



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.

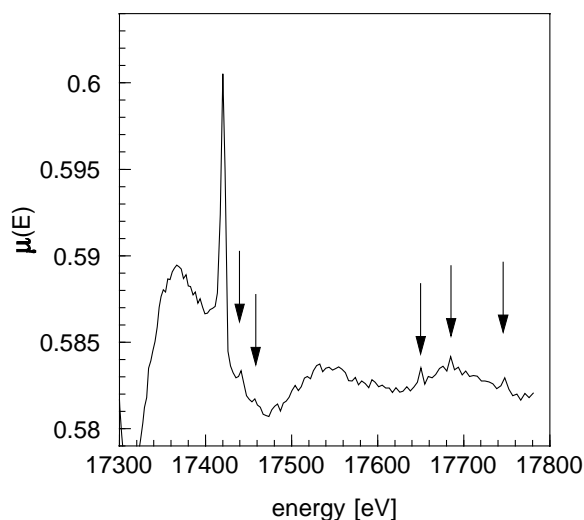
 ROBL-CRG	Experiment title: Adsorption of U(VI) onto FeS and its subsequent reduction	Experiment number: EC279
Beamline: BM 20	Date of experiment: from: 25 / 06 / 2008 to: 30 / 06 / 2008	Date of report: 3 February 2009
Shifts: 15	Local contact(s): Dr. Andre Rossberg	<i>Received at ROBL:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Thilo Behrends * Vasso Alexandratos * Dr. Andreas Scheinost *		

Report:

The goal of experiment EC279 was to evaluate the possibility and kinetics of U(VI) reduction by a) FeS or b) by sulphide in the presence of other mineral phases, and to characterize the reaction product. For this purpose samples from three different types of experiments were analyzed 1) U(VI) added to freshly precipitated FeS suspension at pH 8.0, 2) S(-II) added to aluminum oxide suspension containing adsorbed U(VI), 3) S(-II) added to lepidocrocite suspension containing adsorbed U(VI).

Technical aspects

At the beginning of the experiment we experienced some short storage ring failures, but afterwards it has been possible to make optimal use of the allocated beamtime. The support by the beamline staff was excellent, and collaborating with the staff members during the experiment was very fruitful and inspiring. The very userfriendly software and set-up of the beamline as well as the general performance of the beamline is outstanding. The only drawback was that the new monochromator crystal created glitches in the spectra (see figure, the arrows indicate minor glitches observed in addition to the major glitch at around 17.43 keV). Nevertheless, we consider the outcome of the experiment



as very successful and the results enabled us to answer major questions related to the research objectives. In total EXAFS spectra of 17 frozen wet paste samples were collected in fluorescence mode at about 30K.

Scientific results

Performing iterative transformation factor analysis of the XANES spectra from all samples with the program ITFA (ROSSBERG et al., 2003) revealed that two components are sufficient to reproduce the features of the XANES spectra. The two components can be conceived as representing the XANES spectra of U(VI) and U(IV), respectively. Based on this approach, the relative fraction of reduced U was derived from the ITFA analysis. Practically no reduction of U(VI) occurred within a period of 4 days in experiments with Al oxides to which S(-II) solution was added, irrespective of pH (6 or 8), or S(-II) addition (1 or 5 mM). Uranium became reduced when added to iron oxide suspension, which have been reacted with S(-II) solution prior to U(VI) addition. Up to 65 % of initially added U(VI) was reduced within 2 days. However, the rate of U(VI) reduction varied considerably in the different experiments depending on the age of the suspension and the occurrence of Fe(II) and S(-II) in solution. When added to freshly precipitated FeS, U(VI) was completely reduced within 1h. However, over time reoxidation occurred and after two weeks incubation only about 10% of initial U was still in its reduced form.

At least four components are required to reproduce the EXAFS chi (k^3) spectra, indicating that U(VI) coordination is not identical in all the samples and that also different U(IV) species might occur. One component can be assigned to the group of samples from Al oxide experiments, whereas the EXAFS spectra are very similar in this group. Hence, addition of S(-II) seems not to have an effect on the coordination of U(VI) adsorbed onto Al oxides, and, secondly, U(VI) speciation on Al-oxides differs from U(VI) speciation in suspensions containing iron oxides or iron sulfides. Interestingly, the results of the ITFA analysis suggest, that U(VI) coordination at the surface of precipitated FeS is different compared to that of U(VI) adsorbed to the surface of the transformation product of Fe oxide reduction by S(-II), which, in turn, both differ from U(VI) coordination at iron oxide surfaces. EXAFS fitting is still ongoing and will hopefully provide more information about the difference of U(VI) binding at the surface of the different iron containing phases.

Literature

Rossberg A., Reich T., and Bernhard G. (2003) Complexation of uranium(VI) with protocatechuic acid-application of iterative transformation factor analysis to EXAFS spectroscopy. *Analytical and Bioanalytical Chemistry* **376**, 631-638.