Modelling of Cs sorption in natural mixed-clays and the effects of ion competition

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ABSTRACT

Cs migration in the environment is mainly controlled by sorption onto mineral surfaces, in particular on clay minerals. With the objective of designing a geochemical reactive barrier to treat ^{137}Cs accidental pollution in an industrial waste repository, different natural clayrocks were studied to analyse their capacity to retain Cs.

The simple semi-empiric K_d-approach for experimental data analysis, is unsatisfactory to describe the variability of sorption upon chemical changes. Indeed, due to the high salinity of the site, the effects of competitive ions must be evaluated and quantified. Thus, the development of sorption models, capable of reproducing experimental data obtained under conditions representative of the contaminated site, and applicable to reactive transport studies, is needed.

In this study, a model for Cs sorption, which takes into account the main mineralogy of the sorbent, the composition of the natural water (and ion competition) was successfully applied to interpret the non-linear Cs sorption under natural conditions.

The selectivity coefficients of Cs with respect to the most important cations present in the site water (Na, K, NH_4, Ca) were derived by means of experiments in single clay minerals and synthetic mono-component solutions. Then, these parameters were tested in systems of increasing complexity.

Considering the mineralogical composition of raw materials, it was shown that the principal contribution to Cs sorption is given by the mineral illite, while smectite starts to be relevant only at very high Cs loadings. Kaolinite, even in concentrations around 10 wt% of the clayey fraction, played only a minor role.

With respect to the solution composition, the model was able to predict Cs sorption in electrolyte concentrations up to twice than that of seawater and up to 500 mg/L NH_4^+. The effect of highly competing ions, especially NH_4^+ and K^+, on Cs retention is more important at low ionic strengths and low Cs loadings, where adsorption is dominated by illite selective frayed edge sites, FES. Divalent cations are not especially relevant as competing cations for Cs.

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1. Introduction

Cesium-137 is an important fission product from the irradiation of uranium-based fuels and it has been released in the past to soils and waters as a result of nuclear accidents or weapon testing. Radiocesium always exists as the monovalent cation Cs^+, which presents very high solubility and mobility, thus being a very relevant element from an environmental point of view.

For preventing radionuclide migration, the use of engineered barriers is often required. In addition, to predict contaminant retention under different chemical conditions, geochemical modelling must be applied, but adequate methodologies are needed to

test models and make realistic predictions (Wang and Staunton, 2010).

Suitable materials for the construction of barriers for contaminant migration must fulfill several properties; they must be *reactive*, i.e. they must interact with the contaminant and retain it and, at the same time, they must be more *permeable* than the surrounding soil, to facilitate the income of the contaminated water and its cleaning. After the selection of reactive materials, the permeability of the barrier is achieved mixing the reactive components with a porous filling, for example wood shavings (Rötting et al., 2008). All the materials must be durable, environmentally suitable, reasonably cheap and accessible, as large quantities are often needed to construct the barriers.

After the accidental contamination by ^{137}Cs of an industrial water repository, located in a marsh zone from Andalusia (Southern Spain), different studies were carried out to design a permeable

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reactive barrier to ensure that the water outflowing from the repository to the environment is depleted of ^{137}Cs (Ayora et al., 2012). Many solids have been under study for Cs retention (Borai et al., 2009; Park et al., 2012), but the barriers comprised of argillaceous materials, are reported to be the most effective for its retardation (Krumhans et al., 2001). Cs is, in fact, rather strongly sorbed onto clays by ionic exchange. The extent of Cs uptake mainly depends on the cation exchange capacity (CEC) of the sorbents and their content in mica-like minerals, which present highly selective sorption sites for alkali cations (Cornell, 1993).

Several argillaceous rocks, available near the ^{137}Cs contaminated site or commercials, were selected and their retention capacity was studied (García-Gutiérrez et al. (2012)). Amongst the analysed materials, two of them were particularly suitable for sorbing Cs, presenting high illite content: the San Juan (SJ) and the Rojo Carbonero (RC) clays. The sorption behaviour of these two clayey materials had to be studied more in depth, with the objective of understanding and describing in quasi-mechanistic form the retention of Cs in the marsh contaminated environment, because the simple K_d approach is not enough to predict contaminant migration under natural variable conditions.

Furthermore, the porewater from the studied site is industrial and seawater-derived with high amounts of Na (up to 23 g/L), K (up to 1.2 g/L) and NH_4 (up to 0.7 g/L). Since these cations are expected to compete with Cs for the exchange sites, the existing models have to be tested for such high concentrations of K^+, NH_4^+, Ca^{2+} and Na^+ and ion competition must be explicitly accounted for.

To accomplish the mentioned objectives, in this study, detailed experiments of Cs sorption on single minerals (illite and kaolinite, as main components of clayey materials) and on these two natural clays was carried out. Previously obtained data on smectite as other main component of natural clayrocks (Missana et al., 2014) were used for the modelling of the natural system.

Cs sorption dependence on ionic strength and main exchanging ions was evaluated for the selected minerals converted in different homoionic forms. Basic selectivity coefficients were obtained from sorption experiments in simplified (mineral + simple electrolyte) systems; afterwards, Cs sorption onto raw materials and natural waters was experimentally studied and interpreted using the thermodynamic parameters calculated in the simplified systems.

The migration/retention of Cs in clayrocks has been studied by different authors Van Loon et al. (2009), Tachi et al. (2011), Fuller et al. (2014), Poinssot et al. (1999), Bradbury and Baeyens (2000), Zachara et al. (2002) and Liu et al. (2003). In general, illite is very important for cesium sorption, and Bradbury and Baeyens (2000) proposed a generalized cation exchange sorption model for the uptake of Cs by illite, based on the existence of different sorption sites, which cause non-linear Cs sorption.

