Adsorption of strontium and caesium onto an Na-MX80 bentonite: Experiments and building of a coherent thermodynamic modelling

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ABSTRACT

Multi-site ion exchange modelling permits describing the different adsorption behaviour of cations onto clay minerals. Considering several adsorption sites in the clay minerals' structure allows accurately representing the overall variations of adsorption behaviours. For a wider applicability in soils and sediments, it appears necessary to build a coherent thermodynamic adsorption database for radionuclides. ^{90}Sr and ^{134,137}Cs are major radionuclides to be considered in the case of nuclear accidents, but thermodynamic data on their adsorption on purified smectites are scarce. Therefore, a detailed study to determine Sr^{2+} and Cs^+ adsorption parameter on smectite seems necessary. To provide this kind of information, this study is proposing multi-site ion exchange modelling of the adsorption of Sr^{2+} and Cs^+ onto a pure Na-MX80 montmorillonite. The intrinsic parameters—site concentration and corrected selectivity coefficient for the Na^+/H^+ exchange—were first fitted using an already available Na saturation curve of a purified smectite. The adsorption of Sr^{2+} and Cs^+ on a purified Na-MX80 bentonite was explored, including a kinetic study for Sr, as a function of pH and equilibrium concentration. The isotherms were modelled to determine the corrected selectivity coefficients for the $2Na^+/Sr^{2+}$ and Na^+/Cs^+ exchange reactions. This study provides a part of a wider databasis that is currently under construction, which can be used to predict the adsorption of Sr and Cs in soils and sediments.

1. Introduction

With the use and development of nuclear energy, the knowledge of the behaviour of the ^{235}U daughters in the environment is essential and has widely been studied. ^{90}Sr and ^{137}Cs, with half-lives of 29 and 30 years, respectively, are amongst the major by-products from the fission of ^{235}U (England and Rider, 1993). These isotopes were spread in the environment after the fall-out of the different nuclear weapon detonations, and after the nuclear accidents at Chernobyl (IAEA, 2006) and Fukushima-Daiichi (Sahoo et al., 2016). Because of its capacity to substitute with calcium in the food chain, ^{90}Sr can disturb ecological systems (Comar et al., 1957). Concerning ^{137}Cs, it is considered as a dangerous element because its high sol to plant transfer and radioactive decay includes ^{137}Ba and its gamma radiation.

Strontium and caesium are known to be greatly adsorbed onto soils, more specifically by clay minerals as illite (Bilgin et al., 2001) or kaolinite (Erten et al., 1988; Galamboš et al., 2013). If illite and vermiculite are known to be the strongest adsorbents for caesium, particularly due to the presence of the low concentration of high affinity frayed edge sites (Brouwer et al., 1983; Dzene et al., 2015; Sawhney, 1972),

montmorillonite could also play an important role in the adsorption of Sr^{2+} and Cs^+ due to its high cationic exchange capacity (CEC).

The study of the adsorption behaviour of Sr^{2+} onto pure Na-montmorillonite has been mainly led on smectite-rich soils (Galamboš et al., 2010; Kasar et al., 2014) or non-purified bentonite (Wang et al., 2004). Studies on purified smectite remain scarce in the literature. Missana and García-Gutiérrez (2007) have worked on a purified Na-FEBEX bentonite, which contains illite-smectite interstratified layers that provide specific fixation sites for Cs^+ or K^+. Thereby, FEBEX bentonite cannot be considered as a pure smectite. Nevertheless, the similarity of the adsorption behaviour of Sr^{2+} onto illite and smectite (Missana et al., 2008) could permit comparing these results with those obtained on purified smectite.

Only a few papers deal with Cs^+ adsorption onto pure Na-montmorillonite. As for Sr^{2+}, most of these works deal with smectite-rich soils (Vejsada et al., 2005), non-purified (Galamboš et al., 2010; Montavon et al., 2006; Wang et al., 2010) or not mono-ionic conditioned bentonite (Wu et al., 2009). Gorgeon (1994) reported trace Cs^+ adsorption onto a pure Na-saturated Wyoming montmorillonite in 1 mol per kg of water ($mol.kg_w^{-1}$) NaCl. As the ionic strength is well

outside the validity domain of the Davies (1962) equation, they will not be included in our discussion. As the specific interaction parameter $\varepsilon(Cs^+, Cl^-)$ is not available, and in view of the specific $\log_{10}\gamma_{\pm, CsCl}$ vs. m_{CsCl} variation (Hamer and Wu, 1972), a complete refitting using the specific interaction theory (Ciavatta, 1980) would be necessary, which is out of the framework of this study. This data can only be used as qualitative comparison. Missana et al. (2014a) studied the adsorption of caesium onto an Na-FEBEX bentonite, which carries a significant part of interstratified illite-smectite (vide ante). The illite part from these interstratified is well known to show specific adsorption behaviour towards Cs^+ partly due to the FES. As explained in Ogasawara et al. (2013), even a slight proportion of illite in clay minerals tends to drive the adsorption of Cs^+ at trace level and prevents the direct comparison between the results of Missana et al. (2014a) with results that could be obtained on purified smectite. Even at high concentration of Cs, illite could dominates the adsorption, as shown by Missana et al. (2014b) in San Juan clay (illite, smectite, kaolinite mixture).

The adsorption onto bentonite, as for many clay minerals (Carroll, 1959), is mainly controlled by an ion-exchange mechanism. Semi-empirical approaches of these adsorption mechanisms onto bentonite were used (Dyer et al., 2000; Guimarães et al., 2015; Mahoney and Langmuir, 1991; Rafferty et al., 1981; Shaban and Macášek, 1998), but few works used a mechanistic, or semi-mechanistic, approach. Bradbury and Baeyens (1999) have developed a model based on a mechanistic description of the cation adsorption between a clay minerals and a liquid phase—namely the two-site protolysis non-electrostatic surface complexation and cation exchange model or 2SPNE SC/CE. This model is combining both cation exchange reactions based on the Gaines and Thomas (1953) formalism—with no account for the Na^+/H^+ exchange—, and non-electrostatic surface complexation terms. Missana et al. (2008) applied a model derived from 2SPNE-SC/CE to study the adsorption of Sr^{2+} onto illite, smectite, and illite/smectite mixtures. This approach allows representing the global adsorption behaviour. Within the framework of this model, the pH dependency is given by the adsorption on edge sites > S-OH—either silanol or aluminols sites. Adsorption onto cation exchange sites is not pH dependent. Conversely, adsorption of electrolyte cations only occurs on cation exchange sites. From their basic hypotheses these models do not allow modelling the saturation of a homo-ionic exchanger by a major cation, e.g. the Na^+/H^+ exchange all over the pH range. Conversely, within the multi-site ion exchange modelling framework the Na^+/H^+ exchange is considered intrinsically, as well as the exchange between a metal cation and Na^+ or H^+ exchange (Gaucher, 1998; Gorgeon, 1994; Motellier et al., 2003; Nolin, 1997; Peynet, 2003; Reinoso-Maset and Ly, 2014; Stammose et al., 1992).

In this study, a multi-site ion exchange modelling has been used. This model is based on the ion exchange theory (Tremillon, 1965) and has been developed to represent the adsorption processes on clay minerals (Gaucher, 1998; Gorgeon, 1994; Motellier et al., 2003; Nolin, 1997; Peynet, 2003; Reinoso-Maset and Ly, 2014; Stammose et al., 1992), mixtures of minerals (Peynet, 2003), or soils (Jacquier et al., 2004). The model does not aim to describe clay minerals at the microscopic scale—nature of adsorption sites, particularly affectation of sites defined by the model to the FES sites, surface charge, etc.—but takes into account the adsorption behaviour of major and trace elements in order to represent clay mineral characteristics. The model considers clay minerals as multi-site ion exchangers that bear negative adsorption sites (X_i^-) in contact with the solution. The exchanger(s) and the aqueous solution are considered as non-miscible phases. Each site i can potentially adsorb any cation. It is defined by a site concentration (SC_i in mmol per g of exchanger), and a corrected—of adsorbed species activity coefficient—selectivity coefficient for the exchange reaction between cations, e.g. $K^{*i}_{Na^+/H^+}$ for the Na^+/H^+ exchange.

