



Reversibility of La and Lu sorption onto smectites: Implications for the design of engineered barriers in deep geological repositories

Evgeny Galunin^a, María D. Alba^b, Miguel A. Avilés^b, Maria J. Santos^c, Miquel Vidal^{a,*}

^a *Departament de Química Analítica, Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain*

^b *Instituto de Ciencia de Materiales de Sevilla, Consejo Superior de Investigaciones Científicas – Universidad de Sevilla, Av. Américo Vespucio 49, 41092 Sevilla, Spain*

^c *Departamento de Química, Universidade Estadual de Londrina, Londrina, PR, 86051-990, Brazil*

ARTICLE INFO

Article history:

Received 15 April 2009

Received in revised form 29 July 2009

Accepted 29 July 2009

Available online 5 August 2009

Keywords:

Lanthanides
Smectitic clays
Radioactive waste
Engineered barriers
Sorption reversibility

ABSTRACT

The sorption reversibility of La and Lu (considered as actinide analogues) onto a set of smectites (bentonite FEBEX; hectorite, HEC; MX80; saponite, SAP; Otay montmorillonite, SCA-3; and Texas montmorillonite, STx-1) was studied to estimate actinide retention by smectites that are candidates for use as engineered barriers in deep geological repositories. The sorption distribution coefficients (K_d) and the reversibility parameters (desorption distribution coefficients ($K_{d,des}$), adjusted distribution coefficients ($K_{d,adj}$), and desorption rates (R_{des})) were determined from batch tests in two ionic media: deionized water and Ca 0.02 mol L⁻¹. The latter simulates possible conditions due to the presence of concrete leachates. The results varied greatly depending on the ionic medium, the lanthanide concentration and the clay structure. The high values of $K_{d,des}$ obtained (up to 1.1×10^5 and 9.2×10^4 L kg⁻¹ for La and Lu in water, and 2.8×10^4 and 4.1×10^4 L kg⁻¹ for La and Lu in the Ca medium) indicate the suitability of the tested smectites for lanthanide (and therefore, actinide) retention. Based on all the data, SCA-3, HEC and FEBEX clays are considered the best choices for water environments, whereas in Ca environments the suitable clays depended on the lanthanide considered.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Managing radioactive waste containing actinides is a key issue for the protection of the environment. Deep geological disposal is an accepted approach for the management of long-lived nuclear waste worldwide. In a deep geological repository, based on a multi-barrier system (engineered and natural barriers), the most feasible way by which a radionuclide may be transported to the earth's surface and the biosphere is by groundwater-induced dissolution of the canister and subsequent transport through the barriers. The effectiveness of radionuclide retention and isolation depends mostly on the engineered barriers, often composed of clays [1]. Among other factors, the clay geometry, total charge and isomorphous substitutions all have a significant effect on the sorption of pollutants onto the clays [2]. Among clay minerals, those rich in smectites are considered to be the most efficient for isolation of hazardous waste. This is due to their ability to undergo strain without fracturing, their very low hydraulic conductivity, their high cation sorption capacity and their ability to expand and enter into close contact with both waste and rock [3]. Beside the clay barrier, repositories contain concrete bulkheads in contact with

the smectitic barriers. It has been observed that cement degradation releases hyper-alkaline fluids rich in calcium that may induce geochemical transformations and modify the properties of the smectitic clay barriers [4,5]. Therefore, it is important to study the potential loss of isolation capacity of the clays due to this process.

Actinide sorption–desorption processes are usually studied via lanthanides, which are good analogues for the actinides due to their structural and chemical similarities (similarities in valence state, speciation, complexation, ionic radius, etc.) [6]. The available data regarding lanthanide sorption onto clays point to two main sorption mechanisms: surface complexation at the edges of the clay particles and cationic exchange [7–9]. Thus, the pH [10], the nature of the interlayer cations [11] and ionic strength [12] are all important for sorption. However, despite this identification of the factors affecting sorption, sorption data cannot yet be predicted from clay characteristics.

There is considerable controversy concerning sorption reversibility of lanthanides in smectites. Some researchers conclude that the sorption process is completely reversible [13] while other authors report the irreversibility of the sorption process due to the strong attractive forces between trivalent lanthanide cations and clay interlayer exchange sites [14], or a complete reversibility under acidic conditions and incomplete under basic conditions [15].

* Corresponding author. Tel.: +34 93 403 9276; fax: +34 93 402 1233.
E-mail address: miquel.vidal@ub.edu (M. Vidal).

This study was designed to evaluate the lanthanide sorption–desorption pattern in a set of smectites. As the sorption–desorption mechanisms of lanthanides may vary through the lanthanide series [16], here the lightest (La) and the heaviest (Lu) elements were chosen for the sorption studies. The smectites included some of the montmorillonites considered as candidates for engineered barriers. Furthermore, to simulate deep geological repository conditions, lanthanide sorption reversibility was examined in two media with varying initial concentrations of the lanthanides and Ca (to include secondary effects of cement leaching on the lanthanide–clay interaction). Additionally, the XRD characterization of the smectitic structure before and after the sorption–desorption experiments is included.

2. Materials and methods

2.1. Clay samples

The clay samples examined are 2:1 phyllosilicates. Table 1 summarizes their structural formula, geometry and isomorphous substitutions [17–22]. In all the samples, the <2 μm-fraction was obtained, and the carbonates and organic matter were eliminated to ensure purity. The samples were tested with their natural inter-laminar cations, except for saponite and Otay montmorillonite, which were also homoionized with Ca and Na cations (SAP(Ca), SCA-3(Na)). This homoionization was achieved by suspending the SAP and SCA-3 samples in 1 mol L⁻¹ CaCl₂ or NaCl solution, respectively. The suspension was stirred continuously and every 24 h it was centrifuged and subsequently the precipitate was resuspended in a fresh 1 mol L⁻¹ solution of CaCl₂ or NaCl. After four days, the samples were washed with deionized water until the chloride excess was eliminated. Finally, they were air-dried and ground [23].