Micaceous minerals, as illite, in addition to *planar* sites, possess *frayed edge sites*, FES, arising from the weathering of the clay particles edges. Cations like Cs^+, Rb^+, Li^+ or NH_4^+, characterised by low hydration energy and small dehydrated radius, can replace K^+ at these illite weathered edges and be selectively sorbed. Three exchange sites are usually considered to explain Cs sorption behaviour on illite (Bradbury and Baeyens, 2000; Brouwer et al., 1983; Poinssot et al., 1999).

Even when the presence of illite traces or interstratified with illite can give rise to the existence of selective sites for Cs, similar to illite FES (Missana et al., 2014), the surface of smectite and kaolinite is expected to be uniform and, in these pure minerals, Cs exchange is expected to occur mainly onto planar sites.

In this work, the modelling of Cs sorption on the natural clays will be done by a component additivity (CA) approach considering illite, smectite and kaolinite. A three-site exchange model will be used for the component illite; only exchange in planar sites will be included for smectite and kaolinite (thus, "FES-like" sites are all attributed to illite).

2. Materials and methods

2.1. Clays

Two different natural clays were studied: the Rojo Carbonero (RC) and the San Juan (SJ) clays. The RC clay is a commercial product by Cerámicas Bailén S.L. (Spain). Its mineralogy, provided by the supplier is, in wt%: quartz (27%), phyllosilicates (58%), dolomite (8%), feldspar (2%) and hematite (5%). The clay fraction (<2 μm) is composed by illite (98%) and chlorite. The total cation exchange capacity (CEC) of the RC was determined on the raw material to be 11 meq/100 g (Fernandez, 2012) and its BET surface area, 43.71 ± 0.21 m²/g.

The SJ clay was sampled near the contaminated site and it contains (in wt%): quartz (15–20%), illite (30–50%), kaolinite (10–15%), smectite (5–20%), calcite (3–10%) and clinochlore (10–20%).

From the RC material, the clay fraction (mostly illite), which has a size <2 μm, was separated by sedimentation (Stokes' law), to perform detailed sorption studies on this individual mineral. The obtained illite has a CEC of approximately 19 meq/100 g, in agreement with previous published CEC data (Bradbury and Baeyens, 2000) and its surface area is 77 m²/g.

In addition to illite, Cs sorption onto kaolinite (and smectite) and was also analysed, as they are the main clay minerals present in the SJ solid. These sorption studies on the individual minerals allow obtaining basic selectivity coefficients to be tested in more complex systems.

The kaolinite used in the present study was the natural KGa-1-b, obtained from the Clay Mineral Society (CMS, EEUU). The purity of this material is higher than 93%. The main characteristics were provided by the supplier. It has a CEC of 2 meq/100 g and a BET area of 10 m²/g. The main characteristics of the minerals used in this study are included in Table 1.

As reported in Missana et al. (2014), the smectite was obtained from the Spanish FEBEX bentonite, which has (in wt%) a 93 ± 2% content of smectite, and as main accessory minerals: quartz (2 ± 1%), plagioclase (3 ± 1%), cristobalite (2 ± 1%), calcite (1 ± 0.5%) and potassic feldspar (traces). The BET surface area of this clay is 33 m²/g and its CEC 102 meq/100 g. More details on its composition and properties can be found in Fernandez et al. (2004) and Huertas et al. (2000). Previous mineralogical studies also showed that the smectite phase is made up by illite–smectite mixed layer with a 10–15% of illite layers (Cuadros and Linares, 1996; Huertas et al., 2000). Sorption of Cs in this smectite has been previously studied in detail by Missana et al. (2014) and, in the present work, we refer to those results.

2.2. Preparation of exchanged clay minerals

The details on the preparation of purified smectite can be found in Missana et al. (2014). In the present work, the clay minerals illite and kaolinite were purified and converted into different exchanged forms (Na, K, NH_4 and Ca). To exchange the minerals, they were suspended in 1 M of the respective electrolyte (NaCl, KCl, NH_4Cl or $CaCl_2$): the suspensions were stirred overnight and decanted;

Table 1
Main characteristics of clay minerals used in this work.

	Illite	Smectite	Kaolinite
BET (m²/g)	77	33	10
CEC (meq/100 g)	19	102	2

the process was repeated 3 times. After elimination of the supernatant from the last washing, the exchanged minerals were placed in centrifuge tubes with deionised water. Particles of less than 0.5 μm, to be used in sorption tests, were separated by centrifuging the suspensions (2500g, 10 min). The clay washing/centrifuging procedure was repeated until enough fine fraction was collected. Then, the suspensions were brought to the ionic strength required in the experiments. The concentration of the clay material in the suspension was determined by gravimetry. The solid to liquid ratio (S), used for sorption experiments was 1–3 g L^{-1} approximately for illite and smectite and 10 g L^{-1} for kaolinite and the natural RC and SJ solids.

2.3. Aqueous solution

Sorption experiments were carried out with the clays and minerals suspended in different simple electrolytes (NaCl, KCl, NH$_4$Cl and CaCl$_2$) and natural water sampled in the marsh zone (natural saline water, NSW). The chemical composition of this natural water is detailed in Table 2: it is quite saline (its ionic strength is approximately 0.52 M), with high chlorine content, typical for a marsh with marine intrusion, and high concentration of sodium and calcium, but also of other monovalent ions (K$^+$ and NH$_4^+$) which are known to be potentially strongly competitive for Cs sorption (Eberl, 1980; Sawhney, 1972).

