

	<b>Experiment title:</b> <p style="text-align: center;"><b>Am(III) sorption on montmorillonite</b></p>	<b>Experiment number:</b> <p style="text-align: center;">EC-541</p>
<b>Beamline:</b> <p style="text-align: center;">BM 20</p>	<b>Date of experiment:</b> from: 25/11/2009 to 30/11/2009	<b>Date of report:</b> <p style="text-align: center;">13/12/10</p>
<b>Shifts:</b> <p style="text-align: center;">15</p>	<b>Local contact(s):</b> Dr. Andreas Scheinost	<i>Received at ESRF:</i>
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### Report:

The safety case for radioactive waste repositories is, to a large extent based on the physical and chemical retention of radionuclides on clay minerals which are important constituents in both the man-made engineered barriers and in argillaceous host rock formations. The presence of carbonate, one of the most important inorganic ligands for lanthanide and actinide ions in groundwater and clay porewaters, can have a significant influence on their sorption behaviour on clay minerals. Previous macroscopic sorption experiments and modelling suggest the formation of Am(III) carbonate complexes at the montmorillonite surface (Marques Fernandes et al., 2007). The aim of this work is to improve the mechanistic understanding at the molecular level of the uptake of Am(III) onto montmorillonite in the absence and the presence of dissolved carbonate.

### Preliminary results

The Am(III) loaded montmorillonite films were measured at the  $L_{III}$  edges of Am(III) (18510 eV) and in fluorescence mode. EXAFS spectra were analyzed and fitted using the IFEFFIT software package. Backscattering phases and amplitudes were obtained from FEFF8.0 calculations. The multiple scattering paths (MS) related to the bidentate coordination of the carbonate group was included into the fit. The parameters  $R$ ,  $N$  and  $\sigma^2$  of the scattering paths Am-O<sub>dist</sub>, Am-O<sub>dist</sub>-C and Am-C-O<sub>dist</sub>-C were linked together during the fitting process.

### Sorption of Am(III) on montmorillonite

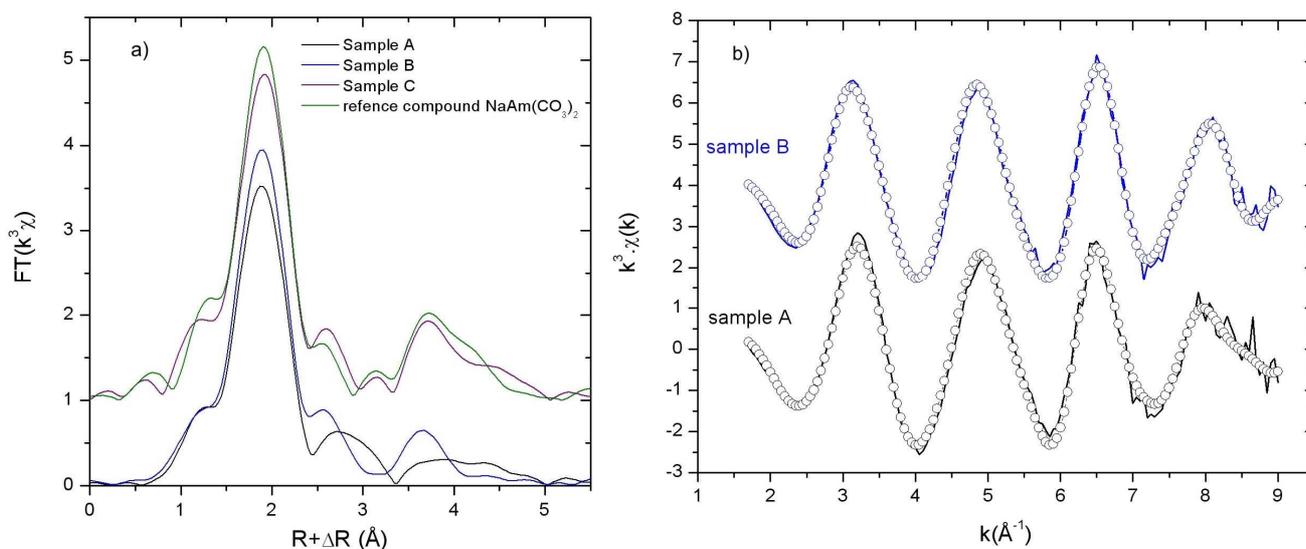
Montmorillonite samples with different Am(III) loadings were prepared in the absence (pH=8) and in the presence of carbonate (equilibrium with the atmospheric  $pCO_2 = 10^{-3.5}$  bar at pH~9.3). In addition the solubility limiting phase  $NaAm(CO_3)_2$  was measured as a reference compound. The experimental

conditions used for the preparation of the EXAFS clay samples A, B and C are summarized in Table 1. EXAFS measurements were performed on Am(III) loaded self supporting STx montmorillonite films.

