby improving energy resolution and sharpening spectral features [6]. The U L3 edge PFY-XANES spectra of the U-magnetite(mag)/maghemite(magh) nanoparticles are shown in Fig. 1 A/B. The U\_mag\_pH8 spectrum shows broadening of the white line (the most intense resonance, WL; see Fig. 1 A). The U\_magh\_pH5, 8, 11 spectra all exhibit similar spectra, with only variations in WL intensity (see Fig. 1 B). The spectra of both pH5 samples have reduced signal-to-noise ratios, indicating having relatively less sorbed U. Representatives of the general two types of spectra observed, U\_mag\_pH8 and U\_magh\_pH11, are compared to U<sup>4+</sup> and U<sup>5+</sup> and U<sup>6+</sup> reference spectra in Fig. 1 C and D. The WL for the U\_mag\_pH8 sample resembles the broad WL exhibited by the U<sup>4+</sup> reference; however, its energy position coincides with the WL energies of the spectra for U\_magh\_pH11 and the U<sup>6+</sup> references. The broad energy distribution of 6d states, leading to the WL broadening, combined with the observed WL energy position, suggests that a U<sup>4+</sup> and U<sup>6+</sup> mixture is present in the U\_mag\_pH8 sample. The similarity of the other U-magnetite/maghemite nanoparticle spectra with the U<sup>6+</sup> reference PFY-XANES indicates that these samples contain predominantly U<sup>6+</sup>. The fact that the PFY-XANES features of the U<sup>5+</sup> reference spectrum differ from those of the U-nanoparticle spectra, notably its lower energy position, is a clear indication that no U<sup>5+</sup> oxidation state species is present in any of the samples. We conclude that this advanced spectroscopic study allows us to exclude the presence of U<sup>5+</sup> in the investigated set of U-magnetite/maghemite nanoparticles, in contrast to results reported in [4]. If U<sup>5+</sup> species were at all formed, the kinetics of the redox reaction leading to its formation must be faster than a few days timescale, which is again in contrast to results in [4].

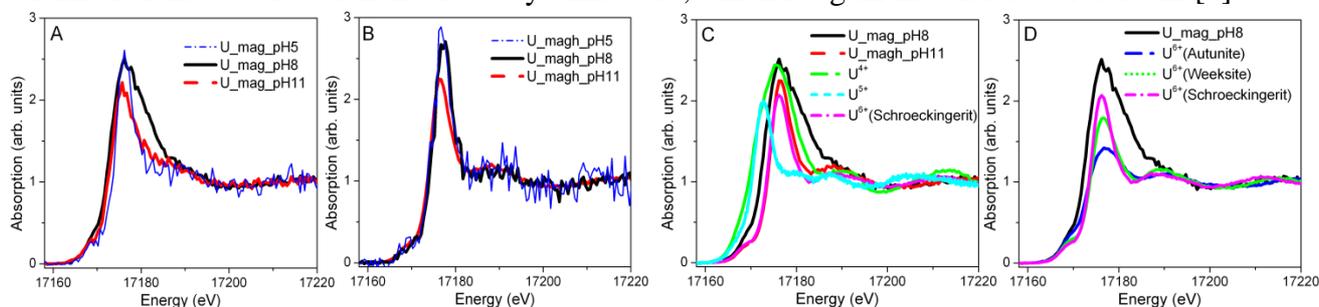


Fig. 1: The U L3 edge PFY-XANES spectra of U magnetite/maghemite nanoparticles for pH 5, 8 and 11 (A/B) and U\_mag\_pH8 and U\_magh\_pH11 compared with reference materials (C and D).

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## Acknowledgement:

We gratefully acknowledge ESRF for the provided beamtime and Kristina Kvashnina for the support during the experiment.