This approach requires a careful and thorough characterisation of adsorption. First, the ion exchange properties (SC_i and corrected selectivity coefficients) have to be measured in a wide parametric domain

of pH, ionic strength, and metal concentration (Jacquier et al., 2004; Motellier et al., 2003; Reinoso-Maset and Ly, 2014; Robin et al., 2015; Stammose et al., 1992), forming a coherent thermodynamic database for adsorption. All the exchange properties are experimentally measurable with adsorption isotherms. Afterwards, these properties can be used to study the metal adsorption (Tertre et al., 2009), or diffusion (Lu et al., 2014; Savoye et al., 2012), in different mineral contexts.

In order to continue building a coherent database, including Sr and Cs, and in light of the few amount of data on the adsorption of these cations onto pure smectite, the aim of this paper is first to ascertain the exchange properties of smectite—SC_i and corrected selectivity coefficient for the Na^+/H^+ exchange—, and second to acquire experimental data on the adsorption of Sr^{2+} and Cs^+ on a homo-ionic pure smectite—here the MX80 bentonite—as a function of pH, ionic strength, and initial concentration of cations. Then, the isotherms will be fitted using multi-site ion exchange modelling to determine the corrected selectivity coefficients for the $2Na^+/Sr^{2+}$ and Na^+/Cs^+ exchange reactions. The overall objective is to propose a coherent set of data for describing the adsorption behaviour of Na^+, H^+, Sr^{2+}, and Cs^+ on a pure smectite. This set of data could then be used to predict the adsorption of Sr and Cs in Na-rich soils.

2. Materials and methods

2.1. Materials

Wyoming MX80 bentonite was used as the adsorbent. It was purified to keep only the montmorillonite part, and conditioned under Na-saturated form following protocols in Gaucher (1998) and Peynet (2003). The organic matter potentially present in the material was removed using H_2O_2 at 80 °C, and calcite was dissolved using 0.1 M HCl solution. The montmorillonite was Na-conditioned by several washings using a 1 M NaCl solution. The reported CEC for the MX80 varies from 0.71 to 1.03 mmol.g^{-1} (Alonso and Ledesma, 2005; Karnland, 2010; Meier, 1999). This value depends upon the measurement protocol or the sample purity. A CEC of 1.03 mmol.g^{-1} was measured for this MX80, extracting all exchangeable cations with a KCl solution at pH ca. 10 (KOH). Supernatant was removed and the MX80 was washed with milli-Q water, then with ethanol. The adsorbed K^+ cations were extracted with a CsCl solution, and analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). This high CEC value tends to confirm the high purity of the montmorillonite extracted from the MX80 bentonite. The purity was also confirmed by X-ray crystallography (XRG 3000, Inel)—see Fig. A1 of the Appendices. Moreover, the material only presents traces of exchangeable K and Mg (less than 1%) and is Na-saturated.

The chemicals used were at least of analytical grade. Stable Sr solutions were prepared from a $SrCl_2 \cdot 6H_2O$ salt (99.995% trace metals basis, Sigma Aldrich). Stable Cs solutions were from CsCl (99.999% trace metals basis, Sigma Aldrich). ^{85}Sr and ^{137}Cs solutions were obtained from Cerca LEA. Ionic strength was fixed using NaCl (Analar Normapur, VWR).

2.2. Adsorption experiments

2.2.1. Experimental protocols

All experiments were performed by batch method at room temperature (22 ± 2 °C) with the same 3.8 g.L^{-1} solid/solution ratio. Polycarbonate Nalgene centrifuge tube (10 mL, 3138–0010, Thermo Scientific) were used. All the solutions and suspensions were made by weighing.

In all experiments the MX80 bentonite was first equilibrated under agitation with the NaCl electrolyte for 24 h. The pH values were adjusted with 1, 0.1 or 0.01 mol.kg$_w^{-1}$ solutions of HCl or NaOH, and suspension were left under agitation for 24 h. A total concentration of stable strontium—1.5 10^{-5} mol.kg$_w^{-1}$ of $SrCl_2$ for the kinetic

experiment, 10^{-6} mol.kg$_w$$^{-1}$ for the adsorption of Sr vs. pH, and from 10^{-2} to 10^{-7} mol.kg$_w$$^{-1}$ for the adsorption of Sr as a function of the concentration—or Cs (10^{-7} mol.kg$_w$$^{-1}$) was added from the stock solution, and the suspensions were then spiked with ^{85}Sr or ^{137}Cs (ca. 3000 Bq) and left under agitation—1 day for Sr studies and 2 days for Cs study from the kinetic experiment, *vide infra*. Finally, the suspensions were ultra-centrifuged (70.1 Ti Rotor, Optima LE-80R, Beckman) during 30 min at 9000 g; 1 mL aliquots of the supernatant were collected, and activity was counted by gamma spectrometry.

A set of kinetic experiments was also prepared without the ^{85}Sr spiking. Mixtures were left under agitation from 0 to 4 days and the equilibrium concentrations were analysed by ICP-AES.

The initial activities in the spiked experiments were determined using a blank procedure – same protocol but without Na-MX80 montmorillonite in batches. The partition coefficients R$_D$ (L.kg^{-1}) were calculated using:

$$R_D = \left(\frac{C°}{C_{eq}} - 1\right) \cdot \frac{V}{m}$$

(1)

where C° and C$_{eq}$ are respectively the initial and equilibrium concentrations (kinetic experiments) or activities (pH and concentration isotherms) of either Sr or Cs, V is the total volume of solution (L), and m is the total dry mass of solid phase (kg).
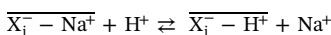
2.2.2. Analytical methods

The aqueous concentrations of inactive Sr and Na in solutions were measured by ICP-AES (Activa, Horiba Jobin Yvon). Samples were diluted with 2% sub-boiling HNO$_3$ (DuoPur, Milestone). Measurements were made with five points calibration curves at 407.771 nm for strontium and 589.592 nm for sodium.

Supernatant activities of ^{85}Sr and ^{137}Cs were determined after sampling of 1 mL aliquots using a gamma counter (1480 Wizard 3, Perkin Elmer). The pH values were measured with a combined microelectrode (pH InLab, Mettler Toledo) by redetermination of the potential/pH plot of the electrode, and by calculating the value of the solutions from their potentials (buffer solutions 4.01, 7.00, 9.18, Merck). Uncertainties from the linear regression are typically in the range of 0.05 units of pH.

2.3. Modelling

The competitive adsorption onto clays is described by a multi-site ion exchange model. This model is detailed in the Appendices and only the main expressions are recalled here without demonstration. First, the adsorption of major cations—Na$^+$ in this study—is studied on a homoionic conditioned montmorillonite under Na-saturation conditions. The evolution of the retention of Na$^+$ as a function of pH is measured in order to describe the exchanger in terms of site concentrations and corrected selectivity coefficients for Na$^+$/H$^+$ exchange (K$_{Na^+/H^+}^{*i}$). In an aqueous solution containing only Na$^+$ and H$^+$, the equilibrium of a given negatively charge type of site X$_i^-$ saturated with Na$^+$ from the montmorillonite with the solution is described by the following equilibrium.

$$\overline{X_i^- - Na^+} + H^+ \rightleftarrows \overline{X_i^- - H^+} + Na^+$$

The corresponding corrected selectivity coefficient of this equilibrium can be written as,

$$K_{Na^+/H^+}^{*i} = \frac{[\overline{X_i^- - H^+}] \cdot [Na^+]}{[\overline{X_i^- - Na^+}] \cdot [H^+]} \times \frac{\gamma_{Na^+}}{\gamma_{H^+}}$$

(2)

where [ ] is the solution (mol.kg^{-1} of water) concentration, [-] is the adsorbed concentration (mol.kg^{-1} of solid) of species, and γ are the activity coefficient of aqueous species—calculated here using Davies (1962) equation.

