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Brice Siroux

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1.2 Objectifs de projet de thèse

Le projet de thèse présenté ici s'inscrit au sein du système 6 du projet. Ce système a pour objectif l'étude et la modélisation du comportement d'adsorption et de migration des radionucléides relâchés suite à un accident nucléaire dans les différentes matrices de l'environnement et notamment dans les sols agricoles autour des principales installations nucléaires françaises. Il permet donc d'apporter un soutien scientifique aux différents systèmes sur les questions du devenir de ces radionucléides dans l'environnement afin d'ajuster les stratégies de décontamination et de remédiation. Il est piloté par le département de physico-chimie (DPC) de la direction de l'énergie nucléaire (DEN) du CEA Saclay dans le Laboratoire de Mesure et Modélisation de la Migration des Radionucléides (L3MR) et le Laboratoire de développement Analytique Nucléaire, Isotopique et Élémentaires (LANIE).

L'étude menée dans le cadre de cette thèse porte toute particulièrement sur les interactions entre le césium et le strontium avec les argiles des sols et la matière organique naturelle. Elle intègre donc parfaitement les thématiques du système. **Elle a pour objectifs de mieux appréhender le comportement du césium et du strontium dans l'environnement afin d'en définir l'état chimique et de mettre en place un outil capable de prédire l'état d'adsorption de ces deux éléments dans un sol agricole français.** Le manuscrit porte donc principalement sur l'étude du comportement d'adsorption des isotopes 134 , 135 , ^{137}Cs et ^{90}Sr , principaux produits de fission de ^{235}U ayant un temps de demi-vie long (environ 30 ans pour le ^{137}Cs et le ^{90}Sr) dans les sols (voir Figure I. 3).

De plus, à l'échelle moléculaire, les molécules humiques tendent à se lier étroitement aux argiles. On parle alors de complexes argilo-humiques.

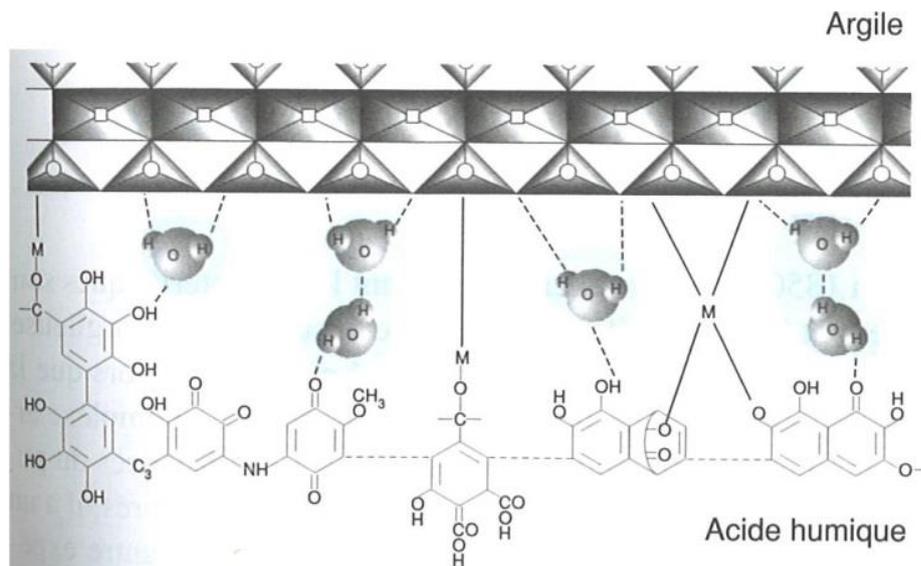


Figure I. 8 Niveaux d'organisation structurale du sol, des macroagrégats aux molécules (GOBAT *et al.*, 2010).

Le calcium et le fer assurent la liaison entre ces deux éléments. Cette liaison confère au sol de nouvelles propriétés (GOBAT *et al.*, 2010) :

- Aération de la structure du sol par floculation des colloïdes argileux et humiques ;
- La liaison entre les molécules humiques et les argiles ralentissent la minéralisation de la matière organique ;
- Elle permet également de limiter la dispersion de l'argile et donc d'éviter le colmatage et la compaction du sol ;
- L'ajout de matière organique au sol augmente sa capacité de rétention des bioéléments.

BELLENGER & STAUNTON (2008) ont montré que la MON semble avoir une affinité plus importante avec les illites qu'avec les montmorillonites ou les kaolinites.

Ainsi, du fait de sa réactivité avec les cations métalliques, elle peut également modifier directement la réactivité de surface des minéraux. Elle a la capacité de favoriser la fixation des ions métalliques sur les surfaces (REILLER & BUCKAU, 2012, et références incluses), mais elle peut également empêcher ces cations, notamment Cs^+ , de se fixer sur les minéraux en

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.

Yong R.N., Nakano M., & Pusch R. (2012) *Environmental Soil Properties and Behaviour*. CRC Press.

CHAPITRE II. ADSORPTION OF STRONTIUM AND CESIUM ONTO AN NA- MX80 BENTONITE: EXPERIMENTS AND BUILDING OF A COHERENT THERMODYNAMIC MODELLING

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Concernant le Sr, une étude cinétique de l'adsorption à $I = 0.1$ M (NaCl) et $\text{pH} = 7$ a montré que l'équilibre est atteint dès les premières minutes de contact. Deux isothermes d'adsorption de Sr en fonction du pH ont été réalisées à $I = 0.1$ et 0.05 M. Ces isothermes montrent que, comme attendu, l'adsorption augmente lorsque la force ionique baisse. A 0.1 M, l'adsorption augmente jusqu'à $\text{pH} 4$ puis atteint un plateau avant de continuer à augmenter à partir de $\text{pH} 7$. A 0.05 M, l'adsorption augmente graduellement jusqu'à $\text{pH} 7$ puis semble atteindre un plateau. Une dernière isotherme, en concentration cette fois-ci, a été menée à $I = 0.15$ M et $\text{pH} = 6.6$, dans laquelle on observe une adsorption constante sur une large gamme de concentrations en Sr à l'équilibre, suivi d'une chute de l'adsorption aux concentrations les plus élevées. Cette chute est une conséquence logique de la saturation de l'échangeur par l'ion Sr^{2+} . Toutes ces isothermes ont été modélisées par ajustement simultané des coefficients de sélectivités pour l'échange $2\text{Na}^+/\text{Sr}^{2+}$, afin d'obtenir un jeu de données cohérentes à différentes forces ioniques. Les coefficients, ainsi obtenus, permettent donc une bonne représentation de ces isothermes d'adsorption.

Concernant l'ion Cs^+ , seule une isotherme d'adsorption en fonction du pH à $I = 0.1$ M a été effectuée et modélisée selon le formalisme des échangeurs d'ions multi-sites afin de déterminer les différents coefficients de sélectivité Na^+/Cs^+ . L'adsorption de Cs^+ augmente légèrement aux pH les plus acides avant de rester relativement constante. Les coefficients obtenus permettent de bien rendre compte ce comportement d'adsorption.

Cette étude a donc permis de réaliser une base de données des comportements d'adsorption de Sr^{2+} et de Cs^+ vis-à-vis de Na^+ et du proton sur une smectite purifiée sodique, selon le formalisme des échangeurs d'ions multi-sites. Cette étude pourra donc servir de base pour mettre en place une base de données plus vaste du comportement d'adsorption des cations majeurs environnementaux et des contaminants tels que le Cs^+ et le Sr^{2+} vis-à-vis des différents minéraux argileux (kaolinite, illite, chlorite, etc.)

2 Abstract

The 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 finely representing the overall variations of adsorption behaviours. For a wider applicability in soils and sediments, it appears necessary to build

(COMAR *et al.*, 1957). Concerning ^{137}Cs , it is considered as a dangerous element because its radioactive decay includes ^{137}Ba and its gamma radiation.

Strontium and cesium 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 cesium, due to the presence of the low concentration high affinity frayed edge sites (SAWHNEY, 1972 ; BROUWER *et al.*, 1983 ; DZENE *et al.*, 2015), montmorillonite could also play an important role in the adsorption of Sr and Cs due to its high cationic exchange capacity (CEC).

The study of the adsorption behaviour of Sr onto pure Na-montmorillonite has been mainly explored on smectite-rich soils (GALAMBOŠ *et al.*, 2010 ; KASAR *et al.*, 2014) or unpurified bentonite (WANG *et al.*, 2004) but studies on purified smectite remain rare in the literature. MISSANA & GARCÍA-GUTIÉRREZ (2007) have worked on a purified Na-FEBEX bentonite, but FEBEX bentonite contains illite-smectite interstratified layers that provided 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 on 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 on pure Na-montmorillonite. As for Sr, most of these works deal with smectite-rich soils (VEJSADA *et al.*, 2005), unpurified (MONTAVON *et al.*, 2006 ; GALAMBOŠ *et al.*, 2010 ; 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 $1 \text{ mol.kg}_w^{-1} \text{ NaCl}$. 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 $\epsilon(\text{Cs}^+, \text{Cl}^-)$ is not available, and in view of the particular $\log \gamma_{\pm, \text{CsCl}}$ vs. m_{CsCl} variation (HAMER & WU, 1972), a complete refitting using the specific interaction theory (CIAVATTA, 1980) would be necessary. This data can only be used as qualitative comparison. MISSANA *et al.* (2014) studied the adsorption of cesium onto a Na-FEBEX bentonite, which carries a significant part of illite-smectite interstratified (*vide ante*). The illite part from these interstratified is well known to show specific adsorption behaviour towards Cs^+ 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.* (2014) with results obtained on purified smectite.

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 (RAFFERTY *et al.*, 1981 ; MAHONEY & LANGMUIR, 1991 ; SHABAN & MACÁŠEK, 1998 ; DYER *et al.*, 2000 ; GUIMARÃES *et al.*, 2015), but few works used a mechanistic (or semi-mechanistic) approach. BRADBURY & BAEYENS (1999) have developed a model based on a mechanistic description of the cation adsorptions between a clay minerals and a liquid phase—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 & THOMAS (1953) formalism—with no account for the Na⁺/H⁺ exchange—, and non-electrostatic surface complexation terms. MISSANA *et al.* (2008) applied a derivative model from 2SPNE-SC/CE to study the adsorption of Sr²⁺ onto illite, smectite, and illite/smectite mixtures. This approach allows representing the global adsorption behaviour. In this model, the pH dependency is only given by the adsorption on edge sites SOH. Sorption onto Cation exchange site is not pH dependent. Conversely, adsorption of electrolyte cations only occurs on cation exchange site. The construction of this model prevents to model the saturation of an exchanger by a major cation.

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 clays (GORGEON, 1994 ; NOLIN, 1997 ; GAUCHER, 1998 ; MOTELLIER *et al.*, 2003 ; PEYNET, 2003 ; REINOSO-MASET & LY, 2014). The model does not aim to describe clay minerals in the microscopic scale (nature of adsorption 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 and is defined by its site concentration (SC_i in mmol.g⁻¹) and its corrected - of adsorbed species activities - selectivity coefficient for the exchange between cations.

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 (MOTELLIER *et al.*, 2003 ; JACQUIER *et al.*, 2004 ; REINOSO-MASET & LY, 2014 ; ROBIN *et al.*, 2015), 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 diffusion (SAVOYE *et al.*, 2012 ; LU *et al.*, 2014) or adsorption (TERTRE *et al.*, 2009) of metals on the exchanger(s).

In order to continue building the coherent database, including Sr and Cs, and in light of the low body of work 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 and initial concentration of cations. Then, the obtained isotherms will be modelled using the multi-site ion exchange modelling in order to determine the corrected selectivity coefficients for the $2Na^+/Sr^{2+}$ and Na^+/Cs^+ exchange reactions. The overall objective is to propose a set of data for describing the adsorption behaviour of Na^+ , H^+ , Sr^{2+} and Cs^+ on a pure smectite in the framework of the multi-site ion exchange modelling formalism. In the future, this set of data could serve to predict the adsorption of Sr and Cs in Na-rich soils.

3.2 Materials and methods

3.2.1 Materials

Wyoming MX80 bentonite was used as the adsorbent. It was purified to only keep the montmorillonite part and Na-conditioned following GAUCHER (1998) and PEYNET (2003) protocols. The organic matter potentially present in the material was removed using H_2O_2 , and calcite was dissolved using 0.1 M HCl solution. The montmorillonite was Na-conditioned by several washings with a 1 M NaCl solution. The reported CEC for the MX80 varies from 0.71 to 1.03 $mmol.g^{-1}$ (MEIER, 1999 ; ALONSO & LEDESMA, 2005 ; KARNLAND, 2010). This value depends upon the measurement protocol or the sample purity. The CEC

measured for this MX80 is 1.03 mmol.g⁻¹. It was measured by extracting all exchangeable cations with a KCl solution at pH around 10 (KOH). Supernatant was removed and the MX80 was washed with milli-Q water, then with ethanol. The adsorbed K⁺ were extracted with a CsCl solution, and analysed by inductive-coupled plasma by atomic emission spectroscopy (ICP-AES). This high 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 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 SrCl₂·6H₂O salt (99.995% trace metals basis, Sigma Aldrich). Stable Cs solutions were from CsCl (99.999% trace metals basis, Sigma Aldrich). ⁸⁵Sr and ¹³⁷Cs solutions were obtained from Cerca LEA. Ionic strength was fixed using NaCl (Analar Normapur, VWR).

3.2.2 Sorption experiments

3.2.2.1 Experimental protocols

All experiments were obtained by batch method. They were conducted at room temperature (22 ± 2°C) with the same 3.8 g.L⁻¹ solid/solution ratio. These experiments were performed in 10 mL polycarbonate Nalgene centrifuge tube (3138-0010, Thermo Scientific). 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 SrCl₂ for the kinetic experiment, 10⁻⁶ mol.kg_w⁻¹ for the adsorption of Sr as a function of pH, and from 10⁻² to 10⁻⁷ mol.kg_w⁻¹ for the adsorption of Sr as a function of the concentration—or cesium (10⁻⁷ mol.kg_w⁻¹) was added from the stock solution, and the suspensions were then spiked with ⁸⁵Sr or ¹³⁷Cs (≈ 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 minutes at 9.000 g and 1 mL aliquot of the supernatant was collected and activity was counted by gamma spectrometry.

A set of kinetic experiments was also prepared without spiking with the radionuclides. 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 ($\text{mL}\cdot\text{g}^{-1}$) were calculated using:

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

where C_i and C_{eq} are respectively the initial and equilibrium concentrations (kinetic experiments) or activities (pH and concentration isotherms) of either Cs or Sr, V is the total volume of solution and m is the total dry mass of solid phase.

3.2.2.2 Analytical methods

The aqueous concentrations of 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 at 407.771 nm for strontium and 589.592 nm for sodium.

Supernatant activities were determined after sampling a 1 mL aliquot 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 pH units.

3.2.3 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

As explained in the Appendices, determining of $[(X_i^-)_m - M^{m+}]$ permits calculating the experimental partition coefficient using the following expression:

$$R_D = \frac{[M]}{[M]} = \frac{\sum_i [(X_i^-)_m - M^{m+}]}{[M]} \quad (5)$$

The methodology to study the retention of a trace element in 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).

3.3 Results and discussion

In presented results, MX80 bentonite was supposed being fully saturated by Na⁺. Despite their possible interactions in the adsorption process, other exchangeable cation (Ca²⁺ and K⁺) presents in the exchanger (cf. § 3.2.1) were neglected in this study. Their trace level concentrations were supposed to be low enough to not interfere in experimental results. Furthermore the possible dissolution of smectite was not considered either. It is known that at acidic (< 4) or highly alkaline pH (> 10) the dissolution of clay minerals is important (BRADBURY & BAEYENS, 1997 ; AMRAM & GANOR, 2005). The dissolution cans lead to a release of aluminium, silicon iron and other structural cations as potassium and magnesium. Thus released cations could compete with the adsorption of Sr²⁺ and Cs⁺ in MX80 and lower modelling nay misrepresent experimental results at highly acidic or alkaline pH.

