



ROBL-CRG

Experiment title:

Polarized EXAFS measurements at uranyl sorbed montmorillonite

Experiment number:

20-01-024

Beamline:

BM 20

Date of experiment:

from: 03/09/00

to: 04/09/00

from: 22/09/00

to: 25/09/00

Date of report:

26/03/01

Shifts:

18

Local contact(s):

C. Hennig

Received at ROBL:

26/03/01

Names and affiliations of applicants (* indicates experimentalists):C. Hennig^{1*}, T. Reich^{1*}, H. Funke^{1*}, A. Roßberg^{1*}, R. Dähn², A. Scheidegger²¹Forschungszentrum Rossendorf e.V., Institute of Radiochemistry, D-01314 Dresden²Paul Scherrer Institut, Waste Management Laboratory, CH – 5232 Villigen**Report:**

EXAFS sorption studies of uranium with montmorillonite and related natural clays in the pH ranging from 3 to 5 have shown that uranyl complexes almost preserve the equatorial shell arrangement comparable to the structure observed in aqueous solution [1,2]. It is shown that uranyl adsorption occurs via ion-exchange as outer-sphere complexation. This result of intact uranyl aquo-ion structure is indicated by a lack of higher shells in the Fourier transform of the uranium L_{III}-edge EXAFS spectra. At near-neutral pH, two additional equatorial shells are observed indicating an inner-sphere complexation with the surface [3,4].

The used montmorillonite STx-1, (Si₄Al_{1.67})(Fe²⁺,Mg)_{0.33} O₁₀(OH)₂(Na_{0.33},H₂O), was purchased from Source Clay Minerals Repository of the Clay Minerals Society. Na⁺-STx-1 was converted by ion exchange in the Ca²⁺ form. The samples were prepared by mixing 2g/L STx-1 with uranyl nitrate solution and NaClO₄ buffer (Tab. 1). This clay suspension was in contact for 24 h. In order to avoid carbonate species the preparation was taken in a glove box. Aliquots of the supernatant solution were analyzed by ICP-MS in order to determine the amount of U(VI) sorbed onto the montmorillonite. The pH of each dispersion was measured prior to filtration.

	NaClO ₄ [mol]	[U] _{init} [10 ⁻⁴ mol]	pH _{final}	[U]/[solid] [μmol/g]	uptake [%]
A	0.1	5.0	5.06	14.53	5.9
B	0.1	2.5	5.11	14.53	11.8
C	0.1	1.0	5.25	12.45	25.2
D	0.0033	2.5	5.20	23.87	19.3

Tab. 1: Experimental conditions of sample preparation and amount of U(VI) sorbed onto montmorillonite

Polarization dependent EXAFS investigations were performed to study the orientation of the linear uranyl moiety and the equatorial oxygen atoms regarding to the basal plane {001} of montmorillonite. For that purpose highly oriented self-supporting films were prepared according a procedure described in [5]. The pole density maximum of layer silicates is typical the basal plane {001}. Quantitative texture measurements shows that this procedure lead to an orientation distribution between $\sim 20^\circ$ and $\sim 35^\circ$ full width of half maximum [5,6].

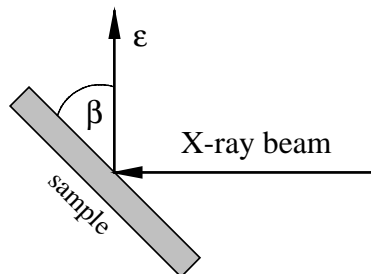


Fig. 1: Geometry of polarization dependent EXAFS experiments. The angle β is defined as tilt angle between the sample surface and the polarization vector ϵ . As angles β are used 10° , 35° , 55° and 80° .

The uranium L_{III} -edge EXAFS spectra measured at angles indicated by β are shown in Fig. 2. The EXAFS amplitudes show a very weak, but nevertheless systematic shift. From low to high β values their shift direction is marked by the arrows in Fig. 2. This is connected mainly with an reducing in the amplitude of the axial oxygen atoms.

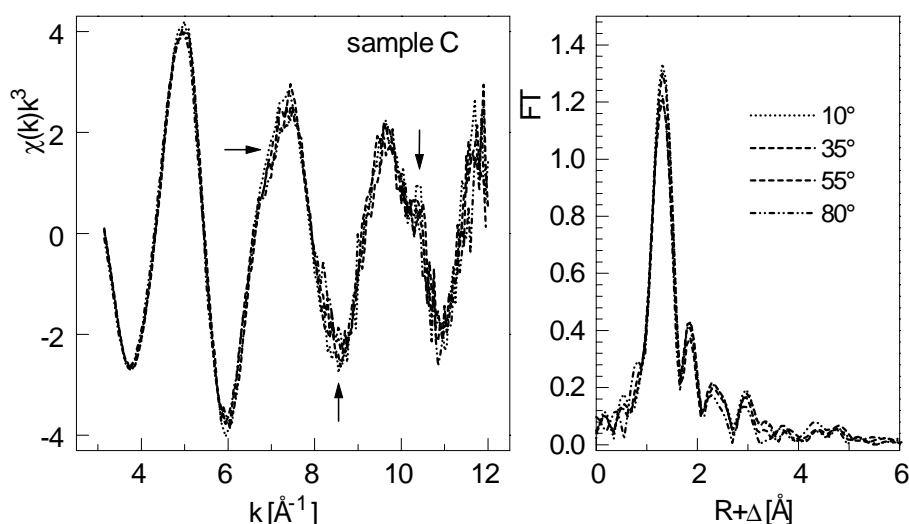


Fig. 2: U L_{III} -edge EXAFS (left side) and their Fourier transform (right side) of sample C.

References

- [1] Chrisholm-Brause, C.: Geochim. Cosmochim. Acta **58** (1994) 3625
- [2] Dent, A.J.: J. Colloid Interface Sci. **159** (1992) 45
- [3] Sylwester, E.R.: Geochim. Cosmochim. Acta **64** (2000) 2431
- [4] Thompson, H.A. et al.: in adsorption of metals by geomeia(ed. Jenne, E.A.) **16** (1998) 349
- [5] Manceau, A. et al.: Synchrotron X-ray methods in clay science, Clay Mineral Society (1999) 68
- [6] Schlegel, M.L. et al.: J. Colloid Interface Sci. **215** (1999) 140