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Forschungszentrum Dresden Rossendorf

Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the FZD. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

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 / experiment 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.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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ROBL-CRG	**Experiment title:** **Uranium solid-phase speciation in presence of pyrite (FeS_2) at slightly alkaline conditions**	**Experiment number**: EC-205
Beamline: BM 20	**Date of experiment**: from: 01-02-2008 to: 05-02-2008	**Date of report**: 31-03-2009
Shifts: 12	**Local contact(s)**: Andreas SCHEINOST	*Received at ROBL:*

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Report:

Several authors have noted a partial reduction of U(VI) (mostly to $UO_{2+x(s)}$) by pyrite in lightly acidic (pH 3-6) conditions and at relatively high initial U concentrations (> 10^{-4} mol·l^{-1}) (Wersin *et al.*, 1994; Aubriet *et al.*, 2006; Eglizaud *et al.*, 2006; Scott *et al.*, 2007). In the present study, the uptake of U(VI) by pyrite was investigated under slightly alkaline conditions (pH 8-9) at variable U concentrations (10^{-8} – 10^{-4} mol·l^{-1}) and in the presence of 0.014 M $NaHCO_3$. As an additional parameter, also the presence of dissolved organic carbon (DOC) was researched. The uranium solid phase speciation in batch systems with high initial U concentration was analysed using X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

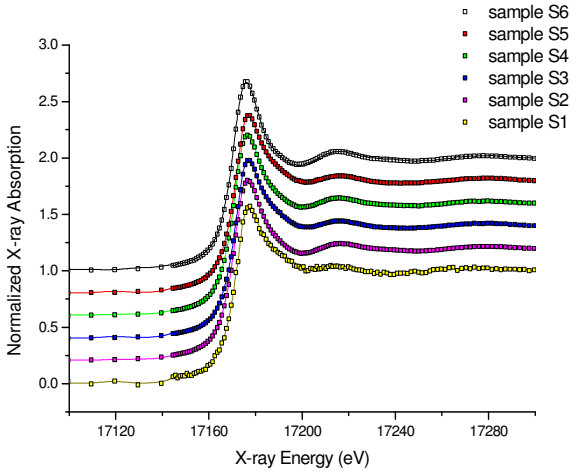
A total of six samples were analysed, which comprised the presence and absence of DOC, different equilibration times (10 and 120 days), and different FeS_2 solid-to-liquid ratio. Uranium was added initially as $UO_2(NO_3)_2$. Table 1 gives an overview of these samples, together with some experimental details concerning solution analysis after equilibration. Apart from the six experimental standards, a number of U standards (e.g., 0.1 mol·l^{-1} solutions of $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(NO_3)_2$ and UO_2(OAc), and $U_3O_{8(s)}$, $UO_{2(am)}$, $UO_{2(s)}$, U^{VI} adsorbed onto FeOOH solid phases in absence and presence of DOC) were equally analysed.

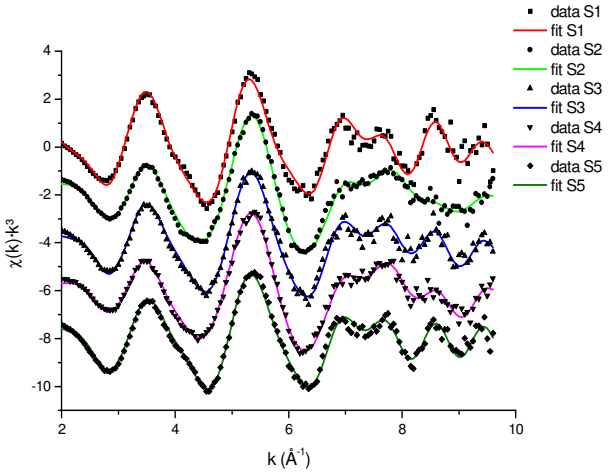
In the figures presented below, the XANES and k³-weighted EXAFS spectra (top figures), and their Fourier transform (FT) and the FT's imaginary part (bottom figures) are shown. XANES spectra were interpreted using Principal Component Analysis and Linear Combination Fitting. A combination of two standards, $UO_{2(s)}$ and U(VI) adsorbed onto FeOOH, was sufficient to adequately reconstruct the spectra of all six samples. The EXAFS spectra were equally interpreted and fitted using a combination of the crystal structure of uraninite and uranyl surface complex, similar to the analysis of U speciation in sediments performed by Kelly *et al.* (2008). This resulted in good fits for all samples.