3.3.1 Choice 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 homoionic sodic exchanger with Na⁺ 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 SC₁ with

a concentration of $0.422 \text{ mmol.g}^{-1}$; PEYNET (2003) reported two major sites ($\Sigma \text{SC}_i = 0.605 \text{ mmol.g}^{-1}$); NOLIN (1997) proposed three sites ($\Sigma \text{SC}_i = 0.886 \text{ mmol.g}^{-1}$). The saturation study from NOLIN (1997) is the only one that reached a total site concentration close to the typical montmorillonite CEC (BRADBURY & BAEYENS, 1997 ; STAUNTON & ROUBAUD, 1997). The montmorillonite used by GORGEON (1994) was not completely saturated with Na^+ and carried 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 sodium and distort the Na saturation curve. Contrary 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. It is worthy to notice that the saturation curve of NOLIN (1997) has been used by others authors (TERTRE *et al.*, 2009 ; TERTRE *et al.*, 2013 ; ROBIN *et al.*, 2015 ; SAVOYE *et al.*, 2015).

The saturation curve obtained by NOLIN (1997) is presented in Figure II. 1. The adsorbed concentration of Na^+ is quickly increasing with pH until pH 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 are representatives of the different fixation sites of the exchanger. As previously explicated, 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.

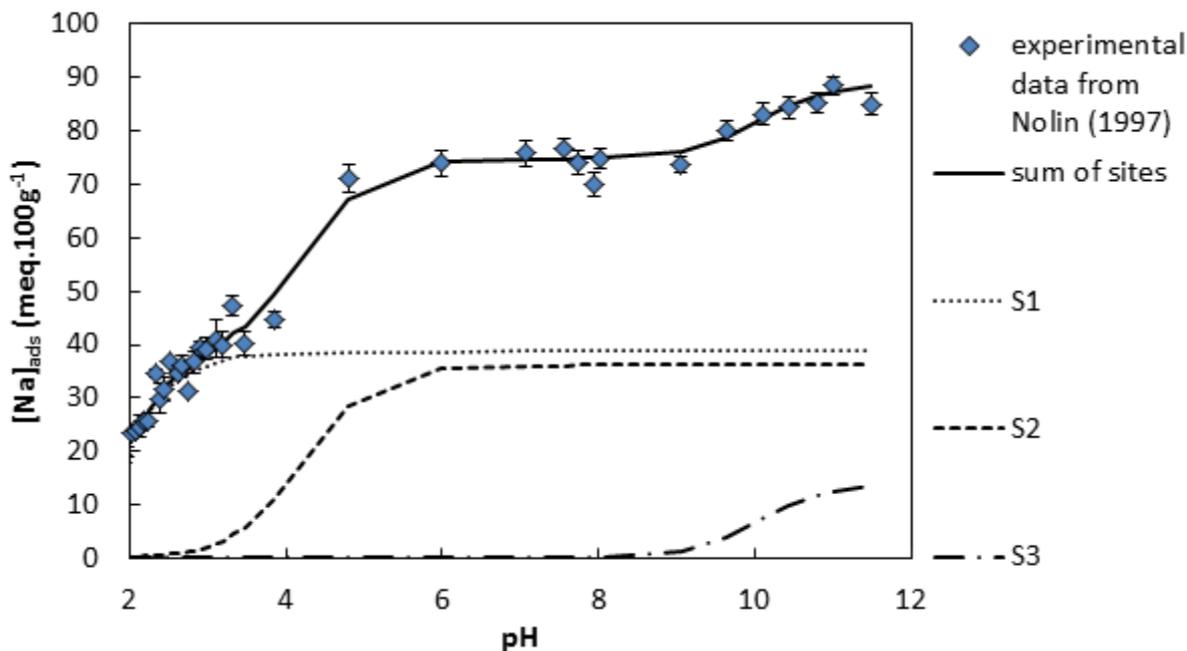


Figure II. 1. Saturation of a montmorillonite with Na^+ vs. pH at constant $I = 0.02 \text{ M}$ (NaClO_4) and solid/liquid ratio (S/L) of 8 g.L^{-1} from NOLIN (1997).

NOLIN (1997) calculated the corrected selectivity coefficients for the Na^+/H^+ exchange for his smectite, but the reported uncertainties were unexpectedly high ($> 40\%$) compared to the correlation with the saturation curve. As the fitting protocol of $\log_{10} K_{\text{Na}^+/\text{H}^+}^{*i}$ and uncertainties estimations were not given, we propose a new fitting of these data in Figure II. 1. The site concentrations from NOLIN (1997) and the obtained $\log_{10} K_{\text{Na}^+/\text{H}^+}^{*i}$ are summarized in Table II. 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 (NOLIN, 1997) vs. MX80 this study—could explain the differences. With the aim of proposing a general database for montmorillonite, the value of $0.886 \text{ mmol.g}^{-1}$ seems in good agreement with those proposed by different authors for a Wyoming montmorillonite (BRADBURY & BAEYENS, 1997 ; STAUNTON & ROUBAUD, 1997).

Table II. 1. Site concentrations and corrected selectivity coefficients for the Na⁺/H⁺ exchange onto a montmorillonite. a site concentrations taken from NOLIN (1997).

Site	SC _i (mmol.g ⁻¹)	ΣSC _i (mmol.g ⁻¹)	log ₁₀ K _{Na⁺/H⁺} ^{*i}
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

3.3.2 Strontium adsorption

Multiple facets of the adsorption of strontium onto our MX80 montmorillonite were explored in this study. The kinetics of adsorption has been examined to determine the necessary equilibrium time. The adsorption behaviour of Sr²⁺ as a function of the equilibrium pH and the Sr concentrations were studied by realizing adsorption isotherms. The role of the ionic strength was also examined. In the aim of building a coherent set of data, the adjustment of all the corrected selectivity coefficient of Sr²⁺ towards Na⁺ was made, in order to model the different adsorption isotherms as a function of the equilibrium pH and the Sr concentration.

The Sr²⁺ cation is the main specie of Sr 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. § 3.6.2)

3.3.2.1 Kinetic experiments

Figure II. 2 shows the adsorption kinetic of Sr onto the Na-MX80. The evolution of R_D measured for Sr is expressed as a function of the contact time. The equilibrium is instantly reached. The R_D value is constant all through the experiment with an average value of R_D = (192 ± 35) L.kg⁻¹.

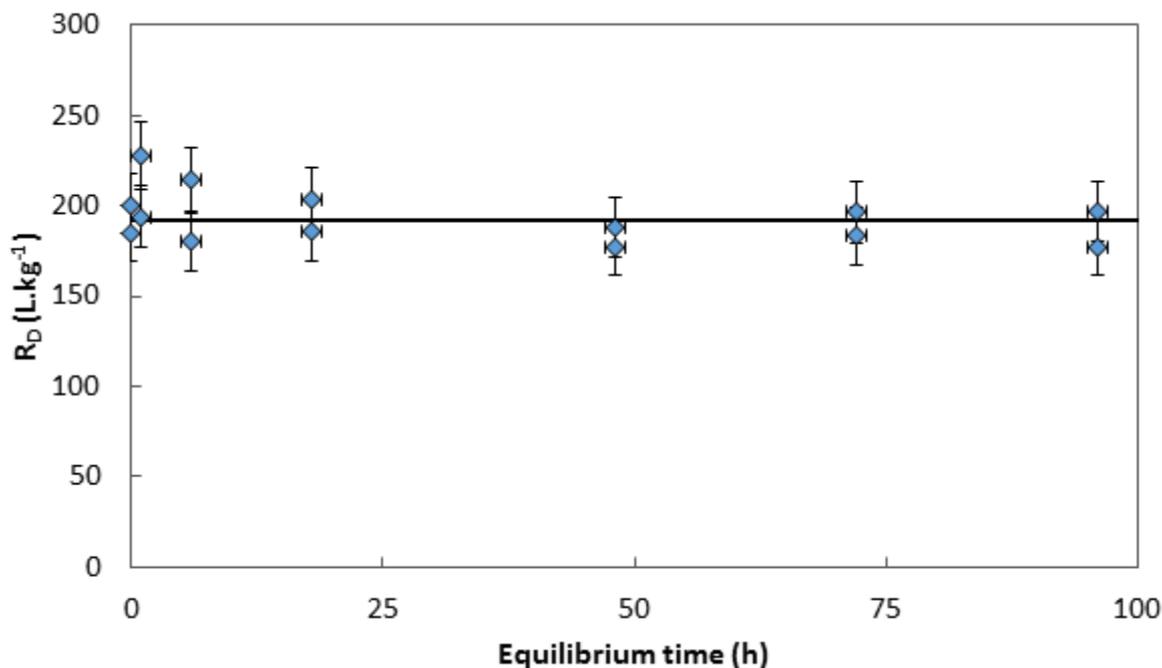


Figure II. 2. Kinetic study of the adsorption at $[Sr]_i = 1.5 \cdot 10^{-5} \text{ mol.kg}_w^{-1}$, $\text{pH} = 7$, $I = 0.1 \text{ mol.kg}_w^{-1}$ (NaCl) and $S/L = 3.8 \text{ g.L}^{-1}$ – time 0 is corresponding to the centrifugation time (30 min) without prior agitation.

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 seconds, 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 hours to be sure to achieve the equilibrium.

3.3.2.2 Sorption experiments and modelling

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

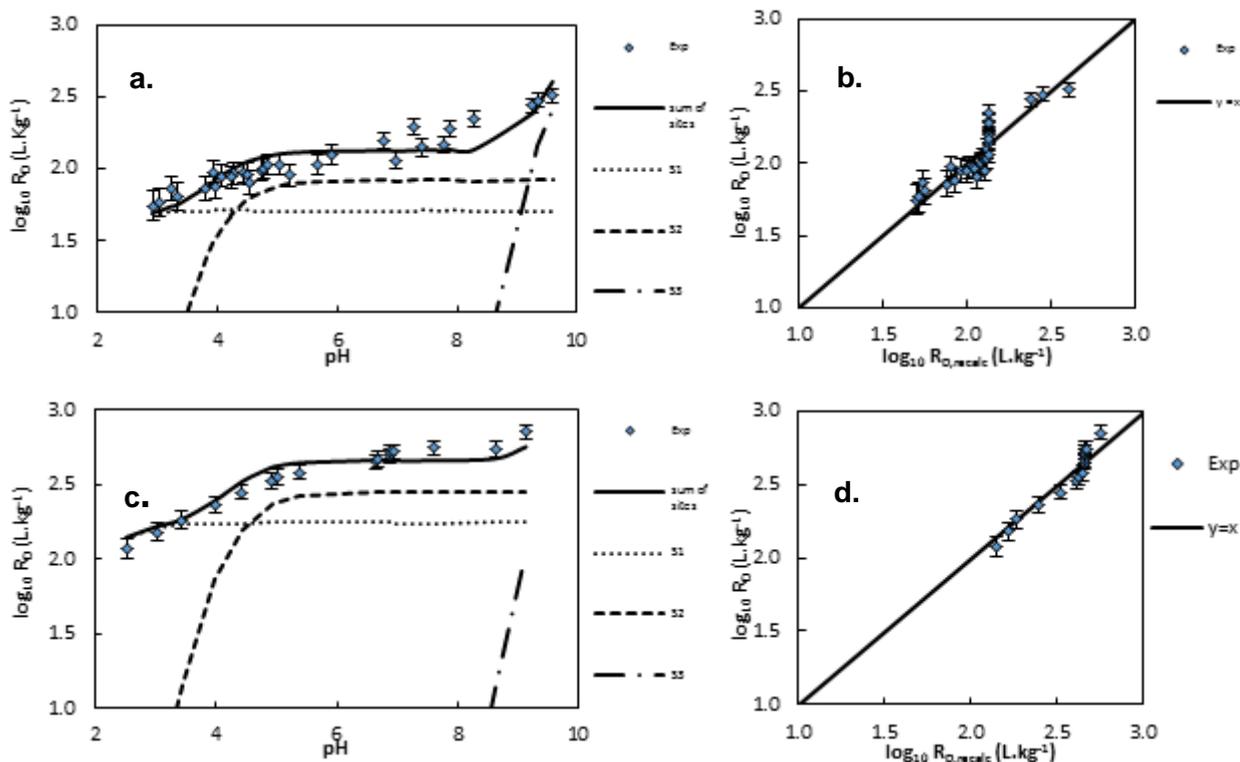


Figure II. 3. Adsorption isotherms of Sr ($[Sr]_i = 10^{-6} \text{ mol.kg}_w^{-1}$) as a function of pH and comparison of experimental results with modelling results at (a, b) $I = 0.1$ and (c, d) $I = 0.05 \text{ mol.kg}_w^{-1}$ (NaCl) and $S/L = 3.8 \text{ g.L}^{-1}$, and representation of the contribution of the different fixation sites.

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

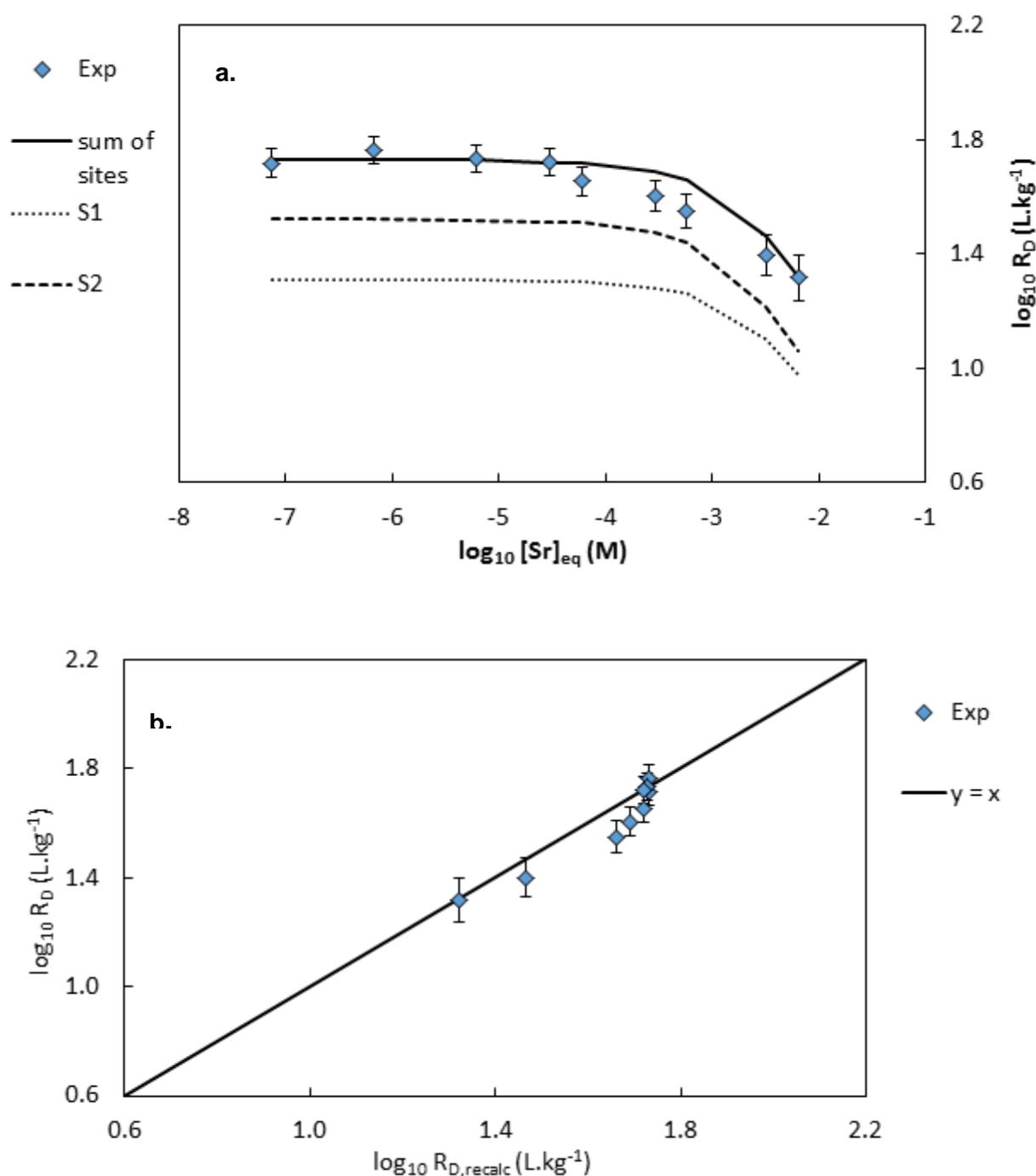


Figure II. 4. (a) Adsorption isotherm in concentration of Sr on MX80 bentonite at $I = 0.15 \text{ mol.kg}_w^{-1}$ (NaCl), $\text{pH} = 6.6$ and $S/L = 3.8 \text{ g.L}^{-1}$, and representation of the influence of the different exchange sites.*The S_3 site does not appear onto the isotherm because of its minor contribution. (b) Comparison of the experimental results with the modelling results.

