

A robust and parsimonious model for caesium sorption on clay minerals and natural clay materials

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ARTICLE INFO

Keywords:

Modelling

Caesium

Sorption

Pure clay minerals

Natural clay materials

ABSTRACT

Caesium (Cs) is one of the most studied radionuclides in the fields of nuclear waste disposal and environmental sciences. The overall objective of this work is to improve the tools designed to describe and predict migration, retention, and bioaccumulation processes in the geosphere and the biosphere, particularly in the soil/solution soil/plant roots systems. Cs sorption on clay minerals has been extensively measured and modeled because these minerals control Cs mobility and (bio)availability in the environment.

A critical analysis of published experimental data on Cs sorption by clay minerals and natural clay materials along with the different models was performed in an attempt to elaborate and evaluate a generic model for Cs sorption. This work enabled us to propose a robust and parsimonious model for Cs sorption, which combines the surface complexation and cation exchange approaches invoking only two types of surface sites: frayed edge and exchange sites. Our model, referred to as the “1-pK DL/IE model”, takes into account the competition between Cs and other cations as well as the influence of the ionic strength and pH of the solution.

This model was successfully calibrated for Cs sorption on three reference clay minerals (illite, montmorillonite and kaolinite), in a wide range of Cs concentrations and physicochemical conditions. Using the same parameters, we tested our model on several natural clayey materials containing a single to several clay minerals. The goodness-of-fit obtained with natural materials containing a single clay mineral demonstrates the robustness of the model. The results obtained with natural mixed clay materials confirm the predictive capability of the model and also allowed us to test the sensitivity to the mineral composition of these materials (uncertainties). We found that illite is usually the most reactive clay mineral with respect to Cs sorption and that component additivity is applicable when the contribution of other clay minerals becomes non negligible. The whole set of model-measurement comparisons performed in this study provides a high level of confidence in the capabilities of the 1-pK DL/IE model as an interesting predictive tool.

1. Introduction

Since decades the pollution of natural ecosystems by radionuclides has become a major concern for society. In particular, caesium (Cs) is widely studied by environmental scientists using different analytic and experimental techniques (Benedicto et al., 2014; Bostick et al., 2002; Chorover et al., 2003; Missana et al., 2014a; Savoye et al., 2012; Wendling et al., 2005). One of the Cs radio-isotopes, ¹³⁷Cs, is an important fission product from the irradiation of uranium-based fuels, has a relatively long life ($t_{1/2} = 30$ years), and constitutes a significant radioecological hazard due to its hard gamma emission. After release of radioactivity into the environment, this radioelement is considered as the main source of contamination of soils (Avery, 1996; Strebl et al.,

1999) and the principal source of radioactivity of nuclear waste in the timeframe of the first one hundred years. Moreover, radiocaesium always exists as the monovalent cation Cs⁺, with chemical properties similar to potassium (K⁺) (Kamei-Ishikawa et al., 2011; Roca and Vallejo, 1995), having very high solubility (Benedicto et al., 2014; Fuller et al., 2014; Missana et al., 2014b; NDA, 2010). Cs mobility in soils environment is also known to be significantly influenced by retention capacity for Cs⁺ (Avery, 1996; Strebl et al., 1999).

Understanding the processes that control the bioavailability and mobility of Cs in the biosphere and geosphere constitutes a major challenge that has to be tackled in order to provide a good estimate of its health and ecological hazard. Geochemical reactions, particularly those occurring at mineral/water interfaces, closely control the fate and

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behavior of the major elements or trace in these systems (Koretsky, 2000). The adsorption/desorption process (i.e. sorption) generally dominates the interactions between Cs and soil as this element hardly forms solid species in natural environments (Dzene et al., 2015).

Clay minerals are often invoked as the most important minerals that control the bioavailability and mobility (migration-retention) of Cs in subsurface (e.g. soils and sediments) and groundwater environments (Bostick et al., 2002; Chorover et al., 2003; Missana et al., 2014a; Savoye et al., 2012; Shenber and Eriksson, 1993; Wendling et al., 2005). In soils, the most efficient carrier phases of Cs⁺ are clay minerals, especially 2:1 layer clays, with a permanent charge arising from isomorphous substitution (Bostick et al., 2002; Comans et al., 1991; Comans and Hockley, 1992; Cornell, 1993; Maes and Cremers, 1986; Nakano et al., 2003; Sawhney, 1972; Watanabe et al., 2012); firstly because of their ubiquity and secondly because they have large specific surface areas with a high density of (negatively and positively) charged surface sites (Kraepiel et al., 1999; Langmuir, 1997).

Among the different properties of Cs/clay mineral interactions, the non-linear Cs sorption isotherms on phyllosilicate clays, such as illite (Bradbury and Baeyens, 2000; Cornell, 1993; Eliason, 1966; Missana et al., 2004; Poinssot et al., 1999; Staunton and Roubaud, 1997; Wahlberg and Fishman, 1962), is considered to be the result of the heterogeneity of the surface adsorption sites. (i) High affinity sites, which adsorb strongly and specifically Cs, are located on the edges of clay minerals and are therefore usually termed as « Frayed Edge Sites » (FES) (Brouwer et al., 1983; Eberl, 1980; Francis and Brinkley, 1976; Jackson, 1963; Maes and Cremers, 1986; Poinssot et al., 1999; Rich and Black, 1964; Sawhney, 1972; Zachara et al., 2002). (ii.) The remaining sites, which have a lower, non-specific, affinity for Cs, are present in large quantities and located on planar surface and mainly constitute the cation exchange capacity (CEC). On these sites, the adsorption of Cs strongly depends on the composition of the cationic exchangeable population, since the adsorption reaction partly proceeds as cation exchange (Cornell, 1993; Rigol et al., 2002; Staunton and Roubaud, 1997; Zachara et al., 2002). Cs can also be selectively fixed on interlayer sites of phyllosilicate clays (Rigol et al., 2002; Salles et al., 2013). Adsorption therefore depends on the relative affinities of Cs, the nature of the competitive exchanging cations, pH and the ionic strength.

Caesium adsorption mechanisms on illite has received a lot of attention for several decades and different studies were produced that inferred the prevailing mechanism (Sawhney, 1972) and, more recently, gave spectroscopic evidence that Cs initially sorbs on illite FES and can eventually enter into the interlayer and be incorporated into the mineral structure (Fuller et al., 2015; Lee et al., 2017). Caesium adsorption on vermiculite and montmorillonite was described by Bostick et al. (2002) as a function of surface coverage using EXAFS. These authors also found that inner-sphere surface complexes may form within the interlayer or at frayed edge sites and were less accessible than outer-sphere complexes. None of these studies exclude the possibility of having Cs adsorbed onto amphoteric sites, at least in the early stage of sorption which would account for the pH-dependency of Cs sorption as opposed to ion exchange in the interlayer. This aspect has received much less attention and experimental data is still lacking, especially for illite. Furthermore, the partial reversibility of Cs is difficult to reconcile with the “collapsed” interlayer resulting from Cs incorporation into the structure of illite (Comans et al., 1991; Comans and Hockley, 1992; De Koning and Comans, 2004; Durant et al., 2018).

Several models have been developed in the last two decades in order to interpret and model non-linear Cs sorption onto mineral phases under specific conditions (homoionized mineral phases, many fixed experimental parameters such as pH and ionic strength) (Baeyens and Bradbury, 1997; Benedicto et al., 2014; Bradbury and Baeyens, 2000; Brouwer et al., 1983; Chen et al., 2014; Gutierrez and Fuentes, 1996; Liu et al., 2004; Marques Fernandes et al., 2015; Missana et al., 2014a, 2014b; Montavon et al., 2006; Poinssot et al., 1999; Savoye et al., 2012; Silva et al., 1979; Zachara et al., 2002). However, no compilation or

comparison study of these models has ever been proposed. Moreover, these models, whose parameters are obtained in a semi-empirical manner, do not take into account the effect of pH on the mineral surface charge: this implies that their transferability to heterogeneous environments is limited (Koretsky, 2000; Missana et al., 2008). Another important point is that these models were calibrated for specific physicochemical conditions proper to each study without considering the transferability to other conditions. This constitutes the major limitation of cation exchange models found in literature, which appear to be unsatisfactory to predict Cs sorption a wide range of conditions in natural systems without any modification of the thermodynamic parameters.

The objective of this work was (i) to establish a compilation of the current models describing Cs sorption on natural clayey materials and (ii) to perform a cross-comparison of all these models with all the data available in the literature for pure clay minerals and for clay materials. (iii) An alternative model was finally developed in order to improve the performance, the robustness and the predictability of the existing models, based on the combining approach (i.e. cation exchange and surface complexation models) described above, and requiring fewer parameters (i.e. parsimonious) than most of the others modelling approaches. It is designed to be capable of modelling Cs adsorption without any parameter changes over a larger range of chemical conditions (i.e. robustness). We calibrated this model with all the data available in the literature for pure clay minerals (illite, montmorillonite, and kaolinite) and we assessed its validity for clay materials of increasing complexity, ranging for relatively simple materials containing only a single clay mineral to materials such as bentonite and claystones containing several types of clay minerals.

2. Material and methods

2.1. Available data on clay minerals and clay materials

A compilation of existing experimental and modeled data found in the literature was performed in order to evaluate the existing models for Cs sorption on clay minerals and the one developed here. These data are mostly constituted by Cs sorption isotherms on the most common clay minerals, i.e. illite, montmorillonite, and kaolinite (243 observations), and on a variety of clay materials (378 observations) (Tables 2 and 4). The adsorption data usually presented in the form of a distribution coefficient (K_d) for the adsorbed Cs as a function of Cs concentration in solution at equilibrium or as a function of pH. The distribution coefficient between the solid and the liquid phase, K_d (L kg⁻¹), is calculated using the following relationship:

$$K_d = \frac{[Cs]_{tot} - [Cs]_{eq}}{[Cs]_{eq}} \frac{V}{m} \quad (1)$$

where $[Cs]_{tot}$ is the total Cs concentration of the suspension (mol L⁻¹), $[Cs]_{eq}$ is the Cs concentration in solution at equilibrium (mol L⁻¹), m/V is the solid: liquid ratio with m the mass of the clay (kg), and V is the volume of the liquid (L).

Table 1 shows the different clay minerals considered in the present investigation, together with their mineralogical properties and the experimental conditions used in the studies. The most abundant set of experimental data concerns illite with a total 191 observations. Fewer experimental data were found for montmorillonite (51 observations) and kaolinite (67 observations). All the clay minerals had been purified and homoionized in Na, K, Ca or NH₄ before performing Cs sorption. The different types of illite considered in this investigation have different origins (Le Puy, Rojo Carbonero and Morris), but exhibit consistent values for the cationic exchange capacities (CEC) and Specific Surface Area (SSA) (Table 1). Note that the illite from Le Puy-en-Velay is usually considered as the “reference” illite and its parameters are preferentially used in several studies (Bradbury and Baeyens, 2000; Chen et al., 2014; Maes et al., 2008; Marques Fernandes et al., 2015).

Table 1

List of clay minerals considered in the present investigation, together with mineralogical properties and the experimental conditions used in different studies. n stands for the number of observations, I corresponds to the ionic strength, and m/V stands for the solid: liquid ratio.

Clay mineral	CEC (meq kg ⁻¹)	SSA (m ² g ⁻¹)	Reference	n	Major cations	I (mol L ⁻¹)	m/V (g L ⁻¹)	pH	[Cs] _{tot} (mol L ⁻¹)
Le Puy-en-Velay illite, Haute-Loire, France	225 ^a /900 ^b	97	Benedicto et al. (2014)	33	Na ⁺ /Ca ²⁺ / K ⁺	0.01	1	7	10 ⁻⁹ - 10 ⁻⁴
	127	97/129	Poinssot et al. (1999)	15	Na ⁺	0.1	1	6.8	8·10 ⁻⁹ - 10 ⁻⁴
Rojo Carbonero illite, Spain	190	77	Missana et al. (2014b)	96	Na ⁺ /K ⁺	0.01–1	1	2–10	10 ⁻⁹
				35	Na ⁺ /Ca ²⁺ / K ⁺ /NH ₄ ⁺	0.1	1	7	10 ⁻⁹ - 2·10 ⁻⁴
Morris illite, Illinois, USA	200	62	Brouwer et al. (1983)	12	K ⁺	0.002/0.02	1	7	2·10 ⁻⁹ - 4·10 ⁻⁴
SWy –montmorillonite, Wyoming, USA	940	–	Staunton and Roubaud (1997)	26	Na ⁺ /Ca ²⁺ / K ⁺	0.01	10	7	10 ⁻⁹ - 5·10 ⁻⁴
	838	740	Gorgeon (1994)	25	Cs ⁺	0.02	10	1–12	0.02
KGa–1–b Kaolinite, Washington, USA	20	10	Missana et al. (2014b)	37	Na ⁺ /Ca ²⁺ / K ⁺ /NH ₄ ⁺	0.1/0.2	10	7	6·10 ⁻¹⁰ - 10 ⁻³
Sigma Kaolinite, synthetic	28	13.2	Gorgeon (1994)	30	Na ⁺ /Cs ⁺	1/0.01	10–50	1–12	10 ⁻⁸ /0.01

^a Collapsed.