From the results it appears that at alkaline pH, and at the investigated bicarbonate concentration, U(VI) uptake by FeS_2 is almost quantitative, and a partial redox transformation to $UO_{2(s)}$ occurs. The presence of dissolved organic carbon was the major factor hindering this reduction. Although the nominal amounts of U(IV)/U(VI) from analysis of the XANES and EXAFS spectra do not agree completely, the same trends were clearly demonstrated.

Table 1: Overview experimental samples measured by XAFS

Sample	**FeS_2**	**U(VI)*ini*** (M)	**U_{liq}*fin*** (M)	**U_{solid}*fin*** (mol/kg)	**Equilibration time**	**DOC**
S1	19.2 g/L	1.5×10^{-4}	2.3×10^{-6}	7.9×10^{-3}	120 days	0 mg/L
S2	19.3 g/L	1.5×10^{-4}	1.7×10^{-6}	7.6×10^{-3}	120 days	58 mg/L
S3	21.0 g/L	1.7×10^{-4}	3.2×10^{-6}	7.8×10^{-3}	10 days	0 mg/L
S4	21.1 g/L	1.7×10^{-4}	1.9×10^{-5}	7.0×10^{-3}	10 days	38 mg/L
S5	4.1 g/L	1.7×10^{-4}	9.4×10^{-5}	1.8×10^{-2}	10 days	0 mg/L
S6	4.1 g/L	1.7×10^{-4}	2.6×10^{-5}	3.4×10^{-2}	10 days	63 mg/L





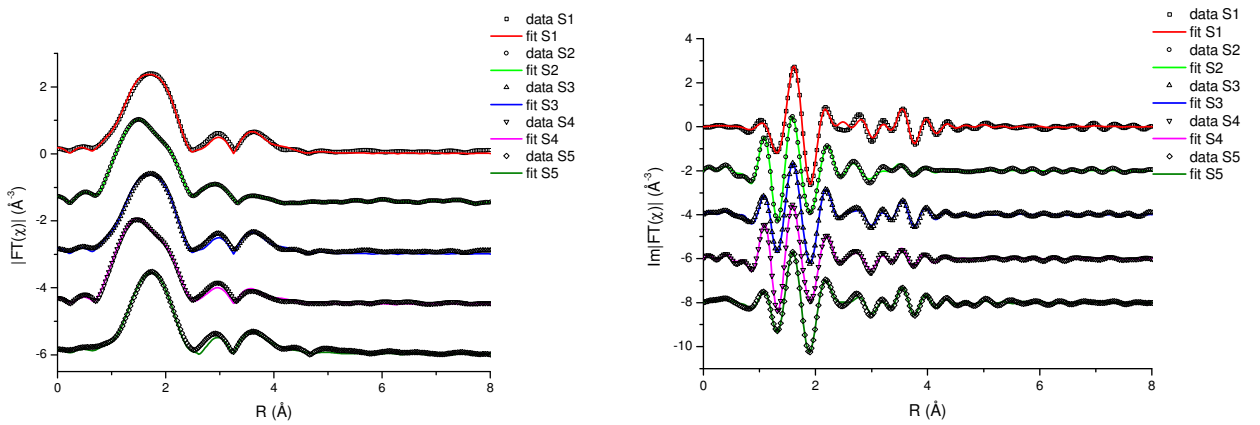


Figure: Normalised XANES (upper left), EXAFS X(k)·k³ (upper right), magnitude of the Fourier Transform (FT) (lower left), and imaginary part of the FT (lower right) of U-FeS_2 samples S1 to S6 (EXAFS spectra of sample S6 not included due to poor data quality). Open symbols represent experimental data, full lines are best fits.

References

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