

## Aqueous U(VI) interaction with magnetite nanoparticles in a mixed flow reactor system: HR-XANES study

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**Abstract.** The redox variations and changes in local atomic environment of uranium (U) interacted with the magnetite nanoparticles were studied in a proof of principle experiment by the U L<sub>3</sub> and M<sub>4</sub> edges high energy resolution X-ray absorption near edge structure (HR-XANES) technique. We designed and applied a mixed flow reactor (MFR) set-up to maintain dynamic flow conditions during U-magnetite interactions. Formation of hydrolyzed, bi- and poly-nuclear U species were excluded by slow continuous injection of U(VI) (10<sup>-6</sup> M) and pH control integrated in the MFR set-up. The applied U HR-XANES technique is more sensitive to minor changes in the U redox states and bonding compared to the conventional XANES method. Major U(VI) contribution in uranyl type of bonding is found in the magnetite nanoparticles after three days operation time of the MFR. Indications for shortening of the U-O<sub>axial</sub> bond length for the magnetite compared to the maghemite system are present too.

### 1. Introduction

The safety assessment of long-term repositories for high-level radioactive waste (HLW) motivates speciation studies of actinides (An) and fission products in relevant systems. The element under particular interest is uranium (U), which occurs in the environment mainly as highly mobile U(VI) and sparingly soluble U(IV) form. Over long periods of time ground water might potentially enter the HLW repository, accelerating corrosion processes of steel containers. To model the U interaction mechanisms with one of the main iron corrosion products, magnetite, various laboratory experiments were performed mainly in static conditions. Such static experiments facilitate formation of secondary phases and might not be representative for potential dynamic conditions in a HLW repository. Up to date only one study is available on the interaction of U with magnetite in dynamic conditions coupled with conventional X-ray absorption fine structure (XAFS) investigations [1]. There are still open questions which need to be addressed: 1) What is the speciation of U after continuous redox and phase transformation processes induced by the interaction of U with magnetite; 2) Are the reduced U species long term stable; 3) Are these species incorporated in the vacancies created by the removal of Fe(II), which is favourable at about pH 5.5?

We present benchmark experiment with a mixed flow reactor (MFR) set-up designed for U(VI) interaction with magnetite nanoparticles in aqueous media. For the first time a combination of the U L<sub>3</sub> and U M<sub>4</sub> edge HR-XANES investigations is used to characterize the U oxidation states and the local atomic environment

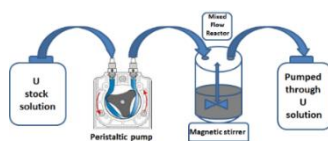


of U in such a system. Reduced core-hole lifetime broadening effects result in better resolved spectral features in the HR-XANES compared to conventional XANES spectra [2]. The method facilitates the detection of minor contributions of U redox states in mixtures. For example the U  $M_4$  edge HR-XANES was successfully applied to characterize U(V) in  $U_4O_9$  [3].

## 2. Experimental part

### 2.1. MFR experiment

A MFR set-up for continuous interaction of U(VI) with magnetite nanoparticles in aqueous suspension employed a 80 mL Plexiglas reactor equipped with a magnetic stirrer and 0.4  $\mu\text{m}$  Millipore filter to prevent loss of particles from suspension (see figure 1). 2 g/L magnetite suspension with pH 7.3 and ionic strength of 0.01 M NaCl was used. Three liters of U(VI) containing aqueous solution ( $[U]=1 \cdot 10^{-6}$  M, pH=5.5) were pumped continuously through the MFR during three days with the help of a Peristaltic pump. pH values were recorded before and after the experiment. Aliquots of aqueous solution after the reactor were sampled every day and the total U concentration was analyzed. The PHREEQC 2.18 code and the Nagra/PSI thermodynamic database [4] for geochemical modelling was used to estimate the U species in the initial U solution. After three days operational time of the MFR, an aliquot of the magnetite suspension was taken and dried in Ar atmosphere. The sample and the references were placed in a Plexiglas holder with two separated Polyethylene windows each with 10  $\mu\text{m}$  thickness. The samples were placed into a gas tight aluminum cylinder for transportation in anoxic conditions and opened shortly prior the HR-XANES measurements.