2.2. Clay characterization: X-ray powder diffraction (XRD) and textural properties

XRD patterns of powdered samples were obtained for original clay samples and clay residues from the sorption–desorption tests, originated from those experiments with the lowest (0.03 meq L⁻¹) and highest (3 meq L⁻¹) initial lanthanide concentration. Diffraction patterns were obtained using a diffractometer (Kristalloflex D-500, Siemens) operating at 40 kV and 35 mA with Ni-filtered CuKα radiation and a graphite monochromator. Diffractograms were obtained for 2θ = 3–70° with a step of 0.05° and a counting time of 3 s. The basal spacing was obtained from XRD patterns of oriented aggregates in water [24].

The textural properties were studied by N₂ adsorption measurements at liquid nitrogen temperature. The experiments were carried out with a Micromeritics ASAP 2010 equipment. Before analysis, the samples were degassed for 2 h at 150 °C in vacuum.

2.3. Sorption–desorption tests

Batch sorption tests were carried out in 50-mL centrifuge tubes, with equilibration of 0.2 g of clay sample with 30 mL of the lanthanide solutions in two ionic media: deionized water and 0.02 mol L⁻¹ Ca(NO₃)₂ (Prolabo, RP Normapur). Due to the low solubility of lanthanide at basic pH at the highest concentrations tested, the initial pH of the solutions of lanthanide in Ca medium was adjusted to 7. Single solutions were prepared from La(NO₃)₃ and Lu(NO₃)₃ (99.9%, Aldrich). The initial concentrations of lanthanide were held to 3, 0.3 and 0.03 meq L⁻¹. The clay suspensions were end-over-end shaken at 30 rpm at room temperature for 24 h. The final suspensions were centrifuged at 10,000 rpm for 25 min (Hettich Universal 30 F) and filtered (Whatman 41, 0.22 μm). The

Table 1
Characteristics of smectitic clays selected for sorption–desorption experiments.

Clay	Structural formula	Geometry	Isomorphous substitutions	CEC ^c (cmol _c kg ⁻¹)	pH	External surface area (m ² g ⁻¹)	Microporous surface area (m ² g ⁻¹)
FEBOX	(Ca _{0.5} Na _{0.08} K _{0.11})(Si _{7.78} Al _{0.22})(Al _{2.78} Fe ^{III} _{0.33} Fe ^{II} _{0.02} Mg _{0.81})O ₂₀ (OH) ₄	Dioctahedral	Tetrahedral and octahedral sheets	1582	9.6	36.1	16.7
HEC	Ca _{0.33} (Si _{7.96} Al _{0.04})(Mg _{5.3} Al _{0.04} Li _{0.66})O ₂₀ (OH) ₄	Trioctahedral	Octahedral sheet	871	10.4	77.2	59.4
MX80	(Na _{0.36} Ca _{0.20})(Si _{7.96} Al _{0.04})(Al _{3.1} Mg _{0.56} Fe ^{III} _{0.18} Fe ^{II} _{0.16})O ₂₀ (OH) ₄	Dioctahedral	Octahedral sheet	1021	7.6	13.2	3.0
SAP ^a	Na _{0.8} (Si _{7.2} Al _{0.8})(Mg _{5.79} Fe _{0.14})O ₂₀ (OH) ₄	Trioctahedral	Tetrahedral sheet	1030	9.5	8.3	n.d.
SCA-3 ^b	(Mg _{0.45} Ca _{0.15} Na _{0.26} K _{0.01})(Si _{7.81} Al _{0.19})(Al _{2.55} Mg _{1.31} Fe _{0.12} Ti _{0.02})O ₂₀ (OH) ₄	Dioctahedral	Tetrahedral and octahedral sheets	1979	9.0	64.0	27.6
STX-1	(Ca _{0.27} Na _{0.04} K _{0.01})(Si ₈)(Al _{2.41} Mg _{0.71} Fe _{0.09} Ti _{0.03})O ₂₀ (OH) ₄	Dioctahedral	Octahedral sheet	828	8.6	54.8	8.1

FEBOX–bentonite FEBOX (ENRESA, Spain); HEC–hectorite (Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, USA); MX80–bentonite MX80 (CIEMAT, Spain); SAP–saponite (Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, USA); SCA-3–Otay montmorillonite (Solvay Alkali GmbH); STX-1–Texas montmorillonite (Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, USA).

^a Clay also used as homoionized modification with Ca ions: SAP(Ca).

^b Clay also used as homoionized modification with Na ions: SCA-3(Na).

^c CEC, theoretical cationic exchange capacity value, mathematically deduced from clay molecular formula.

supernatants were collected in polyethylene bottles, diluted with 1% HNO₃ and stored at 4 °C until analyzed.

Batch desorption tests were performed the day after the sorption tests, by bringing the clay residues from the sorption tests into contact with the two ionic media mentioned above, but without the lanthanide. The other experimental conditions were as described for the sorption tests.

2.4. Determination of the lanthanide concentration in the solutions derived from sorption–desorption tests

The lanthanide contents were analyzed by ICP-OES (PerkinElmer Optima-3200RL), for the samples at the high concentration range, and ICP-MS (PerkinElmer Elan-6000), for the samples at the low concentration range. The detection limit of the ICP-OES instrument is 50 µg L⁻¹ for La and 10 µg L⁻¹ for Lu, and that of the ICP-MS instrument is 5 ng L⁻¹ for both lanthanides. To correct instabilities in the ICP-MS measurements, ¹⁰³Rh was used as an internal standard, with a concentration of 200 µg L⁻¹ in all samples.

