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Modeling cesium retention onto Na-, K- and Ca-smectite: Effects of ionic strength, exchange and competing cations on the determination of selectivity coefficients

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Abstract

Cesium (^{137}Cs) retention onto three homoionic smectites (Na-, K- and Ca-smectite), obtained from natural Spanish FEBEX bentonite, was studied. Special emphasis was given to the analysis of non-linear sorption behaviour and the dependence of selectivity on the ionic strength.

A very large set of experimental sorption data was generated from sorption tests under a wide range of pHs (2–11), ionic strengths (10^{-3} to 10^{0} M), and radionuclide concentrations (10^{-10} to 10^{-3} M). The aqueous phase, in contact with the clay, was analysed to quantify the effects of the presence of trace aqueous ions on Cs retention.

For all the exchanged clays, Cs sorption was non-linear and a two-site exchange model approach was adopted to interpret and model sorption data. Highly selective sites for Cs sorption (Type 1 sites, T1), resembling those present in micaceous materials, with very low capacity but controlling uptake of Cs at low concentration, were observed. The logarithm value of selectivity coefficients determined for Cs^+ in respect to Na^+, K^+ and Ca^{2+} in these sites is: $Log^{Cs}_{Na}K_{SEL}(T1) = 7.59 \pm 0.15$, $Log^{Cs}_{K}K_{SEL}(T1) = 5.15 \pm 0.15$ and $Log^{Cs}_{Ca}K_{SEL}(T1) = 14.41 \pm 0.17$, respectively.

The exchange sites at the surface of smectite sheets (planar sites), with a capacity approximately equivalent to the cation exchange capacity (CEC) of the clay, constitute the second type of sorption sites (Type 2 sites, T2). The logarithm of the selectivity coefficients determined for Cs^+ with respect to Na^+, K^+ and Ca^{2+} is: $Log^{Cs}_{Na}K_{SEL}(T2) = 1.68 \pm 0.15$, $Log^{Cs}_{K}K_{SEL}(T2) = 1.16 \pm 0.15 Log^{Cs}_{Ca}K_{SEL}(T2) = 3.02 \pm 0.15$, respectively.

The analysis of the dependence of sorption values on the ionic strength clearly indicated that for a correct interpretation of data, competition effects of trace ions in solution must be always accounted for.

Data obtained in this work and performed analyses are basic to explain the behaviour of *raw* FEBEX bentonite, and other smectite-based clay materials, under more complex experimental conditions.

1. INTRODUCTION

^{137}Cesium (Cs) is an important fission product of the irradiation of uranium-based fuels and it is a major component of high-level nuclear waste: ^{135}Cs is of concern because of its very long half-life ($\sim 2.3 \times 10^6$ years). From both nuclear accidents and weapons testing, Cs has been released into soils and waters; environmentally radiocesium is of particular concern because it exists always as the highly soluble monovalent cation Cs^+; and also because it's chemically similar to potassium, an element required for important functions of all living cells – making it easily incorporated into living organisms.

Upon environmental release, cesium migration is mostly controlled by sorption onto mineral surfaces; it is especially strongly adsorbed onto clays by ionic exchange. For clay,

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Cs uptake is largely dependent on the clay's cation exchange capacity (CEC) and on the presence of mica-like minerals. These minerals offer sorption sites with high selectivity for alkali cations (Sawhney, 1972; Eberl, 1980).

Smectite and illite are 2:1 clays: their structural unit is formed by two tetrahedral (T) and one octahedral sheet (O), present in a T–O–T configuration (Van Olphen, 1977). The characteristic combination of sheets in clay is called a *layer* and various stacked layers form the mineral particle. For T sheets, tetravalent Si is usually replaced by trivalent elements (such as Al) and, for O sheets, trivalent Al can be replaced by divalent elements (such as Mg). These replacements in the clay structure lead to an excess of negative charge; to compensate for this negative charge and to maintain electro-neutrality, cations are adsorbed at TOT layers surfaces (*planar sites*).

For swelling clays, such as smectite, exchangeable cations are present both at the surface of the particles and at the region between layers (*interlayer*). These cations, however, can be readily exchanged with other cations present in solution. The amount of exchangeable cations determines the CEC of the clay.

The non-expandable illite usually shows a lower CEC than smectite, because the main cation that compensates for the structural negative charge is potassium. Potassium sorption causes the dehydration and collapse of the interlayer and, therefore, this collapsed interlayer is not available for cation exchange (Van Olphen, 1977).

Bentonite, a material envisaged for engineered barriers of radioactive waste repositories (Pusch, 2006), is a clay rock with a high smectite content and low permeability, good plasticity and selling properties, in addition to a high sorption capability for many cations.

Although Cs sorption onto smectite (as a pure mineral) or smectite rich clayrocks, such as bentonite, has been widely studied (Wahlberg and Fishman, 1962; Erten et al., 1988; Staunton and Roubaud, 1997; Dyer et al., 2000; Tsai et al., 2001; Krumhansl et al., 2001; Missana et al., 2004; Tertre et al., 2005; Wu et al., 2009; Galambos et al., 2010; Yllera de Llano et al., 1998; Galambos et al., 2012, amongst others), most of these studies described sorption with the variation of one or several parameters (ionic strength, pH, temperature, concentration of some ion or different ligands) – but with no sorption model capable of comprehensively interpreting Cs uptake.

The comparison of sorption results is obstructed by semi-empiric approaches to the analysis of experimental data obtained under different experimental conditions, above all when sorption is non-linear. These semi-empiric approaches limit the application of predictive models of contaminant migration in the environment.

In this study, two controversial points for the interpretation of some features of Cs sorption onto smectite are addressed: (1) the (apparent) variation of exchange selectivity coefficients as a function of the ionic strength and (2) the (sometimes) observed non-linear sorption.

Sorption is non-linear when distribution coefficients (K_d) depend on the aqueous Cs concentration (Cornell, 1993). For clay rocks, this behaviour is generally related to the existence of different sorption sites, attributed to the presence of micaceaus minerals, such as illite. Micaceous minerals, in addition to *planar* sites, possess *frayed edge sites*, FES, arising from the weathering of the clay particlés edges. Cations including Cs^+, Rb^+, Li^+, NH_4^+, characterised by low hydration energy and small dehydrated radius, can replace K^+ at these weathered edges (Sawhney, 1972; Cornell, 1993). Other monovalent ions, such as Na^+, can access these sites when their concentration is high enough. Yet at these sites, divalent cations with larger sizes and high hydration energy are improbably found (Sawhney, 1972).

In spite of the very low density of FES (<1% of the CEC), they clearly dominate Cs sorption at low concentrations (Sawhney, 1972; Brouwer et al., 1983; Cremers et al., 1988; Poinssot et al., 1999; Bradbury and Baeyens, 2000).

Smectite's surface is expected to be nearly uniform (Gaudette et al., 1966): Kim et al. (1996a) demonstrated, by spectroscopic techniques, the heterogeneity of sorption sites for Cs in illite; whereas at the surface of smectite, multiple sites were not found (Kim et al., 1996b). Thus, Cs sorption on smectite is expected to occur mainly onto planar sites.

