



# Sorption of trivalent lanthanides and actinides onto montmorillonite: Macroscopic, thermodynamic and structural evidence for ternary hydroxo and carbonato surface complexes on multiple sorption sites



M. Marques Fernandes<sup>a, \*</sup>, A.C. Scheinost<sup>b, c</sup>, B. Baeyens<sup>a</sup>

<sup>a</sup> Paul Scherrer Institute, Laboratory for Waste Management, 5232 Villigen PSI, Switzerland

<sup>b</sup> Helmholtz Zentrum Dresden Rossendorf e.V. (HZDR), Institute of Resource Ecology, 01314 Dresden, Germany

<sup>c</sup> The Rossendorf Beamline at ESRF, 38043 Grenoble, France

## ARTICLE INFO

### Article history:

Received 22 January 2016

Received in revised form

5 April 2016

Accepted 17 April 2016

Available online 21 April 2016

### Keywords:

Trivalent actinides

Clay minerals

Carbonate complexation

2SPNE SC/CE model

Strong and weak sites

TRLFS

EXAFS

## ABSTRACT

The credibility of long-term safety assessments of radioactive waste repositories may be greatly enhanced by a molecular level understanding of the sorption processes onto individual minerals present in the near- and far-fields. In this study we couple macroscopic sorption experiments to surface complexation modelling and spectroscopic investigations, including extended X-ray absorption fine structure (EXAFS) and time-resolved laser fluorescence spectroscopies (TRLFS), to elucidate the uptake mechanism of trivalent lanthanides and actinides (Ln/An<sup>III</sup>) by montmorillonite in the absence and presence of dissolved carbonate. Based on the experimental sorption isotherms for the carbonate-free system, the previously developed 2 site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) model needed to be complemented with an additional surface complexation reaction onto weak sites. The fitting of sorption isotherms in the presence of carbonate required refinement of the previously published model by reducing the strong site capacity and by adding the formation of Ln/An<sup>III</sup>-carbonato complexes both on strong and weak sites. EXAFS spectra of selected Am samples and TRLFS spectra of selected Cm samples corroborate the model assumptions by showing the existence of different surface complexation sites and evidencing the formation of Ln/An<sup>III</sup> carbonate surface complexes. In the absence of carbonate and at low loadings, Ln/An<sup>III</sup> form strong inner-sphere complexes through binding to three Al(O,OH)<sub>6</sub> octahedra, most likely by occupying vacant sites in the octahedral layers of montmorillonite, which are exposed on {010} and {110} edge faces. At higher loadings, Ln/An<sup>III</sup> binds to only one Al octahedron, forming a weaker, edge-sharing surface complex. In the presence of carbonate, we identified a ternary mono- or dicarbonato Ln/An<sup>III</sup> complex binding directly to one Al(O,OH)<sub>6</sub> octahedron, revealing that type-A ternary complexes form with the one or two carbonate groups pointing away from the surface into the solution phase. Within the spectroscopically observable concentration range these complexes could only be identified on the weak sites, in line with the small strong site capacity suggested by the refined sorption model. When the solubility of carbonates was exceeded, formation of an Am carbonate hydroxide could be identified. The excellent agreement between the thermodynamic model parameters obtained by fitting the macroscopic data, and the spectroscopically identified mechanisms, demonstrates the mature state of the 2SPNE SC/CE model for predicting and quantifying the retention of Ln/An<sup>III</sup> elements by montmorillonite-rich clay rocks.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

A major concern with high-level radioactive waste repositories

in deep geologic formations is the potential release of radionuclides (RNs) into the biosphere, which needs to be prevented for hundreds of thousands of years due to the long half-life of critical actinides and fission products. An important component of the safety case is the long-term prediction of RN binding to mineral components along the transport path. Sorption onto clay minerals as major constituents of engineered barriers and – in case of argillaceous

\* Corresponding author.

E-mail address: [maria.marques@psi.ch](mailto:maria.marques@psi.ch) (M.M. Fernandes).

host rocks – of the natural barriers, is a crucial process in the retardation chain, which needs to be understood on several length- and time-scales in order to predict reliably the macroscopic RN migration through such clay-rich barriers.