2.4. Radionuclide

The radionuclide used in this study was ^{137}Cs (as CsCl in 0.1 HCl M, Isotope Products). The half-life of ^{137}Cs is 30.2 years. This radionuclide decays by beta emission to ^{137m}Ba, responsible for the emission of gamma rays (662 keV). The activity of Cs in solution was measured by γ-counting with a NaI detector (Packard Autogamma COBRA 2), with a counting efficiency for ^{137}Cs of 0.26. The detection limit for Cs is approximately 5×10^{-11} M.

2.5. Sorption measurements

Experiments were performed at room temperature and under atmospheric conditions. Sorption isotherms were carried out both with the exchanged minerals and with the natural materials.

The distribution coefficient, K_d (mL g^{-1}), is calculated by:

$$K_d = \frac{Cs_{in} - Cs_{eq}}{Cs_{eq}} \cdot \frac{V}{m} \tag{E.1}$$

Cs_{in} and Cs_{eq} are the initial and equilibrium concentration of Cs in the liquid phase (Bq mL^{-1}), m the mass of the sorbent (g) and V the volume of the liquid (mL). Sorption onto vessels was always

Table 2
Chemical composition of the natural saline water, NSW (mg/L), pH and conductivity.

Element	NSW
F$^-$	1
Cl$^-$	16019
Br$^-$	144
SO$_4^{2-}$	3358
NO$_3^-$	<0.1.
PO$_4^{3-}$	<0.1.
NH$_4^+$	352
Ca^{2+}	920
Mg^{2+}	501
Na$^+$	9081
K$^+$	727
pH	9.4
Cond. (mS/cm)	39.7

lower than <2%, therefore it was not accounted for in K_d calculations.

Sorption isotherms were carried out by varying the Cs concentration from 1×10^{-10} M to 1×10^{-3} M approximately. For the experiments 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 selected contact time was 14 days. After the solid separation, three aliquots of the supernatant (2 mL) were extracted from each tube for the analysis of the final activity.

2.6. Sorption modelling

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 solid surface ($\equiv$X) is defined by:

$$z_B A \equiv X + z_A B \Longleftrightarrow z_A B \equiv X + z_B A \tag{E.2}$$

The exchange reaction can be expressed in terms of selectivity coefficients (Gaines and Thomas, 1953):

$$^B_A K_{SEL} = \frac{(N_B)^{z_A}}{(N_A)^{z_B}} \frac{(a_A)^{z_B}}{(a_B)^{z_A}} \tag{E.3}$$

where a_A and a_B are the activities of the cations A and B and N_A and N_B are the equivalent fractional occupancies.

As shown in Bradbury and Baeyens (1994), selectivity coefficients of a cation at trace concentration can be determined by means of sorption measurements; if the cation B is present at trace levels, N_A (E.3) is approximately 1; and if the distribution coefficient due to the exchange process (K_d) is known, the selectivity coefficient can be determined by:

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

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

$$\text{Log}\gamma_i = -0.51 \cdot z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \cdot I\right) \tag{E.5}$$

where I represents the ionic strength of the solution in molal units.

For the experiments with the exchanged minerals (X = Na, K or NH$_4$), E.4 becomes:

$$^{Cs}_X K_{SEL} = \left(\frac{K_d}{CEC}\right) \frac{\gamma_X}{\gamma_{Cs}} (X) \tag{E.4a}$$

For the experiments with Ca-exchanged minerals, E.4 is:

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

These expressions, valid for a cation exchange process in a single site, would allow the determination of selectivity coefficients directly from the sorption data obtained in the exchanged minerals. Additionally, once the selectivity coefficients of Cs with respect to Na, K, and Ca are (experimentally) determined, $^K_{Na} K_{SEL}$ and $^{Ca}_{Na} K_{SEL}$ can be calculated by the following expressions:

$$^K_{Na} K_{SEL} = \frac{^{Cs}_{Na} K_{SEL}}{^{Cs}_K K_{SEL}} \tag{E.6a}$$

$$^{Ca}_{Na} K_{SEL} = \frac{^{Cs}_{Na} K_{SEL}}{^{Cs}_{Ca} K_{SEL}} \tag{E.6b}$$

The verification of the experimentally determined parameters, in addition to other modelling calculations, regarding the effects of multiple sites and/or competing ions on cesium sorption, were aided with the CHESS v 2.4 code (Van der Lee and de Windt, 1999).

3. Results and discussion

3.1. Sorption in exchanged minerals and modelling

Fig. 1 shows Cs sorption isotherms obtained in the exchanged illite (Na-; K-; NH$_4$- and Ca-illite), suspended in the respective electrolytes at ionic strength of 0.1 M. The isotherms are presented as the logarithm of the distribution coefficient, Log (K_d) in mL/g, versus the logarithm of the Cs in solution at the equilibrium, Log (Cs$_{eq}$), expressed in (M). Additional experimental data were obtained at the ionic strength of 0.2 M (data not shown).

Fig. 1 shows that Cs sorption onto illite is non-linear: at low Cs concentration, Log (K_d) values are significantly higher (especially in Na- and Ca- illite) than those at high Cs concentrations. At low Cs concentration, sorption onto illite is dominated by the frayed-edge sites (FES), typically existing in micaceus minerals (Jackson, 1968; Cornell, 1993; Poinssot et al., 1999). These sites have very small concentration, but they are particularly selective for cations like potassium, ammonium, rubidium and cesium. The strong competition of potassium and ammonium with Cs for sorption on these sites is evident, as the Log (K_d) in K- and NH$_4$-illite (Log $K_d \sim 2$) are more than two orders of magnitude smaller than those in Na- and Ca- illite (4.5 and 5 approximately). At medium and high Cs loading, sorption takes place within sites presenting higher density but less selectivity, thus distribution coefficients decrease.