2.5. Data treatment

From the initial lanthanide concentration (C_{init} , meq L⁻¹), and the concentration in the supernatant after sorption (C_{sorb} , meq L⁻¹) and desorption experiments (C_{des} , meq L⁻¹), the following parameters were calculated:

(a) sorption distribution coefficient (K_d , L kg⁻¹):

$$K_d = \frac{(C_{\text{init}} - C_{\text{sorb}})}{C_{\text{sorb}}} \left(\frac{V}{m} \right) \quad (1)$$

where V is the liquid phase volume, in L; and m is the clay sample weight, in kg

(b) desorption distribution coefficient ($K_{d,\text{des}}$, L kg⁻¹):

$$K_{d,\text{des}} = \frac{(C_{\text{init}} - C_{\text{sorb}} - C_{\text{des}})}{C_{\text{des}}} \left(\frac{V}{m} \right) \quad (2)$$

(c) desorption rate (R_{des} , %):

$$R_{\text{des}} = \frac{C_{\text{des}}}{(C_{\text{init}} - C_{\text{sorb}})} 100 \quad (3)$$

(d) adjusted sorption distribution coefficient ($K_{d,\text{adj}}$, L kg⁻¹):

$$K_{d,\text{adj}} = \left(\frac{K_d}{R_{\text{des}}} \right) 100 \quad (4)$$

Sorption–desorption tests were carried out with a minimum of 3 replicates and a maximum of 6 replicates, thus allowing the mean and standard deviation of the derived parameters to be calculated.

3. Results and discussion

3.1. XRD clay characterization

3.1.1. Characterization of clays before sorption–desorption experiments

Diffraction patterns of smectites generally include basal and general reflections [25]. The basal reflections are due to the random superposition of the clay sheets and appear as symmetric lines. Their position varies in accordance with the separation of the sheets, which depends on the sample state. Conversely, the general reflections, designated hk , are asymmetric lines generated by the two-dimensional lattice of the clay sheets, and their position in the diffraction pattern depends only on the structure characteristics of the silicate sheets.

Examination of the XRD diffraction patterns of the smectites (not shown) demonstrated that smectites were hydrated and that they did not exhibit other crystalline impurities. However, the bentonites (FEBEX and MX-80) had crystalline impurities, such as quartz and cristobalite, which were reflected in their XRD diffraction patterns.

3.1.2. Clay characterization after sorption–desorption tests

The smectite basal spacing depends on the water–vapour pressure under which the sample has been prepared, the particular smectite group mineral analyzed, and the exchangeable cation present in the interlayer space. In the case of smectites, the water involved in the sorption–desorption processes corresponds to water layers in the interlamellar space. The basal d_{001} spacing varies with the number of these water layers. The basal space of smectite could vary from 9.6 (no water layers) to 12.5 Å (monolayer), 15.5 (bilayer) and 18.8 Å (trilayer) [26]. The maximum hydration state that can be reached in the smectites depends on the nature of the interlamellar cation.

The values of basal spaces for the original samples and after sorption–desorption experiments are summarized in Table 2. In the saponite, an expansion of the lamellar space up to approximately 15.0 Å was observed, which is compatible with the sorption–desorption of multivalent cations (such as a lanthanide or Ca) in the interlamellar space by ion exchange. Maximum expansion corresponded to the highest initial lanthanide concentration, and intermediate expansion to the lowest initial lanthanide concentration. However, in the Ca medium, this expansion took place at the lowest concentration as well. The only difference found when the smectite was homoionized with Ca (SAP(Ca)) was that the expansion was already total at the lowest concentration. The oriented aggregates of hectorite (HEC) led to conclusions similar to those for SAP.

In the SCa-3 clay, only a slight expansion of the interlamellar space was observed due to the fact that in the initial sample this already corresponded to a bilayer of water molecules. The expansion increased when increasing the initial lanthanide concentration, and it varied with the presence of Ca in the sorption medium. The only difference found when the original sample was homoionized with Na (SCa-3(Na)) is that this expansion was only total at the highest lanthanide concentration.

No significant changes in the diffraction patterns of the oriented aggregates of STx-1 were observed due to the sorption–desorption experiments and the changes observed on the FEBEX (from 14.9 Å in the initial samples to 14.6–15.1 Å depending on the medium) were minor compared with those observed in other silicates. Finally, in the MX80 bentonite, an expansion of the lamellar space up to 15.0 Å was observed, which is compatible with the sorption–desorption of multivalent cations in the interlamellar space by ion exchange. This expansion was total in the Ca medium but only at the highest concentration in the case of the water medium. At the lowest concentration and in the water medium, the layer expansion was higher with La than with Lu.

3.2. Lanthanide sorption

Table 3 summarizes the sorption data from both lanthanides in all the smectites tested, including the resulting pH in the supernatants. There was a general decrease in the K_d values with increasing initial concentration, with differences between the minimum K_d and the maximum K_d of up to two orders of magnitude. For a given ionic medium, the variation of K_d due to the changes in the lanthanide initial concentration was larger than that due to changing the smectite. The maximum K_d value depended on the lanthanide, clay and medium, and it was difficult to derive clear univariant relationships among clay properties and the K_d variation.

Table 2
Basal space of the initial clays and after sorption–desorption experiments.

