

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: Studies on the coordination environments of UO_2^{2+} on gibbsite surface in the presence of natural ligands	Experiment number: 20-01-671
Beamline: BM 20	Date of experiment: from: 23.02.2008 to: 27.02.2008	Date of report: 10.11.2009
Shifts:	Local contact(s): A. Scheinost	<i>Received at ROBL:</i>
Names and affiliations of applicants (* indicates experimentalists): T. Saito*, T. Hattori*, K. Ishida* and S. Nagasaki Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN		

Report:

Structures of sorption complexes that hazardous radionuclides or heavy metals form on mineral surfaces are key information to develop thermodynamic models for reliable prediction of their adsorption amounts in soils, ground waters and deep geological environments. Such information is never obtained from macroscopic adsorption experiments only and must be determined independently via *in-situ* spectroscopy and/or theoretical calculations. In this study we investigated the structures of uranyl (UO_2^{2+}) sorption complexes on gibbsite ($\alpha\text{-Al}(\text{OH})_3$) with silicic acid (H_4SiO_4) by extended X-ray absorption fine structure (EXAFS) spectroscopy. The obtained structural parameters were used to constrain density functional theory (DFT) calculations and to optimize plausible sorption geometries of UO_2^{2+} on gibbsite.

The EXAFS measurements of U-L_{III} edge were carried out in fluorescence mode at 15 K. All sorption samples were prepared in N_2 -filled glove box. The concentrations of UO_2^{2+} , H_4SiO_4 , gibbsite and NaClO_4 were 10 μM , 0.5 mM, 2 g/L and 0.1 M, respectively, and the pH was adjusted to 5.5 or 9.6. For comparison the sorption samples without H_4SiO_4 were also prepared in a similar way. Gibbsite with adsorbed UO_2^{2+} was separated by centrifugation and the resulting wet pastes were loaded into EXAFS sample holders. The concentrations of UO_2^{2+} in the supernatants were measured by an ICP-MS to determine the surface loading of UO_2^{2+} on gibbsite. In all samples more than 90 % of UO_2^{2+} adsorbed on gibbsite both with and without H_4SiO_4 . Adsorption structures of uranyl onto gibbsite were optimized by DFT calculations with B3LYP functional. A neutral Al hexamer cluster, $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$, was used as a model of gibbsite surface. Model clusters with adsorbed UO_2^{2+} and H_4SiO_4 , if present, were fully optimized without any symmetry and structural constraints. Solvation

was taken into account by explicitly placing water molecules on the equatorial plane of UO_2^{2+} in geometry optimization and further performing conductor-like polarizable continuum model calculation with the optimized structures.

In the absence of H_4SiO_4 EXAFS spectroscopy revealed the same interatomic distances of the UO_2^{2+} coordination environment, $R_{\text{U-O}_{\text{ax}}} \approx 1.80 \text{ \AA}$, $R_{\text{U-O}_{\text{eq}}} \approx 2.40 \text{ \AA}$, and towards the gibbsite surface, $R_{\text{U-O}} \approx 2.87 \text{ \AA}$, $R_{\text{U-Al}} \approx 3.38 \text{ \AA}$. In addition, two U-U distances were observed, 3.92 \AA at pH 9.7 and 4.30 \AA at pH 5.6, both with coordination numbers (CN) of ~ 1 . The shorter U-U distance is close to that of the aqueous uranyl hydroxo dimer, $\text{UO}_2(\text{OH})_2$, reported as 3.875 \AA in the literature [1]. The longer U-U distance (4.30 \AA) at acidic pH, however, is not in line with known aqueous uranyl polymer complexes. The DFT calculations of monomeric uranyl sorption complexes show an energetic preference of the corner-sharing versus the edge-sharing configuration on the edge face of gibbsite. The energy difference is so small, however, that possibly both surface species may coexist. In contrast to the edge sites, sorption to the basal face was energetically not favorable. Based on the EXAFS findings we further refined dimeric surface complexes with DFT. Two structural models were obtained: in the acidic region, the observed long U-U distance can be explained with a distortion of the uranyl dimers to form both a corner-sharing and an edge-sharing linkage to neighboring Al octahedral, leading to $R_{\text{U-U}} = 4.150 \text{ \AA}$ (Figure 1 (a)). In the alkaline region, a corner-sharing uranyl dimer complex is most favorable (Figure 1 (b)). The U-O path at $\sim 2.87 \text{ \AA}$ in the EXAFS spectra arises from the oxygen atom linking two Al cations in corner-sharing arrangement.