^b Decollapsed.

Table 2

List of clay materials containing a single type of clay mineral, together with mineralogical properties and the experimental conditions used in different studies. n stands for the number of observations, I corresponds to the ionic strength, and m/V stands for the solid: liquid ratio.

Clay material	CEC (meq kg ⁻¹)	SSA (m ² g ⁻¹)	Reference	n	Content and type of clay mineral	Major cations	I (mol L ⁻¹)	m/V (g L ⁻¹)	pH	[Cs] _{tot} (mol L ⁻¹)
Rojo Carbonero clay, Spain	110	43.7	Missana et al. (2014b)	48	57% illite	Na ⁺ /K ⁺ / NH ₄ ⁺	0.5–0.54 (NSW ^a)	10	7	2·10 ⁻⁹ - 10 ⁻²
MX-80 montmorillonite, Wyoming, USA	787 ± 48	–	Montavon et al. (2006)	38	75–84% montmorillonite	Na ⁺ / Ca ²⁺ / K ⁺ /Mg ²⁺	0.037 (EBPW-1 ^b)	10	7.8	4·10 ⁻⁹ - 8·10 ⁻²
		30/31.3	Bradbury and Baeyens (2011)	38			0.7 (EBPW-2 ^b)	60	7.6	6·10 ⁻⁸ - 3·10 ⁻³
Hanford sediment, Texas, USA	42.6 (Na) 82.5 (K) 46.9 (Ca)	–	Zachara et al. (2002)	93	NA	Na ⁺ /K ⁺ / Ca ²⁺	0.005–5	2–100	7	1·10 ⁻⁹ - 9·10 ⁻²
Boda Clay, Mecsek, Hungary	113	–	Marques Fernandes et al. (2015)	18	50% illite	Na ⁺ / Ca ²⁺ / K ⁺ /Mg ²⁺	0.033 (SPW1 ^c)	2.2	8	10 ⁻⁷ - 10 ⁻²

^a Natural Saline Water.

^b Equilibrium Bentonite Pore Water.

Table 3

Chemical composition of pore water used in the experiments with natural clay materials containing only one type of clay mineral.

Clay material	Rojo Carbonero clay	MX-80 montmorillonite	Boda Clay	
Reference	Missana et al. (2014b)	Montavon et al. (2006)	Bradbury and Baeyens (2011)	Marques Fernandes et al. (2015)
Pore water	NSW ^a	EBPW-1 ^b	EBPW-2 ^b	SPW1 ^c
Units	mol L ⁻¹			
Na ⁺	3.95·10 ⁻¹	5.65·10 ⁻¹	3.7·10 ⁻²	1.7·10 ⁻²
K ⁺	1.9·10 ⁻²	2.8·10 ⁻³	4·10 ⁻⁴	1.8·10 ⁻⁴
Mg ²⁺	2.1·10 ⁻²	2.2·10 ⁻²	3·10 ⁻³	2.4·10 ⁻³
Ca ²⁺	2.3·10 ⁻²	3·10 ⁻²	5.9·10 ⁻³	3.1·10 ⁻³
NH ₄ ⁺	2·10 ⁻²	–	–	–
Str ²⁺	–	2.92·10 ⁻⁴	–	–

^a Natural Saline Water.

^b Equilibrium Bentonite Pore Water, two samples.

^c Synthetic Pore Water.

The experimental conditions (i.e. ionic strength and major cation concentration) used in Cs sorption experiments performed on simple clay materials (Rojo Carbonero clay, MX-80 bentonite, Boda claystone and Hanford sediments) are listed in Tables 2 and 3, along with their mineralogical properties, the type and content of clay mineral. The experimental data obtained with clay materials containing different clay minerals (FEBEX clay, San Juan clay, Callovo–Oxfordian samples, Opalinus clay and Boom clay) and the corresponding experimental conditions are summarized in Tables 4 and 5.

2.2. Sorption models

2.2.1. Ion exchange

The theory of ion exchange is a macroscopic approach developed by Bolt (1982). This exchange involves the structural negative charge of mineral clays, which is compensated by cations adsorption within the interlayer space. In general, several exchange sites can be used to calibrate the exchange data. For the model developed here, we chose to start with a model containing only a single site with a capacity equal to the cationic exchange capacity (CEC).

The exchange of ions at the solid-water interface is usually

Table 4

List of natural clay materials containing several clay minerals (i.e. mixed-clays), together with the experimental conditions used in different studies. n stands for the number of observations, I corresponds to the ionic strength, and m/V stands for the solid: liquid ratio.

Clay material	Reference	n	Contents and types of clay minerals	Major cations	I (mol L ⁻¹)	m/V (g L ⁻¹)	pH	[Cs] _{tot} (mol L ⁻¹)
FEDEX clay, Almeria, Spain	Missana et al. (2014a)	106	93% I/S mixed layer, with 10–15% of illite	Na ⁺	0.001–0.2	1–1.39	6.5	10 ⁻¹⁰ - 10 ⁻⁴
		33		Ca ²⁺	0.1–0.3	1	6.5	10 ⁻⁹ - 5·10 ⁻⁴
		39		K ⁺	0.01–0.1	1	6.5	2·10 ⁻⁹ - 8·10 ⁻⁴
		18		Na ⁺	0.01–0.1	1	2–10	2.3·10 ⁻⁶
		12		Ca ²⁺	0.3	3.3	2–10	4·10 ⁻⁶ / 4·10 ⁻⁹
8	K ⁺	0.1	1	2–10	9.5·10 ⁻⁶			
San Juan clay, Spain	Missana et al. (2014b)	72	30–50% illite, 10–15% kaolinite, 5–20% montmorillonite	Na ⁺ /K ⁺ /NH ₄ ⁺ and NSW ^a	0.46–0.54	10	9.4	2·10 ⁻⁹ - 10 ⁻²
Callovo–Oxfordian claystone, Paris basin, France	Chen et al. (2014)	50	illite–montmorillonite (I/M)	SPW-1 ^b SPW-2 ^b	0.1	2	7.2	5·10 ⁻⁹ - 10 ⁻⁴
	Savoie et al. (2012)	18		RPW ^c	0.1	1100	7.3	2·10 ⁻⁵ - 6·10 ⁻²
Opalinus Clay, Benken, Switzerland	Marques Fernandes et al. (2015)	16	17% illite, 30% I/M mixed layers, 21% kaolinite	SPW-3 ^b	0.23	13.5	7.8	10 ⁻⁸ - 10 ⁻²
Boom clay, Antwerp, Belgium	Maes et al. (2008)	6	10–45% illite, 10–30% I/S mixed layer, 5–20% kaolinite	RBCW ^d	0.016	6.7	8.5	10 ⁻⁹ - 10 ⁻²

^a Natural Saline Water.

^b Synthetic Pore Water, three samples.

^c Reference Pore Water.

^d Reference Boom Clay Water.

Table 5

Chemical composition of pore water used in the experiments with natural clay materials containing several clay minerals (i.e. mixed-clays).

Clay material	San Juan clay	Callovo–Oxfordian claystone			Opalinus clay	Boom clay
Reference	Missana et al. (2014b)	Chen et al. (2014)		Savoie et al. (2012)	Marques Fernandes et al. (2015)	Maes et al. (2008)
Pore water	NSW ^a	SPW-1 ^b	SPW-2 ^b	RPW ^c	SPW-3 ^b	RBCW ^d
Units	mol L ⁻¹					
Na ⁺	3.95·10 ⁻¹	4.6·10 ⁻²	4.2·10 ⁻²	4.1·10 ⁻²	1.64·10 ⁻¹	1.56·10 ⁻²
K ⁺	1.9·10 ⁻²	1·10 ⁻³	5.7·10 ⁻³	5.4·10 ⁻³	3.15·10 ⁻³	1.84·10 ⁻⁴
Mg ²⁺	2.1·10 ⁻²	6.7·10 ⁻³	7.7·10 ⁻³	7.7·10 ⁻³	8.69·10 ⁻³	6.58·10 ⁻⁵
Ca ²⁺	2.3·10 ⁻²	7.4·10 ⁻³	9.7·10 ⁻³	9.7·10 ⁻³	1.21·10 ⁻²	5·10 ⁻⁵
NH ₄ ⁺	2·10 ⁻²	–	–	–	–	–
Sr ²⁺	–	2·10 ⁻⁴	–	–	–	–

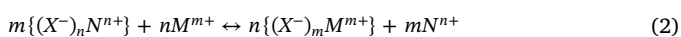
^a Natural Saline Water.

^b Synthetic Pore Water, three samples.

^c Reference Pore Water.

^d Reference Boom Clay Water.

described by reactions in which an equivalent amount of counter-ion charge is conserved. For a single negatively charged site $\equiv X^-$ (e.g. cationic exchange sites of the clays), the ionic exchange reaction involving ions N^{n+} at M^{m+} is expressed as follows:



Being reversible, the thermodynamic constant of cation exchange reactions is expressed by:

$$K_c = \frac{[(X^-)_m M^{m+}]^n \cdot [N^{n+}]^m \left(\frac{f_{(X^-)_m M^{m+}}^n}{f_{(X^-)_n N^{n+}}^m} \right) (\gamma_{M^{m+}}^n)}{[(X^-)_n N^{n+}]^m \cdot [M^{m+}]^n \left(\frac{f_{(X^-)_n N^{n+}}^m}{f_{(X^-)_m M^{m+}}^n} \right) (\gamma_{N^{n+}}^m)} \quad (3)$$

where $[·]$ is the concentration of species in solution (mol L⁻¹) or adsorbed to the solid surface (mol kg⁻¹), and f and γ are the activities of the adsorbed and aqueous species, respectively.

In solutions of constant total molality, frequently, the ratio of the

activity coefficients of the adsorbed species is nearly constant (the ratio is set to 1) (Gaines and Thomas, 1953), and the selectivity coefficient K_c is defined as follows (Jacquier et al., 2004; Savoie et al., 2012):

$$\frac{M}{N} K_c = \frac{[(X^-)_m M^{m+}]^n \cdot [N^{n+}]^m \gamma_{M^{m+}}^n}{[(X^-)_n N^{n+}]^m \cdot [M^{m+}]^n \gamma_{N^{n+}}^m} \quad (4)$$

2.2.2. Surface complexation

Analogous to ion complexation in solution, ‘Surface Complexation Models’ (SCM) (Avena and De Pauli, 1998; Bradbury and Baeyens, 2002; Davis et al., 1978; Davis and Kent, 1990; Ikhsan et al., 2005; Sposito, 1984) provide a molecular description of ion adsorption using an equilibrium approach that defines surface species, chemical reactions, equilibrium constants, mass balances, and charge balances (Goldberg, 2013). This molecular approach was developed by Schindler et al. (1976) who have demonstrated that the adsorption of a cation on

a positively charged surface is possible. These conceptual models take into account both the intrinsic affinity of surface sites for solutes and the coulombic interaction between the charged surface and the dissolved ions (Davis et al., 1978; Hayes and Leckie, 1987; Schindler et al., 1976).

Several chemical SCM have been developed during the last three decades to describe potentiometric titration and metal adsorption data at the oxide-metal solution interface and have been very successful in describing adsorption processes (Goldberg and Criscenti, 2007). These models are distinguished by differences in their respective molecular hypotheses: each model assumes a particular interfacial structure, resulting in the consideration of various kinds of surface reactions and electrostatic correction factors to mass law equations (Davis and Kent, 1990). The description of the most common models is supplied in the Appendix.