The density of FES can be easily determined from the adsorption isotherms. The first inflexion point in the isotherms indicates when their saturation occurs (approximately 4.6×10^{-7} mol/g (or 6×10^{-3} μeq/m^2), see the arrow in Fig. 1). This value, experimentally determined, is considered as a fixed parameter in the modelling.

As reported elsewhere (Bolt et al., 1963; Bradbury and Baeyens, 2000; Brouwer et al., 1983) a three-site exchange model is considered the most adequate to reproduce sorption data on illite. In the case of Na- and Ca-illite, the existence of three sites can be verified by the analysis of the experimental data, but in the case of K- and NH$_4$-clays, it is not easy to assess the existence of more than two sorption sites. Nevertheless, to model sorption data in the natural clays and in the natural system, the selectivity coefficients have to be determined in respect to a major ion, either Na or Ca. As in both Na- and Ca-illite sorption behaviour fits with the existence of three sites, a three-site model must be applied in all the cases.

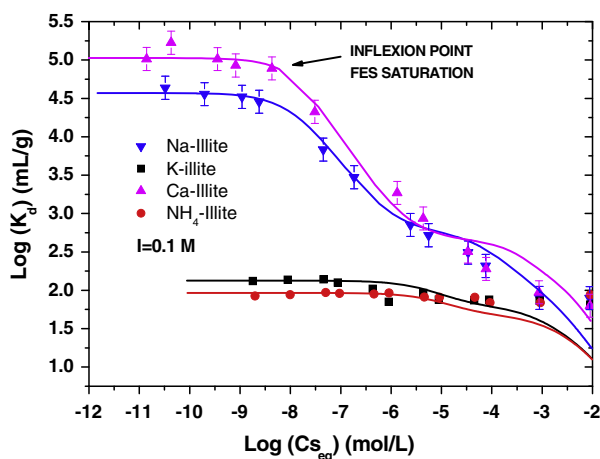As previously mentioned, the FES density can be straightforwardly determined from the sorption isotherms. Instead, the determination of the density of the other two sorption sites (Site 2 and Site 3) is somewhat arbitrary. Bradbury and Baeyens (2000), proposed to assign to the other two sorption sites a density of 20% and 80% of the total CEC (2.52 μeq/m^2), and this assumption will be also adopted in this study. Thus, Site 2 has a density of 0.504 μeq/m^2 and Site 3 of 2.016 μeq/m^2.

The parameters used to fit sorption isotherms in the exchanged illite, with the three-site model, are summarized in Table 3 and the results superimposed to the experimental points in Fig. 1. With the experiments performed in the exchanged illite, the selectivity coefficients of Cs with respect to Na, K, Ca and NH$_4$ (Eq. (E.4)) were determined. From these values, the selectivity coefficients of Ca, K and NH$_4$ were recalculated with respect to the major ion in the system (Na), considering the appropriate relations (E.6a), (E.6b), and the values are summarized in Table 4.

A similar procedure was carried out in Missana et al. (2014), to obtain the selectivity coefficients for smectite, which will be used in this paper for the modelling of the sorption in the natural clays. The sorption behaviour in this smectite was also non-linear, and it could be fit using a two-site model. The two identified sorption sites were FES-like (high affinity) sites and Site 2 (planar) sites. High affinity sites were related to the presence of illite/smectite interstratified layers; therefore their behaviour is supposed to depend on the existence of sites similar to illite FES (Missana et al., 2014).

In the modelling of natural clays, the contribution of FES-like sites will be thus considered to come exclusively from the illite. The contribution of smectite to Cs sorption will be described only by ionic exchange in planar sites. The selectivity coefficients for smectite, from Missana et al., 2014, are summarized in Table 3 and only those corresponding to planar sites will be used in the modelling of the mixed system. The selectivity coefficient of Cs with respect to NH$_4$ (which was not obtained experimentally) was considered equal to the selectivity coefficient with respect to K.

Fig. 2 shows Cs sorption isotherms obtained with the exchanged kaolinite (Na-, Ca-, K- and NH$_4$-kaolinite) at the ionic strength of I = 0.1 M (I = 0.2 M for Na-kaolinite). In the case of K- and NH$_4$-kaolinite, K_d values are similar and nearly constant within the experimental errors, in a very wide range of Cs concentrations. In the case of Ca- and Na-kaolinite, Cs sorption is not linear, indicating the existence of more than one sorption site.

The modelling of Cs sorption isotherms presented in Fig. 2, was carried out considering a two-site exchange model: the selectivity coefficients obtained are summarized in Table 3 and the modelling results superimposed to the experimental points in Fig. 2. As previously observed for smectite, the existence of high affinity (FES-like) sites for Cs sorption in kaolinite is most probably due to the existence of traces of micaceous minerals or interstratified and therefore the contribution of kaolinite to Cs sorption in mixed clays, for sake of simplicity, will be represented only by the ionic exchange in planar sites (Site 2), similarly as the case of smectite.

3.2. Cs sorption in natural clays and modelling

Cs sorption was also studied in two natural materials (RC and SJ), which contain different clay minerals. Sorption on RC is easier to be analysed, as the principal clay mineral is illite (98%), and it is the preferential sorbing mineral. In the case of SJ, in addition to illite (30–50%), also smectite (5–20%) and kaolinite (10–15%), are present and their contribution has to be evaluated. Furthermore, to analyse the extent of sorption variability under real conditions, the effects of competing ions must be studied either.