Yet non-linear Cs sorption has also been observed, in several cases, for smectite (Wahlberg and Fishman, 1962; Eliason, 1966; Staunton and Roubaud, 1997; Missana et al., 2004). This non-lineal sorption of smectite was attributed by Staunton and Roubaud (1997) to both changes in entropy, as Cs occupies an increasing fraction of the exchange complex and to the possible partial collapse of clay layers, but not to the heterogeneity of the exchange sites. Other authors related these differences in selectivity either to the possible formation of inner sphere complexes (Sposito, 1984; Xu and Harsh, 1990) or to the existence of a different charge location in external or internal smectite layers (Staunton and Roubaud, 1997; Onodera et al., 1998, Liu et al., 2008).

Non-linear sorption has been generally modelled by Langmuir or Freundlich-like isotherms (Staunton and Roubaud, 1997; Wu et al., 2009; Galambos et al., 2010; Tachi et al., 2011; Yildiz et al., 2011), but this approach is of little value for the understanding of radionuclide retention mechanisms.

Selectivity coefficients were found to vary with ionic strength for different clays by several authors (Wahlberg and Fishman, 1962; McBride, 1979; Staunton and Roubaud, 1997). Staunton and Roubaud (1997) stated that purely electrostatic considerations did not explain the exchange reactions of Cs on clays and Xu and Harsh (1990) suggested a covalent interaction between Cs and the clay surface. Wahlberg and Fishman (1962) considered the possibility that at the lower ionic strengths, the separation between the solid and the aqueous phase might be not perfect because of the existence of smaller particles, biasing K_d values determination; according to their hypothesis, as the ionic strength increases there might be affects related to the increase of the size of clay particles.

However, in the absence of a sorption model with the capability for the description of the variability of Cs sorption, with its concentration or water chemistry, it is quite difficult to assess whether these hypothesis are plausible.

Multisite cation exchange models were proposed to explain Cs sorption for illite: three sites with different affinity

for Cs were proposed by Brouwer et al. (1983) and Bradbury and Baeyens (2000), but two-site models were also proposed (Zachara et al., 2002; Liu et al., 2004).

Multisite models have not been reported for Cs sorption onto smectite, but modeling of Cs sorption by surface complexation with the triple layer model has been published (Gutierrez and Fuentes, 1996).

Thus, the objective of the present study is to analyse and model Cs sorption on smectite under the widest possible range of chemical conditions and Cs concentrations; assessing the affects of ionic strength, exchange and solution cations, and Cs concentration on selectivity coefficients determination.

For an adequate description of Cs sorption and to test the modeling approach, a large set of experimental data is required but such large datasets are quite scarce in the literature.

Furthermore, competitive cations present in solution may play a significant role in Cs retention, above all when high affinity sites are present. Even in purified and homoionic systems, trace elements coming from the dissolution of the clay exist, and it is impossible to get rid of them (Baeyens and Bradbury, 2004). Thus, it is strictly necessary to account for them for the accurate description of the system (Baeyens and Bradbury, 2004). This is of special importance for the determination of selectivity coefficients that can be biased if solute trace elements are not accounted for.

2. MATERIALS AND METHODS

2.1. Smectite clay

The clay for this study (FEBEX bentonite), was mined from the Cortijo de Archidona deposit Almeria (Spain). FEBEX clay has been used as reference material in many international projects involving radionuclide migration at geological repositories of radioactive waste: *Full-scale Engineered Barriers EXperiment*, FEBEX I and II (Fuentes-Cantillana et al., 1997; Huertas et al., 2000); *Colloid and Radionuclide Retardation*, CRR, and *Colloid Formation and Migration*, CFM (information of both available at www.grimsel.com); *Fundamentals of Radionuclide Migration*, FUNMIG (Buckau et al., 2009) and *Bentonite Erosion: effects on the long term performance of the engineered barrier and radionuclide transport*, BELBAR (www.skb.se).

The raw FEBEX clay has a $93 \pm 2\%$ content of smectite; its accessory minerals include the following: quartz ($2 \pm 1\%$), plagioclase ($3 \pm 1\%$), cristobalite ($2 \pm 1\%$), potassic feldspar, calcite, and tridymite. Previous mineralogical studies showed that the smectite phase is comprised of randomly interstratified illite–smectite mixed layers with 10–15% of illite layers (Cuadros and Linares, 1996; Huertas et al., 2000; Leguey et al., 2002; Fernandez et al., 2004); but illite, as a *pure* trace mineral, was never detected.

The FEBEX clay cation exchange capacity, CEC, is 102 ± 4 meq/100 g and its N_2-BET surface area is 33 $m^2\ g^{-1}$. A summary of the main properties of the FEBEX clay are shown in Table 1: more details can be found elsewhere (Huertas et al., 2000; Fernandez et al., 2004).

2.2. Radionuclide

The radionuclide used for this study, was ^{137}Cs (as CsCl in 0.1 HCl, Isotope Products). The half-life of ^{137}Cs is 30.2 years. This radionuclide decays by beta emission to ^{137m}Ba, causing the emission of gamma rays (662 keV). Cs activity in solution was measured by γ-counting with a NaI detector (Packard Autogamma COBRA 2). The detection limit is 5×10^{-11} M. The counting efficiency for ^{137}Cs is 0.26. A calibrated and certified ^{137}Cs sample was prepared by CIEMAT's "Laboratory of ionising radiation metrology" (Ref: MRC 2008-016, 3/4/2008 CIEMAT, Spain) for the verification of the efficiency of the counting system. The uncertainty for the counting procedure is less than 2%.

2.3. Preparation of the clay suspensions

Previous to use in sorption experiments, the clay was purified and homoionised in Na, K or Ca. The raw clay was washed three times with 1 M $NaClO_4$, KCl or $Ca(NO_3)_2$ to eliminate the soluble salts and to obtain the homoionic smectite (Na-, K- or Ca-smectite). After elimination of the supernatant from the last washing, the exchanged clay was placed in centrifuge tubes with deionised water. Smectite particles of less than 0.5 μm, for use in sorption tests, were separated by centrifuging the suspensions (2500*g*, 10 min). For the prevention of extensive dissolution of the clay, this fine fraction was precipitated in a glass container with 1 M $NaClO_4$, KCl or $Ca(NO_3)_2$, (for Na-, K- or Ca-smectite, respectively). The clay washing/centrifuging procedure was repeated approximately 20 times for Na-smectite and approximately 30 times for Ca-and K-smectite.

When enough of the fine fraction was collected, the clay suspension was introduced into dialysis bags that were sealed and placed in 3 L containers filled with the electrolyte ($NaClO_4$/KCl/$Ca(NO_3)_2$) to bring the suspension to the desired ionic strength.

The electrolyte was changed two or three times per day until both the conductivity of the suspension in the bags and the external electrolyte were the same.

The concentration of the clay material in the suspension, for later utilisation in sorption experiments, was determined by gravimetry. The solid to liquid ratio (S), used in these experiments was 0.5–3.5 g L^{-1} approximately.

2.4. Analysis of the supernatant

The solution, in equilibrium with the clay suspensions, was analysed for the detection of cations (other than those of the main electrolyte used for each case) present in the equilibrium solution because of the partial dissolution of the clay or trace minerals. These cations are always present at trace concentrations but could compete with Cs for sorption sites, requiring their presence to be evaluated.

After 15 days of contact with the clay, the equilibrium solution of different samples, coming from different batches of suspensions at different pH or ionic strengths, was analysed. The separation of the supernatant from the solid was carried out by ultracentrifugation (504,000*g*, 1 h). The concentration of monovalent cations (K^+, Na^+ Li^+

Table 1
Summary of FEBEX clay main properties needed for sorption modeling.