3. Modelling approaches

3.1. Overview of existing models for Cs sorption on clay minerals

A wide range of multi-site ion exchange models were proposed in the literature to simulate experimental data and understand the non-linear Cs sorption behavior on clay minerals. For illite, cation exchange (CE) models with three exchange sites are usually considered (Benedicto et al., 2014; Bradbury and Baeyens, 2000; Brouwer et al., 1983; Cornell, 1993; Fuller et al., 2014; Marques Fernandes et al., 2015; Missana et al., 2014b; Steefel et al., 2003). Such models have also been reported for Cs sorption onto smectites and kaolinite (Missana et al., 2014b). Furthermore, one-site CE models (Bradbury and Baeyens, 2010; Chen et al., 2014) and two-site models can also be found for smectites (Liu et al., 2004; Missana et al., 2014b; Poinssot et al., 1999; Zachara et al., 2002).

Poinssot et al. (1999) proposed a two-site CE model for illite, but they only considered the exchange reactions between Na^+ , or K^+ and H^+ . Savoye et al. (2012) have developed a 5-sites CE model for which selectivity coefficient values were calculated from Poinssot et al. (1999). Selectivity coefficients of CE models are usually obtained from batch-type experiments, measured with pure mineral phases in dispersed state at specific physicochemical conditions (nature of exchange cations, ionic strength, pH, contact time, concentration of some ion). The major differences between these models are the number of Cs sorption sites and the capacities of each site. These semi-empirical parameters calculated for each study fall in a relatively close range, considering that the uncertainty is up to $\pm 0.2 \text{ L kg}^{-1}$ (log unit) due to measurement uncertainty. Missana et al. (2014a) also note that selectivity coefficients vary with ionic strength for different clays.

The analysis of these models shows that only the “generalized caesium sorption” (GCS) model of Bradbury and Baeyens (2000) has been applied to different experimental data (Brouwer et al. (1983), Comans et al. (1991), Staunton and Roubaud (1997), and Poinssot et al. (1999)). No other data compilation and/or model comparison on experimental sorption data has been performed, leaving a wide range of choices for cation exchange modelling of Cs sorption onto illite without clear selection criteria. Note that the model proposed by Poinssot et al. (1999) corresponds to the GCS model without the planar site.

A large number of studies suggest that Cs adsorption depends on pH for various clay minerals (Akiba et al., 1989; Cornell, 1993; Torstenfelt et al., 1982). For instance, Poinssot et al. (1999) observed a small decrease in Cs sorption on illite, at pH lower than 4 and at low Cs concentration ($< 10^{-8} \text{ M}$), where sorption onto the FES dominates (Fuller et al., 2014). This pH-dependent adsorption of trace elements, such as Cs^+ can easily be explained by analogy with the sorption properties of oxides (Kraepiel et al., 1999). The FES result from broken bonds at the edges of clay crystals and hydroxyl groups, and contribute to the development of negative and positive charge (Cornell, 1993). They can potentially react with ions in solution to yield surface complexes

(Koretsky, 2000) like pure oxides phases (Angove et al., 1997; Ikhsan et al., 1999; Kraepiel et al., 1999; Lackovic et al., 2003; Zachara and McKinley, 1993). These surface reactions may be described with a SCM, in which the FES are commonly called ‘variable charge sites’ and noted $\equiv \text{SOH}$ (Davis and Kent, 1990; Davis and Leckie, 1978; Sposito, 1984).

Metal and radionuclide (Ni^{2+} , Zn^{2+} , Eu^{3+} , Al^{3+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Sr^{2+} , Co^{2+} , Cs^+ , Ca^{2+} , Na^+ , Se^{2-} , F^- , Br^- and I^-) adsorption on clay minerals was successfully modeled in many studies using an approach combining cation exchange and surface complexation (Baeyens and Bradbury, 1997; Bruggeman et al., 2010; Charlet et al., 1993; Du et al., 1997; Gu and Evans, 2007, 2008; Gutierrez and Fuentes, 1996; Lund et al., 2008; Mahoney and Langmuir, 1991; Missana et al., 2009; Missana and Garcia-Gutiérrez, 2007; Stadler and Schindler, 1993; Tertre et al., 2006; Weerasooriya et al., 1998; Zachara and McKinley, 1993). This approach usually involves two distinct types of surface sites at the interface between the solid and the solution: (i) $\equiv \text{X}^-$ groups bearing a permanent negative charge which account for the cation exchange part of sorption. Cations (e.g., Na^+ , K^+ , Ca^{2+}) binding at this type of surface sites occurs through electrostatic interactions; (ii) amphoteric $\equiv \text{SOH}$ groups on FES with high affinity for metals and radionuclides but low site density which control protonation/deprotonation (i.e., pH-dependent) which account explicitly for the adsorption of background electrolyte.

Several authors have proposed sorption on amphoteric surface hydroxyl as a suitable mechanism for pH-dependent sorption, as opposed to mineral dissolution or H^+ exchange (Baeyens and Bradbury, 1997). Studies therefore considered the surface complexation mechanism for the description of trace Cs sorption on amphoteric hydroxyl groups of montmorillonite (on $\equiv \text{SOH}$ edge sites). For instance, Gutierrez and Fuentes (1996) used the triple layer model (TLM) to simulate the adsorption of Cs^+ onto Ca-montmorillonite. Two types of adsorption sites were considered to be responsible for Cs adsorption: interlayer and (frayed) edge sites. The dominant mechanism of adsorption was identified as specific adsorption in the edge sites which, although composing only 5% of the total adsorption sites, accounted for as much as 94% of Cs adsorption. Silva et al., 1979 proposed a combined approach for montmorillonite: (i.) a two-site ($\equiv \text{SOH}$ and $\equiv \text{TOH}$ groups) with a 1-pK Double Layer Model (DLM) and (ii.) a one-site cation exchange model. The authors have considered the complexation of Cs^+ and the Na^+ on $\equiv \text{SOH}$ and $\equiv \text{TOH}$ edges groups. This approach requires the fitting of 12 parameters which represents a major drawback. Hurel et al. (2002) have used another surface complexation model for the adsorption of cations (Cs^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) on bentonite. Cs sorption was modeled on the silanol edge sites as well as cation exchange. Wang et al. (2005), also found that at high pH Cs^+ sorption onto bentonite was dominated by surface complexation.

To model Cs sorption on MX-80 bentonite, Montavon et al. (2006) used the simplified two-pK non-electrostatic model (NEM) from Bradbury and Baeyens (1997) to describe the pH-dependent interactions with clay edge surfaces in combination with a cation exchange in the interlayer and on the basal plane surfaces. This model is also very “expensive” in terms of number of adjustable parameters (four SCM and two cation exchange sites). The authors noted that the parameters were only applicable for the conditions of their study. Bradbury and Baeyens (2010) proposed a unique selectivity coefficient ($K_c = 15$) for all the Cs concentration range, which does not allow to account for the non-linearity of Cs sorption isotherm on MX-80 bentonite.

In summary, existing models are usually successful in reproducing a specific set of experiments but are often complex in terms of the number of adjustable parameters and implementation (2-pK TLM, 2-pK DLM ...). Moreover, the applicability of these models is restricted to the data on which they were calibrated and their ability to predict Cs sorption in heterogeneous environments or natural systems appears therefore limited.

Table 6
Mineral properties and parameters for the 1-pK DL/IE model used to model Cs sorption onto illite, montmorillonite, and kaolinite.

Input Parameters	Illite	Montmorillonite	Kaolinite
Site capacity = X- (meq kg ⁻¹) (CEC)	225 ^d	870 ^b	20 ^c
Site density = SOH (sites nm ⁻²)	2.7·10 ⁻³ ^d	3.6·10 ⁻⁵ *	1.5·10 ⁻⁴ *
Surface Specific Area (SSA) (m ² g ⁻¹)	97 ^a	800 ^c	10 ^c
Surface complexation reactions on =SOH sites	logKSC		
SO ^{-0.5} + H ⁺ ↔ SOH ^{0.5}	3.46 ^f	3.4 ^g	5 ^h
SOH ^{0.5} + Cs ⁺ ↔ SOCs ^{0.5} + H ⁺	5.2 [*]	4.3 [*]	3 [*]
SOH ^{0.5} + Na ⁺ ↔ SONa ^{0.5} + H ⁺	-1.8 ⁱ	-1.3 ^j	-3.6 ^j
SOH ^{0.5} + K ⁺ ↔ SOK ^{0.5} + H ⁺	0.6 [*]	0.1 [*]	-1.75 ^k
SOH ^{0.5} + NH ₄ ⁺ ↔ SONH ₄ ^{0.5} + H ⁺	1.5 [*]	-	-1.75 ^j
SOH ^{0.5} + Ca ²⁺ ↔ SOCa ^{1.5} + H ⁺	-5 ^m	-1.4 ^l	-5.9 ⁿ
SOH ^{0.5} + Mg ²⁺ ↔ SOMg ^{1.5} + H ⁺	-5 [§]	-1.4 [§]	-5.9 [§]
SOH ^{0.5} + Sr ²⁺ ↔ SOSr ^{1.5} + H ⁺	-5 [§]	-1.4 [§]	-5.9 [§]
Cation exchange reactions on =X- sites	logKc[*]		
XNa + Cs ⁺ ↔ XCs + Na ⁺	2.45	1.39	2.1
XK + Cs ⁺ ↔ XCs + K ⁺	0.95	0.8	2.1
XNH ₄ + Cs ⁺ ↔ XCs + NH ₄ ⁺	1.6	0.8	2.1
X ₂ Ca + 2Cs ⁺ ↔ 2XCs + Ca ²⁺	5.2	1.7	4.49
X ₂ Sr + 2Cs ⁺ ↔ 2XCs + Sr ²⁺	5.2	2.37	-
X ₂ Mg + 2Cs ⁺ ↔ 2XCs + Mg ²⁺	5.2	2.45	-

*This study.

§Values for Ca²⁺ = Mg²⁺ = Sr²⁺ is assumed.

^a Savoye et al. (2012).

^b Bradbury and Baeyens (2002); Tertre et al. (2006).

^c Missana et al. (2014b).

^d Calculated from the mean of FES site density values given by Benedicto et al. (2014) and Missana et al. (2014b).

^e Avena and De Pauli (1998); Mahoney and Langmuir (1991).

^f Liu et al. (1999), the logK_H values were derived from the Model I (2-pK formalism) for WC illite using logK_H = (pK_{a1} + pK_{a2})/2.

^g pH of zero point charge (pH_{ZPC}) given by Ijagbemi et al. (2009).

^h Hoch and Weerasooriya (2005), the logK_H values were derived from the Double Layer Model (2-pK formalism) for KGa kaolinite using log K_H = (pK_{a1} + pK_{a2})/2 (noted that the pH_{ZPC} of kaolinite sample KGa was determined at 4.9).

ⁱ Revised value from that proposed by Rafferty et al. (1981) in Mahoney and Langmuir (1991) for =SOH site (LogK_{SONa} = -2.2).

^j Mahoney and Langmuir (1991) for =SOH site.

^k Jung et al. (1998) for =SiOH site.

^l Assumed to be equal to the value for K⁺ on kaolinite.

^m Bradbury and Baeyens (2005).

ⁿ Riese (1982) for =SiOH site.

3.2. Building a new, robust and parsimonious model for caesium sorption

To model Cs sorption onto illite, montmorillonite and kaolinite, we tried to minimize the number of adjustable parameters to fit the largest number of sorption data sets by combining:

- a surface complexation model which is used to describe the adsorption of cations (protons, Cs, and cations from the background electrolyte) on a single FES site (=SO^{-0.5}) with a high affinity for Cs but with very low site density,
- and an Ion Exchange model (IE), which is used to simulate the adsorption of cations on permanent negatively charged sites of planar surfaces of clay minerals, including outer-basal and interlayers sites (=X⁻), which have a low affinity for Cs but a high site density (i.e. large contribution to the global CEC). These sites will be called in this study “exchange sites”.

Our modelling methodology is similar to that introduced by Tournassat et al. (2013) as a “minimalist” modelling approach for sorption on high energy sites of montmorillonite edge surfaces, which

attempts to minimize the number of adjustable parameters for modelling the largest number of sorption data and by using a 1-pK approach. This is an advantage over multi-site models available in the literature for Cs sorption on illite and montmorillonite, which have more than two sorption sites, with the exception of the model used by Poinssot et al. (1999).