The model parameters, obtained from the experiments with the exchanged minerals (Tables 3 and 4), will be used to model the behaviour of the natural RC and SJ materials, analysing systems

Fig. 1. Cs adsorption isotherm in exchanged illite: (▲) Ca-; (▼) Na-; (■) K-; -and (●) NH$_4$-illite. Ionic strength I = 0.1 M. Continuous lines represent the modelling with the parameters included in Table 3.

Table 3

Selectivity coefficients (±0.15, $\log K$ units) used to model Cs sorption sorption data in exchanged illite (Fig. 1); exchanged kaolinite (Fig. 2) and exchanged smectite (Missana et al., 2014). In grey cells the parameters used for the modelling of mixed, natural clays.

	Strong sites (FES) (6×10^{-3} μeq/m^2)	Site 2 (0.504 μeq/m^2)	Site 3 (2.016 μeq/m^2)
Illite			
Na-illite	$Log(_{Na}^{Cs}K^{FES}) = 6.90$	$Log(_{Na}^{Cs}K^{S2}) = 3.10$	$Log(_{Na}^{Cs}K^{S3}) = 1.75$
Ca-illite	$Log(_{Ca}^{Cs}K^{FES}) = 15.33$	$Log(_{Ca}^{Cs}K^{S2}) = 6.71$	$Log(_{Ca}^{Cs}K^{S3}) = 4.65$
K-illite	$Log(_{K}^{Cs}K^{FES}) = 4.20$	$Log(_{K}^{Cs}K^{S2}) = 2.00$	$Log(_{K}^{Cs}K^{S3}) = 1.15$
NH$_4$-illite	$Log(_{NH_4}^{Cs}K^{FES}) = 4.00$	$Log(_{NH_4}^{Cs}K^{S2}) = 1.80$	$Log(_{NH_4}^{Cs}K^{S3}) = 1.15$
	Strong sites (FES-like) 7.0×10^{-4} μeq/m^2	Site 2 30.91 μeq/m^2	
Smectite[a]			
Na-smectite	$Log(_{Na}^{Cs}K^{FES}) = 7.59$	$Log(_{Na}^{Cs}K^{S2}) = 1.68$	
Ca-smectite	$Log(_{Ca}^{Cs}K^{FES}) = 14.41$	$Log(_{Ca}^{Cs}K^{S2}) = 3.02$	
K-smectite	$Log(_{K}^{Cs}K^{FES}) = 5.15$	$Log(_{K}^{Cs}K^{S2}) = 1.16$	
	Strong sites (FES-Like) (5.0×10^{-4} μeq/m^2)	Site 2 (1.99 μeq/m^2)	
Kaolinite			
Na-kaolinite	$Log(_{Na}^{Cs}K^{FES}) = 5.50$	$Log(_{Na}^{Cs}K^{S2}) = 2.10$	
Ca-kaolinite	$Log(_{Ca}^{Cs}K^{FES}) = 10.60$	$Log(_{Ca}^{Cs}K^{S2}) = 4.50$	
K-kaolinite	$Log(_{K}^{Cs}K^{FES}) = 4.00$	$Log(_{K}^{Cs}K^{S2}) = 2.15$	
NH$_4$-kaolinite	$Log(_{NH_4}^{Cs}K^{FES}) = 4.00$	$Log(_{NH_4}^{Cs}K^{S2}) = 2.15$	

[a] From Missana et al. (2014).

Table 4

Selectivity coefficients (±0.15, $\log K$ units) with respect to Na, calculated from the experiments with homoionized minerals (Table 3).

	$Log(_{Na}^{X}K_{SEL})$			
	Cs	K	NH$_4$	Ca
Illite FES sites	6.90	2.70	2.90	−1.53
Illite site 2	3.10	1.10	1.30	−0.51
Illite site 3	1.75	0.60	0.60	−1.15
Smectite-site 2[a]	1.68	0.57	0.57	0.29
Kaolinite-site 2	2.10	−0.05	−0.05	−0.30

[a] From Missana et al. (2014).

of increasing complexity. First, model parameters were checked, using Cs sorption isotherms data obtained on the natural RC in: (a) a simple electrolyte (0.5 M NaCl) with increasing content of K$^+$ and NH$_4^+$ (obtained with the addition of KCl or NH$_4$Cl) and (b) in the natural saline water (NSW, Table 2).

Fig. 3 shows Cs sorption isotherms on the natural RC, dispersed in 0.5 M NaCl and 0.5 M NaCl with the addition of 0.02 M of K$^+$, NH$_4^+$ or both. The shape of the sorption isotherm is similar to that observed in the homoionized minerals, indicating non-linear sorption. The maximum Cs adsorption corresponds to a Log (K_d) value of approximately 3.6, in the presence of sodium as unique competing cation. The addition of potassium and ammonium (0.02 M) decreases Cs uptake: in particular at low Cs loadings, where FES dominate sorption, K_d values decrease approximately one order of magnitude.

Using the selectivity coefficients calculated from the test with the exchanged illite (Table 4), all the sorption isotherms could be reproduced very well: simulations are included in Fig. 3. The effects of the addition of potassium and/or ammonium on Cs sorption could be fit as well, indicating that the model developed with the exchanged illite clay can be successfully transferred to interpret sorption data on the natural RC material in simple electrolytes.