Clay	d_{001} (Å) Initial	Sorption medium	C_{init} (meq L ⁻¹)	d_{001} (Å)	
				La	Lu
FEBEX	14.9	Water	0.03	14.6	14.7
			3	14.9	14.9
		Ca	0.03	15.0	14.9
HEC	12.5	Water	0.03	14.2	14.5
			3	14.6	14.7
				^a (vs)	
		Ca	0.03	14.8	15.2
			3	14.6	15.0
				^a (vw)	
MX80	11.7	Water	0.03	13.0	12.6
			3	14.0 (sh)	13.9 (sh)
				^a (vw)	
		Ca	0.03	13.9	14.5
			3	14.7	^a (vw)
				^a (w)	
SAP	12.4	Water	0.03	12.4	12.6
			3	13.6 (sh)	13.7 (sh)
				14.3	14.3
		Ca	0.03	13.1 (sh)	13.0 (sh)
			3	14.7	14.7
				^a (w)	
SAP(Ca)	–	Water	0.03	14.7	14.7
			3	13.5 (sh)	13.3 (sh)
				14.8	14.8
		Ca	0.03	14.8	15.0
			3	14.9	15.0
				^a (vw)	
SCa-3	14.4	Water	0.03	14.9	15.0
			3	14.9	14.9
				^a (vw)	
		Ca	0.03	14.0	15.0
			3	14.9	15.0
				^a (vw)	
SCa-3(Na)	–	Water	0.03	14.7	14.6
			3	15.2	14.8
				15.1	15.1
		Ca	0.03	14.7	15.1
			3	14.7	15.2
				^a (w)	
STx-1	15.3	Water	0.03	13.1	13.2
			3	15.0 (sh)	15.4 (sh)
				15.3	14.9
		Ca	0.03	14.8	14.8
			3	12.9 (sh)	12.9 (sh)
				14.9	14.9
STx-1	15.3	Water	0.03	13.0 (sh)	13.0 (sh)
			3	^a (w)	
				15.3	15.3
STx-1	15.3	Ca	0.03	15.3	15.3
			3	15.3	15.3
				15.3	15.3

(vw) indicates very weak; (w) indicates weak; (s) indicates strong; (vs) indicates very strong; (sh) indicates shoulder.

^a Peak at $2\theta = 10.3^\circ$ due to crystalline lanthanide nitrate.

The K_d (Lu) values were in general higher than the K_d (La), which is explained by the greater charge density of Lu, due to its lower radius (86 pm for Lu and 101 pm for La), which leads to a stronger electrostatic attraction for a given ligand [27,28]. An exception to this was occasionally observed in the water medium for clays with isomorphic substitutions in the octahedral sheets, such as in MX80 and HEC, and for the Ca-homoionized SAP. This could be explained by the higher electrostatic attraction between the interlayer Lu ions and the tetrahedral sheet in tetrahedrally substituted sam-

ples than in smectites without this kind of substitution, due to the more localized character of the negative charge in the vicinity of the tetrahedral Al.

Comparing the K_d values in those smectites that were homoionized, significant changes were observed between the two cases. This confirms that the substitution of the interlaminal cation in a smectite modified its sorption properties. For the SAP smectite, the inclusion of Ca as the interlaminal cation led to a marked increase in the K_d values in the water medium (for instance, the

Table 3
Sorption parameters for both lanthanides in the tested clays (C_{init} , meq L⁻¹; K_d (mean (SD)), L kg⁻¹).

Clay	Sorption medium	C_{init}	La		Lu	
			K_d	pH	K_d	pH
FEBEX	Water	3	15,100 (550)	6.6	15,900 (1600)	6.5
		0.3	18,000 (2100)	8.8	31,500 (1600)	8.3
		0.03	23,800 (3100)	9.2	32,900 (1400)	9.0
	Ca	3	630 (60)	6.6	1400 (200)	6.8
		0.3	2000 (260)	7.1	8800 (500)	7.3
		0.03	3600 (760)	7.3	13,200 (2700)	7.3
HEC	Water	3	25,100 (1100)	8.7	10,000 (1100)	7.1
		0.3	33,400 (5400)	10.1	12,100 (1600)	9.9
		0.03	50,100 (5700)	10.2	16,300 (2400)	10.1
	Ca	3	660 (30)	7.4	1140 (100)	8.1
		0.3	1700 (90)	7.6	12,700 (1400)	7.7
		0.03	2100 (260)	7.7	13,700 (1200)	7.9
MX80	Water	3	5000 (200)	7.5	3100 (140)	7.2
		0.3	5700 (240)	9.6	3700 (420)	9.7
		0.03	6600 (160)	9.8	4400 (350)	9.9
	Ca	3	600 (20)	6.3	460 (4)	6.6
		0.3	12,100 (1600)	7.6	6900 (250)	7.8
		0.03	13,500 (1200)	7.8	9100 (940)	8.0
SAP	Water	3	2100 (80)	8.5	2100 (110)	7.4
		0.3	2600 (80)	9.8	7300 (740)	9.6
		0.03	4300 (520)	10.0	8000 (470)	10.0
	Ca	3	400 (70)	7.3	1000 (2)	6.6
		0.3	2500 (50)	8.3	2600 (180)	8.7
		0.03	5500 (780)	8.5	27,000 (2100)	8.4
SAP(Ca)	Water	3	13,000 (690)	6.9	1500 (220)	6.5
		0.3	19,000 (1700)	8.6	4700 (380)	7.5
		0.03	24,000 (1300)	8.8	12,200 (800)	8.9
	Ca	3	150 (20)	6.4	300 (50)	6.6
		0.3	250 (30)	7.0	1300 (60)	7.1
		0.03	560 (50)	7.1	2200 (290)	7.3
SCa-3	Water	3	12,800 (1000)	6.9	27,000 (2000)	6.5
		0.3	18,000 (1600)	8.3	35,000 (4300)	7.7
		0.03	33,000 (2400)	9.2	48,500 (5500)	8.9
	Ca	3	430 (70)	6.2	850 (90)	6.5
		0.3	970 (50)	6.8	2200 (20)	6.9
		0.03	16,600 (1700)	7.0	11,200 (990)	7.1
SCa-3(Na)	Water	3	7200 (1300)	5.9	1300 (30)	5.3
		0.3	10,400 (910)	7.2	15,400 (1100)	7.0
		0.03	17,300 (1000)	7.6	24,300 (1500)	7.5
	Ca	3	120 (30)	5.9	260 (30)	6.3
		0.3	220 (10)	6.0	520 (20)	6.7
		0.03	400 (40)	6.5	760 (90)	6.8
STx-1	Water	3	11,100 (880)	6.5	11,300 (460)	6.1
		0.3	13,200 (770)	7.2	12,400 (1400)	7.2
		0.03	19,200 (1200)	7.7	15,600 (1600)	7.8
	Ca	3	250 (10)	6.3	580 (20)	6.1
		0.3	550 (10)	6.5	13,000 (2800)	6.7
		0.03	1200 (560)	6.7	16,700 (2000)	6.8