As in many other studies (Baeyens and Bradbury, 1997; Bruggeman et al., 2010; Charlet et al., 1993; Gu and Evans, 2007; Gutierrez and Fuentes, 1996; Lund et al., 2008; Mahoney and Langmuir, 1991; Missana and Garcia-Gutiérrez, 2007; Stadler and Schindler, 1993; Tertre et al., 2006; Zachara and McKinley, 1993), we used a SCM to model the adsorption of cations on surface hydroxyl groups (=SOH) localized in FES for two reasons: (i) these models allow a mechanistic description based on the chemical nature of the adsorption process, and (ii) they take into account both the intrinsic affinity of surface sites for solutes and the coulombic interaction between the surface charge and the dissolved cations (Davis et al., 1978; Hayes and Leckie, 1987; Schindler et al., 1976). We have chosen the Double Layer Model (DLM) (Dzombak and Morel, 1990; Huang and Stumm, 1973; Stumm et al., 1970), as several previous authors (Bradbury and Baeyens, 1997; Hoch and Weerasooriya, 2005; Silva et al., 1979; Sverjensky and Sahai, 1996; Tertre et al., 2006; Tombácz and Szekeres, 2004; Wanner et al., 1996), because it is one of the simplest model available with fewer fitting parameters than other surface complexation models. Moreover, the values of reaction constants depend only on the nature of the solid and the adsorbing solute not on pH, adsorbate concentration, ionic strength and solution composition; (Koretsky, 2000). For more details, see the DLM description in the Appendix.

We selected the 1-pK approach (Van Riemsdijk (1979); Bolt and Van Riemsdijk (1982)) combined with the DLM, using only one charge reaction, as opposed to the classical 2-pK-DLM approach (adsorbing protons in two consecutive steps, each having its own affinity and charge properties). Hiemstra et al. (1989) and Koopal (1993) suggested that the 1-pK model may be used as a physically most realistic simplified model to describe the protonation/deprotonation reactions of (hydr)oxides, when the structure of a surface is not well known (Avena and De Pauli, 1996).

Surface roughness was not explicitly treated in this paper. We consider that roughness is embedded into the surface area value that we take from the literature.

3.3. Geochemical software and statistical analysis

The modelling of the adsorption of Cs and co-ions using our 1-pK DL/IE model was performed with PHREEQC v2.18 (Parkhurst and Appelo, 1999). The goodness of fit of the simulations was optimized with the adjusted determination coefficient (R_{adj}², Appendix, A.2) and by minimizing the difference between predicted and measured values, using the Root Mean Square Deviation (RMSD). Further details are supplied in the Appendix.

4. Results and discussion

4.1. Calibration of the 1-pK DL/IE model for Cs sorption

The mineralogical properties and parameters values used in the 1-pK DL/IE model to simulate sorption data for Cs under the conditions defined in Table 1 onto the three pure clay minerals (illite, montmorillonite and kaolinite) are shown in Table 6.

The logK_H value for illite was calculated using Eqn. (A.7) with the logK_{a1} and logK_{a2} (logK_{SC} reported by Liu et al. (1999)). Note that the calculated value is comparable to the pH of zero point charge (pH_{ZPC}) of other types of illite (Du et al., 1997; Liu et al., 1999). Similarly, the logK_H value used for kaolinite was derived from the 2-pK DLM developed by Hoch and Weerasooriya (2005) for the KGa kaolinite. Again, the calculated value is close to the pH_{ZPC} (4.9) determined by the same

authors. In the case of montmorillonite, the $\log K_H$ value was assumed to be equal to pH_{ZPC} reported by Ijagbemi et al. (2009).

The equilibrium constants used to simulate cation adsorption on FES ($\log K_{\text{SOM}}$) are shown in Table 6. Some values are taken directly from the literature while others were determined by fitting the experimental data listed in Table 1.

Firstly, the $\log K_{\text{SONa}}$ values for illite and montmorillonite were assumed to be equal to the values reported by Mahoney and Langmuir (1991) (2.2 and -2 , respectively for $\equiv\text{SOH}$ site). Secondly, the $\log K_{\text{SOCs}}$ values for both clay minerals were determined by concurrently fitting the 1-pK DL/IE model to the experimental data (5.2 and 4.3, respectively), and the $\log K_{\text{SONa}}$ values were revised to -1.8 and -1.3 , respectively. Note that revised $\log K_{\text{SONa}}$ values are close to the values proposed by Duputel et al. (2014) for illite (-1.6) and Lumsdon (2012) for both minerals (-1). Similarly, the $\log K_{\text{SOK}}$ value for both clay minerals, and $\log K_{\text{SONH}_4}$ value for illite were determined using the same method.

The values of Ca, Mg and Sr surface complexation constants for illite, montmorillonite and kaolinite have been taken directly from literature: Bradbury and Baeyens (2005) for $\equiv\text{S}^{\text{w}2}\text{OH}$ sites, Mahoney and Langmuir (1991) for $\equiv\text{SOH}$ sites and Riese (1982) for $\equiv\text{SiOH}$ sites, respectively. The $\log K_{\text{SONa}}$ and $\log K_{\text{SOK}}$ values for kaolinite, were taken directly from Mahoney and Langmuir (1991) for $\equiv\text{SOH}$ sites and Jung et al. (1998) for $\equiv\text{SiOH}$ sites. The $\log K_{\text{SONH}_4}$ value for kaolinite was assumed to be equal to $\log K_{\text{SOK}}$ value.

The selectivity coefficients (K_c) values for the cation exchange model were generated by starting from literature values and fitting the 1-pK DL/IE model to published Cs sorption data from Table 1. Note that the values obtained are close to selectivity coefficients of existing cation exchange models.

The values for the site capacity of the permanent negatively charged sites ($\equiv\text{X}^-$), i.e. mainly the CEC, and the specific surface area (SSA) for the three studied clay minerals are within the literature range. The $\equiv\text{SOH}^{0.5}$ site density value used for illite was $2.7 \cdot 10^{-3}$ sites $\text{nm}^{-2} \approx 0.43$ meq kg^{-1} , assumed to be equal to the mean FES site density values reported by Missana et al. (2014b) and Benedicto et al. (2014) (0.58 and 0.29 meq kg^{-1} , respectively). For montmorillonite and kaolinite, the values of $\equiv\text{SOH}^{0.5}$ site density were obtained by fitting the experimental data. Furthermore, $\equiv\text{SOH}^{0.5}$ site density value for montmorillonite ($3.6 \cdot 10^{-5}$ sites $\text{nm}^{-2} \approx 4 \cdot 10^{-2}$ meq kg^{-1} with $\text{SSA} = 800$ m^2 g^{-1}) was in the same order of magnitude than the value proposed by Montavon et al. (2006) for exchangeable interlayer cations site in MX-80 montmorillonite ($2 \cdot 10^{-2}$ meq kg^{-1}). For kaolinite, the value of $\equiv\text{SOH}^{0.5}$ site density ($1.5 \cdot 10^{-4}$ sites $\text{nm}^{-2} \approx 2.4 \cdot 10^{-3}$ meq kg^{-1}) is close to the value suggested by Missana and al. (2014b) for the FES ($5 \cdot 10^{-3}$ meq kg^{-1}).

4.1.1. Cs sorption on illite

Results obtained with the 1-pK DL/IE model (continuous red lines) for illite are shown in Fig. 1. The dotted lines represent results calculated by the different sorption models proposed in the literature. It can be seen that the models globally reproduced well the decrease of K_d with increasing dissolved Cs concentration, as well as the difference between Na and Ca-illite (Fig. 1a, b, g, h) versus K and NH_4 -illite (Fig. 1c–f and i) and ionic strength of the solution. These well-known differences reflect the selectivity of illite (especially on FES) for cations according to the following order of affinity: $\text{Cs}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Sr}^{2+} > \text{Ca}^{2+}$ and Mg^{2+} , (Appelo and Postma, 1993; Brouwer et al., 1983; Dyer et al., 2000; Staunton and Roubaud, 1997). The model results show, in particular, that K^+ competes most effectively with Cs^+ adsorption (Eberl, 1980; Sawhney, 1972). Concerning the effect of ionic strength (I), the modelling also confirms that the K_d increases as the ionic strength of the solution decreases, which is more marked for Na and K-illite than for Ca-illite.

The contribution of each type of sorption site is illustrated for the 1 pK DL/IE model in Fig. A.4 for Na-illite at $\text{pH} = 7$ and

$I = 0.1$ mol L^{-1} . At low total Cs concentrations ($[\text{Cs}]_{\text{tot}} = 10^{-9} - 10^{-7}$ mol L^{-1}), sorption is dominated by FES ($\equiv\text{SOCs}^{0.5}$) which have a high affinity for Cs ($\log K_d$ values are higher), a very small concentration (0.43 meq kg^{-1}), and are therefore quickly saturated. At medium and high total Cs concentrations ($[\text{Cs}]_{\text{tot}} = 10^{-7} - 10^{-4}$ mol L^{-1}), sorption occurs on the remaining sites on planar surfaces (exchange sites) which have a higher capacity (190–225 meq kg^{-1}) and a lower selectivity (i.e. lower $\log K_d$ values).

Results also show that the goodness of fit of the 1 pK DL/IE model is globally better than the other models (dotted lines). These performances were obtained using of a unique set of parameters to simulate all the experimental data. For example, in the case of Na-illite at $I = 0.01$ mol L^{-1} (Fig. 1a, data from Benedicto et al. (2014)), the 1 pK DL/IE model and the 3-sites cation exchange model developed by Benedicto et al. (2014), which was specifically calibrated for these experimental data, adequately reproduce the measured $\log K_d$ (see Table 7). However, their model is out-performed by the 1 pK DL/IE model when simulating experimental data from other authors. The same behavior is observed in the case of K-illite (Fig. 1c and e, data from Brouwer et al. (1983)): the calculated $\log K_d$ values from the 1-pK DL/IE model and the 3-sites cation exchange model proposed by Brouwer et al. (1983) both fall within the experimental errors in the whole range of Cs concentrations, and have the best goodness of fit (RMSD values of 0.21 and 0.11 L kg^{-1} , and R_{adj}^2 of 1.07 and 1.11, respectively). Globally, the cation exchange models provide a satisfactory fit only for a limited Cs concentration range: some underestimate and other overestimate strongly Cs sorption as suggested by RMSD values ≥ 0.65 L kg^{-1} .

Further all the models underestimate Cs sorption on K-illite for high ionic strength and high Cs concentrations ($[\text{Cs}]_{\text{eq}} > 10^{-4}$ mol L^{-1}) (Fig. 1 f). This may be explained by the expansion of the illite layers and the increase of the CEC (de-collapse) which facilitate Cs uptake, as postulated by Benedicto et al. (2014) ($\text{CEC}_{\text{decollapsed}} = 900$ meq kg^{-1}), or by the existence of a low amount of another clay mineral, which becomes relevant at high Cs concentrations when saturation of sorbed Cs is reached for illite.

The global RMSD and R_{adj}^2 index, i.e. the average values of RMSD and R_{adj}^2 corresponding to all the Cs sorption isotherms simulated for illite ($n = 95$ observations) are shown in Table 7. The model proposed in this study performs well for all the conditions (smallest global RMSD index value of 0.25 L kg^{-1} and $R_{\text{adj}}^2 = 0.83$), which confirms its accuracy and robustness. The model proposed by Benedicto et al. (2014) also reproduces reasonably well the experimental sorption isotherms (RMSD = 0.27 L kg^{-1} and $R_{\text{adj}}^2 = 0.8$) but does not account for the effect of NH_4^+ concentrations and pH, and requires small adjustments of the parameters in order to improve the fit in each condition. The global performance of the other models is lower.

The simulations of Cs sorption on illite as function of pH using the 1-pK DL/IE model and the model from Poinssot et al. (1999) are shown in Fig. 2. Our model reproduced the experimental data of Poinssot et al. (1999) with a better global accuracy (global RMSD index of 0.13 L kg^{-1} vs. 0.25 L kg^{-1} for Poinssot et al., 1999) for the range of ionic strength from 1 to 0.01 mol L^{-1} (and particularly at the lower value). At low total Cs concentrations ($[\text{Cs}]_{\text{tot}} < 10^{-8}$ mol L^{-1}), the simulations indicate that sorption on illite weakly depends on pH (sorption decreases only at pH lower than 4) and is dominated by the $\equiv\text{SO}^{-0.5}$ site, as it is also suggested by Poinssot et al. (1999).