Fig. 4 shows Cs sorption isotherms on the natural SJ, dispersed in 0.5 M NaCl and 0.5 M NaCl with the addition of 0.02 M of K$^+$, NH$_4^+$

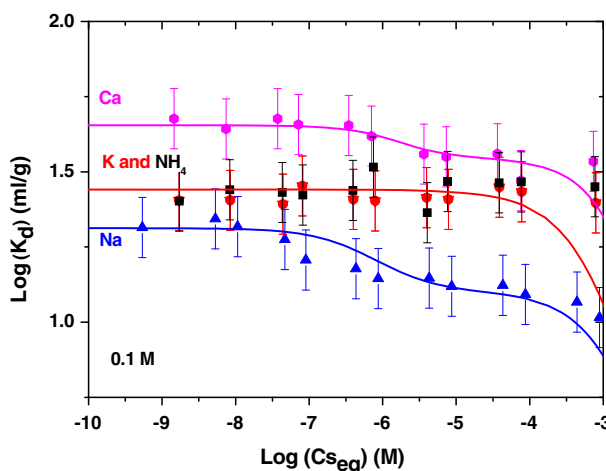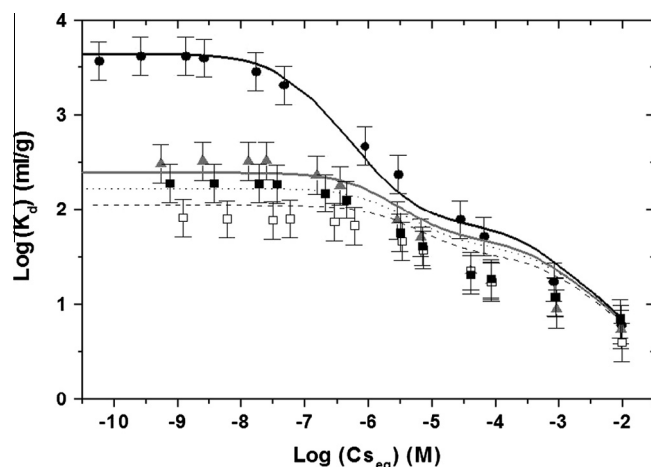**Fig. 2.** Cs adsorption isotherms in exchanged kaolinite: (●) Ca-; (▼) K-, (■) NH$_4$ and (▲) Na-kaolinite. Ionic strength: 0.1 M for Ca, K and NH$_4$-kaolinite, 0.2 M for Na-kaolinite. Continuous lines represent the modelling with the parameters included in Table 3.

Fig. 3. Cesium sorption isotherms with the natural RC clay in: (●) NaCl 0.5 M only; NaCl 0.5 M with addition of 0.02 M (▲) K$^+$ or (■) NH$_4^+$; (□) NaCl 0.5 M with the addition of both 0.02 M K$^+$ and NH$_4^+$. Model with the parameters of Table 4 is superimposed to the experimental points.
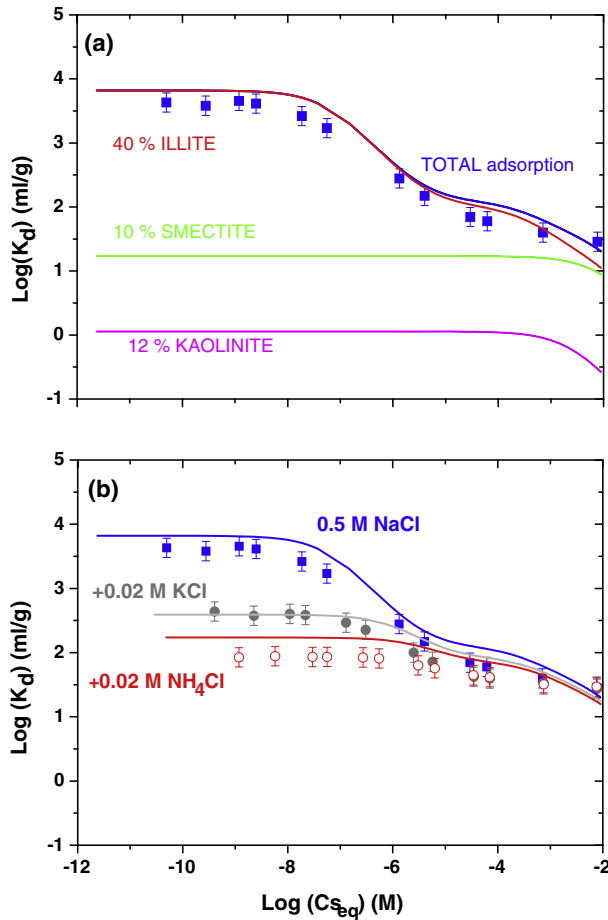
Fig. 4. Cs adsorption isotherms in the natural SJ clay. (a) In NaCl 0.5 M. The contribution to sorption of the different minerals is shown. (b) (■) NaCl 0.5 M only and NaCl 0.5 M with addition of (⬤) 0.02 M K$^+$ or (○) NH$_4^+$ or both. Model with the parameters of Table 4 is superimposed to the experimental points.

or both. To model sorption data in SJ, the contribution of the principal clay minerals had to be considered (illite 40 wt%; smectite 10 wt% and kaolinite 12 wt%, these percentages being mean values obtained in different samples).

The fits obtained with the selectivity coefficients of Table 4, for illite, smectite and kaolinite, are superimposed to the experimental points in Fig. 4. The relative contribution of each mineral to Cs sorption, for SJ suspended in 0.5 M NaCl, is drawn in Fig. 4a. As can be seen in Fig. 4a, illite dominates Cs sorption and smectite starts playing a role only at very high Cs loadings. On the other hand, the contribution of kaolinite could be neglected.

Fig. 4b shows the sorption isotherms in NaCl 0.5 M, with the additions of 0.02 M of K$^+$ or NH$_4^+$. The effect of adding these competitive cations on Cs adsorption in SJ is also quite well reproduced using the parameters of Table 4.