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

Table II. 2. Obtained parameters of the corrected selectivity coefficients for 2Na⁺/Sr²⁺ and Na⁺/Cs⁺ exchange. Values from MISSANA & 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)	$\log_{10}K_{2\text{Na}^+/\text{Sr}^{2+}}^{*i}$	$\log_{10}K_{\text{Na}^+/\text{Cs}^+}^{*i}$
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 & GARCÍA-GUTIÉRREZ (2007)	S ₁	1.02		0.77	
	S ₂			0.80	
	S ₃			1.22	

^a Values from NOLIN (1997)

Modelling of strontium adsorption is represented in Figure II. 3 and Figure II. 4. The modelling represents satisfactorily the pH isotherms at $I = 0.1 \text{ mol.kg}_w^{-1}$ ($r^2 = 0.82$) and at $I = 0.05 \text{ mol.kg}_w^{-1}$ ($r^2 = 0.90$), and the isotherm in concentration ($r^2 = 0.86$). As the modelling strongly depends on the initial parameters used (SC_i and $K_{\text{Na}^+/\text{H}^+}^i$), modelling results cannot be improved without modifying these initial parameters. The choice of adjusting simultaneously all isotherms also constrained the modelling but enhances its applicability at different ionic strengths.

In each isotherm, by using the initial parameters previously discussed, it appears that only the first two sites would be influent to describe Sr adsorption in the pH range 2.5-9 and in the Sr concentration range (10^{-7} - $10^{-2} \text{ mol.kg}_w^{-1}$) at pH 6.6.

The obtained corrected selectivity coefficients for the 2Na⁺/Sr²⁺ can be compared with existing literature. MISSANA & GARCÍA-GUTIÉRREZ (2007) studied the adsorption of Sr onto a FEBEX bentonite at different ionic strengths. These experiments were modelled with

derivative model from BRADBURY & BAEYENS (1999). At $I = 0.1$ and $0.05 \text{ mol.kg}_w^{-1}$ MISSANA & GARCÍA-GUTIÉRREZ (2007) obtained slightly higher $\log_{10}R_D$ values compared to our study— $\log_{10}R_D (0.1 \text{ M}) = 2.16$ and $\log_{10}R_D (0.05 \text{ M}) = 2.82$ for MISSANA & GARCÍA-GUTIÉRREZ (2007) against $\log_{10}R_D (0.1 \text{ mol.kg}_w^{-1}) = 2.12$ and $\log_{10}R_D (0.05 \text{ mol.kg}_w^{-1}) = 2.66$ at pH 7 for this study. Nevertheless, they have founded a $\log_{10}K_{2\text{Na}^+/\text{Sr}^{2+}}$ at 0.66. Despite the fact that they used a different model, it is possible to compare their selectivity coefficient with those from this study. If their selectivity coefficient is transformed according to our multi-site formalism—see Appendices for details—, the corrected selectivity coefficients obtained from MISSANA & GARCÍA-GUTIÉRREZ (2007) are comparable to ours (cf. Table II. 2) - except for S_3 . As this transformation implies the site concentrations and as MISSANA & GARCÍA-GUTIÉRREZ (2007) have used a bentonite with a CEC higher than our sum of site concentrations, the obtained corrected selectivity coefficient from MISSANA & GARCÍA-GUTIÉRREZ (2007) study must be taken with caution. This transformation only serves to compare the order of magnitude.

As mentioned in the introduction, the slight difference in parameters can come from the bentonite used by MISSANA & GARCÍA-GUTIÉRREZ (2007), as the FEBEX bentonite includes a significant part of illite-smectite mixed layers and as illite and smectite have comparable but different selectivity for Sr (MISSANA *et al.*, 2004). The differences in the selectivity coefficients could also arise from the intrinsic properties of used bentonites as their specific surface area.

3.3.3 Cesium adsorption

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

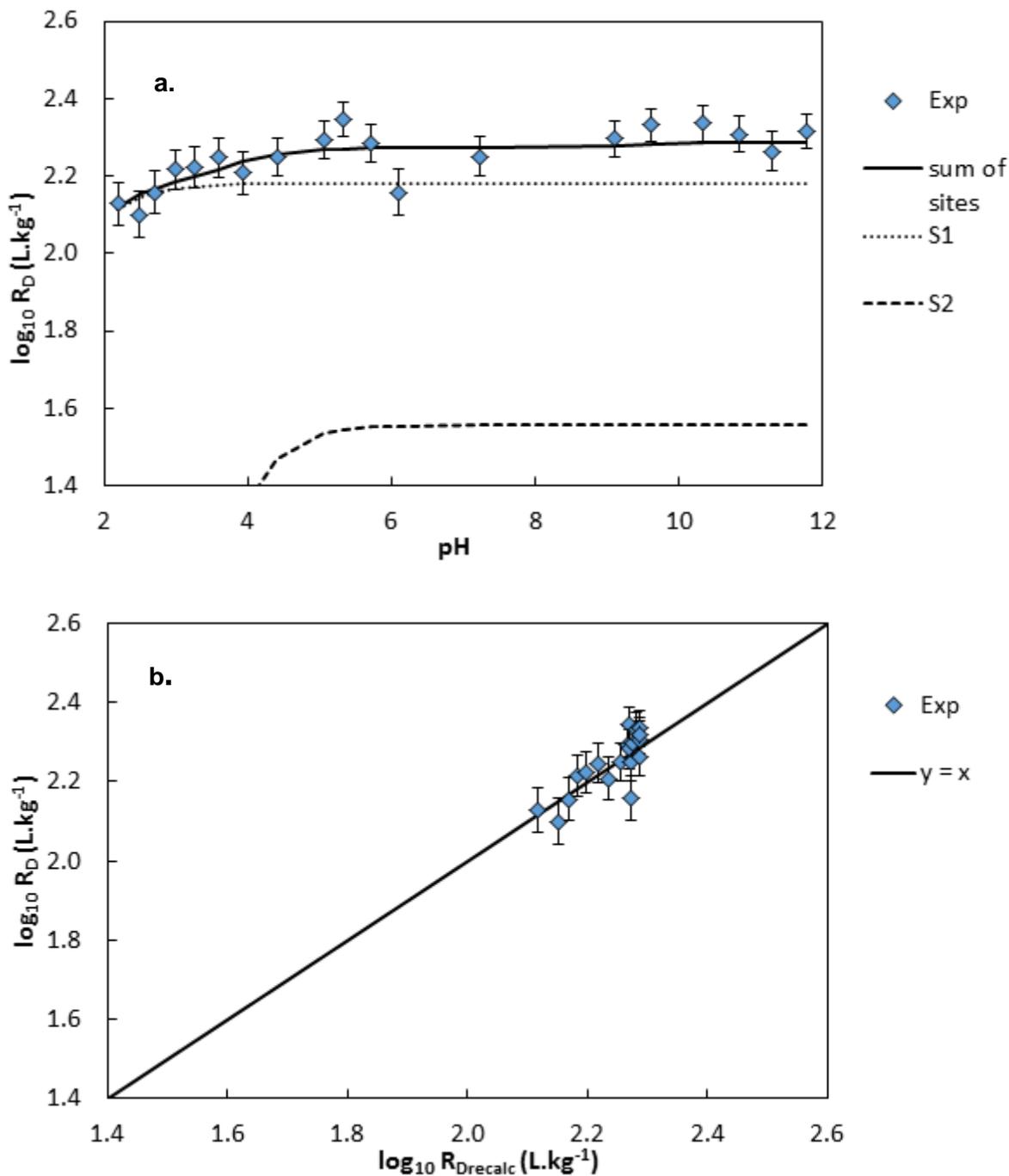


Figure II. 5. (a) Adsorption isotherms of Cs ($[Cs]_i = 10^{-7} \text{ mol.kgw}^{-1}$) as a function of pH at $I = 0.1 \text{ mol.kgw}^{-1}$ (NaCl) and $S/L = 3.8 \text{ g.L}^{-1}$ on a Na-MX80 bentonite and representation of the contribution of the different fixation sites and (b) Comparison of the experimental results with the modelling results.

The adsorption of cesium in the Na-MX80 at $I = 0.1 \text{ mol.kgw}^{-1}$ (NaCl) and its modelling are shown in Figure II. 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 II. 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 $\log_{10}K_{Na^+/Cs^+}^{*3}$ (around 50%).

As explained in the introduction, the great variability of protocol in the literature on the adsorption of Cs onto montmorillonite impedes comparisons between the different results obtained onto not purified or not Na-conditioned bentonite (VEJSADA *et al.*, 2005 ; MONTAVON *et al.*, 2006 ; GALAMBOŠ *et al.*, 2010 ; WANG *et al.*, 2010). Only MISSANA *et al.* (2014) 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 cesium onto illite. This could explain the difference in $\log_{10}K_D$ between MISSANA *et al.* (2014) ($\log_{10}K_D$ 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 Figure II. 5a.

3.4 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 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^+ vs H^+ exchange were obtained from a new fit of the same data. The corrected selectivity coefficients $K_{2Na^+/Sr^{2+}}^{*i}$ and K_{Na^+/Cs^+}^{*i} were obtained from original pH and concentration isotherms into a Na-MX80 montmorillonite, in coherence with the site capacities in NOLIN (1997), and corrected selectivity coefficient K_{Na^+/H^+}^{*i} fitted in this study.

Some parameters were neglected in this work. The Na-MX80 was not entirely saturated with Na⁺ and traces of exchangeable cations still remain in the exchanger. Their concentrations were supposed low enough to not impact the adsorption of Na⁺, Cs⁺ and Sr²⁺. Moreover the possible dissolution of smectite at acidic or alkaline pH leading to a release of exchangeable cation (K⁺, Mg²⁺, Al³⁺, etc.) was not taken into account. These phenomena may affect the adsorption behaviour (decrease of the fixation sites concentrations, competition of adsorption between the different cations). Thus, obtained experimental points and associated modelling at pH below 4 and above 10 must be taken with caution.

Nonetheless, this study can serve as a part of a thermodynamic adsorption database to predict the adsorption of radionuclides, including Sr²⁺ and Cs⁺, onto mixtures of clay minerals. The inclusion of Ca²⁺ 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

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3.6 Appendices

The Appendices contain the XRD diffractogram of the purified Na-MX80 and the development of the modelling formalism

3.6.1 XRD diffractogram of Na-MX80

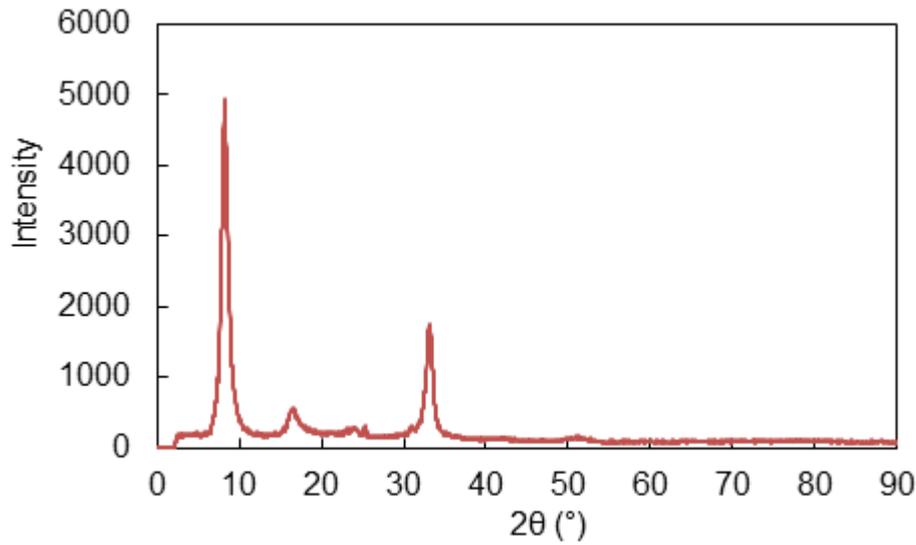
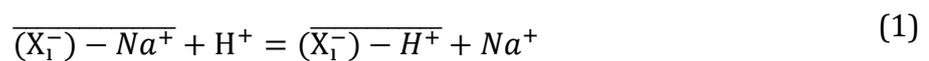


Figure II. 6. XRD powder diffractogram of the purified Na-MX80

3.6.2 Modelling formalism

3.6.2.1 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 :



with the corresponding equilibrium constant:

$$K_{\text{Na}^+/\text{H}^+}^i = \frac{[\overline{(X_i^-) - H^+}] \cdot [\text{Na}^+]}{[\overline{(X_i^-) - Na^+}] \cdot [\text{H}^+]} \times \frac{\gamma_{\text{Na}^+}}{\gamma_{\text{H}^+}} \times \frac{(f_{X_i^- - H^+})}{(f_{X_i^- - Na^+})} \quad (2)$$

where $[]$ is the solution (mol.kg^{-1} of water) or adsorbed concentration (mol.kg^{-1} of solid) of species, $\bar{\gamma}$ 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 unknown, it is assumed that the ratio between these coefficients is constant. Thus, the apparent constants (called corrected selectivity coefficients $K_{\text{Na}^+/\text{H}^+}^{*i}$) are described as follows.

$$K_{\text{Na}^+/\text{H}^+}^{*i} = \frac{[\overline{(X_i^-)} - \text{H}^+] \cdot [\text{Na}^+]}{[\overline{(X_i^-)} - \text{Na}^+] \cdot [\text{H}^+]} \times \frac{\gamma_{\text{Na}^+}}{\gamma_{\text{H}^+}} \quad (3)$$

Each type of site is also described by their site concentrations SC_i in mol.kg^{-1} of solid. The SC_i is equal to the sum of all the adsorbed species concentrations:

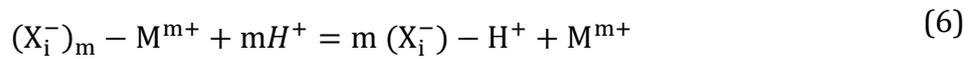
$$SC_i = [\overline{(X_i^-)} - \text{H}^+] + [\overline{(X_i^-)} - \text{Na}^+] \quad (4)$$

By combining equations (3) and (4), the adsorbed concentration of Na can be expressed as:

$$[\overline{Na}] = \sum_i [\overline{(X_i^-)} - \text{Na}^+] = \sum_i \frac{SC_i}{1 + \frac{K_{\text{Na}^+/\text{H}^+}^{*i} \cdot 10^{-pH}}{[\text{Na}^+] \cdot \gamma_{\text{Na}^+}}} \quad (5)$$

3.6.2.2 Adsorption isotherms of trace elements

To model the adsorption of trace elements M^{m+} on Na-saturated exchangers, two reactions are taken into account (1) and:



with the corresponding apparent equilibrium constant:

$$K_{M^{m+}/m\text{H}^+}^{*i} = \frac{[\overline{(X_i^-)} - \text{H}^+]^m \cdot [M^{m+}]}{[(\overline{X_i^-})_m - M^{m+}] \cdot [\text{H}^+]^m} \cdot \frac{\gamma_{M^{m+}}}{\gamma_{\text{H}^+}^m} \quad (7)$$

Since a cation could be complexed in solution, these phenomena are taken into account and the concentration of available M^{m+} is:

$$[M^{m+}] = \frac{[M]}{\alpha_{M^{m+}}} \quad (8)$$

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

The equation of the site concentrations is as follows.

$$SC_i = \overline{[X_1^-] - H^+} + \overline{[X_1^-] - Na^+} + m \overline{[X_1^-]_m - M^{m+}} \quad (9)$$

By combining equations (3), (7) and (9), the site concentration can be expression as a function of the adsorbed concentration $\overline{[X_1^-] - H^+}$:

$$SC_i = \overline{[X_1^-] - H^+} + \frac{\overline{[X_1^-] - H^+} \cdot [Na^+] \cdot \gamma_{Na^+}}{K_{Na^+/H^+}^{*i} \cdot [H^+] \cdot \gamma_{H^+}} + \sqrt[m]{\frac{\overline{[X_1^-] - H^+}^m \cdot [M^{m+}] \cdot \gamma_{M^{m+}}}{K_{M^{m+}/mH^+}^{*i} \cdot [H^+]^m \cdot \gamma_{H^+}^m}} \quad (10)$$

Solving of this equation leads to determine $\overline{[X_1^-] - H^+}$ then $\overline{[X_1^-]_m - M^{m+}}$ using equation (7).