4.1.2. Cs sorption on montmorillonite

Only a few Cs sorption experimental data and models have been published for montmorillonite. Moreover, these models have a large number of adjustable parameters. Note that the data from experiments with MX-80 bentonite have not been used for the calibration of the model but are considered hereafter for its evaluation (cf. Section.4.2).

The CEC of purified SWy-montmorillonite (838 meq kg^{-1}) measured by Gorgeon (1994) was similar to that reported by Staunton and

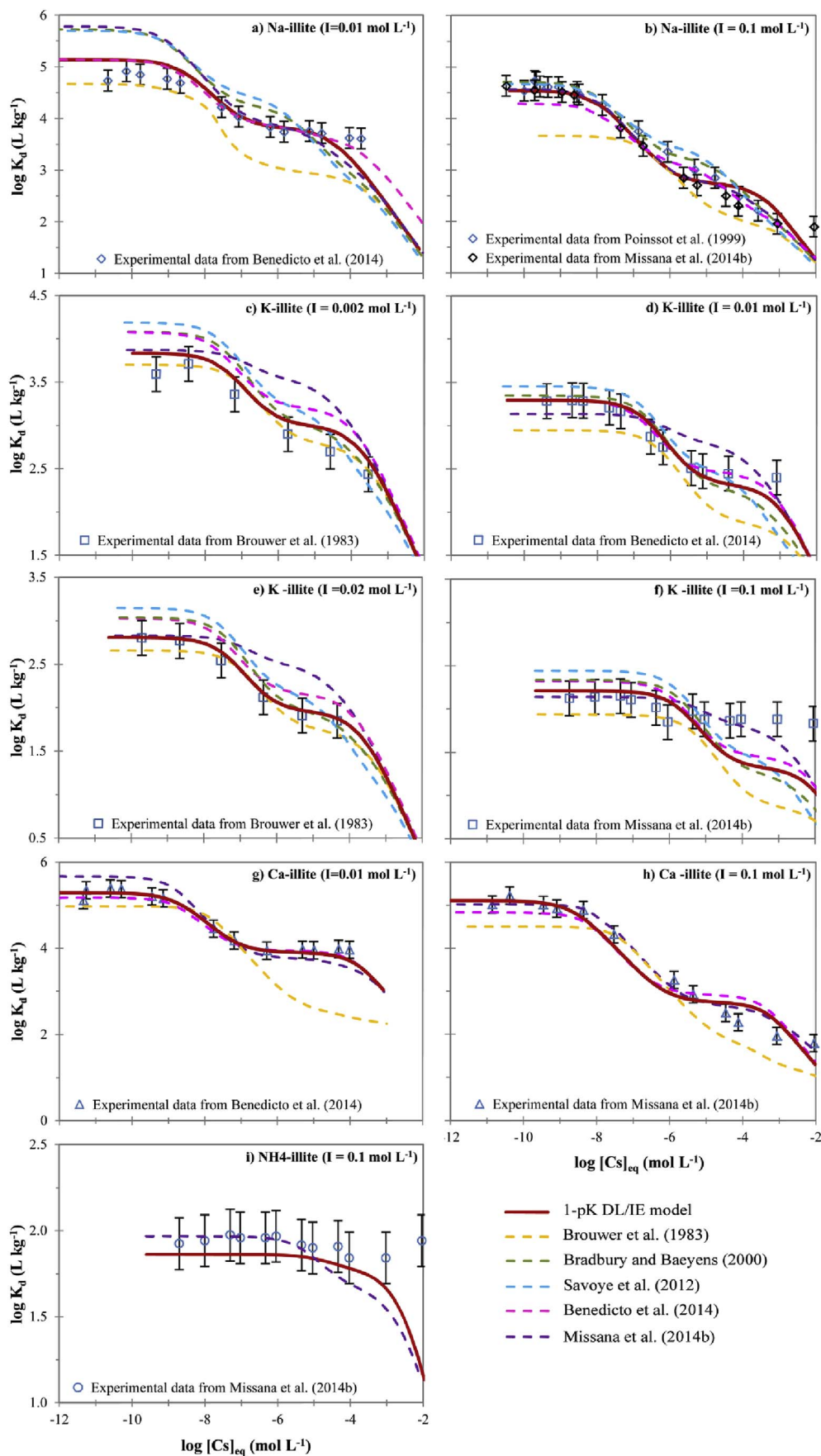


Fig. 1. Cs sorption isotherms measured for Na-, K-, Ca- and NH₄-illite under different physico-chemical conditions (see Table 1). The continuous line represents the results of the modelling performed with our model (1-pK DL/IE model). The dotted lines represent the results of simulations performed using different cations exchange models available in the literature (see legend).

Table 7

Comparison of statistical criteria (RMSD and R_{adj}^2) calculated for the 1-pK DL/IE model and those for the cation exchange models from the literature in the case of sorption onto illite (the R_{adj}^2 takes into account the number of variables, parameters and observations, for the different models).

Statistical criteria	1-pK DL/IE model	Brouwer et al. (1983)	Bradbury and Baeyens (2000)	Savoie et al. (2012)	Benedicto et al. (2014)	Missana et al. (2014b)
RMSD	0.25	0.53	0.38	0.67	0.27	0.39
R_{adj}^2	0.83	0.78	0.81	0.75	0.79	0.81

Roubaud (1997) (940 meq kg⁻¹). In our model we assumed that the CEC for montmorillonite is equal to value proposed by Baeyens and Bradbury (1997) for conditioned Na-montmorillonite, i.e., 870 meq kg⁻¹.

Fig. 3a represents the sorption isotherms of montmorillonite initially saturated with Na, K and Ca, reported by (Staunton and Roubaud, 1997) and Fig. 3b shows the effect of pH on Cs sorption for montmorillonite. Fig. 3 shows that Cs sorption behavior for montmorillonite is similar to that of illite. The sorption isotherms are non-linear especially for Ca-montmorillonite: little changes in log K_d values for Na- and K-montmorillonite were observed, whereas the value of log K_d for Ca-montmorillonite decreases progressively with increasing Cs concentration, which suggests some heterogeneity of the montmorillonite exchange sites and confirms the order of affinity for cations according to the sequence Cs⁺ > K⁺ > Na⁺ > Ca²⁺ (Appelo and Postma, 1993; Brouwer et al., 1983; Dyer et al., 2000; Staunton and Roubaud, 1997).

The analysis of the sorption distribution shows that Cs is adsorbed predominantly on exchange sites for Na- and K-kaolinite. In the case of Ca-illite the distribution of adsorbed Cs follows the same behaviors of

illite (Fig. A.5). Measured log K_d were appropriately reproduced using the 1-pK DL/IE model (Table 6) with the global RMSD index of 0.09 L kg⁻¹ for the sorption isotherms and 0.06 L kg⁻¹ for the sorption on FES.

4.1.3. Cs sorption on kaolinite

Only a few experimental data have been found in literature for the kaolinite, and only the two-site cation exchange model of Missana et al. (2014b) was compared to the model developed here.

Gorgeon (1994) used a synthetic kaolinite (Sigma) which has similar properties than KGa-1-b. The CEC values of KGa-1-b and Sigma kaolinite are equal to 20 and 28 meq kg⁻¹ respectively and their total specific surface area (SSA) are equal to 10 and 13.2 m² g⁻¹, respectively.

Fig. 4 shows that Cs sorption on kaolinite also follows the same pattern as illite, and was appropriately simulated using the 1-pK DL/IE model with a global RMSD index of 0.09 for sorption isotherms (Fig. 4a) and 0.15 L kg⁻¹ for the sorption edge (Fig. 4b). Cs sorption was slightly underestimated at pH 2–3 in the case of Na-kaolinite at high ionic strength I = 1 mol L⁻¹ and [Cs]_{tot} = 10⁻⁷ mol L⁻¹. Our model (Fig. 4a, solid lines) and the cation exchange model proposed by Missana et al. (2014b) (Fig. 4a, dotted lines) show a similar goodness of fit for sorption isotherms.

The sorption isotherms are sensitive to [Cs] except for kaolinite initially saturated with K and NH₄, for which sorption was constant in a very wide range of Cs concentrations. A non-linear change in log K_d values was observed on a small range (0.5 log unit) for Na and Ca-kaolinite. Note that both models failed to reproduce the high K_d value at high Cs concentration (Cs = 10⁻³ mol/L).

Simulations predict that sorption is dominated by exchange site ($\equiv X^-$) for all Cs concentrations range, especially for K-kaolinite (95%). The model could therefore be reduced to a single sorption site, as

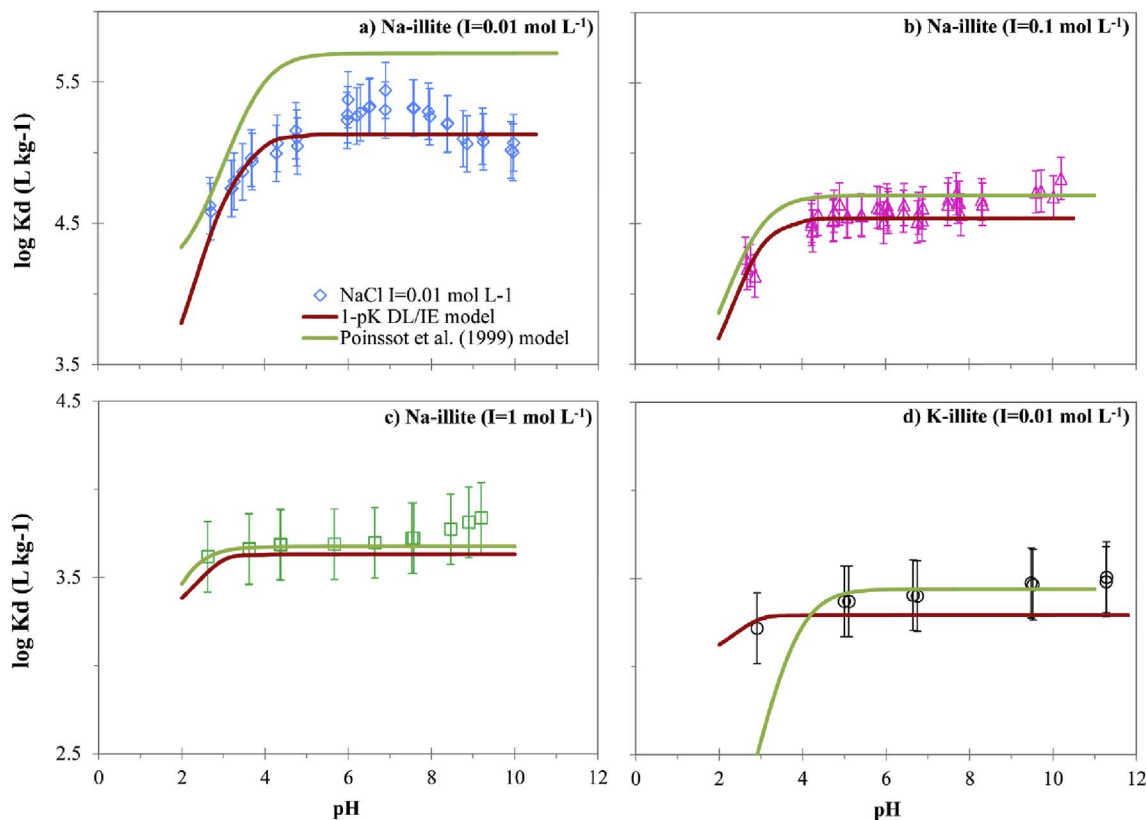


Fig. 2. Cs sorption as a function of pH for illite measured under different physicochemical conditions (Poinssot et al., 1999). The continuous lines stand for results of the modelling. The red line represents the results simulated with our 1-pK DL/IE model and the green line represent results obtained by the model of Poinssot et al. (1999). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