K_d (La) increased from 2100–4300 to 13,000–24,000 L kg⁻¹) but a decrease in the Ca medium (for instance, the K_d (La) decreased from 400–5500 to 150–560 L kg⁻¹), while for SCa-3, the inclusion of Na led to a decrease in the K_d values in both media (for instance, the K_d (Lu) decreased from 27,000–48,500 to 1300–24,300 L kg⁻¹ in the water medium, and from 850–11,200 to 260–760 L kg⁻¹ in the Ca medium).

For many clays, there was a marked decrease in the K_d values when Ca was introduced into the contact solution, over the whole concentration range tested, and it especially influenced the quantification of the maximum K_d (see for instance the case of K_d (Lu) in FEBEX, whose values decreased from 15,900–32,900 L kg⁻¹ in the water medium to 1400–13,200 L kg⁻¹ in the Ca medium). The effect of Ca on K_d can be explained by the fact that the Ca ions tend to sorb at interlayer sites, and are then able to displace the lanthanides to less specific sites. While in terms of K_d the competitive effect of Ca

ions was minor (in the scenarios with the maximum lanthanide K_d , K_d (Ca) ranged for all clays from 3 to 23 L kg⁻¹), the sorbed concentration of Ca was much higher than those of the two lanthanides and thus led to a decrease in lanthanide K_d .

The pH is a major factor affecting lanthanide sorption, since the pH may affect the existence and creation of new sorption sites in clays [16]. However, pH was not controlled in these experiments. While the initial pH in the sorption experiments in the two media was different (around 5.5 in the water medium and 7 in the Ca medium), the resulting pH in the final contact solutions increased in the water medium, while it was closer to the initial pH values in the Ca medium than in the water medium, with final pH values slightly higher or lower than the initial pH (see for instance the case of the FEBEX clay). In fact, the final pH mostly depended on the C_{init} and thus on the C_{eq} of the lanthanides. As seen in Table 3, the range of pH variation (more acidic for the experiments with the

Table 4Desorption parameters and adjusted distribution coefficients for both lanthanides in the tested clays (C_{init} , meq L^{-1} ; $K_{d,des}$ (mean (SD)), L kg^{-1} ; R_{des} (mean (SD)), %; $K_{d,adj}$, 10^3 L kg^{-1} ; $RK_{d,des}$, dimensionless).