Finally, the distribution coefficient can be recalculated with:

$$R_D = \frac{[\bar{M}]}{[M]} \quad (11)$$

3.6.2.3 Transformation of selectivity coefficient from MISSANA & GARCÍA-GUTIÉRREZ (2007) in the multi-site ion exchange formalism

MISSANA & GARCÍA-GUTIÉRREZ (2007) use the GAINES & THOMAS (1953) formalism to express their selectivity coefficient. In this formalism, the selectivity coefficient is equal to:

$$K_{2Na^+/Sr^{2+}}^{*,GT} = \frac{(N_{Sr^{2+}}) \cdot (a_{Na^+})^2}{(N_{Na^+})^2 \cdot (a_{Sr^{2+}})} \quad (12)$$

Where $(N_{M^{m+}})$ is corresponding to the equivalent fractional occupancy on the exchanger and (a) is the activity of cations. The expression of $(N_{M^{m+}})$ is:

$$(N_{M^{m+}}) = \frac{m \cdot [(X^-)_m - M^{m+}]}{CEC} \quad (13)$$

where $[(X^-)_m - M^{m+}]$ 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:

$$K_{2Na^+/Sr^{2+}}^{*,GT} = \frac{\left(\frac{2 \cdot [(X^-)_2 - Sr^{2+}]}{CEC} \right) \cdot [Na^+]^2 \cdot \frac{\gamma_{Na^+}^2}{\gamma_{Sr^{2+}}}}{\left(\frac{[(X^-) - Na^+]}{CEC} \right)^2 \cdot [Sr^{2+}]} \quad (14)$$

By combining with equation (7) and considering the different adsorption sites i , this expression becomes:

$$K_{2Na^+/Sr^{2+}}^{*,i,GT} = 2 \cdot SC_i \cdot K_{2Na^+/Sr^{2+}}^{*,i} \quad (15)$$

CHAPITRE III. RETENTION OF CS AND SR ONTO AN NA-ILLITE: APPLICATION OF THE MULTI-SITE ION-EXCHANGER MODEL.

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1 Résumé en Français

Le second chapitre de ce manuscrit de thèse s'est attelé à étudier l'adsorption des ions Cs⁺ et Sr²⁺ sur une smectite sodique. Les smectites font partie des minéraux argileux majeurs de l'environnement. Leur étude est d'autant plus importante qu'elles sont l'un des minéraux argileux présentant la plus forte capacité d'échange cationique. Ce troisième chapitre étudie, lui, le comportement des illites, faisant également partie des minéraux argileux majoritairement présents dans l'environnement, vis-à-vis de Cs⁺ et Sr²⁺. Cette partie du manuscrit est présentée sous forme de publication soumise dans *Applied Geochemistry*, précédée d'un résumé en français.

En tant que principaux produits de la fission de l'uranium-235, le césium et le strontium apparaissent comme des contaminants environnementaux majeurs lors des tests et accidents nucléaires. Au niveau des sols, ces deux contaminants se retrouvent majoritairement fixés au niveau des minéraux argileux. L'illite est l'un des principaux adsorbants de ces contaminants et plus particulièrement du césium. Dans les illites, les ions Cs⁺ sont réputés pour se fixer de manière forte et quasi-irréversible au niveau des *frayed edge sites*. L'objectif de cette publication est de compléter la base de donnée construite dans le chapitre précédent afin de décrire l'adsorption des ions Sr²⁺ et Cs⁺ sur une illite sodique, selon le formalisme des échangeurs d'ions multi-sites.

Une première partie de cette publication est consacrée à la caractérisation de l'échangeur illitique en termes de concentration de sites (SC_i) et de coefficients de sélectivités corrigés de l'ion Na⁺ vis-à-vis de l'ion H⁺. Elle a été réalisée dans le cadre de la thèse d'Aubéry Wissocq menée conjointement. Cette caractérisation a été effectuée à l'aide d'une courbe de saturation d'une illite sodique par du Na⁺ en fonction du pH. Parmi les courbes de saturation de l'illite par le sodium de la littérature, aucune n'atteint une concentration adsorbée proche de la CEC théorique d'une illite – aux alentours de 25 meq.100g⁻¹ (GORGEON, 1994). Ainsi, une nouvelle courbe de saturation a été obtenue expérimentalement. Cette fois-ci, aux pH les plus basiques, l'adsorption de l'ion Na⁺ par l'illite semble proche de la CEC. Pour modéliser cette isotherme – de manière cohérente avec les données du chapitre précédent – il a été choisi de conserver les concentrations de sites précédemment déterminées par Wissocq et al. (WISSOCQ *et al.* (submitted) et WISSOCQ (2017)), qui ont étudié les processus d'adsorption des ions Cs⁺ et Sr²⁺ sur une illite

calcique. Ainsi, les coefficients de sélectivité Na^+/H^+ ont pu être déduits de cette courbe de saturation.

Ensuite, l'étude du comportement d'adsorption des ions Sr^{2+} et Cs^+ a été réalisée en exploitant, dans le formalisme des échangeurs d'ions multi-sites, des isothermes d'adsorption tirées des travaux de POINSSOT *et al.* (1999a). Dans ces travaux, POINSSOT *et al.* (1999a) ont étudié le comportement d'adsorption de différents cations (Cs, Sr, Ni et Eu) sur une illite du Puy préalablement purifiée et conditionnée sous forme sodique. Les auteurs ont notamment étudié l'adsorption des ions Sr^{2+} et Cs^+ en fonction du pH et de leurs concentrations à l'équilibre, à différentes forces ioniques. La modélisation de toutes ces isothermes a donc permis d'obtenir un jeu de données décrivant l'adsorption des ions Cs^+ et Sr^{2+} sur une illite sodique, valable à différentes forces ioniques.

Cette base de données, qui complète celle obtenue dans le second chapitre de ce manuscrit, a été testée sur des mélanges de phases pures illite/smectite. Le fonctionnement du modèle pour prédire des comportements d'adsorption sur des phases complexes (sols, sédiments) reposant sur le principe d'additivité entre les différentes phases réactives, il a été choisi de tester au préalable ce principe d'additivité en étudiant expérimentalement l'adsorption des ions Cs^+ et Sr^{2+} sur des mélanges de phases pures. Les résultats ont ensuite été confrontés à des simulations. Ces expériences ont été réalisées à $I = 0.1 \text{ mol.kg}_w^{-1}$ (NaCl) et $\text{pH} = 7$. Elles ont été réalisées sur deux mélanges (M1 : 70% smectite – 30% illite et M2 : 30% illite – 70% smectite). Aussi bien pour l'ion Sr^{2+} que Cs^+ , les résultats d'adsorption sur les deux mélanges sont quasiment superposables. Concernant le strontium, étant donné que l'ion Sr^{2+} présente une adsorption similaire pour l'illite et la smectite, l'adsorption est principalement contrôlée par la CEC du mélange. Elle est donc supérieure pour le mélange M1 qui présente le plus de smectite. Pour le césium, c'est l'illite qui contrôle l'adsorption. Dans ce cas, c'est donc le mélange M2 qui présente une adsorption un peu plus forte de l'ion Cs^+ par rapport au mélange M1. En ce qui concerne les simulations, l'adsorption de l'ion Sr^{2+} sur ces deux mélanges est en bon accord avec les simulations effectuées. Pour le césium par contre, l'adsorption à faible concentration est constamment surestimée. Cette surestimation est d'autant plus forte pour M2 que pour M1, et donc pour le mélange présentant la plus grande quantité d'illite. Il semblerait donc que les problèmes proviennent soit de la base de données sur illite, soit de l'illite elle-même.

Au vue des analyses DRX et CEC sur l'illite utilisée, il apparait que l'illite n'est pas totalement pure. Cette pureté a été estimée à 84% et les simulations ont été réalisées à nouveau en corrigeant la pureté. Cependant, si les simulations suivent mieux l'adsorption de l'ion Cs^+ sur le mélange M1, celle sur le mélange M2 est toujours surestimée. Maintenant, il a été montré lors de l'analyse des cations échangeables que du potassium reste présent dans l'illite après son conditionnement sous forme sodique. Etant donné l'affinité du potassium pour les illites, et principalement pour les *frayed edge sites*, il est fort probable que cette différence entre les résultats expérimentaux et les simulations soit due à la présence de potassium.

Cette étude a néanmoins permis de construire une base de données des comportements d'adsorption des ions Sr^{2+} et Cs^+ vis-à-vis de Na^+ et de H^+ sur une illite purifiée sodique, selon le formalisme des échangeurs d'ions multi-sites. L'additivité de cette base de données avec celle développée dans le chapitre 2 a également été démontrée. Ces deux bases de données pourront donc par la suite être utilisées pour essayer de prédire de comportement d'adsorption des ions Cs^+ et Sr^{2+} sur différentes matrices complexes tels que les sols à dominance illitique ou riches en smectites.

2 Abstract

The application of the multi-site ion-exchanger modelling on the prediction of contaminant behaviour onto soils or sediment requires coherent adsorption databases. Following a preceding work on smectite (Siroux et al., submitted, Appl. Geochem.), we are proposing a database of the adsorption behaviour of Cs^+ and Sr^{2+} onto Na-illite, one of the major clay mineral in the environment. To obtain the model parameters for Na^+ and H^+ , a saturation curve of illite with sodium was obtained. Experiments taken from the literature were reinterpreted to model the adsorption behaviour of Cs^+ and Sr^{2+} onto purified and Na-conditioned illite. The modelling of these experiments using the multi-site ion-exchanger model permits constructing a database—site concentrations and corrected selectivity coefficient—to describe their adsorption behaviours. Afterwards, the predictability of the database was verified on simulating experimental adsorption of Cs^+ and Sr^{2+} onto illite/smectite mixtures using the parameters from the database. The application of this

database could permit simulating the adsorption of Cs⁺ and Sr²⁺ onto Na-dominated soils or sediments.

3 Publication

3.1 Introduction

The development of nuclear energy requires the knowledge of its potential consequences. ⁹⁰Sr and ¹³⁷Cs are two of the most important daughters of uranium and plutonium (ENGLAND & RIDER, 1993). Both the radioisotopes were spread in the environment after nuclear accidents such as Chernobyl and Fukushima-Daiichi, but also after the different nuclear weapons testing.

In soils, ⁹⁰Sr and ¹³⁷Cs are strongly retained and their behaviours are mainly dominated by their adsorption onto clay minerals. As clay minerals bear negative surface charges, the adsorption of cation, as Sr²⁺ and Cs⁺, is facilitated. Thus, the adsorption of these radionuclides onto clay minerals, such as bentonite (MONTAVON *et al.*, 2006 ; GALAMBOŠ *et al.*, 2013), illite (MAHONEY & LANGMUIR, 1991 ; FULLER *et al.*, 2015), kaolinite (ERTEN *et al.*, 1988 ; CHEN *et al.*, 2015) or vermiculite (LONG *et al.*, 2014 ; DZENE *et al.*, 2015), has been extensively studied in the literature. Illite is especially referenced as the major adsorbent for cesium. In illite, the strong adsorption of Cs⁺ occurs onto strong affinity low concentration frayed edge sites (SAWHNEY, 1972 ; BROUWER *et al.*, 1983 ; CREMERS *et al.*, 1988).

Many adsorption models were developed in order to represent the adsorption behaviors of Cs⁺ and Sr²⁺ onto clay minerals, sediment or soils. In most of these models, adsorption is described as an ion exchange (ROBIN *et al.*, 2015) or a surface complexation (NIE *et al.*, 2017) reaction. BRADBURY & BAEYENS (1999) have considered both adsorption phenomena and have developed a model based on a mechanistic description of the cation adsorption between a clay minerals and a liquid phase—namely the 2 sites protolysis non-electrostatic surface complexation and cation exchange model or 2SPNE SC/CE.

The application of these models on more complex phases as soils can be done in two ways. Many authors used a generalized composite approach, consisting in fully describing the complex material as a unique phase (MOTELLIER *et al.*, 2003 ; JACQUIER *et al.*, 2004). Actually

this approach allows a good representation of the material and its behaviour but it often impedes the extrapolation of the obtained data onto different materials. Another possibility is to consider a complex phase as an addition of simpler phases. This approach needs more inputs—in soils, it needs the description of all mineral phases—but it allows a better extrapolation of the modelling once the database is completed. MISSANA *et al.* (2014a) have applied a derivative model from the 2SPNE SC/CE and the additivity approach in order to simulate the adsorption of Cs onto two Spanish clays.

The multi-site ion-exchanger formalism (LY *et al.*, 1991 ; STAMMOSE *et al.*, 1992) will be used in this study. This formalism has been also implemented by several studies. Applying the additivity approach on the multi-site ion-exchanger enables simulating adsorption onto complex phases. TERTRE *et al.* (2009) have modelled the Zn²⁺ behaviour onto montmorillonite and has simulated successfully its adsorption onto different soils and sediments applying the additivity approach. The mobility of Cs⁺ (SAVOYE *et al.*, 2012) and Sr²⁺ (SAVOYE *et al.*, 2015) was also successfully simulated using this approach. REINOSO-MASET & LY (2014) have worked on the adsorption of major cations such as Na⁺, Ca²⁺, K⁺, Mg²⁺ onto pure kaolinite and the behaviour of Cs⁺ at trace levels. Finally, in a recent work we have studied the adsorption of Sr²⁺ and Cs⁺ onto an Na-smectite (SIROUX *et al.*, submitted), and onto Ca-illite and -smectite (WISSOCQ *et al.*, submitted).

The aim of this paper is to study the adsorption behaviour of Na⁺ onto a purified illite, and those of Cs⁺ and Sr²⁺ onto a Na-conditioned illite within the multi-site ion-exchanger formalism. First, a purified illite du Puy will be described in terms of site concentrations (SC_i) and corrected—of adsorbed species activity coefficients—selectivity coefficients Na⁺/H⁺ (K^{*i}_{Na⁺/H⁺}) for each site. Then, adsorption isotherms of Cs⁺ and Sr²⁺ onto purified and Na-conditioned illite will be compiled from literature and modelled in order to obtain the K^{*i}_{Mⁿ⁺/nH⁺}. Finally, the obtained database—including the parameters from SIROUX *et al.* (submitted) for Na-smectite—will be used to predictively simulate the experimental adsorption of Cs⁺ and Sr²⁺ onto illite/smectite mixtures.

3.2 Materials and methods

3.2.1 Materials

A SWy-2 smectite purchased from the Clay Mineral Society and an illite du Puy were used in this study. These clay minerals were purified in order to concentrate the montmorillonite and the illite fractions from these clays. The applied purification protocol consists in eliminating the organic matter with H_2O_2 and dissolving the calcite with a $0.1 \text{ mol.kg}_w^{-1}$ HCl solution. The protocol is detailed in GAUCHER (1998), PEYNET (2003) and REINOSO-MASET & LY (2014). The smectite was sieved at $63 \text{ }\mu\text{m}$ and illite at $25 \text{ }\mu\text{m}$. Both clay minerals were next Na-conditioned by several washings with a 1 mol.kg_w^{-1} then $0.1 \text{ mol.kg}_w^{-1}$ NaCl solution. The Na excess was finally removed by washings with Milli-Q water (Millipore, $18. \text{ M}\Omega.\text{cm}^{-2}$), then with ethanol. The clay minerals were analysed by X-ray crystallography (XRG 3000, Inel) in order to determine the impurities. The purified SWy-2 still presents traces of well crystalized quartz, while illite presents traces of quartz, kaolinite, and interbedded minerals.