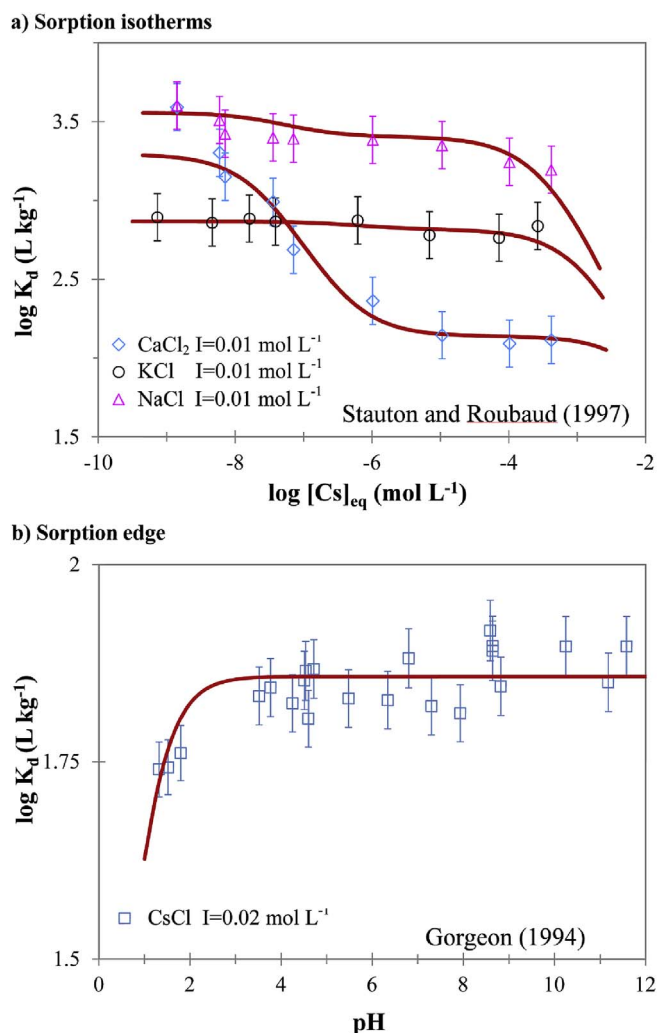


Fig. 3. Cs sorption isotherms as a function of Cs concentration and pH measured for montmorillonite under different physicochemical conditions. These data are from Staunton and Roubaud (1997) and Gorgeon (1994) respectively. The continuous lines represent the results of the modelling performed with our 1-pK DL/IE model.

proposed by Shahwan and Erten (2002). However Missana et al. (2014b) suggested that the existence of high affinity sites (FES) on kaolinite and smectite is most probably due to the existence of traces of micaceous or interstratified minerals.

Fig. A.6 shows (a) the distribution of sorbed Cs on sorption sites ($\equiv SO^{-0.5}$ and $\equiv X^{-}$) and (b) the evolution of species distribution on $\equiv SO^{-0.5}$ site (%) as function of pH as calculated by the 1-pK DL/IE model, for Na-kaolinite at $I = 1 \text{ mol L}^{-1}$ and $[Cs]_{tot} = 10^{-7} \text{ mol L}^{-1}$. At lower pH, the Cs is totally adsorbed by surface planar sites (exchange sites) because $\equiv SO^{-0.5}$ sites are initially saturated by H^+ ($\equiv SOH^{0.5}$). These sites progressively deprotonated in favor of the adsorption of Na and Cs when pH increases from 2 to 5, resulting in an increase of the contribution of FES sites to total Cs sorption. Above pH 5 ($\log K_H = 5$), the $\equiv SOH^{0.5}$ species is negligible and the occupancy of $\equiv SO^{-0.5}$, $\equiv SOCs^{0.5}$, $\equiv SONa^{0.5}$ species represent 3%, 25% and 71%, respectively.

4.1.4. Effect of electrostatic correction factor

The effect of the electrostatic component was also estimated by applying the model without the electrostatic correction factor. The contribution of electrostatic term in Cs sorption on the studied clay minerals was negligible, and the mean difference between K_d values calculated with and without electrostatic term is in order of 0.01%. The maximum of this difference represented only 5% of the mean error of

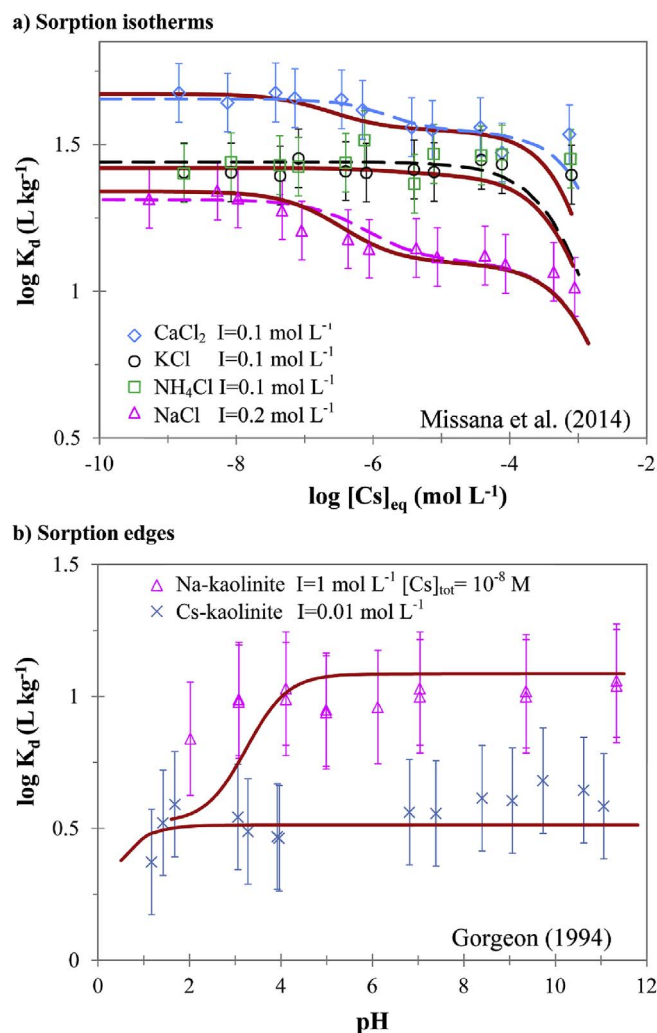


Fig. 4. Cs sorption isotherms as a function of Cs concentration and pH measured for kaolinite under different physicochemical conditions. These data are from Missana et al. (2014b) and Gorgeon (1994) respectively. The continuous and dotted lines stand for results of the modelling obtained by our 1-pK DL/IE model and the cation exchange model of Missana and al. (2014b) respectively.

K_d values ($\pm 0.2 \text{ L kg}^{-1}$) in very isolated cases, which means that the electrostatic correction always remains within the uncertainty range. This ascertainment is in agreement with the observation of Bradbury and Baeyens (1997) who showed that the contribution of the electrostatic term was lower than the range of error. In this study Cs surface complexation at edge sites is treated with very larger stability constants, frequently higher than those for proton adsorption. So as a consequence the chemical contribution is in most cases so strong that it overcomes competition with protons and repulsive electrostatics. So the double layer model can be reduced to a non-electrostatic model. This would also be numerically more easily included into a transport code. Tournassat et al. (2013) have also demonstrated, by testing surface complexation models available in the literature, that a non-electrostatic model is the most efficient model, in terms of simplicity and accuracy, to represent correctly the physical nature of the metal/clay surface interactions.

4.1.5. Performance of the model calibration

Fig. 5 represents the values of $\log K_d$ simulated by 1-pK DL/IE model as function of $\log K_d$ measured for illite, montmorillonite and kaolinite. This figure confirms that the model proposed in this study (1-pK DL/IE model) successfully reproduces the experimental data available in the literature for Cs sorption on these three clay minerals in a wide range of

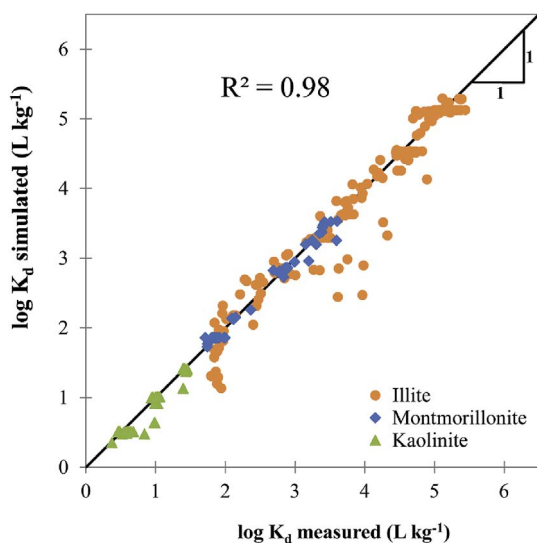


Fig. 5. Relationship between measured and simulated distribution coefficients (K_d) using the 1-pK DL/IE model for the different clay minerals (illite, smectite and kaolinite).

physico-chemical conditions (ionic strength, pH, and solid/liquid ratio). Moreover, these results were obtained with a unique set of parameters for each mineral whereas the selectivity coefficients are often adjusted, for each curve, within a range of $\log K_c \pm 0.2 \text{ L kg}^{-1}$ by authors who want to optimize the fit on their own data (McBride, 1979; Missana et al., 2014a; Staunton and Roubaud, 1997; Wahlberg and Fishman, 1962). The few points further from the 1:1 line correspond mostly to the K_d values obtained for the highest Cs concentrations where all the models have difficulties to simulate the experimental data.

4.2. Model evaluation in natural material made of a single type of clay mineral

The 1-pK DL/IE model was first tested in simple cases with other experimental data obtained on clay materials (Rojo Carbonero clay, MX-80 bentonite, Boda claystone and Hanford sediment) containing only one type clay mineral (illite or montmorillonite). The mineralogical properties of these clay materials, the content and type of clay mineral are listed in Table 2. The experimental conditions (i.e. ionic strength and major cationic environments) used in these experiments are listed in Tables 2 and 3. The 1-pK DL/IE model was applied directly without changing the parameters adjusted previously (Table 6).

For the Rojo Carbonero (RC) clay, the illite content considered was 57%, which result in a capacity of exchange site $\equiv X^-$ of the 1-pK DL/IE model equal to $127.9 \text{ meq Kg}^{-1}$. This hypothesis slightly overestimates the CEC measured by Missana et al. (2014b) (110 meq Kg^{-1}). In the case of MX-80 bentonite, the content of montmorillonite was assumed to be 81.4% (Karnland, 2010), and the CEC equal to 870 meq kg^{-1} . The resulting capacity of the exchange site $\equiv X^-$ of the 1-pK DL/IE model was equal to 705 meq kg^{-1} in agreement with the CEC suggested by Bradbury and Baeyens (2011) ($787 \pm 48 \text{ meq kg}^{-1}$) and the exchangeable interlayer cations site ($\equiv X$) for the model proposed by Montavon et al. (2006) (640 meq kg^{-1}). For the content and type clay mineral in the Hanford sediment (precise data not available), we assumed that only illite was present with a capacity of exchange site $\equiv X^-$ equal to the measured CEC as proposed by Zachara et al. (2002). These authors performed sorption experiments with different ranges of particle size ($63 \mu\text{m}$ and $125\text{--}250 \mu\text{m}$) to demonstrate that the fraction of high affinity sites was independent of size fraction and mineralogical composition. They noted that the concentration of high-affinity sites was very low, making it difficult to identify their location. The edge site density ($\equiv \text{SOH}$) used in modelling was calculated from the fine fraction of sediment ($< 63 \mu\text{m}$), which was 9.2% (i.e. $2.5 \cdot 10^{-4} \text{ sites nm}^{-2}$). Our

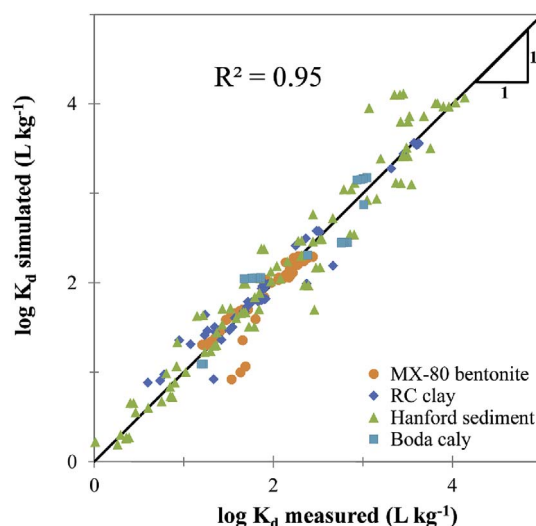


Fig. 6. Relationship between measured and simulated distribution coefficients (K_d) using the 1-pK DL/IE model for the different simple clay materials.

modelling results for Hanford sediments confirmed the dependence of the caesium sorption (K_d) on Cs and competing cation (Na^+ , K^+ , and Ca^{2+}) concentration.

Concerning the Boda clay sample (Breitner et al., 2014) (Marques Fernandes et al., 2015), measured a CEC of 113 meq kg^{-1} . This value is consistent with the measured illite fraction of 50% (considering the reference CEC value of 225 meq kg^{-1} for illite).

