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|  ROBL-CRG | Experiment title: Influence of carbonate on actinides sorption on clay minerals | Experiment number: 20-01-673 |
| | Beamline: BM 20 | Date of experiment: from: 08/04 to: 14/04/08 |
| Shifts: 18 | Local contact(s): Dr. Andreas Scheinost | <i>Received at ROBL:</i> |
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Report:

Clay minerals play an important role in the retention/retardation of radio-contaminants in the near- and far-fields of a radioactive waste repository. In natural environments, the predominant aqueous phase reactions of trivalent actinides and U(VI) are hydrolysis and complexation with dissolved inorganic ligands e.g. carbonates. The formation of strong carbonate complexes in solution can potentially lead to a decrease in metal ion sorption and thus increase the migration rates of actinides. The aim of this work is to improve the mechanistic understanding at the molecular level of the uptake of Am(III) and U(VI) onto clay minerals by investigating the influence of carbonate complexation. This information will prove whether or not ternary complexes form and thereby extend the currently available thermodynamic models for radionuclide sorption (Eu(III)/ Am(III)/ Cm(III)) and U(VI) onto clay minerals by inclusion of carbonates.

Preliminary results

EXAFS spectra were analyzed and fitted using WINXAS and IFEFFIT software package. Backscattering phases and amplitudes were obtained from FEFF8.0 calculations. The Am(III) and U(VI) loaded clays samples were measured at the L_{III} edges of Am(III) (18510 eV) and of U(VI) (17166 eV) resp. in fluorescence mode.

Sorption of Am(III) on *montmorillonite*

EXAFS measurements were performed on Am(III) loaded wet montmorillonite pastes and self supporting montmorillonite films respectively. Samples were prepared in the absence (pH=8) and presence of inorganic carbon (20 mM NaHCO₃ at pH 7.4 and 8.3) at a range of Am(III) loadings down to 200 ppm. Fig. 1 shows the Fourier transform and EXAFS spectra of Am loaded Na-montmorillonite (~350 ppm) at pH 8 in the absence of carbonate. 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. A first shell with 7.9 ± 1.6 O at a distance of 2.48 ± 0.01 Å and a second shell with 1.6 ± 0.5 Si at 3.18 ± 0.01 Å. The identification of Am-Al/Si distances is a clear indication that Am(III) forms inner sphere complexes at the SWy-1 surface. The EXAFS spectra obtained for the samples prepared in the presence and absence of carbonate clearly show different

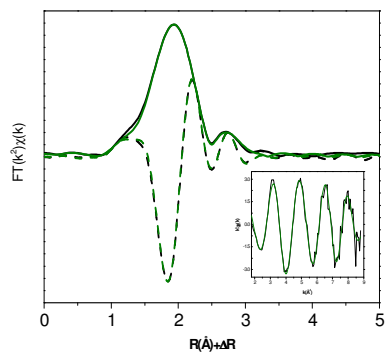


Fig. 1: Fourier transform and k^3 -weighted EXAFS spectra of Am loaded Na-montmorillonite. Black line: experimental data, green line: modelled data, broken lines: imaginary part.

features (Fig. 2). All the measured carbonate samples show additional peaks in the FT ($R \sim 3.8 \text{ \AA}$) which might be an indication of the formation of ternary Am-carbonate surface complexes, but could also be due to the precipitation of the solubility limiting phase $\text{NaAm}(\text{CO}_3)_2$. Evaluation of structural parameters (coordination number, bond length) is on-going. To verify whether these features are due to the formation of ternary Am(III)/carbonate complexes or the precipitation of Am(III) solid carbonates at the clay surface measurements on pure reference compounds as well on sorption samples are necessary.

Sorption of U(VI) on clay minerals

Macroscopic sorption experiments have shown that the presence of inorganic carbonate leads to a strong decrease of the sorption of U(VI) on montmorillonite (Na-SWy-1). P-EXAFS measurements were performed on U(VI) loaded self supporting Na-SWy-1 films. The investigated samples were prepared at $\text{pH} \sim 8$ in the absence and presence of inorganic carbon (1 mM NaHCO_3). Table.1 summarizes the experimental conditions used for the U(VI) sorption on Na-SWy-1.