Clay	Sorption medium	C_{init}	$K_{d,des}$	La			Lu			
				R_{des}	$K_{d,adj}$	$RK_{d,des}$	$K_{d,des}$	R_{des}	$K_{d,adj}$	$RK_{d,des}$
FEBEX	Water	3	24,600 (1700)	0.63 (0.04)	2400	1.8	20,400 (260)	0.77 (0.02)	2060	1.7
		0.3	27,200 (1100)	0.56 (0.04)	3210		25,900 (2500)	0.60 (0.07)	5250	
		0.03	44,900 (490)	0.37 (0.04)	6430		35,100 (300)	0.5 (0.1)	6580	
	Ca	3	670 (110)	19 (2)	3	4.3	1900 (300)	7 (1)	20	7.1
		0.3	2100 (200)	7.0 (0.7)	29		10,300 (1500)	1.5 (0.2)	590	
		0.03	2900 (180)	5.1 (0.3)	71		13,400 (1200)	1.2 (0.1)	1100	
HEC	Water	3	28,600 (900)	0.54 (0.02)	4650	4.0	16,300 (480)	0.95 (0.03)	1050	3.2
		0.3	38,400 (400)	0.38 (0.04)	8790		18,000 (1000)	0.8 (0.1)	1510	
		0.03	114,000 (2500)	0.16 (0.04)	31,300		53,000 (5700)	0.34 (0.08)	4800	
	Ca	3	640 (20)	19.1 (0.6)	4	4.6	1300 (80)	11.3 (0.5)	10	11
		0.3	1840 (70)	7.7 (0.2)	22		12,900 (1100)	1.19 (0.09)	1070	
		0.03	2950 (160)	5.0 (0.3)	42		14,700 (440)	0.71 (0.04)	1930	
MX80	Water	3	7000 (180)	2.13 (0.03)	240	1.4	4000 (550)	3.9 (0.5)	79	1.7
		0.3	8000 (290)	1.95 (0.04)	290		4600 (170)	3.3 (0.1)	110	
		0.03	9600 (530)	1.6 (0.1)	410		6800 (1300)	2.4 (0.4)	180	
	Ca	3	1400 (70)	10.0 (0.6)	6	17	700 (20)	17.7 (0.1)	3	18
		0.3	16,700 (820)	0.90 (0.04)	1340		8600 (480)	1.8 (0.1)	380	
		0.03	24,000 (310)	0.59 (0.06)	2290		12,300 (1000)	1.2 (0.1)	760	
SAP	Water	3	2600 (80)	5.7 (0.1)	37	2.5	2700 (140)	5.6 (0.2)	38	3.1
		0.3	3600 (140)	4.3 (0.2)	60		7500 (400)	2.1 (0.1)	350	
		0.03	6500 (780)	2.4 (0.3)	180		8500 (370)	1.85 (0.06)	430	
	Ca	3	860 (100)	15 (1)	3	5.9	1700 (40)	8.0 (0.2)	13	11
		0.3	2200 (100)	6.5 (0.3)	38		3600 (360)	4.0 (0.4)	65	
		0.03	5100 (80)	2.88 (0.01)	190		18,700 (60)	0.8 (0.2)	3380	
SAP(Ca)	Water	3	20,100 (1200)	0.75 (0.05)	1730	1.6	4000 (570)	3.7 (0.6)	41	3.3
		0.3	23,800 (1400)	0.65 (0.04)	2920		5700 (420)	2.6 (0.2)	180	
		0.03	31,700 (4500)	0.49 (0.07)	4900		13,000 (1500)	1.2 (0.2)	1020	
	Ca	3	330 (60)	31 (4)	0.5	4.8	960 (80)	14.0 (0.3)	2	4.2
		0.3	800 (200)	17 (3)	2		1800 (120)	8.1 (0.3)	16	
		0.03	1600 (410)	10 (2)	6		4000 (420)	3.8 (0.4)	58	
SCa-3	Water	3	38,800 (1900)	0.39 (0.02)	3280	1.9	28,700 (480)	0.55 (0.02)	4910	1.7
		0.3	61,800 (5200)	0.25 (0.03)	7200		41,500 (5000)	0.38 (0.04)	9210	
		0.03	73,000 (4100)	0.22 (0.02)	15,000		49,900 (6200)	0.31 (0.04)	15,600	
	Ca	3	530 (120)	23 (4)	2	53	1800 (35)	11.6 (0.1)	7	6.8
		0.3	1100 (40)	12.2 (0.2)	8		2300 (45)	6.4 (0.4)	34	
		0.03	28,000 (550)	0.57 (0.01)	2910		12,200 (2200)	1.2 (0.2)	930	
SCa-3(Na)	Water	3	11,800 (800)	1.29 (0.08)	560	2.0	4000 (760)	3.7 (0.7)	35	7.4
		0.3	14,400 (1600)	1.1 (0.1)	940		24,100 (2200)	0.62 (0.06)	2480	
		0.03	23,200 (1100)	0.66 (0.04)	2620		29,400 (2400)	0.52 (0.03)	4670	
	Ca	3	140 (30)	51 (5)	0.2	3.6	460 (55)	25.4 (0.6)	1	4.3
		0.3	200 (5)	42.2 (0.5)	0.5		760 (90)	17 (1)	3	
		0.03	500 (40)	24 (2)	2		2000 (660)	8 (3)	10	
STx-1	Water	3	12,300 (320)	1.23 (0.03)	900	1.9	8600 (240)	1.77 (0.04)	640	11
		0.3	14,500 (1500)	1.1 (0.1)	1200		34,500 (3600)	0.44 (0.04)	2810	
		0.03	23,000 (2000)	0.70 (0.06)	2740		92,000 (1400)	0.21 (0.04)	7430	
	Ca	3	740 (20)	17.0 (0.1)	2	2.6	1100 (30)	13.0 (0.3)	4	37
		0.3	790 (10)	16.0 (0.2)	3		15,200 (3200)	1.0 (0.2)	1300	
		0.03	1900 (240)	8 (1)	19		41,000 (11,000)	0.40 (0.09)	4180	

maximum C_{init} and increasing with decreasing initial C_{init}) generally agreed with the K_{d} and C_{eq} variations, since the higher the K_{d} , the lower the C_{eq} and the higher the resulting pH in the contact solution.

3.3. Sorption reversibility

Table 4 summarizes data on sorption reversibility for both lanthanides in the smectitic clays. The $K_{\text{d,des}}$ values increased when the initial lanthanide concentration was decreased, similarly to what was observed with K_{d} . The $K_{\text{d,des}}$ were generally higher than K_{d} (the mean value of the calculated $K_{\text{d,des}}/K_{\text{d}}$ ratios was 1.6 for all the data set), and similarly to the K_{d} they were generally higher in the water than in the Ca medium, with the exception of the MX80 clay. Therefore, it can clearly be stated that the lanthanide sorption in these smectites was partially irreversible. The results obtained agree with those previously reported that predicted sorption irreversibility due to the strong attractive forces between trivalent lanthanide cations and clay interlayer exchange sites [14]. The desorption yields allowed us to draw similar conclusions to those drawn from $K_{\text{d,des}}$ since, as observed for other elements [29], increases in $K_{\text{d,des}}$ were related to decreases in the R_{des} values. For La and Lu, R_{des} ranged from lower than 1% to 6% in water. In the Ca medium, the values ranged from lower than 1% to 50% for La, and from lower than 1% to 25% for Lu. Therefore, not only was the lanthanide sorption lower in the Ca medium, but it was also more reversible.