Each type of site i is also described by a site concentration SC$_i$ in

mol.kg^{-1} of solid. The sum of the SC$_i$ is equal to the sum of all the adsorbed species concentrations.

$$SC_i = [\overline{X_i^- - H^+}] + [\overline{X_i^- - Na^+}]$$

(3)

The methodology to study the saturation of an exchanger with a major cation is detailed elsewhere (Motellier et al., 2003; Reinoso-Maset and Ly, 2014; Stammose et al., 1992).

To determine the corrected selectivity coefficients for the exchange between the trace (Cs$^+$ and Sr^{2+}) and major (Na$^+$) cations, the retention is studied on a homo-ionic sodic conditioned montmorillonite vs. the solution pH and the equilibrium concentration of the trace cation. The corrected selectivity coefficient of a cation M^{m+} with regards to Na$^+$ can be written as follows.

$$K_{mNa^+/M^{m+}}^{*i} = \frac{[\overline{(X_i^-)_m - M^{m+}}] \cdot [Na^+]^m \cdot \gamma_{Na^+}^m}{[\overline{X_i^- - Na^+}]^m \cdot [M^{m+}] \cdot \gamma_{M^{m+}}}$$

(4)

Determining $[\overline{(X_i^-)_m - M^{m+}}]$ permits calculating the experimental partition coefficient using the following expression.

$$R_D = \frac{[\overline{M}]}{[M]} = \frac{\sum_i [\overline{(X_i^-)_m - M^{m+}}]}{[M]}$$

(5)

The methodology to study the adsorption of a trace element onto a homoionic exchanger is also detailed elsewhere (Jacquier et al., 2004; Tertre et al., 2009).

The different site concentrations and corrected selectivity coefficients were obtained fitting the theoretical expression to the experimental data using the MS Excel Solver. The uncertainties of these parameters were obtained using the SolverAid macro from De Levie (2005).

3. Results and discussion

3.1. Preliminary remarks

In this study, MX80 bentonite was supposed to be fully Na-saturated. Despite their possible interactions in the adsorption process, other exchangeable cation, e.g. Ca^{2+} and K$^+$ present in the exchanger (cf. § 2.1), were neglected. Their trace level concentrations were supposed to be low enough not to interfere in experimental results. Furthermore, the possible dissolution of smectite was not considered either. It is known that pH < 4 or pH > 10 the dissolution of clay minerals can be important (Amram and Ganor, 2005; Bradbury and Baeyens, 1997). The dissolution can lead to a release of aluminium, silicon, iron, and other structural cations as K$^+$ and Mg^{2+}. The release of these ions—mainly Al(OH)$_n^{(3-n)+}$ or Fe(OH)$_n^{(3-n)+}$—could compete with the adsorption of Sr^{2+} and Cs$^+$ in MX80. Then, the account of these phenomena is very difficult to manage, see e.g. Bradbury and Baeyens (2005). Hence, one must not forget that these phenomena are intrinsically included into the corrected selectivity coefficients. The deconvolution of these phenomena would require a dedicated study of the clay minerals' structure with pH, and according modifications of the exchangers.

3.2. Selection of the adsorption parameters of the exchanger

The initial parameters of the exchanger (SC$_i$ and log$_{10}$K$_{Na^+/H^+}^{*i}$) are determined by fitting the saturation curve of a homo-ionic Na-exchanger at varying pH. The saturation of a montmorillonite with Na$^+$ has been already studied by Gorgeon (1994), Nolin (1997), and Peynet (2003): Gorgeon (1994) considered only one major site S$_1$ with a concentration of 0.422 mmol g^{-1}; Peynet (2003) reported two major sites (Σ SC$_i$ = 0.605 mmol g^{-1}); and Nolin (1997) proposed three sites (Σ SC$_i$ = 0.886 mmol g^{-1}). The saturation study from Nolin (1997) is the only one that reached a total site concentration close to the typical montmorillonite CEC (Bradbury and Baeyens, 1997; Staunton and
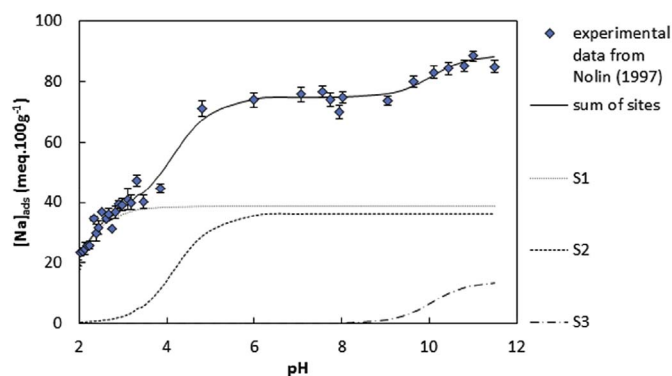
Fig. 1. Modelling of the saturation of a montmorillonite with Na^+ vs. pH at constant I = 0.02 M ($NaClO_4$) and solid/liquid ratio (S/L) of 8 g.L^{-1}, and modelling (plain line) with sites S_1 (dotted line), S_2 (dotted line), and S_3 (dash-dotted line) from Nolin (1997).

Fig. 2. Kinetic study of the adsorption at $[Sr]_{total}$ = 1.5 10^{-5} mol.kg$_w^{-1}$, pH = 7, I = 0.1 mol.kg$_w^{-1}$ (NaCl) and S/L = 3.8 g.L^{-1}—time 0 is corresponding to the centrifugation time (30 min) without prior agitation.

Roubaud, 1997). The montmorillonite used by Gorgeon (1994) was not completely saturated with Na^+ and bared remaining Ca^{2+}. It has been reported by Nolin (1997), and resumed by Tertre et al. (2009), that the remaining Ca^{2+} could compete with the adsorption of Na^+ and distort the Na saturation curve. Compared to Gorgeon (1994) and Nolin (1997), the montmorillonite from Peynet (2003) was less pure, i.e., 80% for Peynet (2003), 98% for Gorgeon (1994), and 96% for Nolin (1997). Thus, the saturation curve obtained by Nolin (1997) was chosen and reinterpreted in the framework of the multi-site ion exchange model, as done by others authors (Lu et al., 2014; Robin et al., 2015; Savoye et al., 2015; Tertre et al., 2009, 2011, 2013).

The saturation curve obtained by Nolin (1997) is presented in Fig. 1. The adsorbed concentration of Na^+ is increasing with pH until 4.5. Then, the adsorption remains practically constant until another increase at pH 9.5. From this saturation curve, three waves are observable. These waves can represent the saturation of the different fixation sites of the exchanger. As previously explained, in the pH range 2–4, the low adsorption of Na^+ is possibly due to the competition with H^+ but also with other cations released from the smectite dissolution.

Nolin (1997) calculated the corrected selectivity coefficients for the Na^+/H^+ exchange for his smectite, but the reported uncertainties were unexpectedly high (> 40% relative uncertainty) compared to the correlation with the saturation curve. As the fitting protocol of $\log_{10}K^{*i}_{Na^+/H^+}$ and uncertainties estimations were not given, we propose a new fitting of these data in Fig. 1. The site concentrations from Nolin (1997) and the obtained $\log_{10}K^{*i}_{Na^+/H^+}$ are summarized in Table 1. The sum of SC_i is supposed to be close to the CEC, but in this particular case, the ΣSC_i is lower than the measured CEC for the MX80. Dissimilarities in used materials—SWy-1 in Nolin (1997) vs. MX80 in this study—could explain the differences. With the aim of proposing a general database for montmorillonite, the value of 0.886 mmol g^{-1} seems in good agreement with those proposed by different authors for a Wyoming montmorillonite (Bradbury and Baeyens, 1997; Staunton and Roubaud, 1997).

3.3. Strontium adsorption

Multiple facets of the strontium adsorption onto the Na-saturated MX80 montmorillonite were explored in this study. The kinetics of adsorption has been examined to determine the necessary equilibrium time. The adsorption behaviour of Sr^{2+} as a function of the equilibrium pH and the Sr concentrations were studied building adsorption isotherms. The role of the ionic strength was also examined. With the aim of building a coherent set of data, all corrected selectivity coefficients of the $2Na^+/Sr^{2+}$ exchange reactions were adjusted to match the adsorption isotherms as a function of the equilibrium pH, ionic strength, and the Sr concentration.