All chemicals were at least of analytical grade. $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ salt (99.995% trace metals basis, Sigma Aldrich) was used to prepare the stable Sr solutions while CsCl (99.999% trace metals basis, Sigma Aldrich) was used for the stable Cs ones. Radioisotopes ^{85}Sr , ^{137}Cs and ^{22}Na were obtained from Cerca LEA. Ionic strength was fixed using NaCl (Analar Normapur, VWR).

3.2.2 Experimental protocol

3.2.2.1 Analytical methods

The aqueous concentrations measurements of Sr, Na, Ca, K and Mg were made by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Activa, Horiba Jobin Yvon) by diluting aliquots with 2% sub-boiling HNO_3 (DuoPur, Milestone). Measurements were made at 407.771 nm for strontium, 589.592 nm for sodium, 317.933 nm for calcium, 766.490 nm for potassium, 273.553 nm for magnesium. The aqueous concentrations of Cs were measured by ICP-MS (Element 2, Thermo Scientific).

The pH values were obtained 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 pH-units.

3.2.2.2 Characterization of clay minerals

The CEC of the purified smectite and illite were measured. The protocol of the CEC and the exchangeable measurement is explained in SIROUX *et al.* (submitted). The CEC measurement consists in extracting all exchangeable cations from clay with a 0.1 mol.kg_w⁻¹ KCl solution with addition of KOH to reach a pH *ca.* 10. Then, adsorbed K⁺ was extracted with a 0.1 mol.kg_w⁻¹ CsCl solution then measured by ICP-AES. For the measurement of the exchangeable cations, a CsCl solution was directly used in order to extract them before being analysed by ICP-AES. Table III. 1 summarizes the measurement results. The sum of the exchangeable cations is close to the measured CEC. As expected, sodium is the major exchangeable cation in purified clay minerals but there are still traces of K⁺ and Mg²⁺.

Table III. 1. Exchangeable cations concentrations and CEC measurement of purified Na-clay minerals

Exchangeable cations

Sample	Exchangeable cations				Sum of exchangeable cations (meq.100g ⁻¹)	CEC (meq.100g ⁻¹)
	Na (meq.100g ⁻¹)	Ca (meq.100g ⁻¹)	Mg (meq.100g ⁻¹)	K (meq.100g ⁻¹)		
Swy-2 smectite	79	<L.O.D.	0.4	2.5	81.9	83.3
Illite du Puy	19.6	<L.O.D.	<L.O.D.	1.1	20.7	20.9

3.2.2.3 Na-saturation curve and adsorption isotherm on pure clay mineral mixtures

Experiments were done by batch method at room temperature (22 ± 5°C). They were performed in 10 mL polycarbonate Nalgene centrifuge tube (3138-0010, Thermo Scientific). All solutions and suspensions were made by weighing.

Chapitre III. Retention of Cs and Sr onto an Na-illite: Application of the multi-site ion-exchanger model

Saturation curve of Na⁺ onto pure Na-illite was made with a 0.02 g.L⁻¹ S/L ratio. Illite was put in contact with 0.02 mol.kg_w⁻¹ NaCl and agitated during 24 h. Solutions of 1, 0.1 or 0.01 mol.kg_w⁻¹ of HCl or NaOH were used in order to adjust the solution pH, then mixtures were left under agitation during one day. Suspensions were spiked with ²²Na and left agitated during 1 day for equilibration. Suspensions were ultra-centrifuged (10.000 rpm during 30 min with Optima LE-80R, Beckman) then 1 mL aliquot of the supernatant was collected and activity was counted by gamma counting (1480 Wizard 3, Perkin Elmer).

The partition coefficients R_D (L.kg⁻¹) were calculated using:

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

where C_i and C_{eq} are respectively the initial and equilibrium activities of either Cs or Sr, V is the total volume of solution (L) and m is the total dry mass of solid phase (kg).

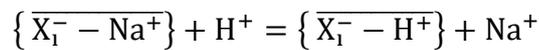
The initial activities were determined using a blank procedure, *i.e.*, using the same protocol without clay minerals in batches. The adsorbed concentrations were then deducted from the initial concentrations—determined by ICP-AES measurement—and the partition coefficient.

Pure clay mixtures experiments were prepared by weighing and dry mechanic stirring. In these experiments, a 3.8 g.L⁻¹ solid/solution ratio was used. Illite/smectite mixtures were first equilibrated under agitation with a 0.1 mol.kg_w⁻¹ NaCl electrolyte for 24 hours. The pH was adjusted around 7 with 1, 0.1 or 0.01 mol.kg_w⁻¹ solutions of HCl or NaOH and suspensions were left under agitation for 24 h. The concentration of stable cesium—from 10⁻² to 10⁻⁹ mol.kg_w⁻¹ in CsCl—or strontium—from 10⁻² to 10⁻⁶ mol.kg_w⁻¹ in SrCl₂—was added in tubes. Suspensions were also spiked with ⁸⁵Sr or ¹³⁷Cs (around 3000 Bq), then left under agitation during five days for Cs, and two days for Sr. Finally, the suspensions were

ultra-centrifuged, a 1 mL aliquot of the supernatant was collected, and activity was counted by gamma counting. The initial concentrations of Sr were determined by analysing of the standard solutions in ICP-AES and the Cs concentrations in ICP-MS.

3.2.3 Modelling

Isotherms were modelled using the multi-site ion-exchanger model. This model is fully detailed elsewhere (MOTELLIER *et al.*, 2003 ; JACQUIER *et al.*, 2004 ; TERTRE *et al.*, 2009 ; SAVOYE *et al.*, 2012 ; REINOSO-MASET & LY, 2014 ; SAVOYE *et al.*, 2015 ; SIROUX *et al.*, submitted). Briefly, in this model exchangers are expressed in terms of site concentrations (SC_i) and corrected—of adsorbed species activity coefficients—selectivity coefficients for Na^+/H^+ exchange (K_{Na^+/H^+}^{*i}). This first description of the exchanger is obtained studying the cation saturation of the homo-ionic exchanger vs. pH. The equilibrium between Na^+ and H^+ on negatively charge type of site X_i^- is described by the following equilibrium reaction.



The equilibrium constant of this equation can be written as,

$$K_{Na^+/H^+}^i = \frac{[\overline{X_i^- - H^+}] \cdot [Na^+]}{[\overline{X_i^- - Na^+}] \cdot [H^+]} \times \frac{\gamma_{Na^+}}{\gamma_{H^+}} \times \frac{(f_{X_i^- - H^+})}{(f_{X_i^- - Na^+})} \quad (2)$$

where [] is the solution (mol.kg⁻¹ of water) concentration, [̄] is the adsorbed concentration (mol.kg⁻¹ of solid) of species, γ are the activity coefficient of aqueous species—calculated here using DAVIES (1962) equation and f is activity coefficient of adsorbed species.

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Since the activity coefficients of adsorbed species f are unknown, it is assumed that the ratio between these coefficients is constant. Thus, the apparent constants—called corrected selectivity coefficients $K_{\text{Na}^+/\text{H}^+}^{*i}$ —are described as follows.

$$K_{\text{Na}^+/\text{H}^+}^{*i} = \frac{[\overline{X_1^- - \text{H}^+}] \cdot [\text{Na}^+]}{[\overline{X_1^- - \text{Na}^+}] \cdot [\text{H}^+]} \times \frac{\gamma_{\text{Na}^+}}{\gamma_{\text{H}^+}} \quad (3)$$

Sites i are also described by their site concentration SC_i in mol.kg⁻¹ of solid which equals to the sum of the adsorbed species concentrations.

$$SC_i = [\overline{X_1^- - \text{H}^+}] + [\overline{X_1^- - \text{Na}^+}] \quad (4)$$

The determination of the corrected selectivity coefficients associated to the trace element (Cs⁺ and Sr²⁺) exchange with Na⁺ is made from the adsorption isotherms of these trace elements on homoionic Na-conditioned exchanger vs. the solution pH or the equilibrium concentration of the trace element in solution. The corrected selectivity coefficient of a cation M^{m+} with regards to Na⁺ can be written as follows.

$$K_{m\text{Na}^+/\text{M}^{m+}}^{*i} = \frac{[(\overline{X_1^-})_m - \text{M}^{m+}] \cdot [\text{Na}^+]^m \cdot \gamma_{\text{Na}^+}^m}{[\overline{X_1^- - \text{Na}^+}]^m \cdot [\text{M}^{m+}] \cdot \gamma_{\text{M}^{m+}}} \quad (5)$$

The calculation of $[(\overline{X_1^-})_m - \text{M}^{m+}]$ permits calculating the experimental partition coefficient using the following expression:

$$R_D = \frac{[\overline{M}]}{[M]} = \frac{\sum_i [(\overline{X_1^-})_m - \text{M}^{m+}]}{[M]} \quad (6)$$

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).

3.3 Results and discussion

3.3.1 Compilation of the existent data from literature

The first part of this study consists in building a database of the adsorption behaviour of Cs^+ and Sr^{2+} onto an Na-Illite. This database was built from experimental data available in the literature that follows several criteria: (i) the illite must be purified; (ii) the illite must be Na-conditioned; and (iii) adsorption isotherms must be built with Na electrolyte (NaCl or NaClO_4).

Sometimes the original experimental data were directly taken from the paper or the manuscript. For other experiments, the retrieval of the experimental data was made using WINDIG (1996) data digitizer software. Once the data were retrieved, the multi-site ion-exchanger modelling was applied in order to determine the selectivity coefficients by fitting with the MS Excel Solver. Uncertainties were finally obtained using the SolverAid macro from DE LEVIE (2005).

3.3.1.1 Saturation of illite with Na^+

First, illite must be characterized in terms of SC_i and $K_{\text{Na}^+/\text{H}^+}^i$ studying the saturation of an Na-illite by Na^+ vs. pH. GORGEON (1994) has previously studied the saturation of an illite du Puy with Na^+ at $[\text{Na}] = 0.02 \text{ M}$: the results are recalled in Figure III. 1. It appears that the saturation curve of GORGEON (1994) increases with pH, and then levels-off to $13.4 \text{ meq}\cdot 100\text{g}^{-1}$ at $\text{pH} = 5.6$. It seems that sodium did not saturate the illite.

New experimental points obtained in this study on Na-illite are also presented in Figure III. 1. At acidic pH the curve follows those from GORGEON (1994) but instead of levelling off, the experimental points continue increasing until $[\text{Na}]_{\text{ads}} = 22 \text{ meq}\cdot 100\text{g}^{-1}$. Contrary to GORGEON

(1994), sodium seems to saturate the Na-Illite and achieves a concentration close to the CEC.

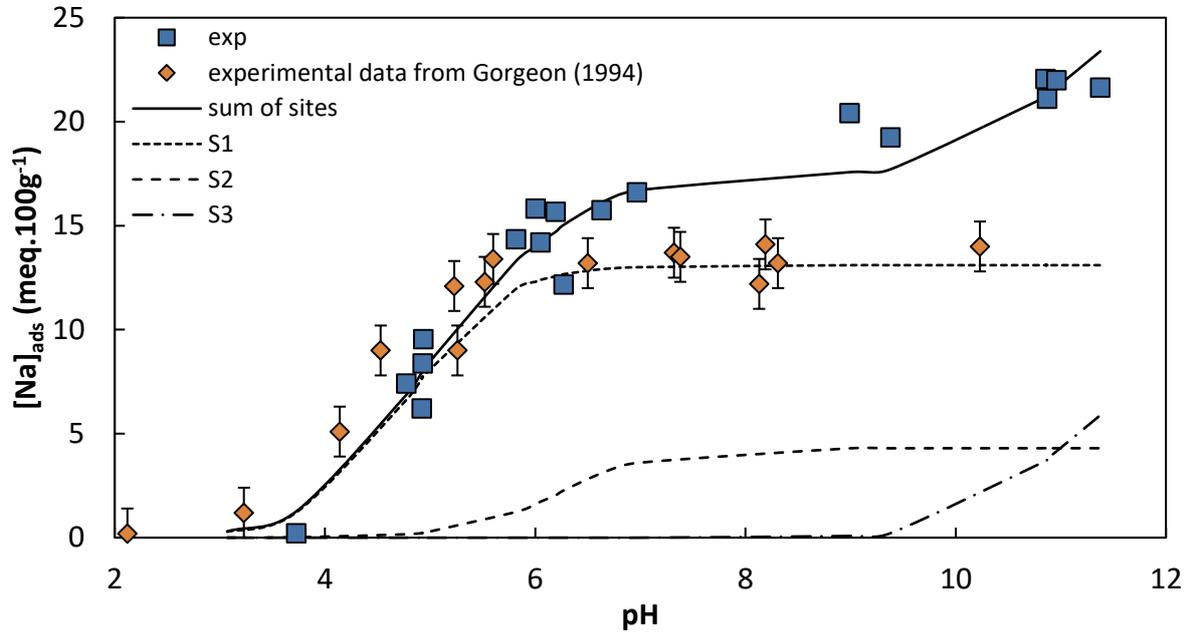


Figure III. 1. Saturation curve of Na-illite in function of the pH at $I = 0.02$ (NaCl) and S/L ratio = 25 g.L^{-1} , and representation of the modelling and the influence of the different fixation sites.

For the sake of consistency the site concentrations determined by *WISSOCQ et al.* (submitted)—who have provided a database of the adsorption of Cs^+ and Sr^{2+} onto a Ca-illite within the same multi-site ion-exchanger formalism—were used for modelling with. The used SC_i and the obtained $\log_{10} K_{\text{Na}^+/\text{H}^+}^i$ are recalled in Table III. 2. The modelling satisfactorily follows the evolution of the experimental results.

Table III. 2. Summary of the site concentrations and selectivity coefficients obtained and used in this study

Mineral	Site	Site concentration (mmol.g ⁻¹)	Selectivity coefficient	Selectivity coefficient value	References
Illite	S ₀	0.001 ^a	$\log_{10}K_{Na^+/H^+}^{*i}$	2.02 ± 1.15	This study
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	-	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	-4.57 ± 0.01	#
	S ₁	0.131 ^a	$\log_{10}K_{Na^+/H^+}^{*i}$	2.77 ± 0.10	#
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	3.97 ± 0.34	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	0.17 ± 0.12	#
	S ₂	0.043 ^a	$\log_{10}K_{Na^+/H^+}^{*i}$	4.19 ± 0.27	#
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	5.65 ± 0.33	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	8.03 ± ∞ ^b	#
	S ₃	0.074 ^a	$\log_{10}K_{Na^+/H^+}^{*i}$	8.95 ± 0.18	#
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	13.76 ± 0.50	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	4.38 ± 0.20	#
Smectite	S ₁	0.387	$\log_{10}K_{Na^+/H^+}^{*i}$	0.24 ± 0.04	SIROUX <i>et al.</i> (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	0.20 ± 0.07	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	-1.31 ± 0.04	#
	S ₂	0.361	$\log_{10}K_{Na^+/H^+}^{*i}$	2.62 ± 0.09	#
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	4.24 ± 0.17	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	1.64 ± 0.17	#
	S ₃	0.139	$\log_{10}K_{Na^+/H^+}^{*i}$	8.45 ± 0.18	#
			$\log_{10}K_{Sr^{2+}/2H^+}^{*i}$	13.99 ± 0.22	#
			$\log_{10}K_{Cs^+/H^+}^{*i}$	7.77 ± 0.37	#

^aSite concentrations of illite taken from WISSOCQ *et al.* (submitted) and WISSOCQ (2017)

^bInfinite uncertainty was attributed to S₂ selectivity coefficient of cesium. This uncertainty is explainable by the absence of constraint during the acquisition of this selectivity coefficient – this fixation sites were not useful to model the experimental isotherms (cf. § 3.3.1.2.1).

3.3.1.2 Adsorption isotherms of trace elements

Adsorption isotherms of Sr^{2+} and Cs^+ onto Na-illite were taken from POINSSOT *et al.* (1999a, 1999b).