In the near-field of deep-geologic high-level waste repositories, reducing conditions will prevail soon after closure, hence long-lived and radiotoxic actinides such as Ac, Pu, Am and Cm will be present in their trivalent oxidation state. In natural environments, the predominant aqueous reactions of trivalent actinides ( $\text{An}^{\text{III}}$ ) and their chemical analogues, the trivalent lanthanides ( $\text{Ln}^{\text{III}}$ ), are hydrolysis and complexation with dissolved inorganic ligands. Dissolved carbonate is of particular interest in this context due its ubiquity in surface and deep groundwaters, but also in the porewaters of host rocks and backfill materials (*i.e.* bentonite, cement). The in-situ porewater of Boom Clay for instance contains up to  $10^{-2}$  M dissolved carbonate, the porewaters of Opalinus Clay, Callovian–Oxfordian clayrock and bentonite about  $10^{-3}$  M (Baeyens et al., 2014; De Craen et al., 2004; Gaucher et al., 2006). Aqueous  $\text{An}^{\text{III}}$  carbonate complexes are very strong, and have been shown to reduce sorption at higher pH, and hence are expected to increase the migration rates of RNs (Guillaumont et al., 2003).

Surface complexation models based on macroscopic sorption experiments of metals on pure minerals are currently state-of-the-art tools to predict the sorption of RNs in clay rich environments under realistic geochemical conditions. Several studies have quantified and modelled the sorption of  $\text{Ln}/\text{An}^{\text{III}}$  on clay minerals in simple electrolyte, *i.e.* without organic and inorganic ligands (Bradbury and Baeyens, 2002, 2006; 2009a, b; Coppin et al., 2002; Gorgeon, 1994; Schnurr et al., 2015; Tertre et al., 2006). In the quasi mechanistic 2 site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) model, sorption of  $\text{Ln}/\text{An}^{\text{III}}$  on montmorillonite and illite is predicted by taking into account three different site types, (1) cation exchange on planar sites, (2) surface complexation on strong sites ( $\equiv\text{S}^{\text{OH}}$ ) with high affinity, but low capacity, and (3) surface complexation on weak sites ( $\equiv\text{S}^{\text{W}1,2}\text{OH}$ ) with high capacity and low affinity (Bradbury and Baeyens, 2002). Such multi-site sorption behavior was also observed for other elements, *e.g.* divalent transition metals,  $\text{UO}_2^{2+}$  and  $\text{NpO}_2^{2+}$  on clay minerals (Bradbury and Baeyens, 2005, 2009a, b).

A quantitative description of the influence of dissolved carbonate on the sorption of  $\text{Ln}/\text{An}^{\text{III}}$  by clay minerals has been little examined until now. To the best of our knowledge, only two studies of  $\text{Ln}/\text{An}^{\text{III}}$  to montmorillonite and illite have focused on this issue (Marques Fernandes et al., 2007; Marques Fernandes et al., 2015). The observed decrease in sorption was less important than predicted by the model, in which  $\text{Ln}/\text{An}^{\text{III}}$  aqueous carbonate complexes were considered as non-sorbing. Only after complementing the model with two carbonate surface complexes on strong sites,  $\equiv\text{S}^{\text{O}}\text{EuCO}_3$  and  $\equiv\text{S}^{\text{O}}\text{EuOHCO}_3^-$ , the data were reproduced. Since the study was conducted at trace concentration only, surface complexation reactions on weak sites were not determined.

Sorption models have a considerably higher reliability and credibility in their application of long-term predictions if they are supported by spectroscopically determined surface complexes. Time Resolved Laser Fluorescence Spectroscopy (TRLFS) is a very efficient speciation tool for  $\text{Ln}/\text{An}^{\text{III}}$  in aqueous solutions or at mineral-water interfaces and enabled the discrimination and quantification of  $\text{Eu}^{\text{III}}$  or  $\text{Cm}^{\text{III}}$  species sorbed by different clay minerals (Geckeis et al., 2013; Schnurr et al., 2015). For instance, the existence of  $\text{Cm}^{\text{III}}$  carbonate complexes at kaolinite and  $\gamma\text{-Al}_2\text{O}_3$  surfaces could be proven by TRLFS (Marques Fernandes et al., 2010). However, TRLFS probes only the ligand field of susceptible metal centers, hence information on the short range structure is limited. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is currently the most appropriate and most widely applied

