



	Experiment title: Determination of U(VI) uptake mechanisms onto purified Na-illite	Experiment number: ME-475
Beamline: BM20	Date of experiment: from: 13.12.2002 to: 19.12.2002	Date of report: 28.08.2003
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Report:

Knowledge on the actinide chemistry in the geological environment is an essential prerequisite for the long-term safety assessment of a high level nuclear waste repository. The aim of the experimental and modelling studies on solid-water interface reactions at the Laboratory for Waste Management at PSI is to elucidate the processes controlling the uptake (sorption) and release (desorption) of safety relevant radionuclides on materials and minerals important in the Swiss radioactive waste management programme. In particular, the saturation of the repository with ground water could cause a release of radionuclides from its containment into the near field (engineered barriers) and the far field (geosphere). The detailed knowledge of the interaction of radionuclides with the natural mineral phases is of great importance to predict their mobility and long term fate. Illite is one of the major clay minerals in argillaceous rocks which are being considered in many countries as potential host rocks for a high-level waste repository (1). U(VI) is an important actinide (spent fuel) and hence its uptake behaviour is of major importance in nuclear waste management.

We have used EXAFS to study the local environment of uranyl (UO_2^{2+}) sorbed onto illite, a 2:1 dioctahedral clay mineral with substantial isomorphic substitution in the tetrahedral sheets. As an example Fig. 1 shows the radial structure functions (RSFs) of samples containing 750 –1650 ppm U(VI) (pH = 5 and 6; 0.1 M NaClO_4 background electrolyte; reaction time 7 days). The figure shows that there are RSF peaks at $R + \Delta R \sim 1.4 \text{ \AA}$ and $\sim 1.8 \text{ \AA}$ (peak A and B), $R + \Delta R \sim 2.5 \text{ \AA}$ (peak C), and at $R + \Delta R \sim 3.0 \text{ \AA}$ (peak D). The intensity and position of the RSF peaks remain essentially unchanged by varying the pH and U(VI) loadings on the clay indicating that the uptake mechanism under the chosen experimental conditions is not affected by these parameters.

Data analysis reveals that the uranium atoms in all samples are coordinated by 2 axial oxygen atoms (O_{ax} , peak A) at a distance of $\sim 1.78 \text{ \AA}$. The multiple-scattering (MS) path of the uranyl moiety was linked during data analysis to the U- O_{ax} scattering parameters without introducing additional variable fit parameters (2). The distances between the uranium and the equatorial oxygen atoms (O_{eq} , peak B) vary slightly between 2.27 \AA and 2.29 \AA and the coordination numbers N (U- O_{eq}) are in the range of 4.9 to 5.7. These U- O_{eq} distances are far from values for mononuclear outer-sphere uranyl aquo-complexes with U- O_{eq} distances of 2.41 \AA - 2.43 \AA obtained at lower pH values (see for example (3)).

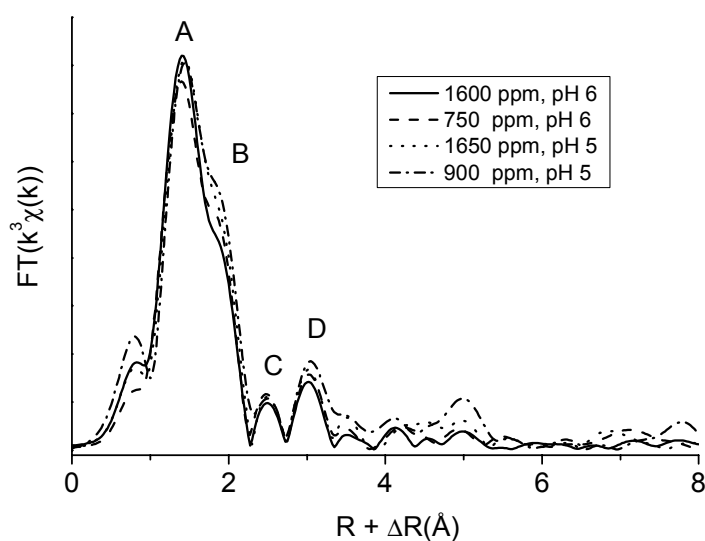


Fig. 1: RSFs of k^3 -weighted U L_{III} -edge EXAFS spectra for U(VI) sorbed onto illite at pH 5 and 6 and various U(VI) concentrations.

The short U-O_{eq} distances indicate that an inner-sphere complexation process dominates the sorption under the used experimental conditions. This finding is supported by analyzing the structural origin of peak D. Data analysis indicates that peak D is caused by U-Al/Si backscattering pairs (1-2 U-Al/Si pairs at 3.35-3.38 Å). The origin of peak C is not yet completely resolved. It is possible to fit this peak with a Si atom at ~3.1 Å. Such short U-Si distances are common in U and Si bearing minerals like e.g. soddyite and coffinite. It should be noted that peak C could be fitted similar well with an oxygen shell (2.9 Å) or a carbon shell (2.9 Å). The uranium-carbon distance is typical for bidentate coordinated carbonate as in ternary uranium(VI)-carbonato surface complexes (4). However, under the experimental conditions employed (i.e., N₂ atmosphere, pH = 5, and 0.1 M NaClO₄) the formation of uranium(VI)-carbonato surface species is highly unlikely. Furthermore, it is not anticipated that peak C is caused by a long oxygen shell (2.9 Å). To the best of our knowledge such long O distances have never been observed in U(VI) sorption experiments. Typically long U-O distances observed in the literature vary from 2.45 to 2.49 Å (e.g. (4-6)).

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