Finally, to test the model under more realistic conditions, the successive step consisted in performing additional Cs sorption isotherms in the natural RC and SJ materials suspended in the saline natural water, whose composition is given in Table 2. The major cation in this water is Na$^+$, but it presents also significant amounts of Ca^{2+}, Mg^{2+}, K$^+$ and NH$_4^+$. All these ions are expected to competitively act for Cs adsorption. For modelling sorption data in this water, for Mg, the same selectivity coefficients as Ca were assumed.

The sorption isotherms of Cs in the natural RC and SJ, suspended in the natural saline water, are shown in Fig. 5. The sorption isotherms are similar in both cases, with maximum distribution
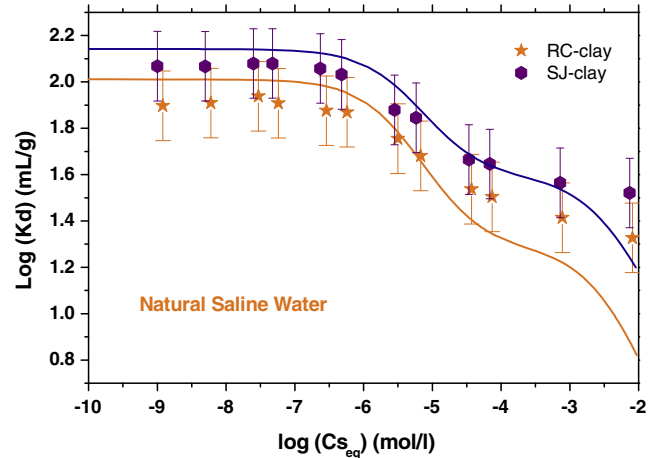

Fig. 5. Cs adsorption isotherms in the natural RC and SJ clay in the natural saline water. Model with the parameters of Table 4 (without changes) is superimposed to the experimental points as continuous line.

coefficients, obtained at low Cs loadings (Log (K_d) around 2); adsorption slightly decreased as Cs concentration increased. The prediction of sorption in this system, using the parameters of Table 4 (without any change), is superimposed to the experimental data as a continuous line. As can be seen, the model developed with the homoionized clay, is able to represent qualitatively and quantitatively the experimental data fairly well, in a very wide range of Cs concentrations, also in this more complex case.

3.3. Model analysis of parameters

For Cs sorption in natural systems two interesting issues can be evaluated: (a) the contribution of the relative content illite/smectite, being these the clay minerals mostly contributing to its sorption and (b) the presence of competing ions. Model calculations were performed to analyse these points.

Fig. 6 shows the simulation of Cs sorption in smectite/illite mixed in different proportions (10/90, 50/50 and 90/10 wt%) in a saline (0.5 M NaCl, Fig. 6a) and less saline environment (0.01 M NaCl, Fig. 6b). In all the cases, it is clear that the higher the illite content, the higher Cs adsorption. Approximately 50% of illite in the system fully dominates adsorption: especially when sorption into FES is relevant, the distribution coefficients in the presence of illite can be up to one order of magnitude higher. Just in the region of the isotherms corresponding to high Cs concentrations, the contribution of smectite (with a larger CEC) might be predominant but in this region the differences in distribution coefficients varying the illite/smectite ratio are negligible.

Fig. 7 shows the dependence of K_d values on the presence of competitive ions (K$^+$, NH$_4^+$ or Ca^{2+}, taken independently). In order to comprehensively analyse the effects of competing ions, a mixture with 50% smectite and 50% illite was considered in two different environments: less saline (0.01 M NaCl, Fig. 7a and c) or high saline (0.5 M NaCl, Fig. 7b and d). Competition effects were analysed both at low Cs concentration (where illite FES site dominates, Fig. 7a and b) and high concentrations (where planar sites dominate, Fig. 7c and d).

