



<b>Experiment title:</b> <b>Uranyl and Th sorption onto illite and montmorillonite</b>	<b>Experiment number:</b> <b>ME-129</b>	
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 01.11.2000 to: 07.11.2000	<b>Date of report:</b> 22-02-01
Shifts: 18	<b>Local contact(s): Tobias Reich</b>	<i>Received at ESRF:</i>

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**Report:**

The Waste Management laboratory at PSI is involved in providing relevant data to assess the performance of future Swiss nuclear waste repositories. In particular, the saturation of the depository with ground water could provoke the 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 hence of great importance to predict their mobility and long term fate. Among the different mineral phases, illite and montmorillonite are of great interest as they are major components of Opalinus clay (up to 50-80 %), a potential host-rock formation for a Swiss high-level nuclear waste repository.

We have used EXAFS to study the local environment of uranyl and Th(IV) sorbed onto illite and montmorillonite (pH= 6). As an example Fig. 1 and 2 show the EXAFS and the pseudo radial distribution function (PRDF) of samples containing 750, 2400 and 3800 ppm Uranium. Data analysis was performed on filtered back transformed data (0.9-3.4 Å) using Feff7 calculated phases and amplitudes. The origin of all features (A-D) in the PRDF's could unambiguously be determined using multiple-shell fitting (Fig. 2 and Tab. 1). A is due to axial uranyl oxygens (1.78 Å), B and C to equatorial oxygens (first shell at ~ 2.29 Å, second shell at ~ 2.47 Å) and D to multiple scattering of the fourth order along the uranyl entity. No further contribution at higher R could be observed.

Fig. 1 and Fig. 2 clearly reveal that the local structure around uranium varies with surface

loading. Data analysis supports this finding and suggests that the number of closest equatorial oxygens increases from 2.8 to 4.3 as the Uranium content in the samples decreases from 3800 ppm to 750 ppm. The splitting of the equatorial oxygen distance suggests the formation of inner-sphere complexes and has been observed in previous studies on uranyl uptake on mineral surfaces [1-4]. Further research is needed to identify the uranyl sorption sites and structurally explain the observed loading-dependant structural changes in the sorption system.

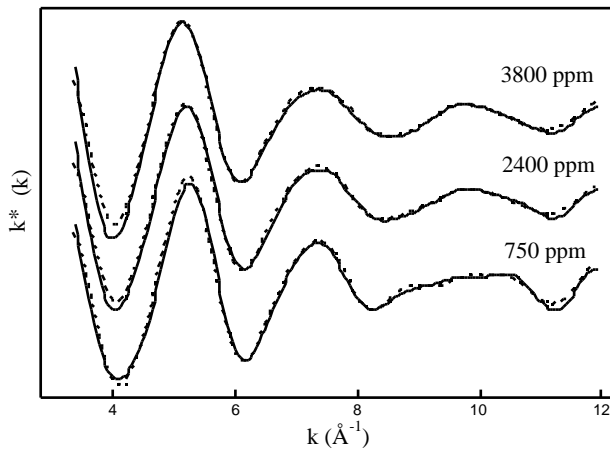


Figure 1: Experimental (—) and calculated (--) EXAFS oscillations at the U L<sub>III</sub> edge for Uranyl sorbed onto illite with different loadings.

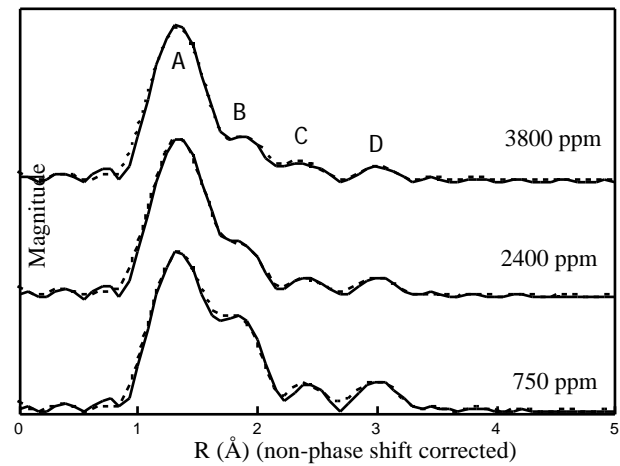


Figure 2: Experimental (—) and calculated (--) modulus of the U L<sub>III</sub> PRDF for Uranyl sorbed onto illite with different loadings.

Table 1: Best fit parameters for the EXAFS oscillations at the U L<sub>III</sub> edge (\*rf means residual factor).

		N	R (Å)	(Å)	E <sub>0</sub> (eV)	*rf (%)
3800ppm	U-O <sub>ax</sub>	2.0	1.78	0.025	-2.1	1.2
	U-O <sub>eq</sub>	2.8	2.30	0.030	-2.1	
		2.5	2.47	0.038	-2.1	
	UO <sub>2</sub> MS	-	3.57	0.091	-2.1	
2400 ppm	U-O <sub>ax</sub>	2.0	1.78	0.025	-2.1	1.5
	U-O <sub>eq</sub>	3.1	2.29	0.038	-2.1	
		2.2	2.46	0.046	-2.1	
	UO <sub>2</sub> MS	-	3.57	0.070	-2.1	
750 ppm	U-O <sub>ax</sub>	2.0	1.78	0.025	-2.1	1.8
	U-O <sub>eq</sub>	4.3	2.29	0.039	-2.1	
		2.0	2.49	0.052	-2.1	
	UO <sub>2</sub> MS	-	3.57	0.001	-2.1	

## References

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