The experimental data were successfully predicted with the 1-pK DL/IE model according to the global $\text{RMSD} = 0.21 \text{ L kg}^{-1}$ and $\text{R}_{\text{adj}}^2 = 0.90$. The $\log K_d$ values simulated are highly correlated (95%) to the $\log K_d$ values measured for the studied simple clay materials (Fig. 6).

Table 8 summarizes the RMSD and R_{adj}^2 index calculated for each material. These results show the good performance of the 1-pK DL/IE model to predict Cs sorption on natural simple clayey materials when complex natural solutions are used (i.e. presence of several competitive cations). Cs sorption isotherms for Rojo Carbonero clay, MX-80 bentonite, Boda claystone and Hanford sediment are supplied in the Appendix (Fig.s A.7 to A.10).

For the RC clay, the results obtained with the 1-pK DL/IE model are a little better than those obtained with the three-site cation exchange model proposed by Missana et al. (2014b) ($\text{RMSD} = 0.18 \text{ L kg}^{-1}$ and $\text{R}_{\text{adj}}^2 = 0.70$). Also, for the Hanford sediment a similar goodness of fit is obtained for the two-cation exchange model proposed by Zachara et al. (2002) (data not shown, $\text{RMSD} = 0.22 \text{ L kg}^{-1}$ and $\text{R}_{\text{adj}}^2 = 0.44$). In the case of Boda clay, the modelling results show that the 1-pK DL/IE model yields a better estimation for Cs sorption than the GCS model (Bradbury and Baeyens, 2000), in terms of accuracy ($\text{RMSD} = 0.64 \text{ L kg}^{-1}$).

Table 8

Root Mean Squart Deviation (RMSD) and adjusted determination coefficient (R_{adj}^2) indices calculated for the 1-pK DL/IE model simulations for simple clay materials. n stands for the number of observations.

Clay material	RMSD	R_{adj}^2	n
Rojo Carbonero clay	0.18	0.78	48
MX-80 montmorillonite	0.13	0.88	72
Hanford sediment	0.21	0.87	87
Boda clay	0.40	0.52	18
Mean	0.21	0.90	–

Table 9
Parameters used for the simulation of sorption on natural mixed-clay materials.

Clay materials	Conditions	Illite	Mont.	I/S Illite	Mont.	kaolinite	CEC measured (meq Kg ⁻¹)	CEC calculated (meq Kg ⁻¹)	CEC meas./CEC calc. (%)	
FEBEX clay	Upper limit for illite	–	–	15%	78%	–	1020.0	712.4	70%	
San Juan clay	Mean value	40%	10%	–	–	12%	–	179.4	–	
Opalinus Clay	Mean value	17%	–	30%	–	21%	183.0	110.0	60%	
Boom clay	Lower limit in clay	20%	–	–	–	–	240.0	45.0	19%	
	Upper limit in clay	45%	–	–	–	–	–	101.3	42%	
	Mean value	30%	–	–	–	–	–	67.5	28%	
	Best fit	20%	–	–	20%	10%	–	221.0	92%	
Callovo–Oxfordian claystone	EST27337	Mean value	16.9%	9%	26.2%	15.5%	–	310.1	–	
	EST26480	Lower limit in clay	14%	–	8.1%	9.9%	–	180.1	135.9	75%
		Upper limit in clay	29%	–	14.9%	18.2%	–	–	257.1	143%
		Mean value	21.5%	–	11.5%	14.1%	–	–	196.9	109%
	EST27861-AB	Lower limit in clay	5%	–	1.8%	2.2%	–	84.7	34.4	41%
		Upper limit in clay	11%	–	4.5%	5.5%	–	–	82.7	98%
	EST27861-B	Lower limit in clay	7%	–	5.4%	6.6%	–	132.9	85.3	64%
		Upper limit in clay	14%	–	7.2%	8.8%	–	–	124.3	93%
	EST27862	Mean I/S value	–	–	0.7%	0.8%	–	14.4	8.5	59%
		Mean I/S value + 1.5% of illite	1.5%	–	0.7%	0.8%	–	–	11.9	83%

4.3. Cs sorption model evaluation for mixed-clays natural materials

Cs sorption was simulated for five clay materials in “prediction mode” by considering only illite as the main reactive clay or using a component additivity approach (CA) to represent the different clay minerals (illite, montmorillonite and kaolinite). Again, the 1-pK DL/IE model was used with the parameters obtained previously for each clay mineral (Table 6). In all simulations, only the clay mineral fractions and pore water compositions were used as input parameters (Tables 4 and 5). The content and the type of clay mineral for each mixed-clay material are shown in Table 9.

4.3.1. FEBEX clay

Fig. 7 shows that Cs sorption isotherms for Na, Ca and K-FEBEX clay were satisfactorily simulated with the 1-pK DL/IE model using the CA approach considering 93% of montmorillonite – illite mixed layers with 15% of interstratified illite and 78% of montmorillonite (global RMSD of 0.18 L kg⁻¹ and R_{adj}² index of 0.89, calculated from 12 sorption curves and 201 measured points). Insignificant differences were calculated between the global RMSD for the 3-site IE model proposed by Missana et al. (2014a) ($\approx 10\%$).

In the case of Na-FEBEX clay at I = 0.001 mol L⁻¹, to obtain a good agreement with experimental data, we followed Missana et al. (2014a) and assumed that the concentration of exchange site ($\equiv X^-$) was reduced by 30% considering that illite affected only the FES (RMSD = 0.18 L kg⁻¹). For the modelling of Cs sorption on Na, Ca and K-FEBEX as function of pH (Fig. A.11), a good fit was also obtained (RMSD = 0.19 L kg⁻¹).

The K_d values predicted by the model are slightly overestimated for Na-, Ca- and K-FEBEX clay at 0.01 mol L⁻¹, 0.3 mol L⁻¹ (only for lower Cs equilibrium concentrations) and 0.1 mol L⁻¹ (only for Cs equilibrium concentrations between 10⁻⁷ and 10⁻⁵ mol L⁻¹) (Fig. 7). Similar results were observed in pH-edge simulations (Fig. A.11).

For the Na-FEBEX clay, with I = 0.01 mol L⁻¹, at low Cs concentration, sorption mostly occurs onto illite, especially on FES (82%, Fig. 8, dotted red line). At higher Cs loading, sorption on montmorillonite exchange sites becomes dominant (solid blue line). At intermediate Cs concentration, sorption is nearly equivalent between illite and montmorillonite. The contribution of montmorillonite FES is always very low and can be neglected. Although the illite fraction in FEBEX clay does not exceed 15%, it has a very important contribution to Cs sorption, particularly at low Cs concentration where sorption on FES dominates (Brouwer et al., 1983; Eberl, 1980; Francis and Brinkley,

1976; Jackson, 1963; Maes and Cremers, 1986; Poinssot et al., 1999; Rich and Black, 1964; Sawhney, 1972; Zachara et al., 2002). It also has a critical role in the non-linear character of the Cs sorption (Missana et al., 2014a, 2014b).

The model reproduces the main features of the experimental data: (i) Cs sorption increases by decreasing the ionic strength of the electrolyte from 0.1 to 0.001 mol L⁻¹, (ii) Cs sorption is non-linear resulting from the existence of two different types of sorption site, as observed by different authors (Eliason, 1966; Missana et al., 2004; Staunton and Roubaud, 1997; Wahlberg and Fishman, 1962). Missana et al. (2014a) explain this behavior by the existence of interstratified illite-montmorillonite mixed-layers (with 10–15% of illite layers).

4.3.2. San Juan clay

Interestingly, the natural San Juan clay material contains a mixture of the three “reference” clay minerals: illite (30–50%), kaolinite (10–15%) and montmorillonite (5–10%) (Missana et al., 2014b). Missana et al. (2014b) have simulated Cs sorption using the CA approach with multi-sites cations exchange models assuming contributions from illite, kaolinite and montmorillonite of 40%, 12% and 10%, respectively.

Cs sorption isotherms were obtained in different conditions: (case A) several simple electrolyte solutions (0.5 mol L⁻¹ NaCl, with addition of 0.02 mol L⁻¹ KCl and 0.02 mol L⁻¹ NH₄Cl) and (case B) the Natural Saline Water (NSW, Table 5). The curves obtained using the CA approach with the 1-pK DL/IE model for illite, montmorillonite and kaolinite (Table 6) are superimposed to the experimental points for all conditions (Fig. 9). A RMSD value of 0.10 L kg⁻¹ was obtained (calculated on all the modeled data including those not shown here), vs. 0.19 L kg⁻¹ for the model of Missana et al. (2014b).

The relative contribution of the different sorption sites to Cs sorption, for the experiment with NSW is presented in Fig. A.12a showing that Cs sorption is dominated by illite, over the whole range of Cs loading. The contribution of kaolinite and montmorillonite FES can be neglected (confirming the hypothesis of Missana et al., 2014b), and montmorillonite (exchange sites) only contributes significantly at high Cs concentration.

The underestimation of the K_d value (1.53 L kg⁻¹) at high Cs equilibrium concentration ($\approx [Cs]_{eq} = 2 \cdot 10^{-2}$ mol L⁻¹) after the saturation of exchange sites of illite and montmorillonite, can be due to the existence of a low amount of another clay mineral which was not taken into account. In Fig. A.12b, the sorption curves are plotted for three different clay mineral fractions in SJ clay: a minimum (30% illite,

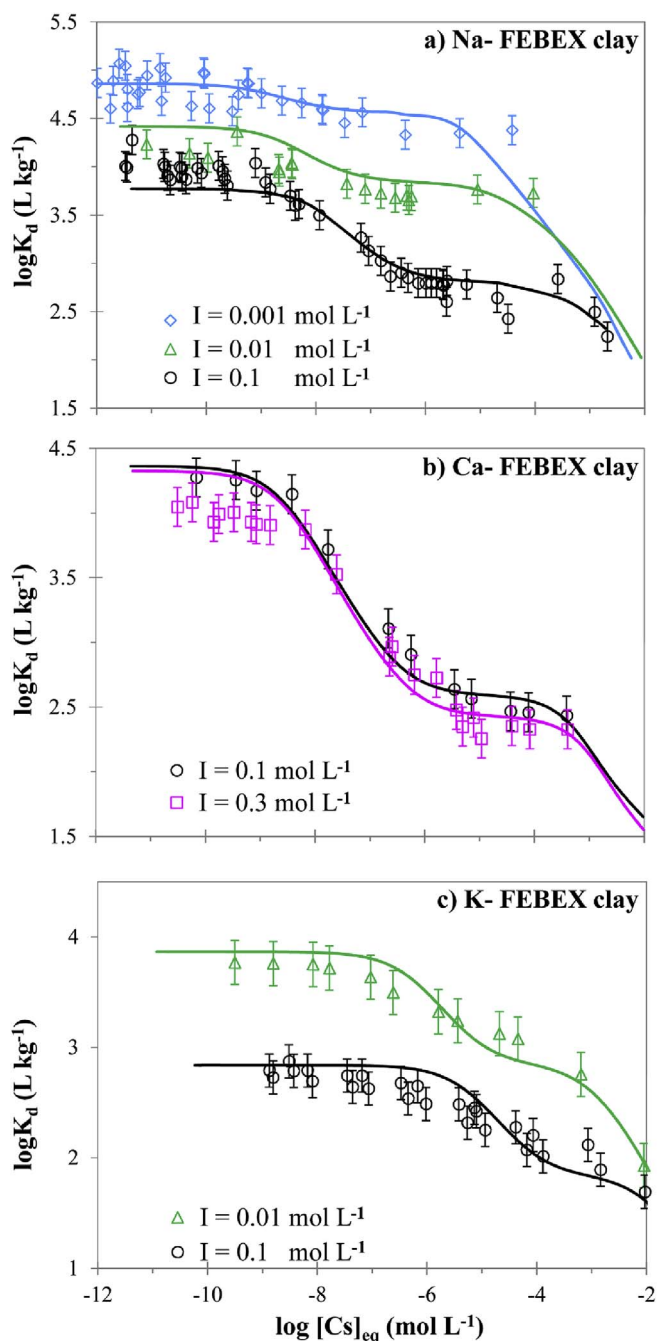


Fig. 7. Cs sorption isotherms measured for (a) Na-, (b) Ca- and (c) K-FEBEX clay at pH 6.5 and at different ionic strengths (Missana et al., 2014a). The continuous lines represent results of the 1-pK DL/IE model using the component additivity approach for illite-montmorillonite interstratified mixed layers (78% montmorillonite and 15% illite).