Table.1: Summary of experimental conditions

| Sample | Conditions | 0.1 M NaClO_4 | pH | Initial U (M) | $\log R_d (\text{L.kg}^{-1})$ | U loading (ppm) |
|--------|--------------------------|------------------------|-----|---------------------|-------------------------------|-----------------|
| A | carbonate free | | 7.9 | $1.5 \cdot 10^{-5}$ | 3.97 | 1680 |
| B | in 1 mM NaHCO_3 | | 7.9 | $2.0 \cdot 10^{-5}$ | 2.7 | 1190 |

Fig.3 shows the experimental EXAFS spectra as well as the experimental and fitted Fourier transform spectra of the U(VI) loaded Na-montmorillonite at pH 8 in the absence (A) and presence of carbonate (B) measured at 35° . The EXAFS parameters obtained by fitting the spectra of both samples are summarized in Table 2. Structural data for both systems show unambiguously that U(VI) forms inner-sphere complexes at the clay surface (splitting of the O_{eq} shell, Si shell and Fe shell). However, no considerable difference is observed for these two samples in the absence and presence of carbonate (no C shell $\sim 2.90 \text{ \AA}$, no O_{dist} shell). This might be an indication that under the given experimental conditions no measurable U(VI)-carbonate ternary complex forms at the clay surface or that the U-C backscattering amplitude is too weak compared to the U-Si backscattering pairs.

Table 2: Structural information derived from the EXAFS analysis of U(VI) loaded self supporting montmorillonite films prepared in the absence and in the presence of carbonate at $\text{pH} \sim 8$.

| Sample | Shell | N | R (\AA) | $\sigma^2 (\text{\AA}^2)$ | E_0 |
|--------|----------------------------|-----|--------------------|---------------------------|-------|
| A | U- O_{ax} | 2* | 1.80 | 0.002 | 8.4 |
| | U- O_{eq1} | 3.6 | 2.29 | 0.008 | |
| | U- O_{eq2} | 3.1 | 2.48 | 0.008 | |
| | U-Si/Al | 0.5 | 3.09 | 0.003* | |
| | U-Fe | 0.3 | 3.41 | 0.003* | |
| B | U-Si/Al | 2.3 | 3.84 | 0.013 | 9.6 |
| | U- O_{ax} | 2* | 1.80 | 0.002 | |
| | U- O_{eq1} | 3.5 | 2.29 | 0.007 | |
| | U- O_{eq2} | 2.9 | 2.50 | 0.007 | |
| | U-Si/Al | 0.8 | 3.10 | 0.003* | |
| | U-Fe | 0.5 | 3.43 | 0.003* | |
| | U-Si/Al | 1.6 | 3.86 | 0.011 | |

*Fixed values, fitting range: $k: 3.6-12.6 \text{ \AA}^{-1}$. MS path of the uranyl moiety was linked to U-O_{ax} scattering as described in [1]

- Hudson, E.A., Allen, P.G., Terminello, L.J., Denecke, M.A. and Reich, T., Polarized x-ray-absorption spectroscopy of the uranyl ion: Comparison of experiment and theory. *Physical Review B*, 1996. 54(1): p. 156.

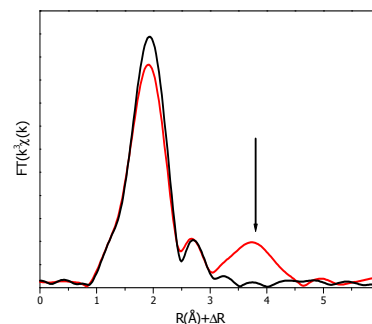


Fig.2. Fourier transform spectra of Am loaded Na-SWy. Black line: in the absence of carbonate, red line: in the presence of carbonate

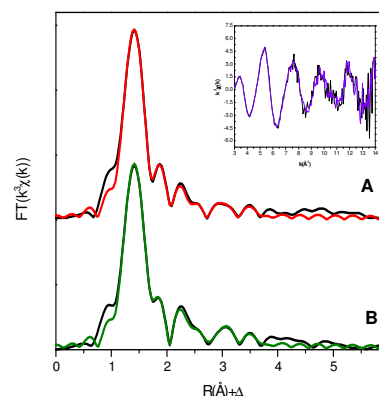


Fig.3. Fourier transform spectra of U(VI) loaded self supporting montmorillonite films. A) in the absence of carbonate, B) in the presence of carbonate. Black line: experimental data, red and green line: modelled data