CEC	30.91 μeq/m^2		
BET	33 m^2/g		
	Na-smectite	Ca-smectite	K-smectite
T1 sites density	7.0×10^{-4} μeq/m^2	3.5×10^{-3} μeq/m^2	1.3×10^{-2} μeq/m^2
T2 sites density	30.91 μeq/m^2	30.91 μeq/m^2	30.91 μeq/m^2

and Rb^+) and divalent cations (Ca^{2+} and Mg^{2+}) was determined to analyse the effects of these trace ions on cesium sorption for the different tests and for the performance of sensitivity analyses. Chemical analyses were carried out by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) and FAAS (Flame Atomic Absorption Spectrometry). The uncertainty of the measurements is less than 5%.

Table 2 shows the summary of these experiments indicating the range of concentration (min–max) of ions found in solution after different tests.

2.5. Cesium inventory of the clay

Acid extractions were performed to determine the intrinsic Cs inventory (exchangeable Cs) of the raw clay. A suspension of 7 g/L was brought to pH 0.5 and maintained by stirring for 1 day; it was then ultra-centrifuged (504,000*g*, 1 h). The supernatant was analysed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry); Cs content was always below the detection limit (<0.2 μg/L, 1.5×10^{-9} M).

2.6. Sorption experiments

Experiments were carried out under atmospheric conditions and at room temperature. Suspensions of Na-, K- and Ca-smectite, at various electrolyte concentrations (from 1×10^{-3} to 1 mol/L of $NaClO_4$, KCl or $CaCl_2$), were used.

The *kinetics* of the sorption process was investigated first to determine the time required for the attainment of the sorption equilibrium. Kinetic tests were carried out between pH 6 and 7 and at a salt concentration of 1×10^{-1} M, with two different (low and high) Cs concentrations ("*low*" refers to [Cs] $<1 \times 10^{-8}$ M and "*high*" to [Cs] $>9 \times 10^{-6}$ M). The solid to liquid ratio, S, was 1 g/L.

The suspensions, traced with ^{137}Cs, were introduced in 12.4 mL polyallomere Beckman Quick-Seal ultracentrifuge tubes. The solid and liquid phases were separated by ultra-centrifuging (694,000g, 30 min), with a Beckman Optima™ L-90 K ultracentrifuge with a 90 Ti rotor. This centrifugation ensures both the deposition of particles larger than 2 nm in diameter and the correct separation between the solid and the aqueous phase, under all the experimental conditions.

After the solid separation, three aliquots of the supernatant were extracted from each tube for the analysis of the final Cs activity. The rest of the solution was used to check the final pH.

Measurements of pH (±0.10) were made using a combined glass pH electrode (Metrohm) incorporating an Ag/AgCl reference electrode. The electrode calibration was made with buffer solutions (Scharlau) at pH 4.00, 7.00, and 10.00.

Sorption edges, (i.e. sorption curves as a function of pH) were carried out by varying the pH of the suspensions from approximately pH 2 to 11 with NaOH or HCl 0.1 or 1 M; the pH was readjusted, if necessary, after the addition of the radionuclide.

Sorption isotherms were carried out, at a fixed pH (6–7) and at a fixed background electrolyte concentration, by varying the radionuclide concentration from [Cs] $= 1 \times 10^{-10}$ M to [Cs] $= 1 \times 10^{-3}$ M, approximately. For the experiment with high Cs concentrations (higher than 1×10^{-6} M), a non-radioactive chemical of high purity (CsCl, Merck) was used in addition to the radiotracer.

The separation and counting procedure for sorption edges and isotherms was the same as that described for kinetic tests.

The distribution coefficient between the solid and the liquid phase, K_d (mL g^{-1}), is calculated with this formula:

Table 2
Concentration of main trace cations found in the supernatant upon the contact with the clays (15 days). Maximum and minimum values obtained after analysing different batches of the suspensions at different ionic strengths and pH. Cs in the aqueous solution was always $<1.5 \times 10^{-9}$ mol/L.

(mol/L)	Na-smectite		K-smectite		Ca-smectite	
	Min	Max	Min	Max	Min	Max
Na^+	–	–	1.7×10^{-5}	5.2×10^{-5}	9.1×10^{-6}	4.9×10^{-5}
K^+	$<2.6 \times 10^{-6}$	8.2×10^{-5}	–	–	3.3×10^{-6}	5.0×10^{-5}
Li^+	$<7.5 \times 10^{-8}$	1.3×10^{-6}	nd	nd	$<7.5 \times 10^{-8}$	
Rb^+	$<9 \times 10^{-9}$					
Ca^{2+}	9.5×10^{-6}	4.2×10^{-4}	1.3×10^{-5}	2.6×10^{-5}	–	–
Mg^{2+}	2.2×10^{-6}	1.5×10^{-5}	1.2×10^{-5}	2.1×10^{-5}	$<2.1 \times 10^{-6}$	1.4×10^{-5}
Sr^{2+}	$<2.1 \times 10^{-6}$					

$$K_d = \frac{C_{in} - C_{fin}}{C_{fin}} \cdot \frac{V}{m} \quad \text{(E.1)}$$

C_{in} and C_{fin} are the initial and final concentrations of Cs in the liquid phase (Bq mL^{-1}), m the mass of the clay (g) and V the volume of the liquid (mL).

For the more in-depth analysis of the affects of ionic strength on Cs retention, single K_d determinations at pH 7 and different ionic strengths were carried out, in addition to sorption edges and isotherms.

Sorption onto vials and ultracentrifuge tubes was checked after sorption experiments. Sorption of Cs onto these vessels was always lower than 2% and therefore it was not accounted for in K_d calculations.

The maximum experimental uncertainty estimated for sorption tests is approximately ±0.15 units on the logarithm of the distribution coefficient. This value has been evaluated considering the maximum uncertainty in the counting procedure (affecting C_{in} and C_{fin}, see (E.1)); and up to 10% error in the solid to liquid ratio (V/m).

3. SORPTION MODELING

Cesium is adsorbed in clays mainly by cationic exchange: the ionic exchange reaction between a cation B, with charge z_B, in the aqueous phase; and a cation A, with charge z_A, at the clay surface (≡X) can be defined by:

$$z_B A \equiv X + z_A B \Longleftrightarrow z_A B \equiv X + z_B A \quad \text{(E.2)}$$

The cation exchange reactions can be expressed with selectivity coefficients (Gaines and Thomas, 1953):

$${}_A{}^B K_{SEL} = \frac{(N_B)^{z_A}}{(N_A)^{z_B}} \frac{(a_A)^{z_B}}{(a_B)^{z_A}} \quad \text{(E.3)}$$

where a_A and a_B are the activities of the cations A and B; and N_A y N_B are the equivalent fractional occupancies. Selectivity coefficients of a cation, at trace concentrations, can be determined by sorption measurements (Bradbury and Baeyens, 1994). If the cation B is present at trace levels, then N_A (E.3) is approximately 1; furthermore if the distribution coefficient of the exchange process (K_d) is known, then the selectivity coefficient can be determined with the following relation:

$${}_A{}^B K_{SEL} = \left(\frac{K_d \cdot z_B}{CEC}\right)^{z_A} \frac{\gamma_A^{z_B}}{\gamma_B^{z_A}} (A)^{z_B} \quad \text{(E.4)}$$

where γ_A and γ_B are the solution activity coefficients of cations A and B. The activity coefficients (γ) at 20 °C, can be calculated with the Davies' approximation:

$$\mathrm{Log}\gamma_i = -0.51 \cdot z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 \cdot I\right)$$

where I represents the ionic strength of the solution. For experiments with Na-smectite or K-smectite, (E.4) becomes:

$${}_{Na}{}^{Cs} K_{SEL} = \left(\frac{K_d}{CEC}\right) \frac{\gamma_{Na}}{\gamma_{Cs}} (Na) \quad \text{(E.4a)}$$

$${}_{K}{}^{Cs} K_{SEL} = \left(\frac{K_d}{CEC}\right) \frac{\gamma_{K}}{\gamma_{Cs}} (K) \quad \text{(E.4b)}$$