spectroscopic technique to probe the atomic-scale environment of metal ions (Brown and Sturchio, 2002). Its use allows identifying the uptake mechanism of actinides and other metal ions including formation of outer- and inner-sphere complexes and the incorporation by the sorbing mineral itself or by surface precipitates (Denecke, 2006; Tan et al., 2010). In experiments containing dissolved carbonate, EXAFS evidenced the formation of  $\text{U}^{\text{VI}}$ -carbonate surface complexes on minerals such as hematite, montmorillonite, and ferrihydrite (Bargar et al., 1999, 2000; Catalano and Brown, 2005; Rossberg et al., 2009). The use of EXAFS together with calculations based on density functional theory (DFT) also enabled the structural visualization of different binding sites for  $\text{Zn}^{\text{II}}$  on montmorillonite, consistent with a multi-site sorption behavior and in particular with the strong-weak site concept of the 2SPNE SC/CE model (Churakov and Dähn, 2012; Dähn et al., 2011). The divalent Zn cation can adopt, due to its size and crystal field stabilization, either an octahedral or a tetrahedral coordination to oxygen ligands, and hence fits into the crystal lattice of montmorillonite. In contrast, the trivalent early actinides and early lanthanides have much larger ionic radii and are therefore typically nine-coordinated, adopting a tricapped prismatic coordination structure (Galbis et al., 2010; Kirsch et al., 2011; Persson et al., 2008). It seems therefore much less likely, that the observed strong-site sorption behavior of  $\text{An}/\text{Ln}^{\text{III}}$  is also based on their partial incorporation into the clay lattice.

In general, structural data of  $\text{An}/\text{Ln}^{\text{III}}$  complexes formed on minerals and particularly on clay minerals are very sparse. In an attempt to probe the structure of  $\text{Am}^{\text{III}}$  sorbed on smectite by EXAFS, only the first oxygen coordination shell could be identified (Stumpf et al., 2004). In three other studies, EXAFS was applied to elucidate the binding mechanism of  $\text{Lu}^{\text{III}}$ ,  $\text{Eu}^{\text{III}}$  and  $\text{Am}^{\text{III}}$  sorbed to and co-precipitated with hectorite (Finck et al., 2012, 2015, 2009). For these three elements, EXAFS allowed to discriminate between surface complexes in case of sorption, and structural incorporation in case of co-precipitation. The sorption mechanism was consistent with the formation of inner-sphere surface complexes at the edges of hectorite platelets.

In the current study, the sorption of trivalent actinides and lanthanides at the montmorillonite surface under different experimental conditions is investigated. Firstly, we measured sorption isotherms across a large concentration range in the presence/absence of dissolved carbonate. Secondly, we refined the 2 SPNE SC/CE model based on these wet chemical data. Finally, we used TRLFS and EXAFS to identify the major surface complexes in the different systems, including postulated ternary surface complexes on strong and weak sites, and to unravel their local structure. The combination of complementary information based on wet chemistry, surface complexation modelling and spectroscopy allowed us to obtain a refined picture of the sorption processes from the atomic to the macroscopic scale.

## 2. Experimental

### 2.1. Materials

Supra-pure grade chemicals and ultra-pure deionized water ( $18\text{ M}\Omega\text{ cm}^{-1}$ ) were used to prepare the solutions. A conditioned and purified Na-montmorillonite<sup>1</sup> suspension in 0.1 M  $\text{NaClO}_4$  was used for the sorption experiments and the TRLFS and EXAFS samples. Details on the clay purification can be found elsewhere (Baeyens and Bradbury, 1995). Based on their very close

<sup>1</sup> Texas montmorillonite (STx-1) from the Clay Minerals Society Clay Repository.

Download English Version:

<https://daneshyari.com/en/article/6364949>

Download Persian Version:

<https://daneshyari.com/article/6364949>

[Daneshyari.com](https://daneshyari.com)