**Figure 1.** Scheme of the MFR set-up.

### 2.2. U $L_3/M_4$ HR-XANES experiments

The U  $L_3/M_4$  edge HR-XANES spectra of U(VI) interacted with magnetite after three days of operation of the MFR (MFR-3d),  $U_4O_9$  and U(VI) adsorbed on maghemite during 55 days (U(VI)-magh) samples were measured at the ID26 beamline at the European Synchrotron Radiation Facility (ESRF) [5]. The incident energy was monochromatized by a Si(111) double crystal monochromator (DCM) (U  $L_3$  17166 eV,  $M_4$  3728 eV). Rejection of higher harmonics was achieved by three Si mirrors at an angle of 3.5 mrad (for the U  $M_4$  edge experiment) and three Pd mirrors at an angle of 2.5 mrad (for the U  $L_3$  edge experiment) relative to the incident beam. The beam size was focused to  $\sim 0.150$  mm vertical and 0.450 mm horizontal size for the measurements at both absorption edges. XANES spectra were measured in high energy resolution fluorescence detection mode using an X-ray emission spectrometer [6]. The sample, analyzer crystal and silicon drift diode (SDD) were arranged in a vertical Rowland geometry. The U HR-XANES spectra at the  $M_4/L_3$  edges were obtained by recording the maximum intensity of the U  $L_{\alpha}/M_{\beta}$  emission lines. Ge(777) (U  $L_{\alpha 1}$  13618 eV) or the Si(220) (U  $M_{\beta}$  3337 eV) diffraction order of five spherically bent Ge/Si crystal analyzers with 1 m bending radius were used. The crystals were aligned at  $75^\circ$  and at  $77^\circ$  Bragg angles for U  $M_4$  and U  $L_3$  edges, respectively. The experimental energy resolution was  $\sim 2.6$  eV for the U  $L_3$  and  $\sim 0.7$  eV for the U  $M_4$  edge and was determined by measuring the full width at half maximum (FWHM) of the elastic peak. The paths of the incident and emitted X-rays through air were minimized in order to avoid losses in intensity due to absorption. Depending on the edge, from ten to forty four scans were measured for each sample. Samples were checked for the radiation damage by measuring a very fast scan (1 sec) with and without 200  $\mu\text{m}$  Al foil attenuating the beam intensity. For the U  $M_4$  edge changes in the spectral shape

were detected after 60 seconds of measuring time, therefore each XANES spectrum has been collected at the fresh sample spot; all spectra were normalized to the maximum absorption intensity.

### 3. Results and discussion

Before interaction with magnetite 90% of the aqueous U is in the form of not hydrolyzed U(VI) uranyl; less than 10% of hydrolyzed species and minor bi- and poly-nuclear hydroxide complexes contribute to the U aqueous solution as well, as predicted by PHREEQC calculations. The U concentration in the outgoing solution was  $5 \cdot 10^{-7}$  M, pH~5.8 validating that about 50% of the initial U was removed by the magnetite nanoparticles. It was demonstrated that at pH = 5.5 Fe(II) can be leached from the magnetite and can reduce U(VI) to U(IV)/U(V). These U(IV)/U(V) species might potentially incorporate in the octahedral Fe(II) vacancies in the magnetite structure [7]. Compared to a static batch sorption setup, the MFR set-up allows for better control of the pH, thereby precipitation of U phases is prevented. In addition, formation of secondary Fe(II) phases is avoided due to the fast Fe(II) removal from the MFR volume.

U  $M_4/L_3$  edge HR-XANES spectra of MFR-3d, U(VI)-magh and  $U_4O_9$  are plotted in figures 2a, a' and 2b, b'. The spectrum of  $U_4O_9$  contains two peaks with energy positions characteristic for U(IV) (line A) and U(V) (line B) [3]. The U(VI)-magh spectrum is used as U(VI) reference as there are no U redox changes occurring during U(VI) interaction with maghemite, having all Fe as Fe(III) but the same spinel ferrite structure as magnetite. The shape of the MFR-3d U  $M_4$  edge HR-XANES spectrum resembles closely that of the U(VI)-magh spectrum (figure 2a, 2a'). The main peak C in figure 2 has the same energy position in both spectra. The energy positions of peaks D and E shift to higher energies in the MFR-3d spectrum (see table 1). The peaks have been assigned to electronic transitions of  $3d_{3/2}$  electrons to  $5f\delta/5f\phi$  line C),  $5f\pi$  (line D) and  $5f\sigma$  (line E) unoccupied valence orbitals of U(VI) in the form of  $UO_2^{2+}$  (uranyl) [8]. The  $5f\sigma$  mainly mixture of U and O valence orbitals [8]. Therefore it is expected that peak E will be sensitive to variations of the U- $O_{axial}$  bond length correlated to the level of hybridization of those valence orbitals.