3.3.1.2.1 Cesium adsorption

For the sake of consistency, the determination of the selectivity coefficients for the Cs^+/H^+ exchange was made by a simultaneous adjustment of the two adsorption isotherms. As we have already noted in a previous work, GORGEON (1994) also reported trace Cs^+ adsorption onto a pure Na-saturated Illite du Puy in 1 mol.kg^{-1} NaCl, which will not be included in our discussion because the ionic strength is well outside the validity domain of the DAVIES (1962) equation—see SIROUX *et al.* (submitted) and references therein.

Figure III. 2 represents the adsorption isotherm of Cs in function of the pH and the modelling of these retrieved data with the influence of the different fixation sites. At this ionic strength ($I = 0.1$ and 0.01 mol.kg^{-1}), the adsorption of Cs seems to be slightly dependent on pH. At very acidic pH the K_D increases greatly then reaches a plateau at pH 4.

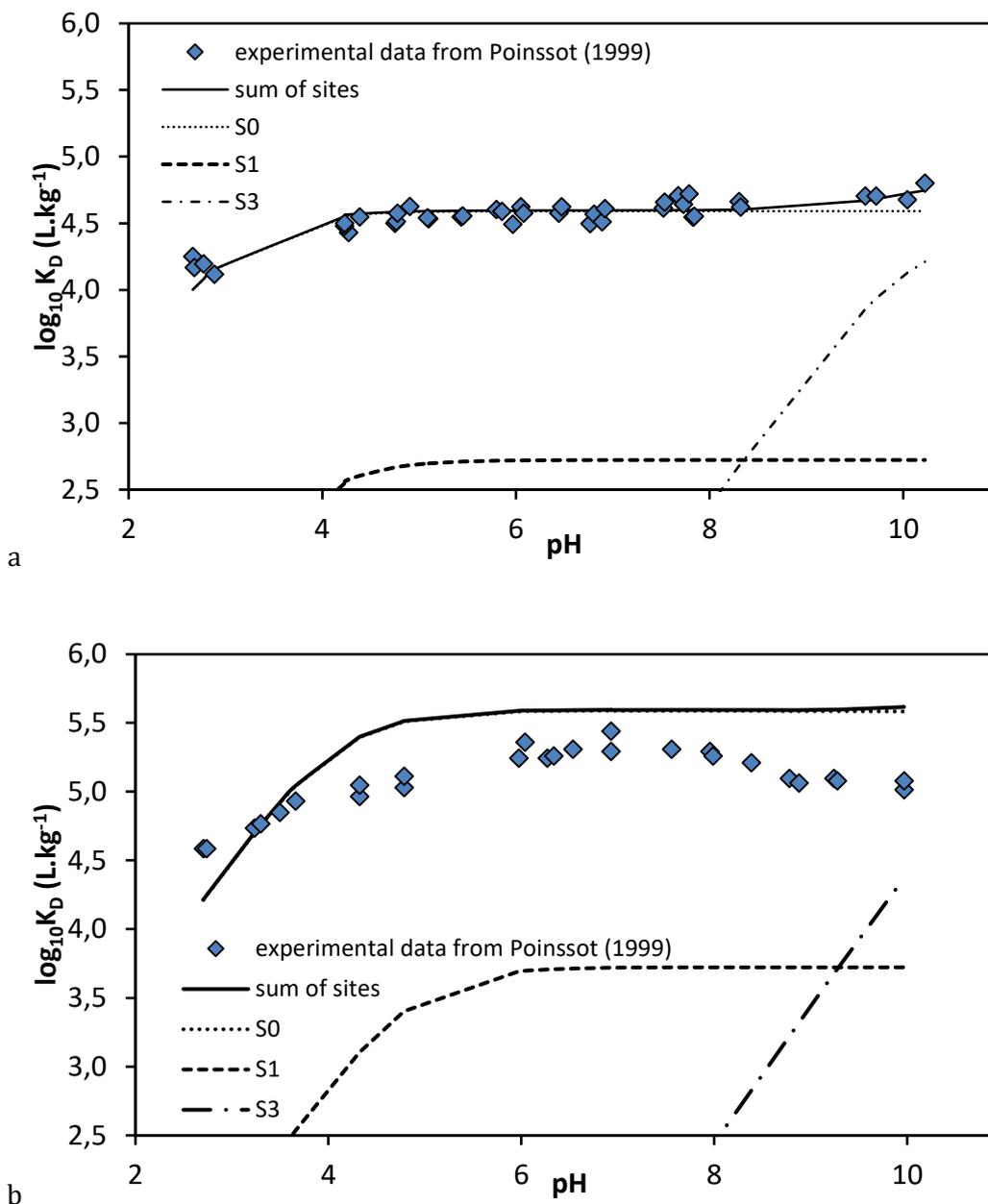


Figure III. 2. Adsorption isotherm in pH of Cs onto Na-illite at a) $I = 0.1$ and b) 0.01 mol.kg^{-1} (NaClO_4) and $[\text{Cs}]_i < 10^{-8} \text{ mol.kg}_w^{-1}$ and modelling with the multi-site ion-exchanger formalism. Data from POINSSOT *et al.* (1999a, 1999b)

Figure III. 3 shows the adsorption isotherm of Cs vs. the equilibrium concentration. This isotherm permits distinguishing specific adsorption behaviour of Cs onto illite. At low concentration, the adsorption of Cs follows a plateau. This adsorption collapses due to the

saturation of the S_0 site then a change in slope is observable, which is highlighting the change of fixation site at a lower K_D value to the S_1 site.

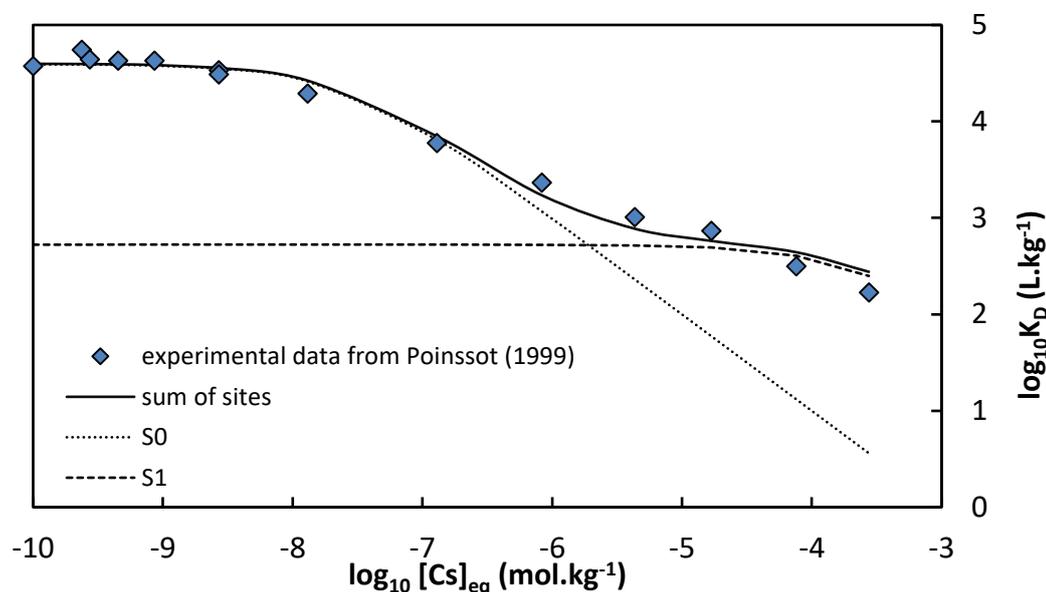


Figure III. 3. Adsorption isotherm in concentration of Cs onto Na-illite at $I = 0.1 \text{ mol.kg}^{-1}$ (NaClO_4), $\text{pH} = 7$ and modelling with the multi-site ion-exchanger formalism. Data from POINSOT *et al.* (1999b).

In adsorption isotherms at $I = 0.1 \text{ mol.kg}^{-1}$, the modelling represents well the experimental data. In Figure III. 2 only three out of the four sites are needed to represent the isotherm. The S_2 does not influence the adsorption of Cs^+ —the contribution to the K_D is $\log_{10} K_D < -4$. In view of the modelling, it is also possible to affirm that the S_0 site drives all the adsorption of Cs. In Figure III. 3 only two of the fixation sites are represented because they drive the adsorption at this pH (*i.e.* $\text{pH} 7$, cf. Figure III. 2). The S_0 site is often referenced as the low concentration high affinity frayed edge site (FES), known to be present in illite (SAWHNEY, 1972 ; BROUWER *et al.*, 1983 ; POINSOT *et al.*, 1999a, b ; MISSANA *et al.*, 2014a) but also in micaceous minerals (ZAUNBRECHER *et al.*, 2015) or vermiculite (DZENE *et al.*, 2015). If the S_0 site and the FES could be connected, this site is not named FES in this study given that the

multi-site ion-exchanger modelling does not aim to study exchanger at a microscopic scale and describes clay exchanger at a macroscopic scale.

At $I = 0.01 \text{ mol.kg}^{-1}$ (Figure III. 2b), the isotherm is overestimated by the modelling. POINSSOT *et al.* (1999b) obtained a similar and unexplained modelling result. By studying the stability of the illite, POINSSOT *et al.* (1999b) have observed a leaching of K^+ in solution. This K^+ could compete with Cs^+ and decrease its adsorption. BRADBURY & BAEYENS (2005) also supposed that this overestimation can come from the dissolution—leaching of measured Al^{3+} , Mg^{2+} and Ca^{2+} —of illite and proposed to take into account the behaviour of these leached cations pH by pH. Applying this proposition requires a measurement of the cationic content in equilibrium solutions or a thermodynamic characterization of the dissolution of illite. Given the aim of this study—to obtain corrected selectivity coefficient of Cs onto Na-illite and smectite—the understanding of the adsorption behaviours at $I = 0.01 \text{ mol.kg}^{-1}$ was abandoned. Nonetheless, the obtained $\log_{10}K_{\text{Cs}^+/\text{H}^+}^{*i}$ are summarized in Table III. 2. These selectivity coefficients—especially associated to the S_0 site or FES—can be compared with the literature. MISSANA *et al.* (2014b) have obtained a $\log_{10}K_{\text{Na}^+/\text{Cs}^+}^{*FES} = 6.90$ comparable with those from POINSSOT *et al.* (1999a, 1999b), *i.e.* = 6.95. In our case, we obtain a similar value with data from Table III. 2.

$$\log_{10}K_{\text{Na}^+/\text{Cs}^+}^{*S_0} = \log_{10}K_{\text{Na}^+/\text{H}^+}^{*S_0} - \log_{10}K_{\text{Cs}^+/\text{H}^+}^{*S_0} = 6.59 \pm 1.15$$

3.3.1.2.2 Strontium adsorption

The adsorption of strontium onto the purified Na-Illite du Puy was taken from POINSSOT *et al.* (1999a) and the selectivity coefficients $\text{Sr}^{2+}/2\text{H}^+$ were also determined by simultaneous adjustment of all the adsorption isotherms (Figure III. 4 and Figure III. 5). ALTMANN *et al.* (2015) have reported as well the adsorption of Sr onto illite, which was similar to those in

POINSSOT *et al.* (1999a). MISSANA *et al.* (2008) have worked on the Na-conditioned Silver Hill illite. At $I = 0.1$ M (NaClO_4), they have also obtained a similar adsorption behaviour vs. pH as POINSSOT *et al.* (1999a) but their medium $\log_{10}K_D$ is slightly higher—2.1 for MISSANA *et al.* (2008) against 2.0 for POINSSOT *et al.* (1999a)—. Their data will not be used given that their representation in $\log K_D$ is using a too wide scale to recover accurate data ($\log K_D$ axis is varying between 1.5 and 6).

Figure III. 4 represent the adsorption isotherm of Sr vs. pH at $I = 0.1$ and 0.01 mol.kg^{-1} (NaClO_4), respectively, and $[\text{Sr}]_i < 10^{-9} \text{ mol.kg}^{-1}$. At $I = 0.1 \text{ mol.kg}^{-1}$, the adsorption is strongly increasing at acidic pH then is reaching a plateau in the pH span 5-8. At more alkaline pH, the adsorption is increasing again. At $I = 0.01 \text{ mol.kg}^{-1}$, the $\log_{10}K_D$ raised to a plateau at pH below 6 (Figure III. 4b). These adsorption behaviours are recalling those of Sr onto smectite (SIROUX *et al.*, submitted).

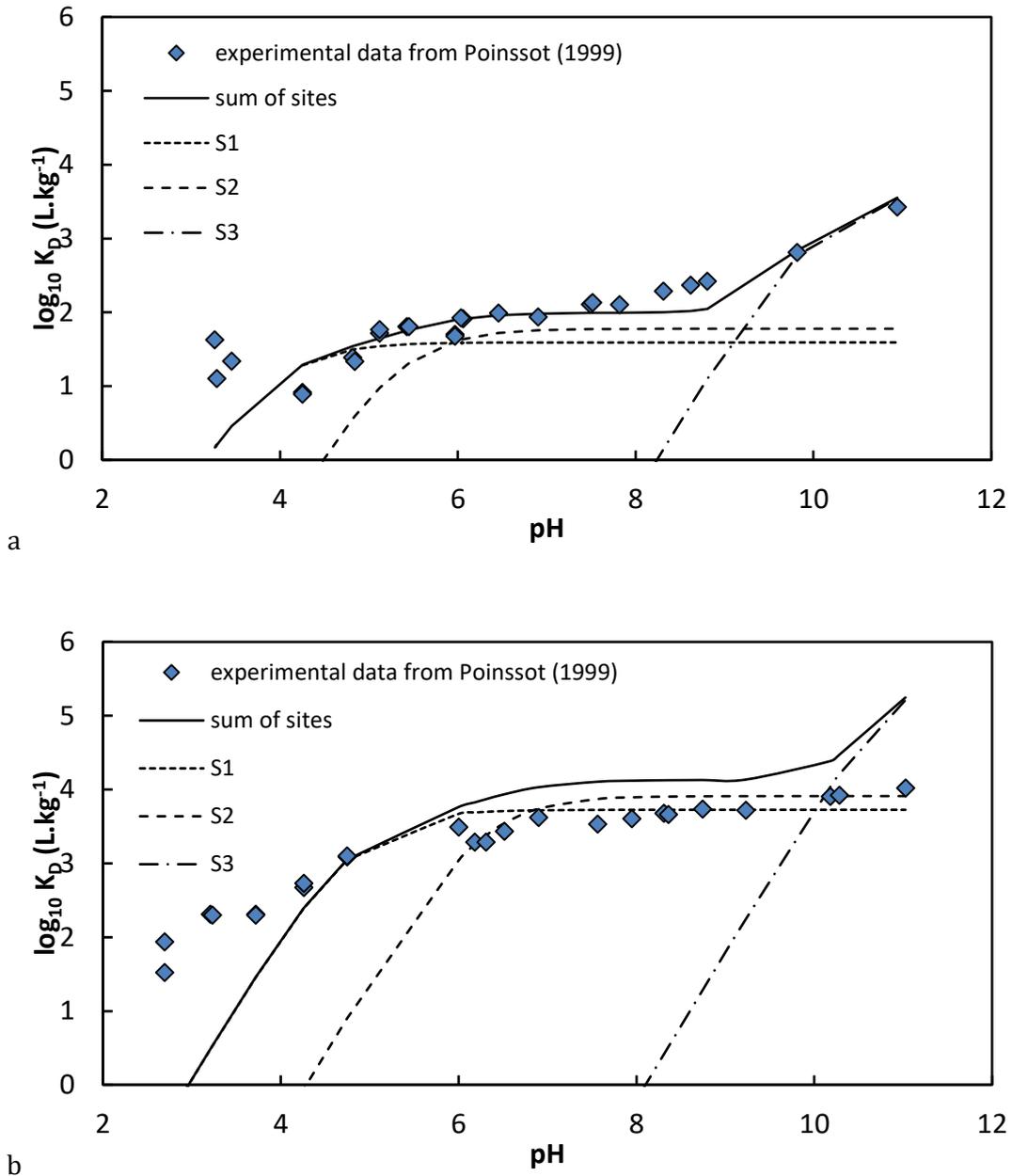


Figure III. 4. Adsorption isotherm in pH of Sr onto a Na-illite at $[Sr]_i < 10^{-9}$ mol.kg $_w^{-1}$ t , a) $I = 0.1$ mol.kg $_w^{-1}$ and S/L ratio = 1.78 g.L $^{-1}$, and b) $I = 0.01$ mol.kg $_w^{-1}$ ($NaClO_4$), and S/L ratio = 1.53 g.L $^{-1}$ and modelling with the multi-site ion-exchanger formalism.