The Sr^{2+} cation is the main Sr specie in solution in all these experiments—$SrCl^+$ represents 3% (I = 0.15 M), 2% (I = 0.1 M) and 1% (I = 0.05 M) of the dissolved species (Sverjensky et al., 1997), and $SrOH^+$ is not significantly present in solution below pH 10 (Shock et al., 1997). Nevertheless, all the speciation effects are taken into consideration in the modelling (cf. Appendix B.2)

3.3.1. Kinetic experiments

Fig. 2 shows the adsorption kinetics (R_D as a function of the contact time) of Sr onto the Na-MX80. The equilibrium is reached within minutes. The R_D value is constant all through the experiment with an average value of R_D = (192 ± 35) L.kg^{-1}.

In similar experiments Galamboš et al. (2013) have studied the kinetic of adsorption of Sr^{2+} onto three different bentonite samples. They showed that the equilibrium was achieved within 10 s, and the adsorption remained constant during at least 10 days, which is in agreement with our results. In our case, the final equilibrium time between bentonite/NaCl mixture and the strontium solution was set at 12 h to be sure to achieve the equilibrium.

3.3.2. Adsorption experiments and modelling

Fig. 3 shows the adsorption isotherm of Sr vs. pH onto the Na-MX80 at two ionic strengths, i.e. I = 0.1 (Fig. 3a) and 0.05 (Fig. 3c) mol.kg$_w^{-1}$ (NaCl). The contributions of the different adsorption sites are also represented. At I = 0.1 mol.kg$_w^{-1}$, the adsorption steadily increases with pH. At I = 0.05 mol.kg$_w^{-1}$, the evolution of R_D is also influenced by pH. The R_D increases gradually up to pH 7 then reaches a plateau. It is worthy to note that Sr adsorption is decreasing with increasing ionic strength as expected for an ion exchange mechanism.

The concentration isotherm as a function of the equilibrium concentration at 0.15 mol.kg$_w^{-1}$ NaCl and fixed pH = 6.6 is shown in Fig. 4a. Strontium adsorption weakly depends on initial concentrations and does not seem to present any specific behaviour. The isotherm is nearly linear in the range $[Sr]_{eq}$ = 10^{-7}–10^{-4} mol.kg$_w^{-1}$ ($\log_{10}R_D$ = 2.1) then decreases at the highest concentrations, due to the

Table 1
Site concentrations and corrected selectivity coefficients for the Na^+/H^+ exchange onto a montmorillonite.

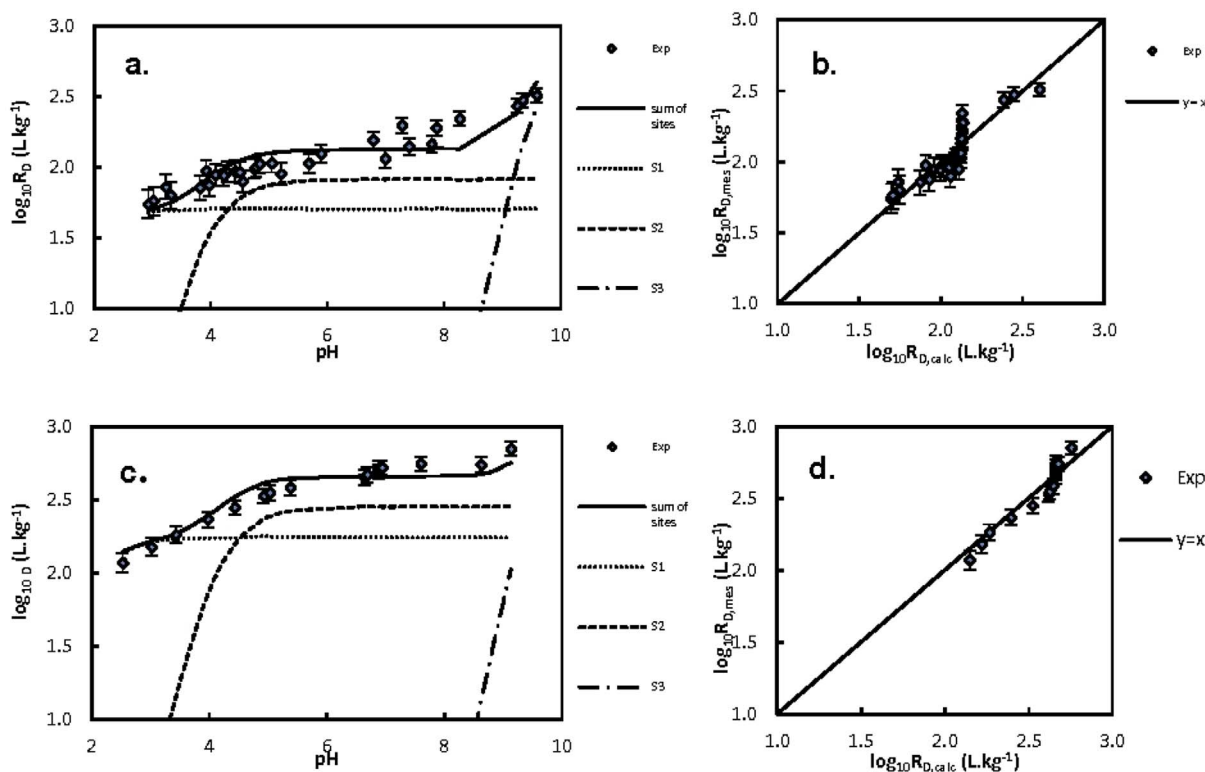| Site	SC_i (mmol.g^{-1})	ΣSC_i (mmol.g^{-1})	$\log_{10}K^{*i}_{Na^+/H^+}$
S_1	0.387 ± 0.038[a]		0.24 ± 0.04
S_2	0.361 ± 0.068[a]	0.887	2.62 ± 0.08
S_3	0.139 ± 0.092[a]		8.45 ± 0.18

[a] Site concentrations taken from Nolin (1997).

Fig. 3. Adsorption isotherms of $[Sr]_{total} = 10^{-6}$ mol.kg$_w^{-1}$ as a function of pH, and comparison of experimental with modelling results at S/L = 3.8 g.L^{-1} and I = 0.1 mol.kg$_w^{-1}$ (NaCl) (a, b) and I = 0.05 mol.kg$_w^{-1}$ (NaCl) (c, d); representation of the contribution of the differents fixation sites, S$_1$ in dotted lines, S$_2$ in dashed lines, and S$_3$ in dash-dotted lines.
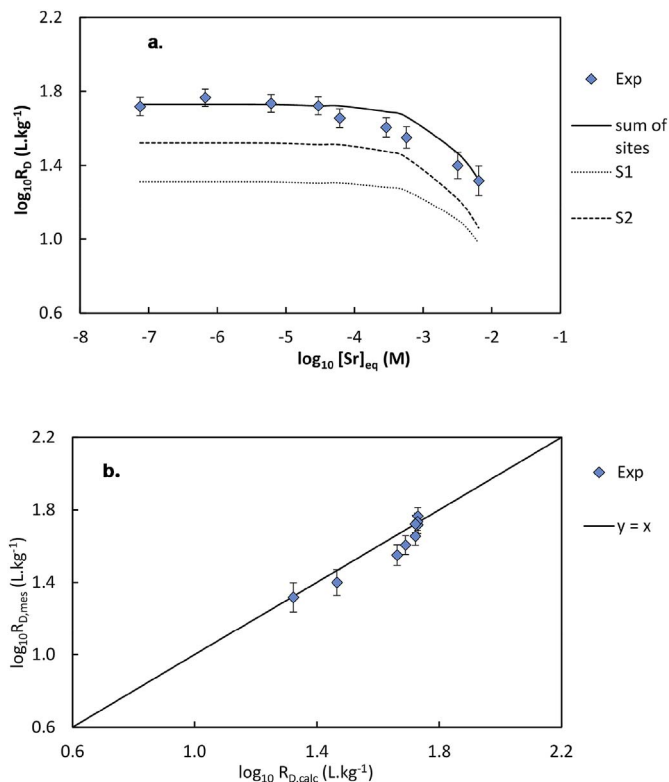

Fig. 4. Adsorption isotherm in concentration of Sr on MX80 bentonite at I = 0.15 mol.kg$_w^{-1}$ (NaCl), pH = 6.6 and S/L = 3.8 g.L^{-1}, and representation of the influence of the differents exchange sites (a)—the S$_3$ site does not appear onto the isotherm because of its minor contribution—; and comparison of the experimental with the modelling results (b).

saturation of the clay mineral.