A complementary approach to examine the sorption reversibility is through the calculation of the adjusted K_{d} ($K_{\text{d,adj}}$). While $K_{\text{d,des}}$ provides information about the equilibrium displacement of a lanthanide between the clay in which it is already incorporated and a contact solution, $K_{\text{d,adj}}$ corrects the initial (reversible) sorption K_{d} by the lanthanide fraction participating in the sorption equilibrium. These two parameters give similar information and were highly correlated (La: $\log K_{\text{d,adj}} = 1.9 \times \log K_{\text{d,des}} - 1.9$; $r = 0.994$; Lu: $\log K_{\text{d,adj}} = 2.0 \times \log K_{\text{d,des}} - 2.3$, $r = 0.985$). Therefore, both parameters satisfactorily describe the lanthanide sorption process including its irreversible character.

3.4. Proposed clays suitable for engineered barriers

In order to select clays suitable for engineered barriers for radioactive waste repositories, various factors have to be considered, such as their physical and hydraulic properties, their sensitivity to damages caused by the radiation and also their chemical properties related to radionuclide retention, the latter being the target properties examined in this work. Although the source term in waste repositories is going to be multipollutant, while our studies are based in single scenarios, the results obtained may give some initial hints on the most suitable smectites, in respect of their retention capacity, to be used in the repositories.

As the values of the sorption–desorption parameters varied not only due to the clay–lanthanide combination, but also due to the initial lanthanide concentration and composition of the sorption medium, a unique proposal for the most suitable clay cannot easily be provided. Suitable clays are those with high $K_{\text{d,des}}$ and $K_{\text{d,adj}}$ values in the conditions expected in deep geological repositories. As stated in the previous section, it was observed that $K_{\text{d,des}}$ and $K_{\text{d,adj}}$ decreased with increasing C_{init} . This was easily deduced from the ratios of the $K_{\text{d,des}}$ ($RK_{\text{d,des}}$), calculated from its maximum and minimum values (quantified at the lowest and highest C_{init} , respectively), which varied from 1.4 to 11 in the water medium, and from 2.6 to 53 in the Ca medium. This could be explained by the fact that the higher C_{init} , the larger the contribution of the mechanism based on sorption at less specific sites that appears to be more reversible. This is in accordance with the XRD analysis of the oriented aggregates, which demonstrated a mayor expansion at the

higher concentrations indicating that at these concentrations ion exchange took place. The decrease in $K_{\text{d,des}}$ and $K_{\text{d,adj}}$ due to the increase in the C_{init} was greater in the Ca than in the water medium, due to the blocking effect of Ca at higher concentrations and its lower hydrated radius than that of any lanthanide [30]. This is consistent with the expansion of sheets observed in a number of clays in Ca, but not in the water medium (FEBEX, MX80, SAP, SCa-3(Na)).

When comparing the sequence of SAP(Ca), FEBEX, SCa-3 clays (smectites with isomorphous substitutions in the tetrahedral sheets) in all scenarios, the sorption reversibility was inversely related to their total charge. This could be due to the fact that a localized charge favours electrostatic interactions and thus sorption by ion exchange. In most cases, the presence of Ca in the interlamellar spacing favours sorption in both media with both lanthanides, which can be observed by comparing SAP and SCa-3 to SAP(Ca) and SCa-3(Na), respectively. This could be explained by a more hydrated initial state of the sheets that maintains the lanthanide access to the interlamellar spacing and would be in accordance with the oriented aggregates at lower concentrations showing larger interlamellar spacing for SAP(Ca) and SCa-3 than for SAP and SCa-3(Na), respectively.

Summarizing, SCa-3, HEC and FEBEX clays (and also STx-1, especially for Lu) appear to be good options in a water sorption medium. In a Ca medium, which can be considered closer to real scenarios due to the potential presence of Ca leachates from the surrounding concrete bulks in the repository, the proposed clays depend on the lanthanide, with MX-80, SCa-3 and SAP the preferred options for La, and STx-1, SAP, FEBEX and HEC suitable for Lu. It is therefore suggested that clays with dioctahedral geometry be chosen for the retention of lanthanides in water media in an engineered barrier system due to their initial high lanthanide sorption and subsequent low sorption reversibility, while the clays with trioctahedral geometry could be used for lanthanide retention in Ca media.

Acknowledgements

This research was supported by the Ministerio de Educación y Ciencia (projects CTM2005-03847/TECNO and CTQ2007-63297), the Junta de Andalucía (project P06-FQM-02179), from PETRI (project PTR95-0996.OP), and from EU – 6th Framework Programme (HRM Activity under the MRTN-CT-2006-035957 contract). The authors are also grateful to the CNPq-Conselho Nacional de Desenvolvimento Científico e Tecnológico and CAPES-Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil for a postdoctoral scholarship. Besides, the authors would like to thank Dr. A. Padró for his technical assistance in the ICP-OES and ICP-MS analyses.

