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Experiment title:
Adsorption of actinide ions on (hydr-)oxide and clay minerals : Influence of the solution chemistry

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Report:

The migration of uranium in the environment is an important issue in the context of groundwater contaminations by radioactive waste repositories. The aim of the present experiment was to gain insights into the coordination of U(VI) -the most stable oxidation state in oxidizing aqueous medium- on two mineral phases (an alumina gel $Al_2O_3.nH_2O$ and a kaolinite $Al_2Si_2O_5(OH)_4$) under chemical conditions relevant to groundwaters (near-neutral pH values and presence of aqueous carbonate ligands). We investigated the influence of an aqueous carbonate complexation of U(VI) on the uranyl surface species by varying the initial uranyl concentration ($[U]_i = 5.10^{-4}$ M or 10^{-4} M) and the carbonate concentration ($C_C=10^{-2}$ M or $C_C \approx 0$ using CO_2-free solutions under a N_2-atmosphere) of the aqueous phase used in our batch sorption experiments. A list of the samples is given in table 1.

Uranium L_{III}-edge EXAFS spectra were recorded in transmission and fluorescence mode at the Rossendorf beamline (ROBL) of the ESRF, using a Si(111) double-crystal monochromator. Energy calibration was obtained by measuring the K-edge absorption of yttrium metal. The EXAFS spectra were analysed according to standard procedures using the program IFEFFIT and theorical scattering phases and amplitudes calculated with the scattering code FEFF [1].

Fourier transforms (not corrected for phase shift) of the k^3-weighted XAFS spectra are presented in figure 1. They exhibit two distinct major peaks in the shorter distance region.

The first one at about 1.5 Å corresponds to the U-O_{ax} single scattering interactions, the second one at about 2 Å corresponds to the U-O_{eq} interactions. All samples display also a weak contribution at 2.7 Å.

The results of the fits are summarized in table 2 for the uranyl species on the alumina gel. The small contribution at 2.7 Å (on the FT) was attributed to a U-C single scattering contribution. A surprising feature is that the presence of carbon is observed not only for the *A75C* sample ($C_C=10^{-2}$ M) but also for all samples maintained under a N_2-atmosphere. This indicates either carbonate impurities on solids -that could not be removed by our minerals pre-treatments- and / or a carbonate contamination of the samples during the sorption experiments or their conditioning for EXAFS analyses. It is to be noticed that the formation of uranyl carbonate species is favoured in uranyl solutions at $C_C=10^{-2}$ M or at equilibrium with atmospheric CO_2 at pH ≈7.5. Uranium is found surrounded by an average of 2 carbon atoms, at a distance of 2.92-2.94 Å (table 2). From such a distance between uranium and carbon, it is possible to conclude on the formation of a bidentate surface complex. A bidendate coordination results indeed in a distance of about 2.9 Å whereas a monodendate coordination would result in a longer distance, of about 3.2 Å [2]. No evidence of an uranium-aluminium interaction was found, leading us to assume that an outer-sphere complexation mechanism is responsable for the formation of a carbonate-uranyl surface species at near-neutral pH values.

The signal for the *k75* sample (uranyl sorbed on kaolinite) was very weak -the specific surface of kaolinite is indeed about sixteen time smaller than the alumina one-. Therefore, we could not perform a stable fit on this spectrum. We however can notice that the O_{eq} contribution at 2 Å is diminished when compared with that obtained on the alumina gel samples. This suggests different chemical environments for uranium sorbed on a kaolinite and on an alumina gel respectively.

Table 1: Summary of samples preparation

Name	**[UO_2^{2+}] (M)**	**[CO_3^{2-}] (M)**	**pH**	**Mineral phase**
A75	5.10^{-4}	*N_2-atm	7.5	Alumina gel
A75C	5.10^{-4}	10^{-2}	7.5	Alumina gel
a75	10^{-4}	*N_2-atm	7.5	Alumina gel
k75	10^{-4}	*N_2-atm	7.5	Kaolinite

*sorption experiments using CO_2-free solutions under a N_2-atmosphere

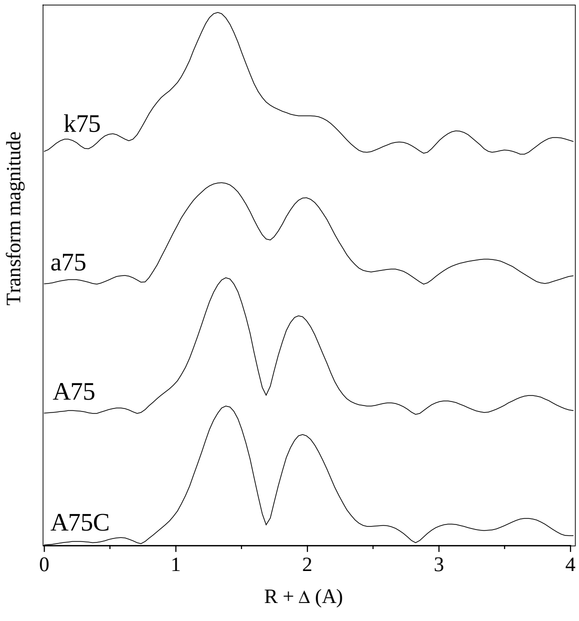

Figure 1: Fourier transform magnitude taken over k = 3-12 $Å^{-1}$ for UO_2^{2+} sorbed on alumina and kaolinite.

Table 2 : Best fit parameters of the uranium L_{III}-edge EXAFS spectra for U(VI) sorbed on alumina. Distances are given in Å and Debye-Waller factors in $Å^2$. The axial oxygen coordination number was held constant (N = 2) for all fits.

	O_{ax}	**O_{eq}**	**C**
A75	R = 1.80 σ^2 = 0.002	N = 5.2 R = 2.44 σ^2 = 0.007	N = 1.7 R = 2.94 σ^2 = 0.002
A75C	R =1.81 σ^2 = 0.002	N =5.3 R = 2.46 σ^2 = 0.005	N = 2.3 R = 2.92 σ^2 = 0.001
a75	R = 1.80 σ^2 = 0.004	N = 6.8 R = 2.45 σ^2 = 0.009	N = 2.7 R = 2.92 σ^2 = 0.003

The same experiments were made in order to study Np(V) sorption on alumina and kaolinite. The signal of the kaolinite samples is too small to be analysed by EXAFS. The evaluation of the alumina spectra is still in progress.

References:

[1] J.J. Rehr, R.C. Alberts, Phys. Rev. B, 1990, 41, 8139.
[2] R.J. Reeder, M. Nugent, G.M. Lamble, C.D. Tait, D.E. Morris, Environ. Sci. Technol. 2000, 34, 638.
[3] P.G. Allen, J.J. Bucher, D.K. Shuh, N.M. Edelstein, T. Reich, Inorg. Chem., 1997, 36, 4676.