The position of peak E is shifted by  $\sim 0.2 \text{ eV} \pm 0.05 \text{ eV}$  to higher energies compared to U(VI)-magh implying shorter average U- $O_{axial}$  bond distance in the MFR-3d sample, compared to U(VI)-magh [9]. A likely explanation is that the shorter U- $O_{axial}$  bond length results from a stronger bonding of uranyl to the magnetite surface compared to maghemite. This is consistent with the observations made for An(III) adsorption on maghemite and magnetite reporting shorter bond distances for the An(III)-magnetite interactions compared to An-maghemite [10].

The U  $L_3$  edge HR-XANES MFR-3d spectrum resembles clearly the spectrum of U(VI)-magh confirming the major U(VI) contribution in the MFR-3d sample (figure 2b, 2b'). The energy position of the multiple scattering H resonance is also sensitive to the U- $O_{axial}$  bond distance. But it does not change significantly for the two spectra. This is a clear indication that the U  $L_3$  edge has lower sensitivity to small variations in the U- $O_{axial}$  bond length compared to the U  $M_4$  edge HR-XANES spectrum.

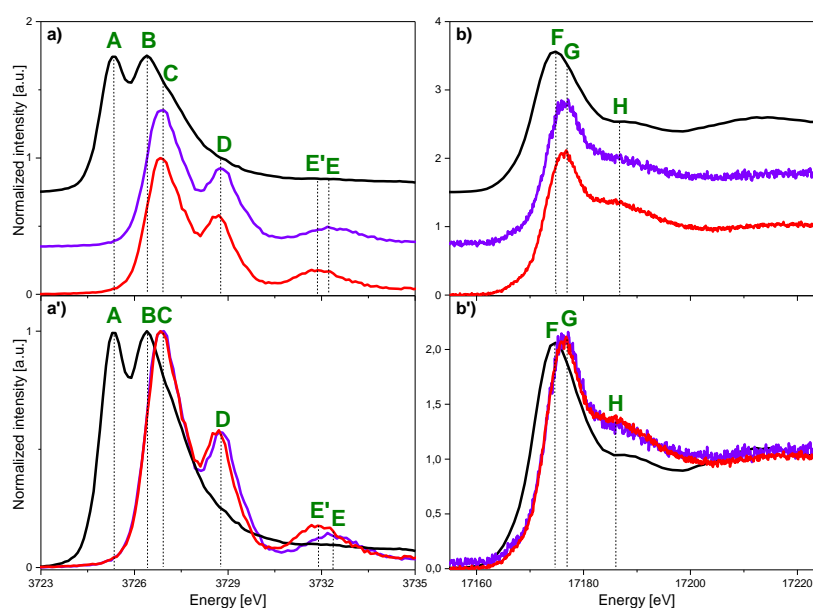
**Table 1.** Energy positions of the spectral peaks.

Edge	U $M_4$ ( $\pm 0.05$ eV)						
Feature	A	B	C	D	E'	E	(E-E')
[eV]	3725.3	3726.4	3726.9	3728.8	3731.9	3732.1	0.2
Edge	U $L_3$ ( $\pm 0.05$ eV)						
Feature	F	G	H				
[eV]	17174.8	17176.8	17188.7				

### 4. Conclusions

A combination of U  $M_4$  and  $L_3$  edge HR-XANES studies is valuable for evaluating minor changes in the redox states and local coordination environment of U in dynamic systems where two or more redox active

couples are influencing the reaction process. The combination of spectroscopy studies with these advanced techniques with precise pH and  $E_h$  measurements is a powerful tool for investigations of redox processes. We have shown that the set-up is functional and can be applied for longer interaction time studies. One necessary improvement is the insertion of online  $E_h$ -measurements. Extended X-ray Absorption Fine Structure (EXAFS) investigations will be beneficial as they can potentially help to distinguish between surface adsorbed and/or incorporated U species in magnetite. No shift of the main spectral features in U  $M_4$  and U  $L_3$  edges HR-XANES spectra indicate no observable change in U redox state after three days of the interaction time with magnetite. Planned additional experiments including longer interaction times and/or different experimental conditions (pH, flow rate) might lead to U redox changes in the system and provide insights about the long term stability of the reduced U species.



**Figure 2.** U  $M_4$  (a, a') and U  $L_3$  (b, b') edge HR-XANES spectra of MFR-3d (violet),  $U_4O_9$  (black) and U(VI)-magh (red).

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