



Experiment title: Use of an electrochemical cell for *in situ* XAFS characterisation of U(IV) coordination and colloid formation with silicate ligands

Experiment number:
EC-788

Beamline: BM20	Date of experiment: from: 13 June 2012 to: 15 June 2012	Date of report: 15 march 2013
Shifts: 6	Local contact(s): Christoph Hennig	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Michel Schlegel*, **Michel Tabarant***

CEA, DEN/DANS/DPC/SEARS/LISL, F91191 Gif-sur-Yvette Cedex

Scientific Background and Aims of the experiment

Operation of pressurized-water nuclear reactors, and disposal of spent fuel in nuclear waste repositories can result in contact between water and UO_2 fuel. Uranium dissolved can then escape confining barriers and migrate in the environment, contaminating aquifers and streams [1]. This $\text{U}^{(\text{IV})}$ mobility may be significantly enhanced by complexation with inorganic ligands such as silicate, which is ubiquitous in the environment. This complexation can further nucleate stable colloids which may further enhance the solubility and mobility of radionuclides, even under reducing conditions [2]. Eventually, this uranium-silicate interaction can lead to precipitation of reduced uranium phases such as coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$, $0 \leq n \leq 4$), a mineral associated to UO_2 in large uranium deposits [3]. It is therefore essential to **identify and characterize the dissolved species and colloids** formed upon interaction of $\text{U}^{(\text{IV})}$ with silicate to predict the long-term fate of this actinide in natural systems.

Contacting $\text{U}^{(\text{IV})}$ in solution with silicate prevented the precipitation of U (or Pu) hydroxides over short periods, suggesting that silicate ligands and the actinides formed (meta)stable complexes [4]. X-ray Absorption Fine Structure (XAFS) spectroscopy can provide this valuable structural information on such complexes stoichiometry and structure in solution. However, a very low potential is needed to reduce and stabilize $\text{U}^{(\text{IV})}$ in solution, meaning that samples prepared in a laboratory and brought to the beamline can be easily oxidized during transport. To overcome these issues, **we developed an electrochemical cell to reduce *in situ* $\text{U}^{(\text{VI})}$ to $\text{U}^{(\text{IV})}$ and determine the structure of $\text{U}^{(\text{IV})}$ -silicate complexes and colloids, and their possible evolution over a short timescale by XAFS spectroscopy.** The cell was tested in our laboratory using the conventional hexacyanoferrate system, and was successfully used to reduce $2 \times 10^{-3} \text{ M } (\text{CN})_6\text{Fe}(\text{III})^{3-}$ to $(\text{CN})_6\text{Fe}(\text{II})^{4-}$ with an electron yield better than 90%.

During the scheduled beamtime, several goals were to be met.

- (1) The cell had to be installed on the ROBL beamline without any geometrical hindrance.
- (2) The cell had to be smoothly operated for electrochemistry with two tight envelopes.
- (3) An $\text{U}(\text{VI})$ solution in presence of the silicate had to be reduced in a convenient time span.

Results

Goals (1) and (2) were met without any flaw, attesting to the flexible nature of the cell. For goal (3) the cell was filled with 1 mL of 10^{-3}

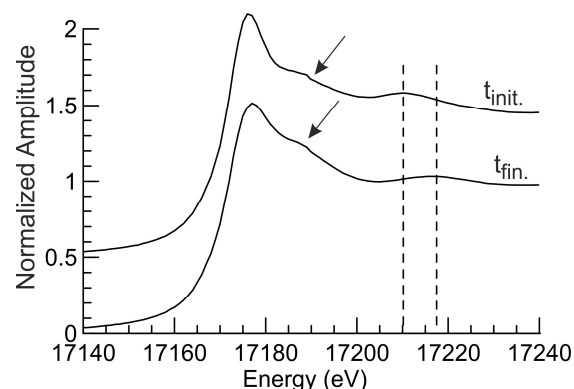


Fig. 1. In situ real-time U L_3 -edge XANES spectra of the U in the electrochemical cell.

M.L⁻¹ U^(VI) in presence of silicate (0.001 M) and carbonate (0.05 M) at pH 7 or 8. Reduction was performed in usually less than 8 h, and could be monitored in real-time by X-ray Absorption Near-Edge (XANES) spectroscopy at the U L3-edge (Figure 1). This monitoring showed changes in position of the shoulder near 17 180 eV and the band near 17 215 eV, revealing changes in uranium environment.

The nature of the U compound at the end of the reaction time was investigated by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Evolution of the EXAFS spectra confirmed the modification of U chemical environment (Figure 2a), which was also visible on the Fourier transforms (FT) of these data as a changes in the number and position of backscattering peaks (Figure 2b).