In the presence of H_4SiO_4 distinct broadening or even splitting of the U-O_{eq} shell was observed. It is also apparent that the backscattering from Si is now recognizable in addition to that from Al around 3.3 \AA : $R_{\text{U-Si}} = 3.09$ and 3.82 with $\text{CN} \approx 1$ for acidic pH; $R_{\text{U-Si}} = 3.07$ with $\text{CN} \approx 1$ for alkaline pH. These findings suggest the formation of $\equiv\text{Al-O-U-O-SiO}_4\text{H}_n$ ternary sorption complexes (the type-B ternary complex [2]). At acidic pH the contribution of neighboring U in the FT modulus was rather small ($< 2 \%$), suggesting that complexation with H_4SiO_4 on gibbsite surface prevented UO_2^{2+} clustering. The structures of the ternary sorption complexes were optimized in DFT calculations on the basis of the obtained EXAFS parameters and the corresponding sorption geometries in the binary system. The obtained structures consistent with the EXAFS results are shown in Figure 1 (c) and (d). It was turned out that silicic acid coordinated to sorbed UO_2^{2+} via monodentate complexation at acidic pH (Figure 1 (c)), while via bidentate complexation at alkaline pH (Figure 1. (d)).

Literature cited

1. Tsushima, S.; Rossberg, A.; Ikeda, A.; Muller, K.; Scheinost, A. C., *Inorg. Chem.* **2007**, 46, 10819-10826.
2. Alcacio, T. E.; Hesterberg, D.; Chou, J. W.; Martin, J. D.; Beauchemin, S.; Sayers, D. E., *Geochim. Cosmochim. Acta* **2001**, 65, 1355-1366.

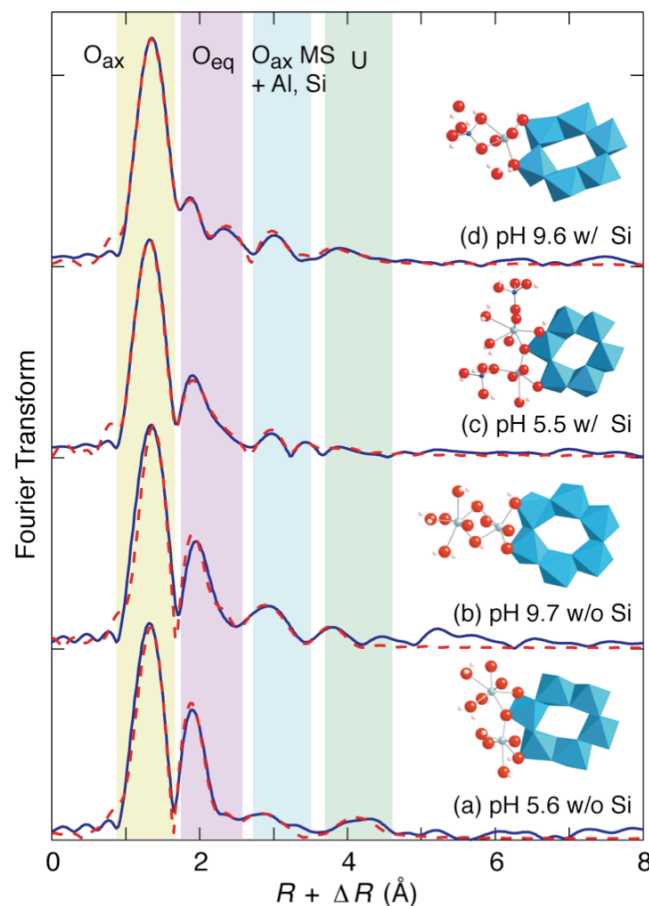


Figure 1. Fourier transform modulus of U-L_{III} edge EXAFS spectra (blue) and theoretical fittings (red) of uranyl adsorbed on gibbsite surface with and without silicic acid. The concentration of UO_2^{2+} , H_4SiO_4 (if present), NaClO_4 and gibbsite were $10 \mu\text{M}$, $500 \mu\text{M}$, 0.1 M and 2 g/L , respectively. The pH values of the samples and the sorption geometries by DFT calculations were inserted in the figure.