For experiments with Ca-smectite, (E.4) is:

$${}_{Ca}{}^{Cs} K_{SEL} = \left(\frac{K_d}{CEC}\right)^2 \frac{\gamma_{Ca}}{\gamma_{Cs}^2} (Ca) \quad \text{(E.4c)}$$

These analytical expressions, valid for a simple cation exchange process at a single site, allow the determination of selectivity coefficients directly from the sorption curves. However, the parameters, thus determined, might be biased either by the presence of other ions competing for the sorption site or by the presence of other sorption sites; the values determined directly by the experimental sorption data will therefore be referred to as "*apparent*" (Table 3).

The verification of the experimentally determined parameters, in addition to other modeling calculations on the effects of multiple sites and/or competing ions on Cs sorption, were performed with the CHESS v 2.4 code (Van der Lee and de Windt, 1999); the fit of the experimental curves was obtained with a trial and error procedure.

4. RESULTS AND DISCUSSION

4.1. Sorption kinetics

Kinetic tests, on the three different smectites (Na-, K- and Ca-smectite), were carried out using two different Cs concentrations: $[Cs] < 1.0 \times 10^{-8}$ M (*low* concentration) and $[Cs] > 9.0 \times 10^{-6}$ M (*high* concentration). Although sorption equilibrium is always reached within hours, for Na-smectite at low concentrations, a slower kinetic behaviour is observed, with the sorption equilibrium attained within 3–4 days. Sorption experiments were carried out with a contact time of 1 week. (All the results from kinetic experiments are shown in the Additional Material, AM, Fig. AM1).

4.2. Sorption edges: affects of pH on sorption

Fig. 1 shows the sorption edges obtained for Na-smectite at *high* Cs concentration (2.3×10^{-6} M) and at two different electrolyte concentrations (1×10^{-1} and 1×10^{-2} M $NaClO_4$). Similar tests were carried out with a low Cs concentration and with K- and Ca-smectite (Results shown in AM, Fig. AM2). For all these cases, sorption does not depend on pH – neither at low nor at high Cs concentrations.

In the aqueous phase, cesium exists as an uncomplexed cation (Cs^+); a change of sorption with pH is expected only with a change of the properties of the solid phase (Hakem et al., 2004). The small decrease in sorption observed, at pH lower than 4, might be related to partial dissolution of the clay and possible ion competition on Cs sorption (Poinssot et al., 1999).

Summarised in Table 3 are the mean K_d values and standard deviations that were calculated with all the experimental points from pH 4 to 11, for all the exchanged clays.

4.3. Sorption isotherms: affects of Cs concentration and ionic strength on sorption

4.3.1. Cesium concentration

Fig. 2 shows the sorption isotherms obtained at pH 6.5 with Na-, K- and Ca-smectite carried out with suspensions

Table 3
Summary of the main results obtained in experimental tests and apparent selectivity constants directly calculated with Equation 4, as explained in the test. (**) Not in a *lineal* zone.

Clay Type (X)	Test type	[Cs] (M)	pH (±0.5)	S (g/L)	I (M)	Log K_dT1 site (ml/g)	Log K_dT2 site (ml/g)	Apparent $Log_X^{Cs}K_{SEL}$(T1)	Apparent $Log_X^{Cs}K_{SEL}$(T2)
Na-	Kinetics	1.1×10^{-9}	6.5	1	1.0×10^{-1}	3.89 ± 0.10	–	**7.51**	–
Na-	Kinetics	9.7×10^{-6}	6.5	1	1.0×10^{-1}	–	2.70 ± 0.04	–	**1.69**
Na-	Edge	2.3×10^{-6}	Var	1	1.0×10^{-1}	–	2.73 ± 0.04	–	**1.72**
Na-	Edge	2.3×10^{-6}	Var	1	1.0×10^{-2}	–	3.63 ± 0.08	–	**1.62**
Na-	Isotherm	Var	6.5	3.75	1.0×10^{0}	3.16 ± 0.02	1.83 ± 0.07	7.79	**1.82**
Na-	Isotherm	Var	6.5	1.0	2.0×10^{-1}	3.53 ± 0.04	2.35 ± 0.04	7.51	**1.64**
Na-	Isotherm	Var	6.5	1.31	1.0×10^{-1}	4.11 ± 0.13	2.74 ± 0.10	7.75	**1.73**
Na-	Isotherm	Var	6.5	1.39	1.0×10^{-2}	4.22 ± 0.17	3.69 ± 0.05	6.86	**1.68**
Na-	Isotherm	Var	6.5	1.39	1.0×10^{-3}	4.80 ± 0.15	4.28 ± 0.12	6.44	**1.27**
								Mean 7.64 ± 0.16	Mean 1.70 ± 0.07
K-	Kinetics	5.3×10^{-9}	6.5	1	1.0×10^{-1}	2.80 ± 0.03	–	**5.15**	–
K-	Kinetics	9.5×10^{-6}	6.5	1	1.0×10^{-1}	–	2.42 ± 0.03	(**)	(**)
K-	Edge	9.5×10^{-6}	Var	1	1.0×10^{-1}	–	2.32 ± 0.07	(**)	(**)
K-	Isotherm	Var	6.5	1	1.0×10^{-1}	2.76 ± 0.03	2.13 ± 0.10	**5.12**	**1.12**
K-	Isotherm	Var	6.5	1	1.0×10^{-2}	3.75 ± 0.02	3.14 ± 0.10	**5.10**	**1.14**
K-	Single Kd	5.4×10^{-9}	6.5	1	5.0×10^{-1}	2.23 ± 0.10	–	**5.28**	–
K-	Single Kd	5.4×10^{-9}	6.5	1	2.0×10^{-1}	2.58 ± 0.10	–	**5.24**	–
K-	Single Kd	5.4×10^{-9}	6.5	1	1.0×10^{-1}	2.84 ± 0.10	–	**5.20**	–
K-	Single Kd	5.4×10^{-9}	6.5	1	5.0×10^{-2}	3.08 ± 0.10	–	**5.13**	–
K-	Single Kd	5.4×10^{-9}	6.5	1	1.0×10^{-2}	3.76 ± 0.10	–	**5.11**	–
K-	Single Kd	5.4×10^{-9}	6.5	1	5.0×10^{-3}	4.05 ± 0.10	–	**5.10**	–
K-	Single Kd	5.4×10^{-9}	6.5	1	1.0×10^{-3}	4.65 ± 0.10	–	**5.01**	–
								Mean 5.14 ± 0.08	**Mean 1.13 ± 0.01**
Ca-	Isotherm	Var	6.5	1.0	3.0×10^{-1}	3.93 ± 0.07	2.30 ± 0.05	**14.46**	**3.32**
Ca-	Isotherm	Var	6.5	1.0	1.0×10^{-1}	4.23 ± 0.06	2.44 ± 0.07	**14.64**	**3.17**
Ca-	Kinetics	9.7×10^{-6}	6.5	1.0	3.0×10^{-1}	–	2.13 ± 0.05		**2.97**
Ca-	Kinetics	1.1×10^{-9}	6.5	1.0	3.0×10^{-1}	3.75 ± 0.10	–	**14.10**	–
Ca-	Edge	4.0×10^{-6}	Vv	2.75	3.0×10^{-3}	–	3.02 ± 0.08	–	**2.97**
Ca-	Edge	4.0×10^{-6}	Vv	3.30	3.0×10^{-1}	–	2.46 ± 0.09	–	(**)
Ca-	Edge	4.9×10^{-9}	Vv	3.30	3.0×10^{-1}	4.06 ± 0.06		**14.72**	
Ca-	Single Kd	2.5×10^{-6}	6.5	1.7	3.0×10^{-2}	–	2.74 ± 0.2	–	**3.32**
Ca-	Single Kd	2.5×10^{-6}	6.5	1.7	6.0×10^{-2}	–	2.48 ± 0.2	–	**3.05**
Ca-	Single Kd	2.4×10^{-6}	6.5	1.7	1.5×10^{-1}	–	2.29 ± 0.2	–	**2.99**
Ca-	Single Kd	1.1×10^{-9}	6.5	0.5	1.5×10^{-1}	4.05 ± 0.04	–	**14.44**	–
Ca-	Single Kd	1.1×10^{-9}	6.5	1.0	3.3×10^{-1}	3.74 ± 0.03	–	**14.12**	–
Ca-	Single Kd	1.1×10^{-9}	6.5	1.0	4.4×10^{-1}	3.66 ± 0.02	–	**14.08**	–
Ca-	Single Kd	1.1×10^{-9}	6.5	1.0	5.7×10^{-1}	3.58 ± 0.02	–	**14.04**	–
Ca-	Single Kd	1.1×10^{-9}	6.5	0.4	9.0×10^{-2}	4.33 ± 0.10	–	**14.80**	–
Ca-	Single Kd	1.1×10^{-9}	6.5	0.2	4.5×10^{-2}	4.45 ± 0.10	–	**14.77**	–
Ca-	Single Kd	1.1×10^{-9}	6.5	0.1	2.3×10^{-2}	4.96 ± 0.10		**15.55**	–
								Mean 14.52 ± 0.45	**Mean 3.11 ± 0.16**