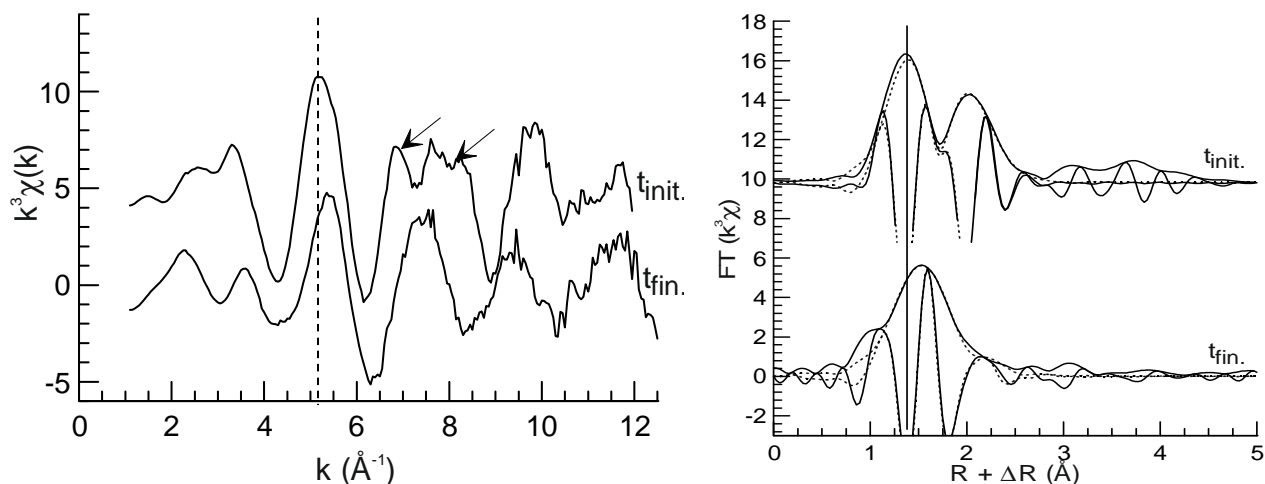


Figure 2. (a) EXAFS spectra and (b) Fourier Transforms for the electrochemical cell at the beginning (t_{init}) and at the end (t_{fin}) of the reduction period.

The spectra for the initial and final U species in solution were fitted using theoretical phase and amplitude functions generated by FEFF8 [5]. Best-fit results for the initial spectrum revealed the presence of a first shell of ~ 2 O atoms at 1.82 Å, corresponding to the axial oxygen of the uranyl moiety. The distances and number of atoms for the more distant shells are in agreement with the formation of an hydrated, carbonate-complexes U(VI) species, as expected in 0.05 M carbonate solution. At the end of the reaction time, the first shell has shifted to larger value (1.86 Å), but it still present, and two O shells of ~ 2.4 and ~ 1.7 atoms at 2.28 and 2.47 Å, respectively, could be successfully fitted. The interatomic distance and number of atoms in these shells compare with the values published for U(VI) present as precipitates in basic solutions [6].

Table 1. Best fit-results for the spectra recorded in the electrochemical cell.

spectrum	Oax			O1			O2/C			ΔE (eV)	Rf
	R (Å)	N	σ (Å)	R (Å)	N	σ (Å)	R (Å)	N	σ (Å)		
t_{init}	1.82	2.3	0.068	2.45	4.3	0.084	2.84	1.5	0.084	4.9	4×10^{-5}
t_{fin}	1.86	2.3	0.076	2.28	2.4	0.077	2.47	1.7	0.077	7.8	4×10^{-5}

The results of the EXAFS quantitative analysis revealed that despite a high overpotential used to reduce U(VI) to U(IV), the oxidation degree of U was little affected. In contrast, the pH of the solution increased significantly to values needed for precipitation of U (hydr)oxide phases. This pH increase can be understood simply from the reaction of water reduction: $H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$. This reaction outcompeted U reduction and trapped U^(VI) in a solid phase, making it much harder to reduce. Future improvements such as optimisation of the nature and geometry of the working electrode will aim at overcoming these limitations.

References

- [1] W.M. Murphy and E.L. Shock. in: *Uranium: mineralogy, geochemistry, and the environment*, (P.C. Burns and R. Finch, eds.). Reviews in mineralogy, **38**, pp. 221-253, Mineralogical Society of America, Washington, D. C. (1999). [2] A.P. Novikov, S.N. Kalmykov, et al. *Science* **314**, 638-641 (2006). [3] R. Finch and T. Murakami. in: *Uranium: mineralogy, geochemistry, and the environment*, (P.C. Burns and R. Finch, eds.). Reviews in Mineralogy, **38**, pp. 91-179, Mineralogical Society of America, Washington, DC (1999). [4] E.M. Pazukhin, A.S. Krivokhatskii, et al. *Radiokhimiya (Soviet Radiochemistry)* **32**, 26-32 (1990). [5] A.L. Ankudinov, B. Ravel, et al. *Phys. Rev. B* **58**, 7565-7576 (1998). [6] P.G. Allen, D.K. Shuh, et al. *Radiochim. Acta* **75**, 47-53 (1996).