Table 1. EXAFS clay samples description: S/L ratio = 2g·l<sup>-1</sup>, background electrolyte 0.1 M NaClO<sub>4</sub>

Sample	pH	pCO <sub>2</sub> (bar)	[ <sup>243</sup> Am(III)] <sub>i</sub> (M)	<sup>243</sup> Am(III) sorbed (mmol·kg <sup>-1</sup> )	log R <sub>d</sub> (L·kg <sup>-1</sup> )
A	8.0	-----	2.09·10 <sup>-06</sup>	2.78	4.85
B	9.3	10 <sup>-3.5</sup>	5.90·10 <sup>-06</sup>	2.74	3.80
C	9.3	10 <sup>-3.5</sup>	2.09·10 <sup>-06</sup>	8.32	4.46

Fig. 1a shows the Am L<sub>III</sub> edge k<sup>3</sup>-weighted FT of all the Am(III) samples. The spectra obtained for the samples prepared in the presence and absence of carbonate clearly show different features (Fig. 1a). All the measured carbonate samples show additional peaks in the FT at R~3.8 Å (R+ΔR). The similarity of the FT spectra of the clay sample C and the reference compound clearly shows that in case of sample C surface precipitation occurred. This is in a good agreement with the increased Rd value of 4.46 obtained for sample C.



Figs. 1. a) Fourier Transforms of experimental EXAFS spectra measured for the Am(III) sorption samples A to C and the reference compound NaAm(CO<sub>3</sub>)<sub>2</sub>; b) experimental (solid lines) and fitted (symbols) k<sup>3</sup>-weighted EXAFS data for the Am(III) samples A and B.

EXAFS spectra of the samples A and B were fitted in the *k*-space and the obtained fits are shown in Fig. 1b (symbols). The results of the data analysis are summarized in Table 2.

The EXAFS parameters obtained by fitting the spectra of the carbonate free sample are consistent with bond lengths from Am-O and Am-Si/Al backscattering pairs. The identification of Am-Al/Si distances is a clear indication that Am(III) forms inner sphere complexes at the STx surface. However, additional EXAFS measurements on carbonate free Am(III) clay samples prepared under different pH and loading

conditions are necessary to derive a reliable structural model for inner sphere complexation of Am(III) at the montmorillonite surface.

The EXAFS parameters obtained by fitting the spectra of the sample B (in equilibrium with atmospheric pCO<sub>2</sub>) are consistent with the formation of 1-2 Am(III) carbonate complexes at the montmorillonite surface. No Am-C shell was necessary to reproduce the EXAFS spectrum. However fitting a weak backscatter such as carbon in our system might be difficult, since the backscattering amplitude produced 1 C (z = 6) is much weaker than the amplitude produced by one Si/Al shell (z = 13/14) originating from the montmorillonite surface. The most reliable structural evidence for the formation of bidentate Am(III) carbonate complexes at the montmorillonite surface is the identification of the distal oxygen O<sub>dist</sub> shell of the carbonate ligand (4.28 Å) and the associated multiple scattering of U-C-O<sub>dis</sub> (4.28 Å) and U-C-O<sub>dist</sub>-C (4.28 Å).

The evaluation of the NaAm(CO<sub>3</sub>)<sub>2</sub> solid phase spectra and of the Am(III) loaded clay film C is still in progress.

Table 2. Structural parameters for the Am(III) loaded montmorillonite films derived from the EXAFS analysis.

Sample	Shell	CN	R (Å)	σ <sup>2</sup> [Å <sup>2</sup> ]	ΔE <sub>0</sub> [eV]
A	Am-O	8 (1)	2.46(1)	0.013(2)	7.83
	Am-Si <sub>1</sub> /Al <sub>1</sub>	1.1(3)	3.20(2)	0.007*	
	Am-Si <sub>2</sub> /Al <sub>2</sub>	1.2(5)	3.75(3)	0.01*	
	Am-Si <sub>3</sub> /Al <sub>3</sub>	5(2)	4.72(2)	0.013(6)	
B	Am-O	7.09	2.46	0.010	10.93
	Am-Si	1.75	3.23	0.010	
	Am-O <sub>dist</sub>	1.53	4.28	0.005*	
	Am-O <sub>dist</sub> -C	3.06	4.28	0.005	
	Am-C-O <sub>dist</sub> -C	1.53	4.28	0.005	

Note: CN: coordination number; R: distance; σ<sup>2</sup>: Debye-Waller factor; \*: value fixed during the fit; number in parentheses represents the errors in the last digit.

#### Reference:

Marques Fernandes, M., Baeyens, B., and Bradbury, M. H., 2007. The influence of carbonate complexation on lanthanide/actinide sorption on montmorillonite. *Radiochim. Acta* **96**, 691-698.