References

- [1] A. Meunier, L. Velde, The reactivity of bentonites: a review. An application to clay barrier stability for nuclear waste storage, *Clays Clay Miner.* 33 (1998) 187–196.
- [2] M.E. Essington, *Soil and Water Chemistry: An Integrative Approach*, CRC Press, Boca Raton, Florida, 2004.
- [3] R. Pusch, Engineered barriers, in: V. Popov, R. Pusch (Eds.), *Disposal of Hazardous Waste in Underground Mines*, Wessex Institute of Technology, UK, 2006, pp. 35–40.
- [4] F. Huertas, Effects of cement on clay barrier performance, *ECOCLAY Project Tech. Rep. F14W-CT96-0032*, European Commission, Brussels, 2000.
- [5] M. Villar, I. Pérez de Villar, P. Martín, M. Pelayo, A. Fernández, A. Garralón, J. Cuevas, S. Leguey, E. Caballero, F. Huertas, C. Jiménez de Cisneros, J. Linares, E. Reyes, A. Delgado, J. Fernández-Soler, J. Astudillo, The study of Spanish clays for their use as sealing materials in nuclear waste repositories: 20 years of progress, *J. Iberian Geol.* 32 (2006) 15–36.
- [6] N. Chapman, J. Smellie, Introduction and summary of the workshop: natural analogues to the conditions around a final repository for high-level radioactive waste, *Chem. Geol.* 55 (1986) 167–173.
- [7] V. Sinityn, S. Aja, D. Kulik, S. Wood, Acid–base surface chemistry and sorption of some lanthanides on K^+ -saturated Marblehead illite: I. Results of an

- experimental investigation, *Geochim. Cosmochim. Acta* 64 (2000) 185–194.
- [8] M. Bradbury, B. Baeyens, Sorption of Eu on Na and Ca-montmorillonite: experimental investigations and modelling with cation exchange and surface complexation, *Geochim. Cosmochim. Acta* 66 (2002) 2325–2334.
- [9] T. Stumpf, C. Hennig, A. Bauer, M. Denecke, T. Fanghanel, An EXAFS and TRLS study of the sorption of trivalent actinides onto smectite and kaolinite, *Radiochim. Acta* 92 (2004) 133–138.
- [10] S. Bruque, T. Mozas, A. Rodriguez, Factors influencing the retention of lanthanides ions by montmorillonite, *Clay Miner.* 15 (1980) 413–420.
- [11] J. Maza-Rodriguez, P. Olivera-Pastor, S. Bruque, A. Jiménez-Lopez, Exchange selectivity of lanthanide ions in montmorillonite, *Clay Miner.* 27 (1992) 81–89.
- [12] M. Bradbury, B. Baeyens, Modelling the sorption of Mn(II), Co(II), Ni(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonites: linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides, *Geochim. Cosmochim. Acta* 69 (2005) 875–892.
- [13] D.R. Turner, R.T. Pabalan, F.P. Beretti, Neptunium (V) sorption on montmorillonite: an experimental and surface complexation modeling study, *Clays Clay Miner.* 46 (1998) 256–259.
- [14] C. Bonnot-Courtois, N. Jaffrezic-Renault, Étude des échages entre terres rares et cations interfoliaires de deux argiles, *Clay Miner.* 17 (1982) 409–420.
- [15] F. Coppin, S. Castet, G. Berger, M. Loubet, Microscopic reversibility of Sm and Yb sorption onto smectite and kaolinite: experimental evidence, *Geochim. Cosmochim. Acta* 67 (2003) 2515–2527.
- [16] Y. Takahashi, A. Tada, H. Shimizu, Distribution pattern of rare earth ions between water and montmorillonites and its relation to the sorbed species of the ions, *Anal. Sci.* 20 (2004) 1301–1306.
- [17] L. Ames, L. Sand, S. Goldich, A contribution on the Hector, California bentonites deposit, *Econ. Geol.* 53 (1958) 22–37.
- [18] R. Grim, G. Kulbicky, Montmorillonite: high temperature reactions and classification, *Am. Mineral.* 46 (1961) 1329–1369.
- [19] J. Post, Saponite from Near Ballarat, California, *Clays Clay Miner.* 32 (1984) 147–153.
- [20] W. Janes, J. Bigham, Charge reduction, octahedral charge and lithium retention in heated Li-saturated smectites, *Clays Clay Miner.* 35 (1987) 440–448.
- [21] A. Fernandez, B. Baeyens, M. Bradbury, P. Rivas, Analysis of the porewater chemical composition of a Spanish compacted bentonite used in an engineered barrier, *Phys. Chem. Earth* 29 (2004) 105–118.
- [22] G. Montes-H, B. Fritz, A. Clement, N. Michau, Modelling of geochemical reactions and experimental cation exchange in MX-80 bentonite, *J. Environ. Manage.* 77 (2007) 35–46.
- [23] A.I. Becerro, Desarrollo de un sistema modelo de análisis estructural de la reactividad química de compuestos de silíceo 2D y 3D aplicado a la formación de $\text{Lu}_2\text{Si}_2\text{O}_7$, Doctoral Thesis, Universidad de Sevilla, 1997.
- [24] D. Moore, R. Reynolds, X-ray Diffraction and the Identification and Analyses of Clay Minerals, Oxford University Press, UK, 1989.
- [25] G. Brown, The X-ray Identification and Crystal Structures of Clay Minerals, Clay Minerals Group, London, 1961.
- [26] M.D. Alba, A.I. Becerro, M.A. Castro, A.C. Perdigón, Hydrothermal reactivity of Lu-saturated smectites: Part I. A long range order study, *Am. Mineral.* 86 (2001) 115–123.
- [27] S. Cotton, Lanthanide and Actinide Chemistry, John Wiley and Sons, Chichester, England, 2006.
- [28] J.E. House, Inorganic Chemistry, Academic Press, San Diego, California, USA, 2008.
- [29] J. Sastre, G. Rauret, M. Vidal, Sorption-desorption tests to assess the risk derived from metal contamination in mineral and organic soils, *Environ. Int.* 33 (2007) 246–256.
- [30] J. Kielland, Individual activity coefficients of ions in aqueous solutions, *J. Am. Chem. Soc.* 59 (1937) 1675–1678.