The site concentrations from Nolin (1997) and $\log_{10}K^{*i}_{Na^+/H^+}$ in Table 1 were chosen to interpret the isotherms. The $\log_{10}K^{*i}_{2Na^+/Sr^{2+}}$ values were adjusted to fit the calculated $\log_{10}R_D$ values to the experimental ones.

Modelling of strontium adsorption is represented in Figs. 3 and 4. The modelling represents satisfactorily the pH isotherms at I = 0.1 mol.kg$_w^{-1}$ (r^2 = 0.82) and at I = 0.05 mol.kg$_w^{-1}$ (r^2 = 0.90), and the concentration isotherm (r^2 = 0.86). As the modelling strongly depends on the initial parameters used (SC$_i$ and $K^i_{Na^+/H^+}$), modelling results cannot be improved without modifying these initial parameters. The choice of adjusting simultaneously all isotherms constrained the modelling, but enhances its applicability at different ionic strengths. For each isotherm, by using the previously discussed initial parameters, it appears that only the first two sites would be influent to describe Sr^{2+} adsorption in the pH range 2.5–9, and in the Sr concentration range 10^{-7}-10^{-2} mol.kg$_w^{-1}$ at pH 6.6.

The obtained corrected selectivity coefficients for the 2Na$^+$/Sr^{2+} exchange can be compared with existing literature. Missana and García-Gutiérrez (2007) studied the adsorption of Sr^{2+} onto a FEBEX bentonite at different ionic strengths. These experiments were described using a model derived from the one proposed by Bradbury and Baeyens (1999). At I = 0.05 and 0.1 mol.kg$_w^{-1}$ Missana and García-Gutiérrez (2007) obtained slightly higher $\log_{10}R_D$ values compared to our study—$\log_{10}R_D$ (0.1 M) = 2.16 and $\log_{10}R_D$ (0.05 M) = 2.82 for Missana and García-Gutiérrez (2007) against $\log_{10}R_D$ (0.1 mol.kg$_w^{-1}$) = 2.12 and $\log_{10}R_D$ (0.05 mol.kg$_w^{-1}$) = 2.66 at pH 7 for this study. Nevertheless, they obtained a $\log_{10}K_{2Na^+/Sr^{2+}}$ of 0.66. Despite the fact that they used a different model, it is possible to compare their selectivity coefficient with the ones obtained here. If the selectivity coefficients from Missana and García-Gutiérrez (2007) are transformed according to our multi-site formalism—see Appendices for details—, the parameters are comparable (cf. Table 2), except for S$_3$. As this transformation implies the site concentrations, and as Missana and García-Gutiérrez (2007) have

Table 2
Obtained parameters of the corrected selectivity coefficients for $2Na^+/Sr^{2+}$ and Na^+/Cs^+ exchange. Values from Missana and García-Gutiérrez (2007) are recalculated within the framework of the multi-site ion exchange model (see Appendices for details).

References		SC_i (mmol.g^{-1})	ΣSC_i (mmol.g^{-1})	$\log_{10}K^{*i}_{2Na^+/Sr^{2+}}$	$\log_{10}K^{*i}_{Na^+/Cs^+}$
This study	S_1	0.387 ± 0.038^a	0.886	0.73 ± 0.03	1.57 ± 0.02
	S_2	0.361 ± 0.068^a		1.00 ± 0.03	0.98 ± 0.13
	S_3	0.139 ± 0.092^a		2.92 ± 0.08	0.69 ± 0.32
Missana and García-Gutiérrez (2007)	S_1	1.02		0.77	
	S_2			0.80	
	S_3			1.22	

^{a} Values from Nolin (1997).

used a bentonite with a CEC higher than our sum of site concentrations, this transformation only serves to compare the orders of magnitude.

As mentioned in the introduction, the slight difference in parameters can come from the bentonite used by Missana and García-Gutiérrez (2007), as the FEBEX bentonite includes a significant part of illite-smectite mixed layers, and as illite and smectite have comparable but yet different selectivity for Sr^{2+} (Missana et al., 2004). The differences in the selectivity coefficients could also arise from the intrinsic properties of used bentonites, as their specific surface areas.

3.4. Caesium adsorption

The adsorption behaviour of caesium was explored as a function of pH to determine the corrected selectivity coefficients $K^{*i}_{Na^+/Cs^+}$. The adsorption of Cs^+ onto montmorillonite seems to quickly reach the equilibrium according to Wu et al. (2009) who reported that the adsorption equilibrium of Cs onto montmorillonite mineral is achieved after 5 min of contact time. Therefore, the adsorption kinetics has not been explored in this study. The equilibrium time used was the same as for Sr.

The adsorption of caesium onto the Na-MX80 at $I = 0.1$ mol.kg$_w^{-1}$ (NaCl) and its modelling are shown in Fig. 5. As for Sr^{2+}, the Cs^+ adsorption is weakly dependent on the equilibrium pH. The adsorption increases up to pH 5, then seems to stay constant. The $\log_{10}R_D$ value at this plateau seems slightly greater than for Sr^{2+}, i.e., ca. 2.30 for Cs^+ and 2.10 for Sr^{2+}. Site concentrations from Nolin (1997) and corrected selectivity coefficients for the Na^+/H^+ exchange in Table 2 were used to model the isotherm and to determine the corrected selectivity coefficients of the Na^+/Cs^+ exchange. Due to the weak variation in adsorption, the S_1 and S_2 sites seem to mainly drive the variation of Cs^+ adsorption in the pH range, while the S_3 site is only needed at high pH and does not greatly contribute to the representation of the adsorption behaviour. This phenomenon explains the high uncertainty of $\log_{10}K^{*3}_{Na^+/Cs^+}$ (around 50%).

As explained earlier, the great variability of protocol in the literature on the adsorption of Cs onto montmorillonite impedes comparisons between the different results obtained onto non-purified or not Na-conditioned bentonite (Galamboš et al., 2010; Montavon et al., 2006; Vejsada et al., 2005; Wang et al., 2010). Only Missana et al. (2014a) used a purified Na-conditioned bentonite, but the significant part of interstratified smectite/illite from this bentonite prevents the comparison with our study owing to the very strong and specific adsorption behaviour of caesium onto illite (Ogasawara et al., 2013). This could explain the difference in $\log_{10}K_D$ between Missana et al. (2014a)—$\log_{10}K_D$ viz. 3.2 at $C_{eq} \approx 10^{-7}$ M, $I = 0.1$ M NaClO$_4$ and pH 6.5—and the $\log_{10}K_D = 2.3$ in Fig. 5a.