Bold values used for the calculations of the initial mean selectivity coefficients.

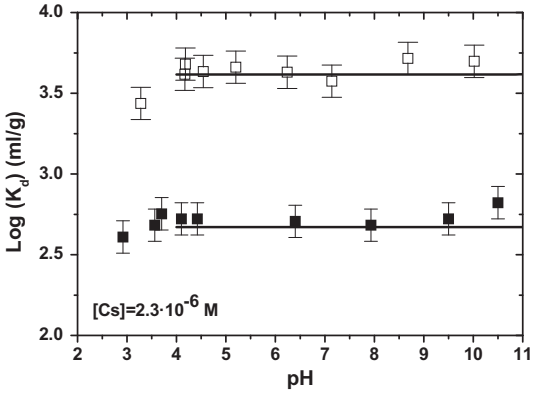

Fig. 1. Cesium adsorption as a function of pH for Na-smectite at two different ionic strengths (■) 0.1 M and (□) 0.01 M in $NaClO_4$. The continuous lines correspond to the fit of the curves with the parameters of Table 6.

at an ionic strength of I = 0.1 M. Fig. 2a shows the data represented as the logarithm of Cs concentration adsorbed (Log(C_{ads}), mol/g) *vs.* the logarithm of Cs concentration in solution at the equilibrium (Log(C_{fin}), mol/L). In such a graph, linear sorption would be represented by a unique straight line with a slope of 1.

Fig. 2b shows the same data represented as the logarithm of the distribution coefficient (Log(K_d), mL/g) *vs.* Log(C_{fin}), to facilitate the comparison of K_d values obtained for the different exchanged smectites.

Fig. 2 shows that in all the exchanged clays, Cs sorption clearly deviates from linearity. The observed behaviour seems to be consistent with the existence of two different sorption sites. The first (Type 1 sites, T1) presents very low capacity: the saturation of T1 sites is evidenced by the small plateau observed in sorption data presented in Fig. 2a. Up to the saturation of these sites, sorption is linear (constant K_d region in the inset of Fig. 2b). The maximum Cs adsorbed at T1 sites (marked by an arrow in Fig. 2a), allows the experimental determination of the concentrations at T1 sites. The maximum Cs adsorbed is within the same order of magnitude for Na- and Ca-smectite (2.3×10^{-8} and 5.8×10^{-8} mol/g, respectively); whereas for K-smectite, this value is approximately one order of magnitude higher (4.4×10^{-7} mol/g). Similar selective sorption behaviour is observed for illite FES.

After the saturation of T1 sites, another region of linear sorption (slope unit in Fig. 2a and constant K_d, in inset of Fig. 2b) can be clearly observed. This is in agreement with the existence of a second sorption site (Type 2 sites, T2). K_d values are higher in T1 sites than in T2 sites; T1 sites, therefore, have a low capacity but higher affinity for Cs – and T2 sites have lower affinity but higher capacity.

As mentioned in the Introduction, for smectite, cation exchange is expected to occur mainly at the planar sites, where exchangeable cations reside for the maintenance of the neutrality of the system. The density of T2 sites must, therefore, roughly correspond to the total CEC of the clay (Table 1).

For smectite, even if sorption sites heterogeneity is not expected, non-linear sorption has been previously observed

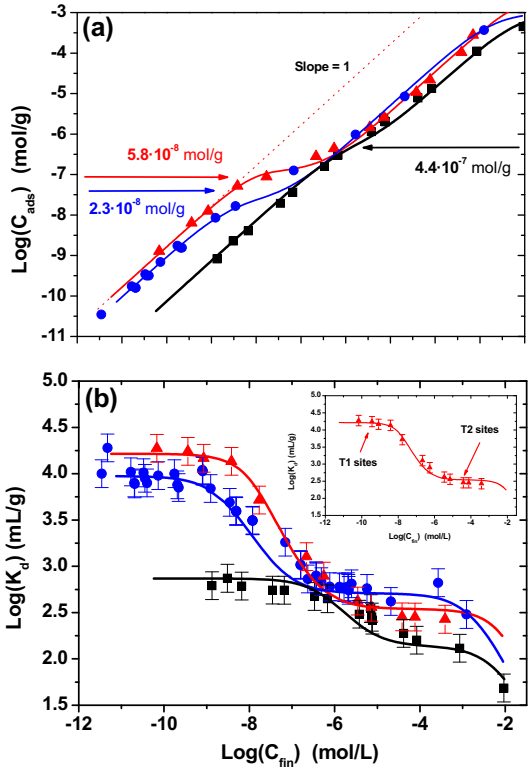

Fig. 2. Comparison of cesium adsorption isotherms obtained at pH 6.5 and ionic strength 0.1 M for the three exchanged smectites: (a) data expressed as Log(C_{ads}) vs. Log(C_{fin}) and (b) data expressed as Log(K_d) vs. Log(C_{fin}). The lines correspond to the fit of the curves with the parameters of Table 6. (■) K-smectite; (▲) Ca-smectite; (●) Na-smectite. Inset: costant K_d regions correspond to sorption onto different sites.

by different authors. As mentioned in the Introduction, different hypothesis to explain this behaviour were considered by other authors; our hypothesis is based on the existence of interstratified mixed-layers.

