



	Experiment title: Structure of uranyl-arsenate complexes sorbed on bentonite	Experiment number: CH-2739
Beamline: BM 20	Date of experiment: from: 10/12/2008 to: 12/12/2008 10/04/2009 to: 14/04/2009	Date of report: 01/09/2009
Shifts: 18	Local contact(s): Dr. Andreas Scheinost	<i>Received at ESRF:</i>
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Report:

Background. The occurrence of solid uranyl-arsenate phases such as Troegerite, $\text{UO}_2(\text{H}_2\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{UO}_2(\text{HAsO}_4) \cdot 4\text{H}_2\text{O}$ in nature and as products of laboratory synthesis¹ indicate interactions between uranium (VI) and arsenate (V) and thus the existence of dissolved uranyl-arsenate species. Yet, little is known about the environmental relevance, stability conditions and structural characteristics of aqueous uranyl-arsenate species. Although solid uranyl-arsenate phases are known to be less soluble in natural waters, Rutsch et al.² were able to identify and report the existence of three aqueous uranyl-arsenate species in the pH range 1 to 3. Based on analogies to their uranyl-phosphate counterparts, they have been assigned as $\text{UO}_2(\text{HAsO}_4)_{(\text{aq})}$, $\text{UO}_2\text{H}_2\text{AsO}_4^+_{(\text{aq})}$, $\text{UO}_2(\text{H}_2\text{AsO}_4)_{2(\text{aq})}$. Since effective strategies for rehabilitation of uranium and arsenic contaminated waters depend on the understanding of the speciation in such waters, the formation of aqueous uranyl-arsenate complexes has to be recognized as a potential factor controlling arsenic and uranium mobility and sorption behaviour. Recent TRLFS studies³ have shown that a fourth uranyl arsenate species ($\text{UO}_2\text{AsO}_4^-$) was identified for the first time in the pH range between 7 and 8.5. With EXAFS, it was aimed to reaffirm the existence of the aqueous uranyl-arsenate species. Although TRLFS is suitable for species identification, this technique provides no structural information of these complexes, necessary to assess the behaviour of uranyl-arsenates in natural systems and for U and As remediation processes. Thus the task of the proposed XAS studies was to characterize the structure of aqueous uranyl-arsenate complexes existing at different pH-values from pH 2 to 8.

Experimental. Uranyl-arsenate solutions were prepared with uranyl to arsenate ratios of 1 to 10 using uranyl concentration levels of 0.01 mM, 0.05 mM and 1 mM at pH values of 2, 4, 5, and 7.5. Filtered solutions (0.2 μm cellulose acetate filters) were pipetted into PE sample holders, covered with kapton® tape and enclosed in a heat-sealed PE body as second confinement against radionuclide release. To guarantee stability of the aqueous complexes, samples were immediately flash-frozen and stored in liquid N_2 prior their analyses with XAS. Furthermore a uranyl-arsenate precipitate was prepared from a solution containing equimolar uranyl and arsenate concentrations of 5 mM at pH 3.3. X-ray absorption spectroscopy spectra were recorded at the uranium L_{III} -edge (17185 eV) at the ESRF beamline BM-20 (Rossendorf Beamline - ROBL). Both transmission and fluorescence modes were used for sample measurements using argon-filled ionization chambers resp. a 13-element Ge-detector (Canberra) with a sample orientation of 45° and a detector

orientation of 90° to the incident beam. To guarantee sample stability, avoid photo-induced redox-processes, and improve complex detectability, samples were measured at 15 K with a closed-cycle He-cryostat⁴. The EXAFS spectra were averaged, deadtime corrected and processed according to standard procedures⁵ using the suit of programs EXAFSPAK⁶. Theoretical scattering phases and amplitudes are calculated using the scattering code FEFF 8.4.

Results. To find a concentration level of uranium where EXAFS measurements could be performed without the formation of uranyl-arsenate precipitates, a wide range of uranyl concentration levels from 0.01 mM up to 1 mM were tested. The pre-experiments to check the essential concentrations necessary to obtain acceptable EXAFS spectra at low uranyl concentrations have shown that extremely long measuring times for the samples were required as well as concentrations above 0.01 mM. Consequently, only part of the proposed samples, i.e. only the liquid samples with the established minimum concentration could be measured in the allocated beamtime span, setting aside the solid samples.

Only one sample with concentration levels of 0.05 mM uranyl and 0.5 mM arsenate at pH 2 showed aqueous uranyl-arsenate species in dissolved state (Tab. 1). This was indicated by the comparison of the determined U-As bond distance of the sample with that of known uranyl-arsenate minerals. The U-As bond distance of 3.3 Å of the sample indicated a bidentate coordination which is significantly different from the U-As bond distance of 3.7 Å characteristic for the monodentate coordination in uranyl-arsenate minerals, e.g. troegerite and the uranyl-arsenate precipitate from the present study (Tab. 1). At higher pH and concentration levels, the measured samples showed U-As bond distances of around 3.7 Å indicating the formation of precipitates. However, in the present study we present for the first time the identification and structural characterization of an aqueous uranyl-arsenate species existing at pH 2 using XAS.

Table 1. Structural parameters of aqueous uranyl-arsenate complexes and precipitate from XAS analyses at the uranium L_{III} –edge.

Samples	Shell	R[Å] ^a	N	σ ² [Å ²]	ΔE0 [eV]
0.05 mM uranyl + 0.5 mM arsenate pH = 2	U-Oax	1.78	2 ^b	0.00351	0.8
	U-Oeq	2.39	4 ^b	0.00533	0.8
	U-As	3.39	2 ^b	0.00288	0.8
uranyl-arsenate precipitate	U-Oax	1.77	2 ^b	0.00139	-2.3
	U-Oeq	2.27	4 ^b	0.00418	-2.0
	U-As	3.68	2.75	0.00220	-2.0
	U-U1	5.37	2.53	0.00192	-2.0

^a R ± 0.02 Å, ^b fixed, σ² Debye-Waller factor.

References.

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