Data digitized from POINSSOT *et al.* (1999a).

Figure III. 5 shows the adsorption isotherm of Sr vs. the equilibrium concentration onto an Na-illite at pH 7 and $I = 0.1$ mol.kg $_w^{-1}$ ($NaClO_4$). Here, the adsorption stays constant, *i.e.* $\log_{10} R_D = 2$, then collapses at the highest concentrations starting from $[Sr]_{eq} = 10^{-5}$ mol.kg $_w^{-1}$. Once again, this adsorption behaviour recalls the one of Sr onto smectite (SIROUX *et al.*,

submitted). Therefore, it is possible to state that Sr has similar adsorption behaviours onto illite and smectite.

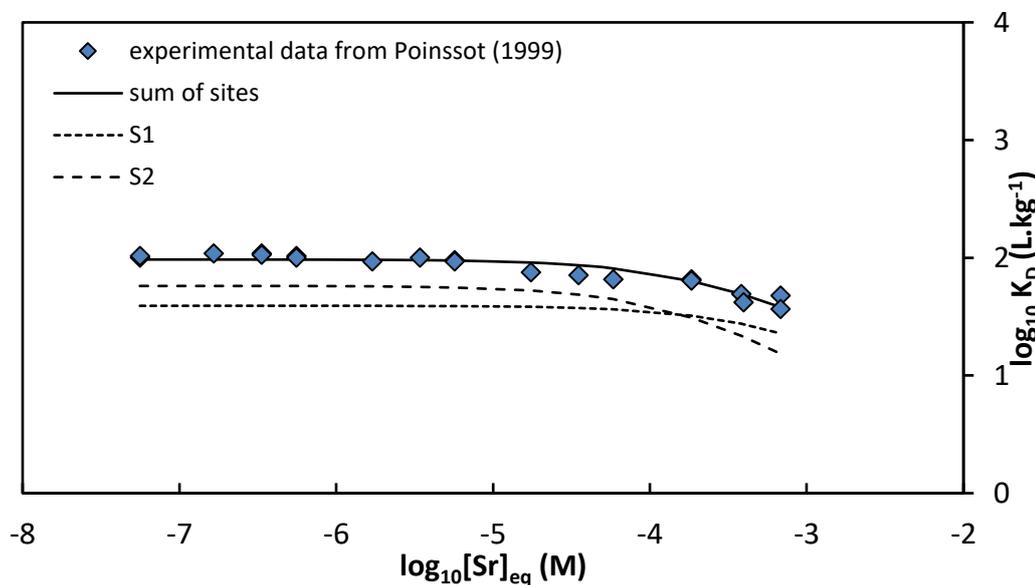


Figure III. 5. Adsorption isotherm in concentration of Sr onto a Na-illite at $I = 0.1$ mol.kg $^{-1}$ (NaClO $_4$), pH = 7 and S/L ratio = 1.75 g. L $^{-1}$ and modelling with the multi-site ion-exchanger formalism. Data digitized from POINSSOT *et al.* (1999a)

The modelling follows well the experimental data except for the adsorption isotherm in pH at $I = 0.01$ mol.kg $^{-1}$. Given that two experiments were made at the same ionic strength, these experiments have driven the adjustment. Thus, the weight of the isotherm at $I = 0.01$ mol.kg $^{-1}$ is weak compared to the two others and the modelling of this experiment overestimates the data. Reasons of this overestimation are probably the same that in 3.3.1.2.1. The obtained $\log_{10} K_{Sr^{2+}/2H^+}^{*i}$ are reported in Table III. 2. As supposed in this study, the $\log_{10} K_{Sr^{2+}/2H^+}^{*i}$ from illite and smectite are similar except for the S $_1$ site.

3.3.2 Verification of the additivity approach of the modelling

To apply the multi-site ion-exchanger modelling with the built database in more complex materials as soils or sediments, it is possible to use the additivity properties between the

different reactive phases. In this study, the additivity property was studied in order to check the efficiency of this database to simulate the adsorption behaviour of Cs^+ and Sr^{2+} onto illite/smectite mixtures. To achieve this aim, adsorption isotherms onto mixtures of pure phase were built. Purified and Na-conditioned SWy-2 smectite and illite du Puy were used for these experiments.

Two mixtures were prepared by mechanic mixture: 30% illite/70% smectite (M1) and 70% illite/30% smectite (M2). The exact percentages from these mixtures are detailed in Table III. 3. Adsorption isotherms in concentration of Cs and Sr were made on these mixtures at pH 7 and $I = 0.1 \text{ mol.kg}^{-1}$. Results were compared with the simulations done with the Na-materials database (cf. Table III. 2).

Table III. 3. Percentage of illite and smectite in M1 and M2 mixtures

Sample	% illite	% smectite
M1	30.2	69.8
M2	70.1	29.9

3.3.2.1 Adsorption of Cs onto illite/smectite mixtures

Figure III. 6 shows the adsorption isotherms of cesium on the two mixtures at pH 7 and $S/L = 3.8 \text{ g.L}^{-1}$. As in § 3.3.1.2.1, the isotherm follows the specific adsorption of Cs onto illite, which seems to drive the adsorption. Despite the greatest percentage of smectite in M1 than in M2, both adsorption behaviours of Cs are almost identical. The shape of the adsorption of Cs is well represented but experimental results are slightly overestimated at low concentration of Cs. This overestimation is especially higher in M2, the most concentrated in illite. The origin of these overestimations will be questioned further in the following.

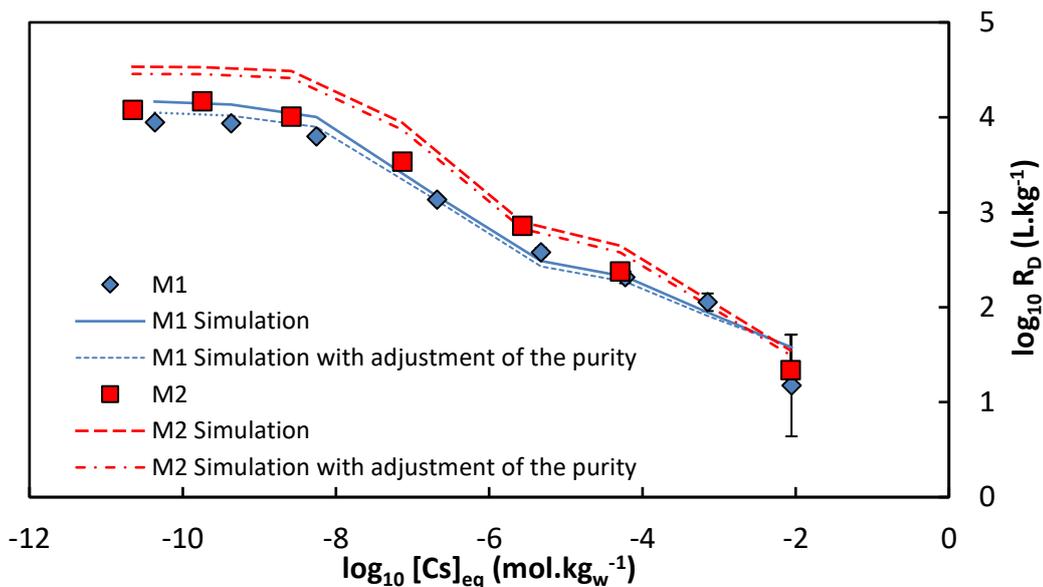


Figure III. 6. Adsorption isotherms in equilibrium concentration of Cs at $I = 0.1 \text{ mol.kg}_w^{-1}$ (NaCl), $\text{pH} = 4$ and S/L ratio = 3.8 g.L^{-1} on mixture M1 and M2 (Table III. 3) with the associated simulations.

3.3.2.2 Adsorption of Sr onto illite/smectite mixtures

The adsorption isotherm of strontium onto both clay mixtures are presented in Figure III. 7. As discussed in § 3.3.1.2.2, smectite and illite have comparable adsorption behaviour for Sr. Thus, the obtained $\log_{10}R_D$ are similar for both mixtures. For Sr, the adsorption is driven by the CEC of the exchanger. Consequently the adsorption of Sr is higher in mixtures greatly concentrated in smectite. This assessment is verified in Figure III. 7. The adsorption of Sr is greater in M1 than in M2.

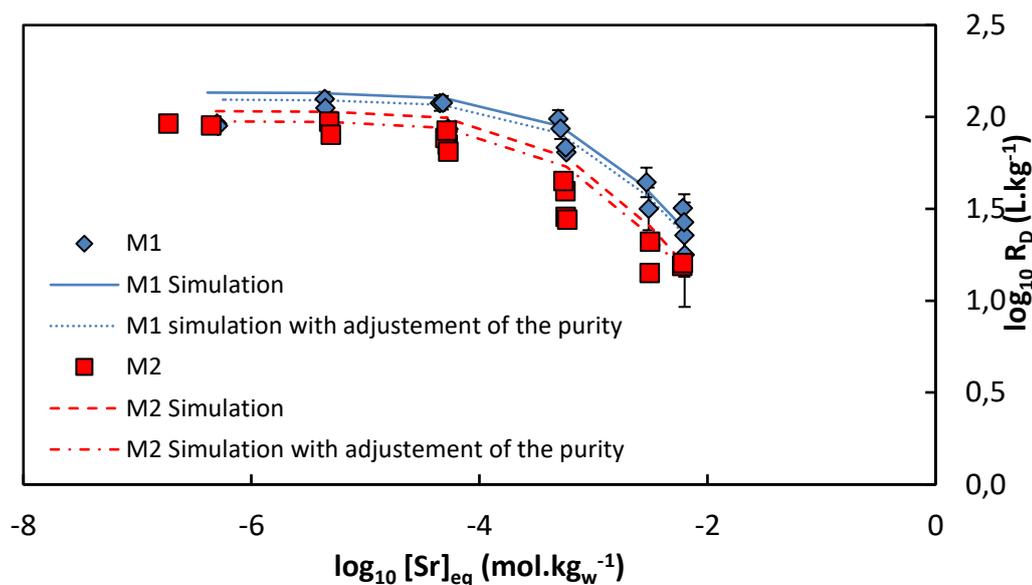


Figure III. 7. Adsorption isotherms in concentration of Sr at $I = 0.1 \text{ mol.kg}_w^{-1}$ (NaCl), $\text{pH} = 4$ and S/L ratio = 3.8 g.L^{-1} on M1 and M2 (Table III. 3) with the associated simulations.

Despite a very slight overestimation, the agreement between simulations and experimental results is good. Simulations also follow well the decrease in adsorption caused by the addition of illite. It seems that in the case of Sr, the database used allows a correct representation of the adsorption behaviour onto illite/smectite mixtures.

3.3.2.3 Discussion on the additivity results

The CEC of the two purified clay minerals has been explored but their values differ from those from the database. Indeed, in the database smectite has a CEC of $88.7 \text{ meq.100g}^{-1}$ against $83.3 \text{ meq.100g}^{-1}$ for our SWy-2 smectite and illite has a CEC of $24.9 \text{ meq.100g}^{-1}$ against $20.9 \text{ meq.100g}^{-1}$ for our illite du Puy. Given the XRD analysis (cf. § 3.2.1), it is not incoherent to postulate that used smectite and illite are not pure. In view of the measured CEC, it is possible to estimate that the smectite and illite are 94% and 84% pure, respectively. This purity difference can be taken into account in the modelling. Figure III. 6

also shows the corrected simulation. The adjustment of the purity causes a decrease of the simulated $\log_{10}K_D$. If this decrease permits a better representation of the adsorption of Cs onto M1, the representation of M2 experiment is still slightly overestimated. In the case of Sr (Figure III. 7), the adjustment of the clay minerals purities does not change significantly simulations.

The purity difference is not sufficient to explain the slight overestimation of the simulation of the adsorption behaviour of Cs onto the clay mixtures. Nevertheless, this problem could come from the clay minerals themselves, especially the illite du Puy. As seen in § 3.2.1, the purified and Na-conditioned illite du Puy still presents traces of exchangeable K^+ (*i.e.* 1.1 meq.100g⁻¹). It represents around 5% of the CEC. As Cs⁺, K^+ is well known to interact strongly with illite especially with the FES. Thus the presence of K^+ could interfere with the adsorption of Cs⁺. MISSANA *et al.* (2014b) show this effect by studying the adsorption of Cs onto various conditioned illite. Onto K-illite the adsorption of Cs⁺ is lower than onto Na-illite—a decrease of around 2.2 units of $\log K_D$ is observed at low Cs concentration.

3.4 Conclusion

The adsorption of Cs and Sr onto a purified illite has been studied and compiled from the literature. These isotherms were modelled within the multi-site ion-exchanger formalism with the aim of obtaining corrected selectivity coefficients Na^+/H^+ , Cs^+/H^+ and $Sr^{2+}/2H^+$. The experiments are well represented by the modelling. These representations insure a good efficiency of the obtained database to simulate the adsorption of Cs⁺ and Sr²⁺ onto Na-illite. Furthermore, the performance of this database, including the parameters from SIROUX *et al.* (submitted), was verified onto illite/smectite mixtures. Despite overestimations observed at low Cs concentration, the good agreement between the experimental

isotherms of the adsorption of Cs and Sr with the simulation tends to confirm the quality of the database. Henceforth, this database could be used to predict the adsorption compartment of Cs^+ and Sr^{2+} onto more complex phases as sediments or soils.

Acknowledgments

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CHAPITRE IV. ON THE USE THE MULTI-SITE ION EXCHANGE MODEL TO PREDICTIVELY SIMULATE THE ADSORPTION BEHAVIOUR OF CESIUM AND STRONTIUM ONTO FRENCH AGRICULTURAL SOIL

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1 Résumé en français

Le principe d'additivité du modèle d'échange d'ion multi-sites ayant été vérifié dans le chapitre précédent sur des mélanges de phases pures illite/smectite. Nous nous proposons ici de vérifier l'applicabilité de ce modèle, ainsi que de la base de données, sur des échantillons de sols afin de prédire le comportement d'adsorption des ions Cs⁺ et Sr²⁺ sur des sols en considérant les différentes proportions de minéraux argileux qui les composent. Cette partie du manuscrit de thèse est présentée sous forme de publication soumise à *Geochimica et Cosmochimica Acta*, précédée d'un résumé en français.

Le modèle d'échange d'ion multi-sites permet de modéliser et de simuler le comportement d'adsorption des ions sur différentes phases argileuses, sédiments, etc. En appliquant le principe d'additivité des phases réactives et à l'aide des bases de données construites sur les smectites et illites, ce modèle a également permis de simuler le comportement d'adsorption des ions Cs⁺ et Sr²⁺ sur des mélanges de phases pures illite/smectite. Ce principe d'additivité doit donc être désormais vérifié sur des échantillons de sols par différenciation de leurs différents minéraux argileux (illite, smectite, kaolinite, etc.).

Après une analyse faite dans le cadre du projet DEMETERRES sur les sols agricoles français près des différentes installations nucléaires, trois sols ont été sélectionnés et prélevés pour cette étude. Il s'agit des sols de Pusignan (Rhône), Étoile-sur-Rhône (Drôme) and Herqueville (Manche). Pusignan ainsi que Herqueville appartiennent à la famille des cambisols, tandis que Etoile-sur-Rhône appartient à la famille des calcosols selon la nomenclature FAO. Ils présentent toutefois différentes spécificités. Pusignan est un sol neutre riche en matière organique (aux alentours de 4%). Étoile-sur-Rhône est également un sol neutre mais cette fois-ci riche en carbonates ([CaCO₃] \approx 5 %), tandis que Herqueville est un sol acide (pH_{eau} = 5.5) riche en matière organique (\approx 5%) et en Al³⁺ dissous échangeables. Les premiers horizons de ces sols ont été prélevés et chaque échantillon a été tamisé à 150 µm afin de concentrer légèrement la fraction argileuse et d'homogénéiser l'échantillon.