4. Conclusions

The adsorption behaviour of Sr and Cs on a purified Na-MX80 bentonite was studied, with the objective to determine the corrected selectivity coefficients of the $2Na^+/Sr^{2+}$ and Na^+/Cs^+ exchanges
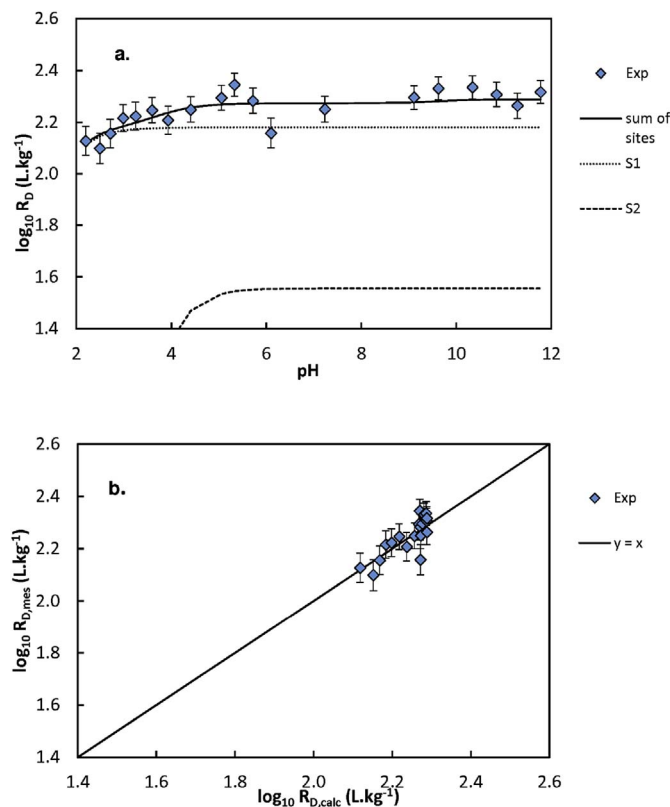

Fig. 5. Adsorption isotherms of $[Cs]_i = 10^{-7}$ mol.kgw^{-1} vs. pH at $I = 0.1$ mol.kg$_w^{-1}$ (NaCl) and $S/L = 3.8$ g.L^{-1} on a Na-MX80 bentonite and representation of the contribution of the different fixation sites (a) and comparison of the experimental to the modelling results (b).

using the multi-site ion exchange formalism. The site repartitions and concentrations of the Na-MX80 montmorillonite were taken from literature (Nolin, 1997), and corrected selectivity coefficients for the Na^+/H^+ exchange were obtained from a new fit. The corrected selectivity coefficients $K^{*i}_{2Na^+/Sr^{2+}}$ and $K^{*i}_{Na^+/Cs^+}$ were obtained from newly acquired pH and concentration isotherms onto an Na-MX80 montmorillonite, in coherence with the site capacities determined by Nolin (1997), and corrected selectivity coefficient $K^{*i}_{Na^+/H^+}$ fitted in this study.

Some parameters were neglected in this work; traces of exchangeable cations still remains in the Na-MX80. Their concentrations were supposed low enough not to impact the adsorption of H^+, Na^+, Cs^+, and Sr^{2+}. Moreover, the possible dissolution of smectite at acidic or alkaline pH—leading to a release of exchangeable cation K^+, Mg^{2+}, Al^{3+}, etc.—was not taken into account. These phenomena may affect the adsorption behaviour in different ways: (i) decrease of the fixation sites concentrations; (ii) modification of the clay minerals structure; and (iii) adsorption competition between the different cations. One can come to the conclusion that these three phenomena are contained—and

not directly expressed—in the corrected selectivity coefficients. Thus, obtained experimental points and associated modelling at pH below 4 and above 10 could be taken with caution, and a more dedicated study on the account of the clay dissolution, and hence of exchanger properties modifications at low and high pH, could be needed.

Nonetheless, this study can serve as a part of a thermodynamic adsorption database to predict the adsorption of radionuclides, including Sr^{2+} and Cs^+, onto mixtures of clay minerals. The inclusion of Ca^{2+} and K^+ as other major cations in clayey environments will be the next step to more fully describe the adsorption behaviour of these radionuclides onto soils or sediments.

Acknowledgment

Appendices

The appendices contain the XRD diffractogram of the purified Na-MX80 and the development of the modelling formalism.
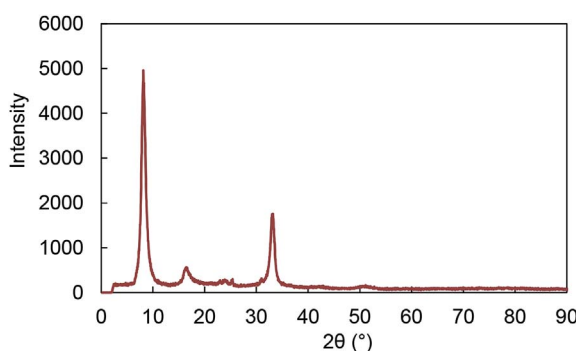
A. XRD diffractogram of Na-MX80

Fig. A1. XRD powder diffractogram of the purified Na-MX80.

B. Modelling formalism

B.1. Saturation curves

The competitive adsorption onto clays is described by a multi-site ion exchange model. The exchange reaction between Na^+ and H^+ in a Na-saturated exchanger can be expressed as follows, where X_i^- is a given type of negatively charged site i,

$$\overline{X_i^- - Na^+} + H^+ \rightleftarrows \overline{X_i^- - H^+} + Na^+ \tag{B1}$$

with the corresponding equilibrium constant,

$$K_{Na^+/H^+}^i = \frac{[\overline{X_i^- - H^+}] \cdot [Na^+]}{[\overline{X_i^- - Na^+}] \cdot [H^+]} \times \frac{\gamma_{Na^+}}{\gamma_{H^+}} \times \frac{(f_{X_i^- - H^+})}{(f_{X_i^- - Na^+})} \tag{B2}$$

where $[\cdot]$ is the solution $(mol.kg_w^{-1})$ or adsorbed concentration $(mol.kg^{-1}$ of solid) of species, f is the activity coefficient of adsorbed species, and γ is the activity coefficient of species in solution.

Since the activity coefficients of adsorbed species f are not known, it is assumed that the ratio between these coefficients is constant. Thus, the apparent constants—called corrected selectivity coefficients K_{Na^+/H^+}^{*i}—are described as follows.

$$K_{Na^+/H^+}^{*i} = \frac{[\overline{X_i^- - H^+}] \cdot [Na^+]}{[\overline{X_i^- - Na^+}] \cdot [H^+]} \times \frac{\gamma_{Na^+}}{\gamma_{H^+}} \tag{B3}$$

Each type of site i is also described by its site concentration SC_i in $mol.kg^{-1}$ of solid, which is equal to the sum of all the adsorbed species concentrations:

$$SC_i = [\overline{(X_i^-) - H^+}] + [\overline{(X_i^-) - Na^+}] \tag{B4}$$

Combining equations (B3) and (B4), the absorbed concentration of Na can be expressed as follows.

$$[\overline{Na}] = \sum_i [\overline{X_i^- - Na^+}] = \sum_i \frac{SC_i}{1 + \frac{K_{Na^+/H^+}^{*i} \cdot 10^{-pH}}{[Na^+] \cdot \gamma_{Na^+}}} \tag{B5}$$

B.2. Adsorption isotherms of trace elements

To model the adsorption of trace elements M^{m+} on Na-saturated exchangers, one has to account both for the Na^+/H^+ reaction (B1) and the M^{m+}/mH^+ reaction,

$$\overline{(X_i^-)_m - M^{m+}} + mH^+ = m\overline{X_i^- - H^+} + M^{m+} \tag{B6}$$

with the corresponding corrected selectivity coefficient.

$$K^{*i}_{M^{m+}/nH^+} = \frac{[\overline{X_i^- - H^+}]^m \cdot [M^{m+}]}{[\overline{(X_i^-)_m - M^{m+}}] \cdot [H^+]^m} \cdot \frac{\gamma_{M^{m+}}}{\gamma_{H^+}^m} \tag{B7}$$

Complexation of cations in solution is taken into account and the concentration of available M^{m+} is expressed as follows,

$$[M^{m+}] = \frac{[M]}{\alpha_{M^{m+}}} \tag{B8}$$

where [M] is the sum of all the M species concentration in solution and $\alpha_{M^{m+}}$ is the Ringböm (1963) coefficient.