It is not uncommon for smectite to form interstratified layers with other phyllosilicate minerals that are often randomly distributed. Interstratified layers are, in fact, very common in clayrock (Fiore et al., 2010).

Cuadros and Linares (1996), Fernandez et al. (2004) and Leguey et al. (2002) agree on the existence of randomly interstratified illite/smectite mixed layers in the FEBEX clay, detected by X-ray diffraction of oriented mounts. For the bentonite <20 μm fraction, some trace impurities of mica were sometimes detected (Cuadros and Linares, 1996), but the <0.5 μm fraction was reported to be almost pure smectite (Leguey et al., 2002). The illite content found in the interstratified illite/smectite was similar for the <20 μm fraction (Cuadros and Linares, 1996, ~15%), for the <2 μm fraction (Fernandez et al., 2004, ~11%) and for the <0.5 μm fraction (Leguey et al., 7–10%).

Therefore, the presence of mixed layers may structurally lead to the existence of selective sites in smectite, such as those present in illite (FES-like) – even though their characteristics and properties might not be necessarily equivalent to those observed for "pure" illite.

In a "standard" Na-illite (Bradbury and Baeyens, 2000), the FES density (approximately 2×10^{-7} to 1×10^{-6} eq/g) is between 0.1% and 0.5 % of the total CEC. The density of T1 sites estimated in this study from the sorption isotherms for the Na-smectite is lower, 2.3×10^{-8} eq/g, and represents only the 0.002% of the CEC ($\sim 1 \times 10^{-3}$ eq/g) of the FEBEX clay (Table 1). For K- and Ca-smectite the values are 4.3×10^{-7} and 1.2×10^{-7} eq/g, corresponding to 0.042% and 0.011% of the CEC, respectively. However, in spite of their low density, these sites clearly dominate Cs sorption at low loadings and therefore they cannot be neglected

4.3.2. Ionic strength and ion competition

Sorption behaviour, as a function of the ionic strength, has been analysed in Fig. 3; this figure shows the sorption isotherms obtained at pH 6.5 and different ionic strengths for Na-smectite (Fig. 3a); K-smectite (Fig. 3b); and Ca-smectite (Fig. 3c). Data are expressed as the Log(K_d) *vs.* Log(C_{fin}).

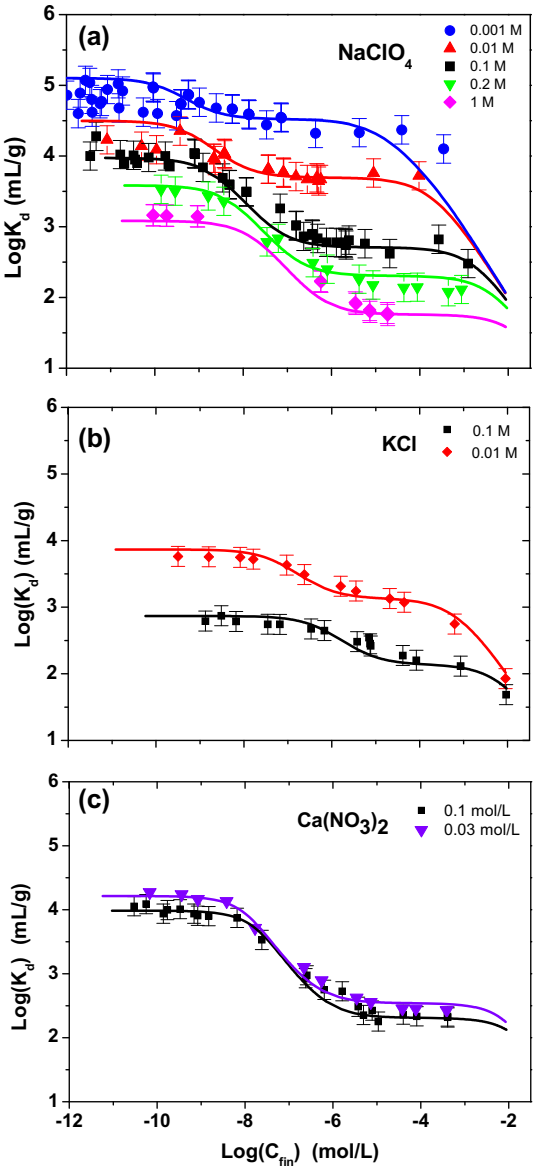

Fig. 3. Cesium adsorption isotherms obtained at pH 6.5 and different ionic strengths: (a) Na-smectite; (b) K-smectite and (c) Ca-smectite. The continuous lines correspond to the fit of the curves with the parameters of Table 6.

At all ionic strengths, sorption isotherms present two regions, where the distribution coefficient is constant within the experimental error – supporting the existence of two different sites, as mentioned before. Summarised in Table 3 are the following: the mean values of the distribution coefficients obtained for each of these sites and for each test and the *apparent* selectivity coefficients calculated by (E.4).

In regard to the dependence of sorption on ionic strength (Figs. 1 and 3), Cs sorption always increases as the ionic strength of the electrolyte decreases, as expected for ionic exchange processes; the effect being more pronounced for Na- and K-smectite than for Ca-smectite.

For ionic exchange processes, the theoretical dependence on ionic strength or electrolyte concentration, A, derived from (E.4) is the following:

$$z_A \cdot \mathrm{Log}(K_d) = -z_B \mathrm{Log}(A) + \mathrm{Log}\left(\frac{{}_A{}^B K_{SEL} (CEC)^{z_A} \gamma_B^{z_A}}{z_B^{Z_A} \gamma_A^{Z_B}}\right) \quad \text{(E.5)}$$

Thus, for a homovalent exchange (Cs–Na or Cs–K), the dependence of Log(K_d) on Log(A) is represented by a line with a slope of −1. For Cs–Ca exchange this dependence should be a line with slope −0.5.

Fig. 4 shows the experimental dependence of Log(K_d) on Log(A) (E.5): for Na- and K-smectite (Fig. 4a, homovalent exchange) and for Ca-smectite (Fig. 4b, heterovalant exchange).

Fig. 4 includes all data for sorption isotherms or edges, as well as additional data obtained by performing single K_d-tests at different ionic strengths (Table 3). The slope of the straight lines of the experimental Log(K_d) *vs.* Log(A) and the correlation coefficients are summarised in Table 4.

For K-smectite (Fig. 4a), the experimental sorption dependence on the ionic strength at both sites compares well with the theoretical behaviour (for T1, slope −0.92 and for T2, slope −1.01); but for Na-smectite, larger variations were observed with the theoretical behaviour: the slope of the curve for T2 sites is −0.85 and for T1 sites is −0.52.

For Ca-smectite, (Fig. 4b) the slope of the curve for sorption at T2 sites is −0.39 – also lower than the expected behaviour (slope −0.5); whereas for T1 sites, the slope is higher than the expected for a Cs-Ca exchange, with a value of −0.89.

For Na-smectite, the deviation from the theoretical behaviour is more pronounced at lower ionic strengths – where K_d values are generally lower than the predicted and the experimental data dispersion higher. For calculated (apparent) selectivity coefficients (Table 3), the effect of ionic strength is also observed, with selectivity tending to decrease when ionic strength decreases.