5% montmorillonite and 10% kaolinite), medium (40% illite, 10% montmorillonite and 12% kaolinite) and maximum value (50% illite, 20% montmorillonite and 15% kaolinite). These simulations show that the uncertainty on the clay mineral fraction results in envelope curves bracketing the experimental error. The average clay minerals content proposed by Missana et al. (2014b) results in the best fit (solid curve).

4.3.3. Callovo-Oxfordian samples (COx)

Cs sorption data for five samples of Callovo-Oxfordian claystone from Chen et al. (2014) and Savoye et al. (2012) are considered here (Table 6). These samples contain pure and interstratified illite and montmorillonite. The sorption isotherms were obtained in synthetic

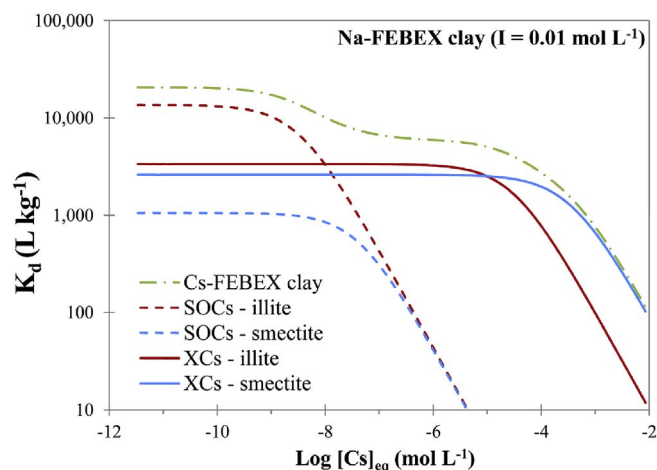


Fig. 8. Distribution of adsorbed Cs between frayed-edge sites (FES) and planar sites of illite-montmorillonite mixed layers (Na-FEBEX clay at pH 6.5 and I = 0.01 M).

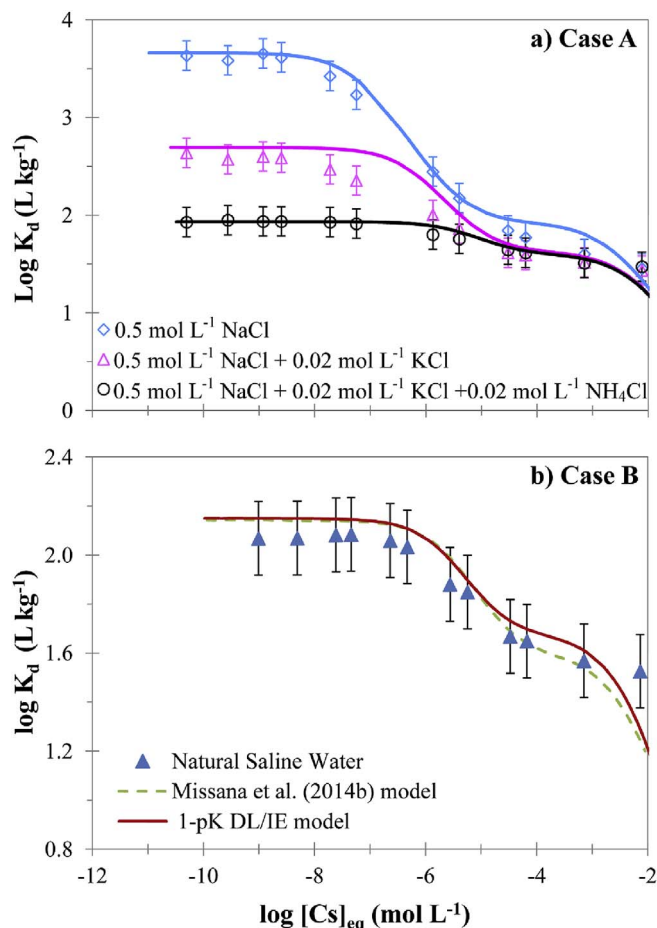


Fig. 9. Cs sorption isotherms for San Juan clay measured (a) at pH 7 and in different physicochemical conditions (case A) and (b) in natural saline water (case B). Experimental data are from Missana et al. (2014b). The continuous and dotted lines represent results of the modelling performed with our 1-pK DL/IE model and with the cation exchange model of Missana et al. (2014b), respectively.

pore waters (SPW) and in a reference pore water (RPW) (Table 5) containing the following cations: Na⁺, Ca²⁺, Mg²⁺, and K⁺ (and also Sr²⁺ in SPW-1).

The mineral fractions used in the calculations correspond to the lower and upper limit, and to the mean values proposed by Chen et al. (2014) (Table 9). We considered also that the contribution of the

$\equiv \text{SO}^{-0.5}$ site exclusively from the pure illite (as confirmed by the previous results). The experiment results are successfully simulated with 1-pK DL/IE model with the different mineralogical compositions (Fig. A.13): Cs sorption is dominated by illite over the whole Cs concentration range and the contribution of montmorillonite (exchange sites) is significant only at high Cs loading. Results obtained with sample EST27861-B show that when the FES from the I/S illite fraction are considered (solid lines), Cs sorption increases by about 10% (Fig. A.13B). The EST27862 sample was modeled alternatively with interstratified illite and montmorillonite only (dotted red line strongly underestimating measured data), and by adding 1.5% of illite (solid line) which greatly improved the fit (Fig. A.13D). Note that the model of Chen et al. (2014) underestimates Cs sorption at medium to high Cs concentration (Fig. A.13A & D).

Cs sorption on another COx sample (EST27337) was also modeled by Savoye et al. (2012). The total clay fraction is 32–65% of clay minerals (Gaucher (1998) with 62% of illite/smectite mixed-layer mineral with 65% of illite, 25% of montmorillonite, and 10% of vermiculite), smectite (9%), illite (26%), kaolinite (2%), and chlorite (1%) Claret et al. (2004). We assumed that this sample is composed by 65% of clay minerals and we used the mineralogy proposed by Claret et al. (2004) (Table 9). Fig. A.14 shows Cs sorption isotherm onto EST27337 sample in RPW (Table 5), with red lines representing the results the 1-pK DL/IE model using CA approach considering clay minerals fraction given in Table 6, and the green line those of the model proposed by Savoye et al. (2012). These authors modeled Cs sorption using multi-site cation exchange model considering four sorption sites for illite and three sites for montmorillonite (for a total of 7 sites). The two models show the same goodness fit of the experimental curves with $\text{RMSD} = 0.4 \text{ L kg}^{-1}$, but the 1-pK DL/IE model required much less sorption sites and fitting parameters than the one used by Savoye et al. (2012).

4.3.4. Opalinus clay

The Opalinus clay (OPA) sample used in the calculations, referenced as SLA-938, contains 30% of illite/smectite mixed layer, 17% of pure illite and 21% of kaolinite, with a CEC value of 183 meq kg^{-1} (Marques Fernandes et al., 2015).

The modelling results are obtained considering that I/S mixed layers (30%) are exclusively constituted by illite (for a total fraction of illite of 47%, as proposed by Marques Fernandes et al. (2015)) using the 1-pK DL/IE and the GCS model (green and red lines, respectively) (Fig. A.15). In addition, our model also integrates the kaolinite fraction. The Cs sorption data are very well reproduced by both models ($\text{RMSD} = 0.23 \text{ L kg}^{-1}$). The results obtained with our model show that the contribution of kaolinite is negligible.

4.3.5. Boom clay

Mineralogical studies of the Boom clay Formation show a variable clay mineral composition with a total fraction in the interval between 30 and 60% and the main components as follows: illite (10–45%), illite/smectite mixed layer (10–30%), kaolinite (5–20%) (Aertsens et al., 2004; De-Craen et al., 2004).

The Cs adsorption isotherm on Boom clay in equilibrium with the Reference Boom Clay Water (RBCW; Table 5) was first modeled using the 1-pK DL/IE and the GCS model considering only illite (20, 30 and 45%), as tested by Maes et al. (2008). The best agreement with experimental data is obtained using 30% illite with both models ($\text{RMSD} = 0.32 \text{ L kg}^{-1}$ for the 1-pK DL/IE and 0.51 L kg^{-1} for the GCS model) (Fig. 10). With this simplified mineral composition, the GCS model and the 1-pK DL/IE model both underestimate measured K_d values for Cs equilibrium concentrations higher than $10^{-4} \text{ mol L}^{-1}$.

To obtain a better fit, we have added a montmorillonite and kaolinite fraction: 20% illite, 20% montmorillonite and 10% kaolinite (Fig. 10, dotted red line). This change significantly improved the sorption at high Cs concentrations and the RMSD value (0.11 L kg^{-1}) (Cs sorption decomposition is shown in Fig. A.16). Note that the

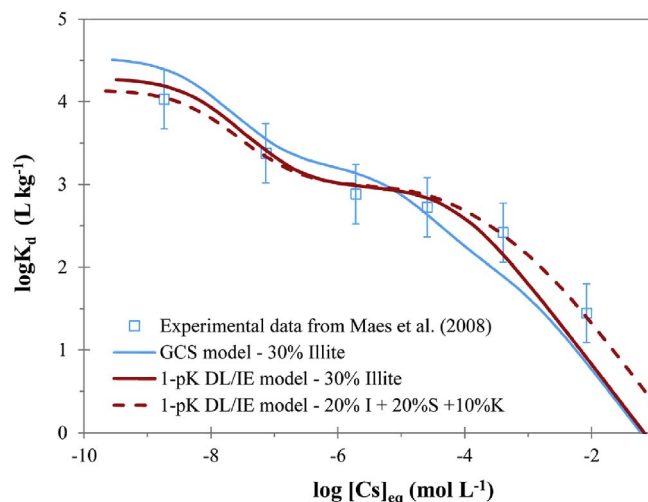


Fig. 10. Cs sorption isotherms for Boom clay in RBC Water (see Table 6). Experimental data are from Maes et al. (2008). The continuous blue and red lines represent results of the modelling performed with the GCS model proposed by Maes et al. (2008) and the 1-pK DL/IE model by considering 30% of illite, respectively. The dotted red line represents the best fit obtained with our model using 20% illite, 20% smectite and 10% kaolinite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

contribution of kaolinite is less than 1% of Cs total sorption.

5. Conclusion

We propose a new model for Cs sorption that combines a one-site 1-pK double layer model and a one-site ion exchange model to account for varying levels of Cs concentrations (10^{-9} – $10^{-4} \text{ mol L}^{-1}$) and physicochemical conditions (pH, ionic strength, and competing ions). A single set of parameters was adjusted for each clay mineral: illite, montmorillonite, and kaolinite. Since only 2 types of sorption site are considered and the same formalism is used for the three clay minerals, this approach reduces the number of parameters compared to existing multi-site model for these clay minerals. The application of this parsimonious model to simple clayey material, even with complex natural pore-water compositions, shows the robustness of our model. The use of the component additivity approach for complex mixed-clay materials, considering the clay mineral fractions, was also successful without any adjustment of parameters.

The simulations performed with the 1-pK DL/IE model on clays-tones show that the uncertainty concerning the clay mineral fraction can be taken into account and results in envelope curves bracketing the experimental measurement error. To this regard, our model outperforms the “generalized Cs sorption” (GCS) model (Bradbury and Baeyens, 2000) which is largely used in the context of radioactive waste management. The GCS model is quite reliable with clay materials that are comparatively rich in illite (e.g. Opalinus clay and Palfris marl) but underestimates Cs sorption when the illite-montmorillonite mixed layer content is comparable or higher than illite (e.g. Boom clay) as also note by Chen et al. (2014). Our model, as well as the other models from the literature, tends to underestimate the K_d values for very high Cs concentrations [10^{-4} to 10^{-3} mol/L].

Another interesting result is that the effect of the electrostatic component in Cs sorption on the clay minerals and natural clayey materials can be neglected. In a next step, the 1-pK DL/IE model will be used to simulate the behavior of Cs in natural soils.

Acknowledgements

The authors are indebted to the Institute for Radiological Protection and Nuclear Safety (IRSN) and to the Provence-Alpes-Côte d’Azur

(PACA) regional authorities for the PhD grant provided to M.A. Cherif.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2017.10.017>.

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