The equation of the site concentrations is written as follows.

$$SC_i = [\overline{(X_i^-) - H^+}] + [\overline{(X_i^-) - Na^+}] + m[\overline{(X_i^-)_m - M^{m+}}] \tag{B9}$$

Combining equations (B3), (B7), and (B9) the site concentration can be expressed as a function of the adsorbed concentration $[\overline{(X_i^-) - H^+}]$:

$$SC_i = [\overline{(X_i^-) - H^+}] + \frac{[\overline{X_i^- - H^+}] \cdot [Na^+] \cdot \gamma_{Na^+}}{K^{*i}_{Na^+/H^+} \cdot [H^+] \cdot \gamma_{H^+}} + \sqrt[m]{\frac{[\overline{X_i^- - H^+}]^m \cdot [M^{m+}] \cdot \gamma_{M^{m+}}}{K^{*i}_{M^{m+}/mH^+} \cdot [H^+]^m \cdot \gamma_{H^+}^m}} \tag{B10}$$

Solving this equation leads to determine $[\overline{(X_i^-) - H^+}]$ then $[\overline{(X_i^-)_m - M^{m+}}]$ using equation (B7).

Finally, the distribution coefficient can be recalculated using:

$$R_D = \frac{[\overline{M}]}{[M]} \tag{B11}$$

B.3. Transformation of selectivity coefficient from Missana and García-Gutiérrez (2007) in the multi-site ion exchange formalism

Missana and García-Gutiérrez (2007) used the Gaines and Thomas (1953) formalism to express their selectivity coefficient. In this formalism, the selectivity coefficient is expressed as:

$$K^{*,GT}_{2Na^+/Sr^{2+}} = \frac{(N_{Sr^{2+}})}{(N_{Na^+})^2} \cdot \frac{(a_{Na^+})^2}{(a_{Sr^{2+}})} \tag{B12}$$

where $(N_{M^{m+}})$ corresponds to the equivalent fractional occupancy on the exchanger and $a_{M^{m+}}$ is the activity of cations.

The expression of $(N_{M^{m+}})$ is written:s

$$(N_{M^{m+}}) = \frac{m \cdot [\overline{(X^-)_m - M^{m+}}]}{CEC} \tag{B13}$$

where $[\overline{(X^-)_m - M^{m+}}]$ is the adsorbed concentration of M in $mmol.g^{-1}$ of solid and CEC is the cationic exchange capacity of the exchanger in $mmol.g^{-1}$.

The selectivity coefficient can be re-expressed as follows.

$$K^{*,GT}_{2Na^+/Sr^{2+}} = \frac{\left(\frac{2 \cdot [\overline{(X^-)_2 - Sr^{2+}}]}{CEC}\right) \cdot [Na^+]^2}{\left(\frac{[\overline{X^- - Na^+}]}{CEC}\right)^2 \cdot [Sr^{2+}]} \cdot \frac{\gamma_{Na^+}^2}{\gamma_{Sr^{2+}}} \tag{B14}$$

Finally, combining with equation (B7) and considering the different adsorption sites *i*, this expression becomes:

$$K^{*i,GT}_{2Na^+/Sr^{2+}} = 2.SC_i \cdot K^{*i}_{2Na^+/Sr^{2+}} \tag{B15}$$

References

Alonso, E.E., Ledesma, A., 2005. Advances in Understanding Engineered Clay Barriers. In: Proceedings of the International Symposium on Large Scale Field Tests in Granite. Taylor & Francis.

Amram, K., Ganor, J., 2005. The combined effect of pH and temperature on smectite dissolution rate under acidic conditions. Geochim. Cosmochim. Acta 69, 2535–2546.

Bilgin, B., Atun, G., Keçeli, G., 2001. Adsorption of strontium on illite. J. Radioanal. Nucl. Chem. 250, 323–328.

Bradbury, M.H., Baeyens, B., 1997. A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part II: modelling. J. Contam. Hydrol. 27, 223–248.

Bradbury, M.H., Baeyens, B., 1999. Modelling the sorption of Zn and Ni on Ca-montmorillonite. Geochim. Cosmochim. Acta 63, 325–336.

Bradbury, M.H., Baeyens, B., 2005. Experimental and Modelling Investigations on Na-illite: Acid-base Behaviour and the Sorption of Strontium, Nickel, Europium and Uranyl. Paul Scherrer Institute, Villigen, Switzerland, pp. 73. Report PSI Bericht 05-02. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/36/111/36111078.pdf.

Brouwer, E., Baeyens, B., Maes, A., Cremers, A., 1983. Cesium and rubidium ion equilibria in illite clay. J. Phys. Chem. 87, 1213–1219.

Carroll, D., 1959. Ion exchange in clays and other minerals. Geol. Soc. Am. Bull. 70, 749–779.

Ciavatta, L., 1980. The specific interaction theory in evaluating ionic equilibria. Ann. Chim. (Roma) 70, 551–567.

Comar, C.L., Russell, R.S., Wasserman, R.H., 1957. Strontium-calcium movement from soil to man. Science 126, 485–492.

Davies, C.W., 1962. Ion Association. Butterworths.

De Levie, R., 2005. Advanced Excel for Scientific Data Analysis. Oxford University Press, pp. 638.

Dyer, A., Chow, J.K.K., Umar, I.M., 2000. The uptake of caesium and strontium radioisotopes onto clays. J. Mater. Chem. 10, 2734–2740.

Dzene, L., Tertre, E., Hubert, F., Ferrage, E., 2015. Nature of the sites involved in the process of cesium desorption from vermiculite. J. Colloid Interface Sci. 455, 254–260.

England, T.R., Rider, B.F., 1993. ENDF-349 Evaluation and Compilation of Fission Product Yields. Lawrence Berkeley National Laboratory, pp. 173. Report LA-UR-3106. http://t2.lanl.gov/nis/publications/endf349.pdf.

Erten, H.N., Aksoyoglu, S., Hatipoglu, S., Gokturk, H., 1988. Sorption of cesium and strontium on montmorillonite and kaolinite. Radiochim. Acta 44/45, 147–151.

Gaines, G.L., Thomas, H.C., 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys. 21, 714–718.

Galamboš, M., Krajnak, A., Rosskopfová, O.g., Viglasova, E., Adamcova, R., Rajec, P., 2013. Adsorption equilibrium and kinetic studies of strontium on Mg-bentonite, Fe-bentonite and illite/smectite. J. Radioanal. Nucl. Chem. 298, 1031–1040.

Galamboš, M., Kufčáková, J., Rosskopfová, O.g., Rajec, P., 2010. Adsorption of cesium and strontium on natrified bentonites. J. Radioanal. Nucl. Chem. 283, 803–813.

Gaucher, E., 1998. Interactions Eaux-argiles. Etude Expérimentale. PhD Thesis. Université Denis Diderot (Paris VII), Paris, France, pp. 260 (In French).

Gorgeon, L., 1994. Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux. PhD Thesis. Université Pierre et Marie Curie (Paris VI), Paris, France, pp. 189 (In French).

Guimarães, V., Azenha, M., Rocha, F., Silva, F., Bobos, I., 2015. Influence of pH, concentration and ionic strength during batch and flow-through continuous stirred reactor experiments of Sr^{2+}-adsorption onto montmorillonite. J. Radioanal. Nucl.

Chem. 303, 2243–2255.

Hamer, W.J., Wu, Y.C., 1972. Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25°C. J. Phys. Chem. Ref. Data 1, 1047–1100.

IAEA, 2006. Environmental Consequences of the Chernobyl Accident and Their Remediation: Twenty Years of Experience. Report of the Chernobyl Forum Expert Group 'Environment'. International Atomic Energy Agency Vienna, Austria, pp. 166. http://www.pub.iaea.org/MTCD/publications/PDF/Pub1239_web.pdf.

Jacquier, P., Ly, J., Beaucaire, C., 2004. The ion-exchange properties of the Tournemire argillite - I. Study of the H, Na, K, Cs, Ca and Mg behaviour. Appl. Clay Sci. 26, 163–170.

Karnland, O., 2010. Chemical and Mineralogical Characterization of the Bentonite Buffer for the Acceptance Control Procedure in a KBS-3 Repository. SKB, Stockholm, Sweden Report TR-10-60. http://www.skb.se/upload/publications/pdf/TR-10-60.pdf.

Kasar, S., Kumar, S., Kar, A., Bajpai, R.K., Kaushik, C.P., Tomar, B.S., 2014. Retention behaviour of Cs(I), Sr(II), Tc(VII) and Np(V) on smectite-rich clay. J. Radioanal. Nucl. Chem. 300, 71–75.