As already mentioned in Section 1, other authors observed this anomalous behaviour and attempted to explain it with several hypotheses as the non-electrostatic character of Cs-clay interactions or biased K_d determination caused

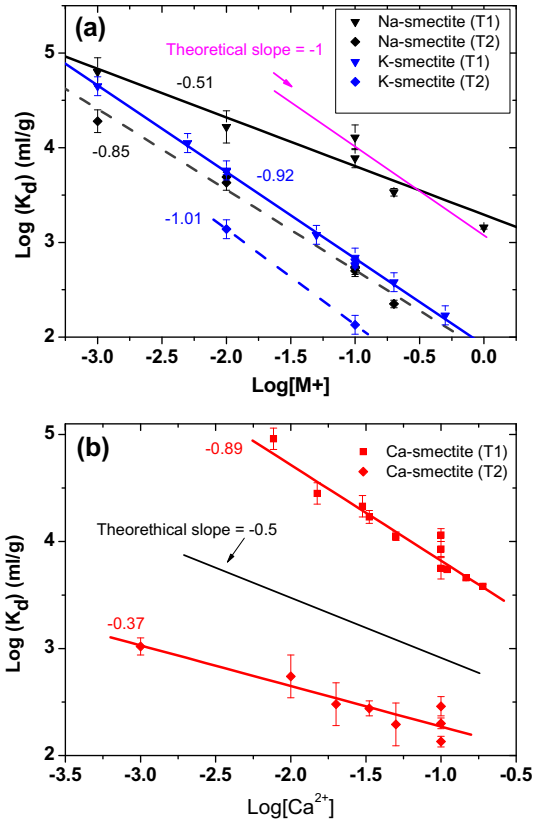

Fig. 4. Analysis of the dependence of Log(K_d) on the concentration of the main ions in solution: (a) Na- and K-smectite and (b) Ca-smectite.

Table 4
Slope determined by linear regression of experimental Log K_d *vs.* the concentration of the main ion of the electrolyte (Ec.5, Fig. 4). R = correlation coefficient.

Clay type		T1 sites		T2 sites	
	Theoretical slope	Measured slope	R	Measured slope	R
Na-smectite	**−1**	−0.51 ± 0.06	−0.96	−0.85 ± 0.06	−0.99
K-smectite	**−1**	−0.92 ± 0.03	−0.99	−1.01 ± 0.00	–
Ca-smectite	**−0.5**	−0.89 ± 0.07	−0.97	−0.39 ± 0.06	−0.93

Bold values used for the calculations of the initial mean selectivity coefficients.

by not appropriated centrifugation (the latter was excluded by this study).

We hypothesize the deviation from the theoretical behaviour – leading to lower selectivity coefficients as the ionic strength decreases – is caused by the competition for sorption sites of the existing trace ions (especially K^+) in the aqueous solution; this competition, in the literature, often is not accounted for.

Even after accurate homoionisation and purification processes, trace elements are always present in solutions equilibrated with the clay (see Table 2), and their affect cannot be ruled out (Baeyens and Bradbury, 2004).

Furthermore, the low density of sorption sites enhances the competition affect. Clearly, for Na-smectite, the deviation from the theoretical behaviour is much more evident for T1 than for T2 sites. Small differences in the quantity of K^+ in samples with a Na electrolyte concentration of 10^{-3} M, for T1 sites, may lead to significant differences in measured K_d and, mainly for this reason, the dispersion of data is higher under these conditions. Competition effects are not so evident for K-smectite, in agreement with the higher selectivity of K^+.

These results indicate that it is strictly necessary to account for the existence of ion competition in Cs sorption for sorption modeling and consider the range of concentrations of the possibly competitive ions in solution as experimentally measured (Table 2). The verification of this hypothesis is found in the modeling section.

However, the observed dependence for Ca-smectite at T1 sites, i.e. the selectivity increase when the ionic strength decreases, deserves additional analyses because this behaviour cannot be explained by ion competition affects. The presence of Ca, at least up to certain concentrations, might be the cause of the expansion (de-collapse) of illite layers of interstratified illite/smectite and increase the accessibility of sorption sites. Comans and Hockley (1992) and Wauters et al. (1994) reported that the presence of large cations, such as Ca^{2+}, improves the process of radiocesium fixation in micaceous clays by expanding the interlayers. A recent study (Benedicto and Missana, submitted) shows that the presence of Ca^{2+} ions significantly increases Cs sorption for illite, although this effect is much more evident for planar sites than for FES sites.

Other possibilities that can explain the observed behaviour are the following: a) Cs interaction with Ca-smectite at these sites is not purely electrostatic, or b) Cs retention could take place by its exchange with the potassium, present in T1 sites, that is not completely displaced by Ca during the homoionisation stage. This last hypothesis will be tested by modeling.

4.4. Modeling approach

Results shown above indicate that Cs sorption for the three smectites could be mostly explained by a two-site (T1 and T2) ionic exchange model, in which ion competition must be accounted for (Fig. 4).

As a first step, based on the hypothesis of the existence of sorption sites at which Cs is adsorbed by cation exchange, the selectivity coefficients were determined using (E.4), as already mentioned. The mean value of the selectivity coefficient, obtained with the different tests, was used as an input value for the initial modeling. The model was then tuned to consider the competitive effects of other ions in solution.

Table 3 shows the selectivity coefficients directly calculated for each experiment (*apparent*). Because the greatest deviation from the theoretical behaviour, as a function of the electrolyte concentration, is observed at the lowest ionic strengths (Fig. 4), where the data are expected to be more affected by ion competition we considered – for the calculation of the initial mean selectivity coefficient – only data at higher

Table 5
Initial parameter derived from experimental data of Table 3. The error on the Log parameters is taken on the basis of the maximum experimental error (±0.15).

T1 sites (±0.15)	T2 Sites (±0.15)
$Log_{Na}{}^{Cs}K$ (T1) = 7.64	$Log_{Na}{}^{Cs}K$(T2) = 1.70
$Log_{K}{}^{Cs}K$ (T1) = 5.14	$Log_{K}{}^{Cs}K$(T2) = 1.13
$Log_{Ca}{}^{Cs}K$ (T1) = 14.52	$Log_{Ca}{}^{Cs}K$ (T2) = 3.11
$Log_{Na}{}^{K}K$ (T1) = 2.50	$Log_{Na}{}^{K}K$(T2) = 0.57
$Log_{Na}{}^{Ca}K$ (T1) = 0.76	$Log_{Na}{}^{Ca}K$ (T2) = 0.29
$Log_{K}{}^{Na}K$ (T1) = −2.50	$Log_{K}{}^{Na}K$(T2) = −0.57
$Log_{K}{}^{Ca}K$ (T1) = −4.24	$Log_{K}{}^{Ca}K$ (T2) = −0.85

ionic strengths (in bold in Table 3).The mean values of the apparent selectivity coefficients for Na–Cs, K–Cs and Ca–Cs exchange, at T1 sites, are the following: $Log_{Na}{}^{Cs}K_{SEL}(T1) = 7.64 \pm 0.16$, $Log_{K}{}^{Cs}K_{SEL}(T1) = 5.14 \pm 0.08$ and $Log_{Ca}{}^{Cs}K_{SEL}(T1) = 14.52 \pm 0.45$.For the consideration of sorption at the planar sites (T2), especially important for medium–high Cs concentrations, the mean values of apparent selectivity coefficients for Na–Cs, K–Cs and Ca–Cs exchange are the following: $Log_{Na}{}^{Cs}K_{SEL}(T2) = 1.70 \pm 0.07$, $Log_{K}{}^{Cs}K_{SEL}(T2) = 1.13 \pm 0.01$ and $Log_{Ca}{}^{Cs}K_{SEL}(T2) = 3.31 \pm 0.16$.

