

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.


Experiment title:

Investigation of uranium and iron speciation in U-magnetite nanoparticles by high energy resolution X-Ray absorption near edge structure spectroscopy

Experiment
number:

EV-64

Beamline: ID26	Date of experiment: from: 18.06.2014 to: 23.06.2014	Date of report: 3.12.2014
Shifts: 18	Local contact(s): Kristina Kvashnina	<i>Received at ESRF:</i>

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Report:

Long-term storage of high-level radioactive waste (HLW) might lead to radioecological hazards. One of the elements under potential interest is uranium (U), which most often occurs in the environment as highly mobile U^{VI} and sparingly soluble U^{IV} form. It is believed that the main inorganic reducing agent for U^{VI} in the environment is ferrous iron dissolved from natural magnetite. Results published from laboratory experiments for interaction of U^{IV} with magnetite particles are very different. They show partial reduction^[1,2] of U^{VI} or the formation of a ~3 nm UO_2 particles on the surface layer^[3]. More recently, the evidence for U^{VI} reduction to intermediate U^V state was found with no direct evidence of U^{IV} state, which is in contradiction with thermodynamic calculations^[4]. The goal of this research work on the interaction of U with magnetite nanoparticle presented here is: 1) to verify the presence of U^V ion state in the system; U^V is thermodynamically relatively stable only within a narrow Eh-pH region, but might be stabilized on the surface of the nanoparticles, 2) to quantify the amount of reduced U^{VI} to U^{IV} state for different interaction times (from 7 to 175 day). We have performed U M_4 edge high-energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) spectroscopy of U in different U-magnetite systems to clarify these questions.

Experimental Details:

We performed U M_4 edge HERFD-XANES spectroscopy measurements of U in three different U-magnetite systems: U sorbed on the magnetite nanoparticles in a mixed flow reactor (MFR) conditions (1 sample); U sorbed on the magnetite/maghemite nanoparticles in a static batch sorption conditions (7 samples); U coprecipitated with magnetite (8 samples) and U oxidation state references: UO_2 (U^{IV}), U_4O_9 (0.5 U^{IV} / 0.5 U^V), U_3O_8 (0.67 U^V / 0.33 U^{VI}), α -, β -, γ - UO_3 (U^{VI}) and U^{VI} -uranyl containing mineral phases: boltwoodite ($HK(UO_2)(SiO_4) \cdot 1.5H_2O$) and meta-schoepite ($UO_3 \cdot 1.5H_2O$). During the experiment, the synchrotron radiation was monochromatized by a Si(111) double crystal monochromator. The energy of the primary

monochromator was scanned from 3722 to 3735 eV with 0.1 eV step width over the U M₄ edge (3726 eV). For each excitation energy, the emitted photons from the sample were monochromatized by five spherically bent Si(220) analyzer crystals and focused on an Ketek detector. At sample points providing highest fluorescence intensity (50 counts/sec), 10 sec long scans were measured to minimize the X-ray induced radiation damage of the samples. 30 to 50 scans were collected for one sample at different sample spots.

Results and discussion:

U M₄ edge HR-XANES spectra of U^{VI} sorbed on magnetite after 3 days of operation of the mixed flow reactor ("3d U^{VI}-magn MFR"), U₄O₉ and meta-schoepite are plotted in **Figure 1**. The main features of the "3d U^{VI}-magn MFR" spectrum resemble closely those of the meta-schoepite spectrum typical for U^{VI}, uranyl type of bonding^[5,6]. However, the main peak is broader and it has approximately 0.1 eV energy shift (line C) towards peak B characteristic for U^V. Additionally, the position of peak E is shifted ~0.25 eV to higher energies (see line E'), suggesting slightly different U-O_{ax} bond length.

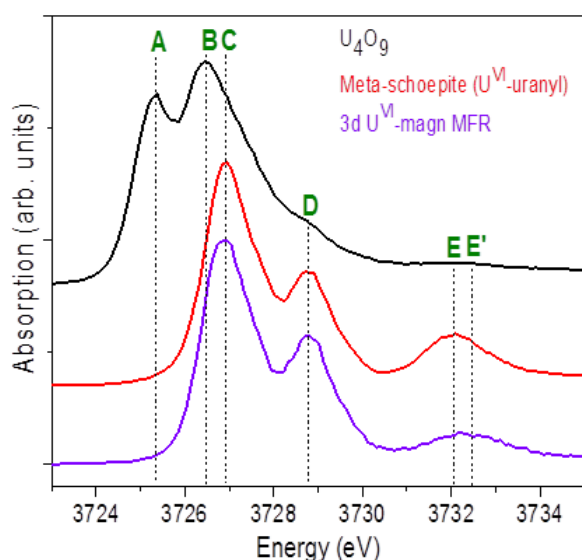


Figure 1: U M₄ edge HR-XANES spectra of the 3 days interacted U^{VI}-magnetite MFR sample, U₄O₉ and meta-schoepite.

The energy positions and shapes of the spectral features of the U M₄ edge HR-XANES spectra of 1-175 days interacted U^{VI} on the magnetite and 55 days U^{VI}-maghemite and boltwoodite (not shown here) are very similar, indicating that U has oxidation state U^{VI} and has formed uranyl type of bonding with axial O atoms in the 1-175 day U^{VI}-magnetite and 55 day U^{VI}-maghemite samples. However, the intensities of features D and E in the spectra of all U-magnetite samples are slightly reduced and there is about 0.2 eV energy shift towards the U^V peak (line B) compared to those of 55 day U-maghemite

and boltwoodite. These findings indicate U^V contribution in these samples. Maghemite and magnetite are isostructural, but maghemite does not contain Fe^{II} necessary for reduction of U^{VI}, therefore the spectrum of the 55 day U-maghemite sample can be considered as a reference spectrum for U^{VI} in U M₄ edge HR-XANES studies. In the spectra of U co-precipitated with magnetite (not shown here) absorption resonances A, B and D with variable intensities present in the spectra of all samples are characteristic for U^{IV}, U^V and U^{VI}-uranyl type of bonding, respectively. U^V has a dominant contribution, whereas the contributions of U^{IV} and U^{VI} vary in the spectra of the 1000-10000 ppm U-magnetite co-precipitated samples. We currently perform linear combination least squares fit analyses to evaluate quantitatively the contributions of the different U oxidation states.

References:

- [1]. Misana, T., et al., 2003, GCA, **67**, 2543-2550; [2]. Regenspurg, S., et al., 2009, Appl. Geochem., **24**, 1617-1625; [3]. Scott, T.B., et al., 2005, GCA, **69**, 5639-5646; [4]. Ilton, E.S., et al., 2010, Env. Sci. & Tech., **44**, 170-176.; [5]. Kvashnina, K., et al., 2013, Phys. Rev. Let., **111**, 25.
- [6]. Vitova, T., et al., 2014, Accepted for Inorg. Chem.

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