Lu, J., Tertre, E., Beaucaire, C., 2014. Assessment of a predictive model to describe the migration of major inorganic cations in a Bt soil horizon. Appl. Geochem 41, 151–162.

Mahoney, J.J., Langmuir, D., 1991. Adsorption of Sr on kaolinite, illite and montmorillonite at high ionic strengths. Radiochim. Acta 54, 139–144.

Meier, P.L., 1999. Determination of the cation exchange capacity (CEC) of clay minerals using the complexes of copper(II) Ion with triethylenetetramine and tetra-ethylenepentamine. Clays Clay Min. 47, 386–388.

Missana, T., Benedicto, A., García-Gutiérrez, M., Alonso, U., 2014a. Modeling cesium retention onto Na-, K- and Ca-smectite: effects of ionic strength, exchange and competing cations on the determination of selectivity coefficients. Geochim. Cosmochim. Acta 128, 266–277.

Missana, T., García-Gutiérrez, M., 2007. Adsorption of bivalent ions (Ca(II), Sr(II) and Co (II)) onto FEBEX bentonite. Phys. Chem. Earth 32, 559–567.

Missana, T., García-Gutiérrez, M., Alonso, U., 2004. Kinetics and irreversibility of cesium and uranium sorption onto bentonite colloids in a deep granitic environment. Appl. Clay Sci. 26, 137–150.

Missana, T., García-Gutiérrez, M., Alonso, U., 2008. Sorption of strontium onto illite/smectite mixed clays. Phys. Chem. Earth 33, S156–S162.

Missana, T., García-Gutiérrez, M., Benedicto, A., Ayora, C., De-Pourcq, K., 2014b. Modelling of Cs sorption in natural mixed-clays and the effects of ion competition. Appl. Geochem 49, 95–102.

Montavon, G., Alhajji, E., Grambow, B., 2006. Study of the interaction of Ni^{2+} and Cs^+ on MX-80 bentonite; effect of compaction using the "capillary method". Environ. Sci. Technol. 40, 4672–4679.

Motellier, S., Ly, J., Gorgeon, L., Charles, Y., Hainos, D., Meier, P., Page, J., 2003. Modelling of the ion-exchange properties and indirect determination of the interstitial water composition of an argillaceous rock. Application to the Callovo-Oxfordian low-water-content formation. Appl. Geochem 18, 1517–1530.

Nolin, D., 1997. Rétention de radioéléments à vie longue par des matériaux argileux - Influence d'anions contenue dans les eaux naturelles. PhD Thesis. Université Pierre et Marie Curie (Paris VI), Paris, France, pp. 221 (d).

Ogasawara, S., Nakao, A., Yanai, J., 2013. Radiocesium interception potential (RIP) of smectite and kaolin reference minerals containing illite (micaceous mineral) as impurity. Soil Sci. Plant Nutr. 59, 852–857.

Peynet, V., 2003. Retention d'actinide et de produits de fission par des phases solides polyminerales. PhD Thesis. Université Pierre et Marie Curie (Paris VI), Paris, France, pp. 273 (In French).

Rafferty, P., Shiao, S.Y., Binz, C.M., Meyers, R.E., 1981. Adsorption of Sr(II) on clay-minerals: effects of salt concentration, loading, and pH. J. Inorg. Nucl. Chem. 43, 797–805.

Reinoso-Maset, E., Ly, J., 2014. Study of major ions sorption equilibria to characterize the

ion exchange properties of kaolinite. J. Chem. Eng. Data 59, 4000–4009.

Ringböm, A., 1963. Complexation in Analytical Chemistry: a Guide for the Critical Selection of Analytical Methods Based on Complexation Reactions. Interscience Publishers, New York, NY, USA, pp. 395.

Robin, V., Tertre, E., Beaufort, D., Regnault, O., Sardini, P., Descostes, M., 2015. Ion exchange reactions of major inorganic cations (H^+, Na^+, Ca^{2+}, Mg^{2+} and K^+) on beidellite: experimental results and new thermodynamic database. Toward a better prediction of contaminant mobility in natural environments. Appl. Geochem 59, 74–84.

Sahoo, S.K., Kavasi, N., Sorimachi, A., Arae, H., Tokonami, S., Mietelski, J.W., Łokas, E., Yoshida, S., 2016. Strontium-90 activity concentration in soil samples from the exclusion zone of the Fukushima daiichi nuclear power plant. Sci. Rep. 6, 23925.

Savoye, S., Beaucaire, C., Fayette, A., Herbette, M., Coelho, D., 2012. Mobility of cesium through the Callovo-Oxfordian claystones under partially saturated conditions. Environ. Sci. Technol. 46, 2633–2641.

Savoye, S., Beaucaire, C., Grenut, B., Fayette, A., 2015. Impact of the solution ionic strength on strontium diffusion through the Callovo-Oxfordian clayrocks: an experimental and modeling study. Appl. Geochem 61, 41–52.

Sawhney, B.L., 1972. Selective sorption and fixation of cations by clay minerals: a review. Clays Clay Min. 20, 93–100.

Shaban, I.S., Macášek, F., 1998. Influence of humic substances on sorption of cesium and strontium on montmorillonite. J. Radioanal. Nucl. Chem. 229, 73–78.

Shock, E.L., Sassani, D.C., Willis, M., Sverjensky, D.A., 1997. Inorganic species in geologic fluids: correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. Geochim. Cosmochim. Acta 61, 907–950.

Stammose, D., Ly, J., Pitsch, H., Dolo, J.-M., 1992. Sorption mechanisms of three actinides on a clayey mineral. Appl. Clay Sci. 7, 225–238.

Staunton, S., Roubaud, M., 1997. Adsorption of ^{137}Cs on montmorillonite and illite: effect of charge compensating cation, ionic strength, concentration of Cs, K and fulvic acid. Clays Clay Min. 45, 251–260.

Sverjensky, D.A., Shock, E.L., Helgeson, H.C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. Geochim. Cosmochim. Acta 61, 1359–1412.

Tertre, E., Beaucaire, C., Coreau, N., Juery, A., 2009. Modelling Zn(II) sorption onto clayey sediments using a multi-site ion-exchange model. Appl. Geochem 24, 1852–1861.

Tertre, E., Ferrage, E., Bihannic, I., Michot, L.J., Prêt, D., 2011. Influence of the ionic strength and solid/solution ratio on Ca(II)-for-Na^+ exchange on montmorillonite. Part 2: understanding the effect of the m/V ratio. Implications for pore water composition and element transport in natural media. J. Colloid Interface Sci. 363, 334–347.

Tertre, E., Hubert, F., Bruzac, S., Pacreau, M., Ferrage, E., Pret, D., 2013. Ion-exchange reactions on clay minerals coupled with advection/dispersion processes. Application to Na^+/Ca^{2+} exchange on vermiculite: reactive-transport modeling, batch and stirred flow-through reactor experiments. Geochim. Cosmochim. Acta 112, 1–19.

Tremillon, B., 1965. Les Séparations par les Résines Échangeuses d'Ions. Gauthier-Villars, Paris, France, pp. 400.

Vejsada, J., Jelínek, E., Řanda, Z., Hradil, D., Přikryl, R., 2005. Sorption of cesium on smectite-rich clays from the Bohemian Massif (Czech Republic) and their mixtures with sand. Appl. Radiat. Isot. 62, 91–96.

Wang, T.-H., Hsieh, C.-J., Lin, S.-M., Wu, D.-C., Li, M.-H., Teng, S.-P., 2010. Effect of alkyl properties and head groups of cationic surfactants on retention of cesium by organoclays. Environ. Sci. Technol. 44, 5142–5147.

Wang, X., Chen, Y., Wu, Y., 2004. Sorption and desorption of radiostrontium on powdered bentonite: effect of pH and fulvic acid. J. Radioanal. Nucl. Chem. 261, 497–500.

Wu, J.J., Li, B., Liao, J.L., Feng, Y., Zhang, D., Zhao, J., Wen, W., Yang, Y.Y., Liu, N., 2009. Behavior and analysis of cesium adsorption on montmorillonite mineral. J. Environ. Radioact. 100, 914–920.