The most competitive cations are NH$_4^+$ and K$^+$, whereas the effects of Ca^{2+} on Cs adsorption are very small in all the cases. Competitive effects are very evident at low concentration of the main cation (Na) and low Cs concentration (Fig. 7a). In this case, the presence of the most competitive ions, is appreciable at a concentration of 1×10^{-4}–1×10^{-3} M (by 0.3–1.4 log units), and can
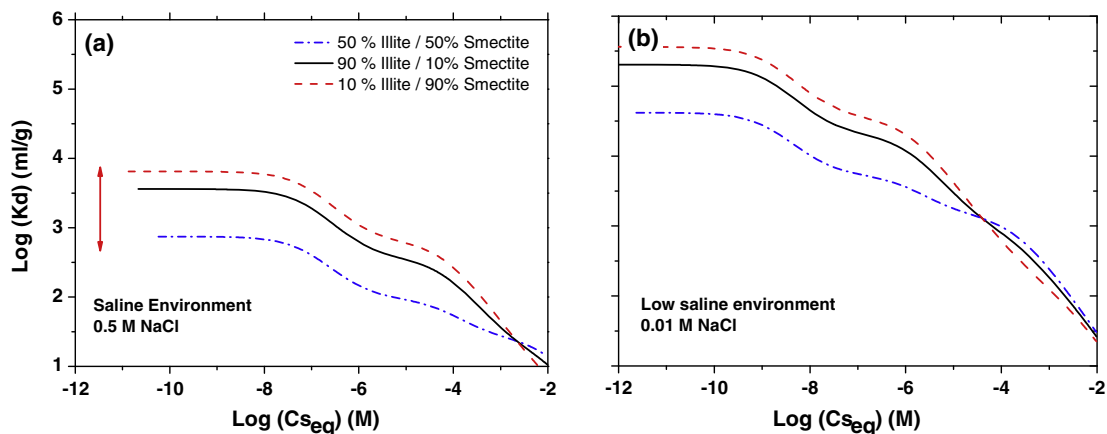
Fig. 6. Simulations of minerals contribution to the Cs sorption in mixed smectite/illite systems (10/90; 50/50; 90/10, 1 g L^{-1}) in: (a) NaCl 0.5 M and (b) NaCl 0.01 M.
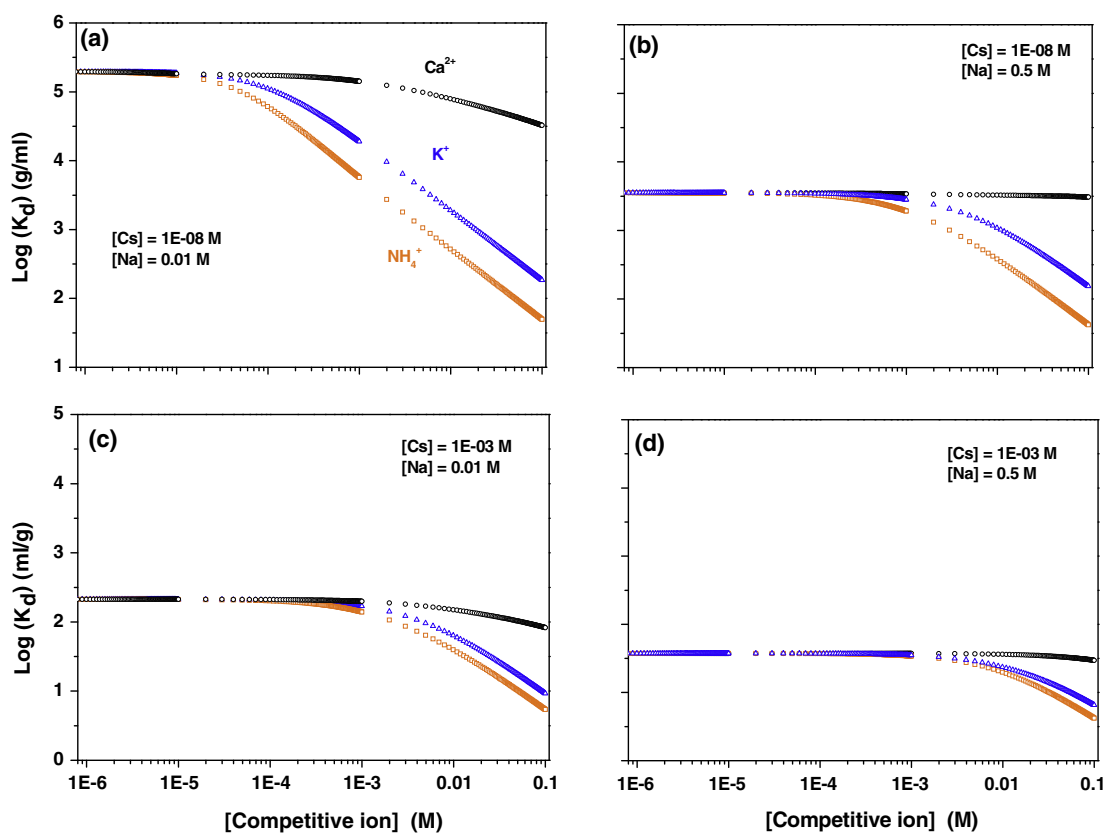

Fig. 7. Simulations of competition effects of ($\bigcirc$) Ca^{2+}; ($\triangle$) K$^+$ and ($\square$) NH$_4^+$ on Cs adsorption in 50% illite and 50% smectite system (1 g/L). (a) Low Cs concentration and low saline water; (b) low Cs concentration and saline water; (c) high Cs concentration and low saline water and (d) high Cs concentration and high saline water.

cause a decrease in K_d values up to four orders of magnitude approximately at K or NH$_4^+$ concentration of approximately 0.1 M.

At low Cs concentration and high concentration of Na (Fig. 7b), the competitive effects can be also important, with a decrease of approximately 2 orders of magnitude in K_d values, but higher concentration of competitive ions are necessary (>1 × 10^{-3} M) to observe this effect.

At high Cs concentration (Fig. 7c and d), competitive effects are not as strong as those discussed above. Concentrations of competitive ions higher than 1 × 10^{-2} M are needed to start observing some effects on K_d values and the maximum decrease is one order of magnitude or less.

4. Conclusions

Sorption of Cs in the two natural clays analysed (San Juan and Rojo Carbonero), was non- linear, and a multisite ion exchange model had to be adopted to fit experimental data. To develop this sorption model, capable of reproducing Cs retention behaviour under the conditions of a high salinity site, the selectivity coefficients of Cs with respect to the most important competing cations were derived by means of sorption experiments in single exchanged clay minerals; then these parameters were tested in systems of increasing complexity: natural clays in different electrolytes and natural waters.

Considering the main mineralogical composition of the natural materials, it was shown that the principal contribution to Cs sorption is given by the mineral illite, while smectite starts to be relevant only at very high Cs loadings. Kaolinite, even in concentrations around 10% of the clayey fraction, played only a minor role.

The developed sorption model was able to represent qualitatively and quantitatively Cs sorption data in a very wide range of Cs concentration and chemical conditions. In particular, it was successful in predicting sorption competition effects caused by high concentrations of NH_4^+, and K^+ and Na^+ in concentrations higher than twice that of seawater. The effect of NH_4^+ and K^+ on Cs retention is more important at low ionic strengths and low Cs loadings, where adsorption is dominated by illite FES. Divalent cations are not especially relevant as competing cations for Cs.

Acknowledgments

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