Starting from the above mentioned experimental initial values, for the consideration of the competing effects of the ions present in solution, additional selectivity coefficients must be calculated.

For example, if ${}_{Na}{}^{Cs}K_{SEL}$, ${}_{K}{}^{Cs}K_{SEL}$ and ${}_{Ca}{}^{Cs}K_{SEL}$ are known, ${}_{Na}{}^{K}K_{SEL}$ and ${}_{Na}{}^{Ca}K_{SEL}$ can be calculated by the following expressions:

$$ {}_{Na}{}^{K}K_{SEL} = \frac{{}_{Na}{}^{Cs}K_{SEL}}{{}_{K}{}^{Cs}K_{SEL}} \quad \text{(E.6a)} $$

$$ {}_{Na}{}^{Ca}K_{SEL} = \frac{({}_{Na}{}^{Cs}K_{SEL})^2}{{}_{Ca}{}^{Cs}K_{SEL}} \quad \text{(E.6b)} $$

Table 5 summarises the calculated selectivity coefficients.

Thus, considering the presence of competing ions, within the experimentally evaluated concentrations, all the experimental data set was fit with a finer tuning of the initial parameters. All the parameters used for the fit of the experimental data are summarised in Table 6. Model calculations are superimposed onto the experimental data of Figs. 1–3, and onto all the additional Figures in AM.

The values of the selectivity coefficients, obtained in this study for T1 sites, compare well with those found in the literature for illite clay at FES sites; the values obtained here for T2 sites are similar to those published (see Table AM1, AM).

Selectivity coefficients for Cs–Ca, were also determined for T1 sites, as previously done in other studies; and with these parameters, the experimental data can be reproduced quite well (Fig. 3). Yet because the sorption behaviour at T1 sites of Ca-smectite does not fit with the theoretical dependence on the ionic strength for an exchange process,

Table 6
Parameters used for the best fit of the experimental sorption curves presented in the Figures of the paper. The concentration of competing ions in solution is also indicated. The error on these parameters will be considered the highest between experimental (±0.15) and the standard deviation obtained in different tests.

	$Log_{X}{}^{Cs}K_{SEL}$(T1)	$Log_{X}{}^{Cs}K_{SEL}$(T2)	$[Ca^{2+}]$(M)	$[Na^{+}]$(M)	$[K^{+}]$(M)
K-smectite					
Isotherm 0.01 M (Fig. 3b)	5.14	1.13	2×10^{-5}	2×10^{-5}	0.01
Isotherm 0.1 M (Fig. 3b)	5.14	1.13	2×10^{-5}	2×10^{-5}	0.1
Kinetics 0.1 M (Fig. AM1a)	5.20	1.30	1×10^{-5}	1×10^{-5}	0.1
Kinetics 0.1 (Fig. AM1b)	5.10	1.10	2×10^{-5}	2×10^{-5}	0.1
Edge (Fig. AM2a)	5.15	1.15	2×10^{-5}	2×10^{-5}	0.1
Mean	5.15 ± 0.04	1.16 ± 0.08			
Na-smectite					
Isotherm 1 M (Fig. 3b)	7.70	1.75	1×10^{-5}	1	1×10^{-5}
Isotherm 0.2 M (Fig. 3b)	7.55	1.60	2×10^{-4}	0.2	7×10^{-5}
Isotherm 0.1 M (Fig. 3b)	7.60	1.70	1×10^{-5}	0.1	1×10^{-5}
Isotherm 0.01 M (Fig. 3b)	7.50	1.70	1×10^{-5}	0.01	8×10^{-5}
Isotherm 0001 M	7.50	1.70	1×10^{-4}	0.001	8×10^{-5}
Edge 0.1 M (Fig. 1a)	7.60	1.65	1×10^{-4}	0.1	5×10^{-5}
Edge 0.01 M (Fig. 1a)	7.60	1.65	1×10^{-4}	0.01	5×10^{-5}
Kinetics 0.1 M (Fig. AM1a)	7.60	1.65	1×10^{-4}	0.1	5×10^{-5}
Kinetics 0.1 M (Fig. AM1b)	7.70	1.70	1×10^{-4}	0.1	1×10^{-5}
Mean	7.59 ± 0.07	1.68 ± 0.04			
Ca-smectite					
Isotherm 0.3 M (Fig. 3c)	14.62	3.10	0.1	1×10^{-5}	1×10^{-5}
Isotherm 0.1 M (Fig. 3c)	14.62	3.10	0.03	1×10^{-5}	1×10^{-5}
Kinetics 0.1 M (Fig. AM1a)	14.24	3.10	0.1	5×10^{-5}	5×10^{-5}
Kinetics 0.1 M (Fig. AM1b)	14.33	2.79	0.1	5×10^{-5}	5×10^{-5}
Edge (Fig. AM2b)	14.24	3.10	0.001	1×10^{-5}	1×10^{-5}
Edge 2 (Fig. AM2b)	14.30	2.90	0.1	1×10^{-5}	1×10^{-5}
Edge 3 (Fig. AM2b)	14.52	2.90	0.1	1×10^{-5}	1×10^{-5}
Mean	14.41 ± 0.17	3.02 ± 0.13			

another hypothesis for the analysis of the experimental data was made. As widely reported in the literature, T1 sites are especially selective for alkali ions, but it is difficult that they could be occupied by calcium or other bivalent ions. Thus, even after the homoionisation process, calcium might not be able to occupy these sites. It could be then assumed that Cs retention can occur *via* exchange with the potassium present at T1 sites – rather than displaced during the homoionisation stage. Following this reasoning, a model was tried and a good fit of the experimental curves could be obtained (see Fig. AM3, in the Additional Material). However, this model is not able to reproduce the sorption behaviour as a function of the ionic strength either (Fig. 4); thus the hypothesis that in this case, the sorption mechanism is different from ionic exchange is strengthened.

For the rest of the cases, as can be seen in the Figures, this approach is quite successful in predicting sorption data, with different exchanging and competing ions and in a wide range of Cs concentration. Both the set of selectivity coefficients obtained in this study and the performed analyses are very useful to explain Cs sorption behaviour onto smectite-based clay materials, even under more complex experimental conditions.

5. SUMMARY AND CONCLUSIONS

The analysis of sorption data from three different exchanged smectites (Na-, K- and Ca-smectite) allowed determining a set of selectivity coefficients essential to model Cs sorption behaviour under a wide range of chemical conditions.

Sorption was shown to be not linear, probably because of the presence of randomly interstratified illite–smectite mixed layers, providing highly selective sorption sites; a two-site exchange model was the most adequate to describe Cs retention.

For Na- and K-smectite, both at planar (T2) sites and T1 sites, resembling the FES sites observed for illite, sorption occurs by ionic exchange, in agreement with theoretical calculations for a 1:1 exchange process, provided one accounts for the competition of trace ions in solution.

For Ca-smectite, ionic exchange also clearly occurred at T2 sites. The nature of Cs retention at Ca-smectite T1 sites is not totally clear, because the observed experimental dependence of sorption with the ionic strength was significantly different from the theoretical one, and not explainable by the existence of competing ions in solution. The very low density of T1 sites makes a clear identification by experimental spectroscopic techniques very difficult, but future studies should aim at elucidating the interaction mechanisms between Cs and Ca-smectite at these sites. The possibility that the presence of large hydrated cations may cause the expansion of clay layers – making more accessible sorption sites – should be considered.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.10.007.

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