Pour appliquer le modèle d'échange d'ion multi-sites selon le principe d'additivité, il a fallu dans un premier temps déterminer la composition minéralogique de chacun de ces sols. Ainsi, chaque sol (fraction < 2 µm) a été analysé par DRX afin de déterminer les

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compositions théoriques en illite, smectite, kaolinite et chlorite. Une analyse CEC de ces sols a également été menée afin de comparer les capacités d'échange cationique calculées, selon les proportions minéralogiques déterminées avec les diffractogrammes DRX, avec celles directement mesurées. Ainsi, chaque sol a été simplifié selon un mélange illite/smectite/kaolinite/chlorite.

Ensuite, la CEC de chaque échantillon de sols (tamisé à 150 μm) a été déterminée afin de recalculer les compositions en minéraux argileux de ces fractions. Pour la première expérience, les sols ont été approximés à des mélange illite/smectite – les deux minéraux argileux possédant les bases de données les plus complètes, mais également les deux minéraux argileux supposés les plus influents dans les processus d'adsorption des ions Cs^+ et Sr^{2+} . L'analyse des cations échangeables de ces différents échantillons de sols a également permis de mettre en évidence que le calcium se trouve être le cation échangeable majoritairement présent sur chacun de ces sols.

Ainsi, des isothermes d'adsorption de Cs et Sr en milieu CaCl_2 ($I = 0.1 \text{ M}$) au pH de l'eau d'équilibre ont été menées par méthode « batch ». Le césium montre une adsorption forte sur les différents sols avec une isotherme d'adsorption semblable à celle que l'on aurait pu obtenir sur une illite pure. Il semblerait donc que l'illite contrôle tout le comportement d'adsorption de l'ion Cs^+ dans les sols. L'adsorption dans le sol de Herqueville est néanmoins plus faible que dans les autres sols. Le strontium possède, lui, une adsorption faible sur chaque sol en suivant l'ordre Étoile-sur-Rhône > Pusignan > Herqueville. Ces isothermes ont été confrontées à des simulations en utilisant le modèle des échangeurs d'ion multi-sites. Lors de ces simulations, il est considéré que chaque sol est constitué d'un mélange illite/smectite saturé en calcium. Les simulations permettent de bien représenter le comportement d'adsorption de Cs sur Pusignan et Étoile-sur-Rhône, mais elle surestime fortement le $\log K_D$ sur celui sur Herqueville. Concernant, le strontium, bien que les simulations surestiment ou sous-estiment constamment les adsorptions, il est considéré que ces simulations représentent néanmoins de manière acceptable les comportements d'adsorption.

Plusieurs expériences ont ensuite été menées afin de mieux comprendre l'influence de différents éléments composants les sols (kaolinite, matière organique naturelle et Al^{3+} échangeable) et de déterminer les limites du modèle. La prise en compte de l'adsorption

sur la kaolinite n'a pas significativement modifié les simulations d'adsorption, du fait de sa faible CEC et de son comportement d'adsorption non spécifique vis-à-vis du césium ou du strontium. La matière organique naturelle a été éliminée par traitement des échantillons de sols avec du H₂O₂ à 80°C. Des isothermes d'adsorption ont à nouveau été réalisées sur ces échantillons traités, mais la suppression de la matière organique n'a pas modifié significativement les précédentes isothermes d'adsorption. Enfin, les cations échangeables Al³⁺ dissous ont été supprimés grâce à de multiples lavages au KCl 1 M à pH = 4. Si la suppression de ces cations a permis une meilleure simulation de l'adsorption de l'ion Sr²⁺ sur le sol d'Herqueville, l'isotherme de l'ion Cs⁺ reste largement inférieure à sa simulation. De ces expériences, il a été conclu, que dans nos conditions, la matière organique naturelle n'influe pas ou peu sur l'adsorption des ions Cs⁺ et Sr²⁺ dans les sols sélectionnés mais que les ions Al³⁺ du système, eux, diminuent l'accessibilité de l'ion Sr²⁺. Les problèmes rencontrés au niveau de l'adsorption de l'ion Cs⁺ sur le sol d'Herqueville peuvent donc provenir de 2 phénomènes. De l'aluminium échangeable, présent en très faible quantité, peut être toujours présent dans le sol de Herqueville au niveau des FES des illites et ainsi bloquer l'accès à ces sites pour le césium. Il est également possible que les problèmes de simulation de l'adsorption de Cs⁺ sur Herqueville proviennent du calcul des proportions minéralogiques dans lesquels les micas – présents en forte quantité dans le sol d'Herqueville – ont été considérés comme de l'illite – du fait de l'impossibilité de les distinguer efficacement par DRX. Les micas possèdent effectivement un comportement d'adsorption fort pour l'ion Cs⁺ mais pas nécessairement aussi fort que les illites. Ainsi, ne pas distinguer les micas de l'illite tend à potentiellement surestimer l'adsorption de l'ion Cs⁺.

Enfin, une dernière expérience a été menée sur le sol d'Étoile-sur-Rhône afin de mesurer l'efficacité du modèle et de la base de données dans des conditions expérimentales plus proches que celles que l'on retrouverait dans la nature. Pour cela, de nouvelles isothermes d'adsorption ont été effectuées avec un ratio solide/liquide plus grand (c.à.d. 0.25 kg.L⁻¹ contre 0.05 kg.L⁻¹ précédemment), à [CaCl₂] aux alentours de 2 mmol.L⁻¹ et avec ajout de 1 puis 2 mmol.L⁻¹ de KNO₃. Dans ces différentes conditions, un accord satisfaisant est observé entre les résultats expérimentaux et les simulations effectuées. Cela tend à confirmer l'efficacité de l'approche mise en place ainsi que du modèle de rétention associé pour prédire des comportements d'adsorption de Sr²⁺ et Cs⁺ dans les sols.

2 Abstract

In case of nuclear accident, ^{90}Sr and $^{134,137}\text{Cs}$ are major radionuclide to account. In a previous work (Siroux et al., *Appl. Geochem.*, submitted), the adsorption of Sr^{2+} and Cs^+ was studied onto purified illite and smectite. In this study, the adsorptions of Sr^{2+} and Cs^+ were obtained onto three less than $150 \mu\text{m}$ fractions of French soil samples—Pusignan, Rhône; Etoile-sur-Rhône, Drôme; and Herqueville, Manche. The less than $2 \mu\text{m}$ fractions of the soil samples were first analysed by X-ray diffraction in order to estimate their clay minerals proportions, which were then approximated to an illite/smectite mixture in consistency with the CEC of $< 150 \mu\text{m}$ fractions. First, Sr and Cs adsorption experiments were made at an ionic strength of $0.1 \text{ mol.kg}_w^{-1} \text{ CaCl}_2$, and at the pH value of the solution equilibrated with water. The experimental isotherms of Sr^{2+} and Cs^+ were then compared with simulations obtained using parameters for the multi-site ions exchanger model from data issued from preceding works including Siroux et al. (*Appl. Geochem.*, submitted). This simulation approach is based the additive adsorption properties between several reactive phases and permits representing satisfactorily the adsorption of Cs and Sr in most cases. In order to highlight the limiting parameters of the modelling predictive ability, treatment were made on soil samples. The major part of the natural organic matter (NOM) from soil was removed using H_2O_2 . Then the adsorption isotherms were repeated. The removal of the NOM does not change significantly the adsorption behaviour of either Sr^{2+} or Cs^+ . In the case of Herqueville soil, the exchangeable Al^{3+} was also removed with several washing with $\text{KCl } 1 \text{ M}$. This removal permits a better simulation of the adsorption isotherm in the case of Sr^{2+} , but not in the case of Cs^+ . The predictive capacities of the modelling were tested onto Etoile-sur-Rhône soil with a synthetic pore water ($[\text{CaCl}_2]$ around 2 mmol.L^{-1} and addition of KNO_3) in order to estimate its efficiency.

3 Publication

3.1 Introduction

The nuclear accident of Fukushima-Daiichi has led to the release of a significant amount of radionuclides in the surrounding environment, out of which cesium-137 and strontium-90 were identified as major contaminants (Tanaka et al., 2012; Kanda, 2013; Sahoo et al.,

2016). ^{137}Cs and ^{90}Sr are two major daughters of the fission of ^{235}U (England and Rider, 1993). In order to understand the aftermath of the Fukushima-Daiichi nuclear events, but also the Chernobyl accident and the different nuclear weapons testing, the scientific community has enhanced the knowledge of the impact and mobility of these two elements in the environment (Bunzl et al., 1998; Matsunaga et al., 1998; Fujikawa et al., 1999; Hou et al., 2003). In France, 19 nuclear power plants are operating and provide the major part of the produced electricity. Thereby, the knowledge of the possible repercussions of such a comparable accident is essential. The objective of this work is to provide a model capable to predict the adsorption of Sr and Cs onto agricultural French soils.

^{90}Sr and ^{137}Cs are well known to have a low mobility (Han et al., 2016; Mishra et al., 2016) in soils due to their strong interactions with clay minerals (Sawhney, 1970; Adeleye et al., 1994; Dyer et al., 2000), out of which illite and vermiculite are known to be the most selective adsorbents for Cs^+ . This high adsorption is due to the weak hydration energy of Cs^+ and mainly attributed to the existence of low concentration high affinity sites, usually referred as frayed edge sites (FES) on illite (Sawhney, 1972; Cornell, 1993; Dzene et al., 2015). Strontium is also greatly retained by clay minerals (Erten et al., 1988; Missana et al., 2008; Galamboš et al., 2013; Siroux et al., submitted) but is not showing any specific high affinity.

In soils, natural organic matter (NOM) also influences the adsorption of Cs^+ . It was evidenced that the NOM coating clay minerals tends to decrease the adsorption of Cs^+ (Dumat et al., 2000). The removal of the initial NOM from soils also enhanced the adsorption of Cs^+ (Dumat et al., 1997). These effects are more important at low concentration of Cs^+ (Dumat and Staunton, 1999). Thus, Staunton et al. (2002) proposed that NOM is fixed in the anion exchange sites around the FES and is blocking physically the access to these sites. The effects of NOM on the adsorption of Sr^{2+} onto soils are scarcely studied. Samadfam et al. (2000) has studied the adsorption of Sr onto a kaolinite by addition of humic acid and only evidenced slight influence.

The adsorption of Cs^+ and Sr^{2+} onto soils was commonly interpreted with semi-empirical approaches as the Langmuir or the Freundlich isotherms (Gutierrez and Fuentes, 1991; Campbell and Davies, 1995; Goto et al., 2008). These approaches only permit a description of the adsorption under fixed physicochemical conditions, and prevent from extrapolating results to other conditions. Thermodynamic modelling, as surface complexation and ionic

exchange modelling, were proposed to improve the knowledge and the description of the adsorption phenomena. Some modelling used both surface complexation and ionic exchange (Bradbury and Baeyens, 1999). This latter model permits a mechanistic description of the cation adsorption onto clay minerals but it does not take into account the pH dependency of adsorption onto cation exchange sites and conversely, major cation from electrolyte cannot be adsorbed on pH dependent sites SOH. With this model, saturation curve of an exchanger by a major cation in function of the pH cannot be explored.

The multi-site ion-exchanger model was successfully used to interpret the adsorption behaviour of multiple cations in various clays minerals and sediments (Stammose et al., 1992; Motellier et al., 2003 ; Jacquier et al., 2004 ; Tertre et al., 2009; Reinoso-Maset and Ly, 2014; Savoye et al., 2015; Siroux et al., submitted). This model is designed to describe the adsorption at a macroscopic scale, and it allows accounting for the solution chemistry of the elements (complexation, hydrolysis, etc.).

By applying the multi-site ion-exchanger model, it is possible to describe an exchanger in two ways: as a unique and specific phase, and through an additive approach. Motellier et al. (2003) characterised directly the Callovo-Oxfordian argillaceous rock in terms of site concentrations and corrected—of adsorbed species activities—selectivity coefficients with the multi-site ion-exchange modelling. Conversely, the additivity approach permits extrapolating the modelling to various types of materials according to their clay minerals compositions. In this study, the predictive character of the modelling approach sits on the additivity of the adsorption properties of reactive phases acting in the studied media. This method consists in i) determining the clay mineral proportions from soil samples; ii) approximating the clay mineral proportions to an illite/smectite mixture in agreement with the original characteristics of soils (mineralogical composition, CEC); and iii) applying the model to simulate the adsorption of Cs and Sr onto these soils. Savoye et al. (2012) used this principle to study the mobility of Cs⁺ through the Callovo-Oxfordian claystones. Tertre et al. (2009) also used this principle for Zn²⁺ in clayey sediments considering an illite/smectite mixture, but the adsorption behaviour of Zn²⁺ has been supposed to be equivalent for illite and smectite. Recently, Missana et al. (2014)—using the Gaines and Thomas (1953) formalism of the ion-exchange—have represented the adsorption of Cs⁺ on various soils and sediments according to their illite, smectite, and kaolinite compositions

In France, the most commonly clay minerals encountered in soils are smectite, illite, kaolinite, and chlorite. Smectite and illite adsorption properties were recently studied by applying the multi-site ion-exchange modelling by Siroux et al. (submitted) and Wissocq et al. (Wissocq, 2017; Wissocq et al., submitted). Reinoso-Maset and Ly (2014) have explored adsorption capacities of kaolinite but the behaviour of Sr²⁺ is missing. Concerning chlorite, studies are missing in the literature. Given its low cation exchange capacity—10-40 meq/100g (Yong et al., 2012)—and the lack of knowledge of any specific behaviour for Cs⁺ or Sr²⁺, chlorite was neglected in the rest of the study.

In this paper, the modelling through the additivity approach was examined to predict the adsorption of Cs⁺ and Sr²⁺ onto three French agricultural soil samples. First, each soil sample was examined in terms of illite/smectite or illite/smectite/kaolinite compositions. Adsorption isotherms of Cs⁺ and Sr²⁺ were built in a large range of concentration on these soil samples. Considering Ca²⁺ as the major cation in the equilibrium solution, the background solution was fixed at an ionic strength of 0.1 mol.kg_w⁻¹ (CaCl₂) at the pH_{water} values measured for each soil. The experimental results were compared to the simulations. In order to improve these simulations the influence of NOM and exchangeable Al³⁺ on the adsorption was explored. Kaolinite was also added in simulations to study its effect. Finally the predictive capacity of the modelling in more relevant environmental conditions was studied.

3.2 Materials and methods

3.2.1 Materials

3.2.1.1 Soils sample collection and characteristics

Three agricultural soil samples were collected near Pusignan (Rhône), Herqueville (Manche) and Etoile-sur-Rhône (Drôme). These soil samples were supposed to be representative of the diversity of the agricultural soil surrounding the French nuclear sites. These soils are classified as cambisol fluvic (Pusignan), cambisol typic (Herqueville), and calcosol (Etoile-sur-Rhône) according to the FAO nomenclature. The first horizon of these soils was collected, air dried, and sieved at 2 mm. Grain-size fractionations were performed

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by wet sieving and sedimentation following the AFNOR NF X31-107 standard. The granulometric repartitions of the three soils are reported in Table IV. 1. It appears that all the samples have a comparable percentage of fine particles (0-2 μm) referenced as clays.

Table IV. 1. Granulometric repartition of soil samples (< 2 mm).

	depth	Clay %	Fine silt %	Coarse silt %	Fine sand %	Coarse sand %
	cm	0-2 μm	2-20 μm	20-50 μm	50-200 μm	200-2000 μm
Pusignan (F-69330)	0-30	16.54	19.53	16.69	18.35	28.89
Etoile-sur-Rhône (F-26800)	0-20	18.22	13.82	33.49	27.28	7.18
Herqueville (F-50440)	0-14	13.13	18.86	35.19	20.98	11.84

Table IV. 2 presents the characteristics of each soil samples in term of organic matter, organic carbon, carbonate, etc. The organic matter (OM) was determined by the volatile loss at 550°C, organic carbon (C_{org}) and nitrogen (N) contents were determined within the standard French procedures NF ISO 10694 and the NF ISO 13878 respectively. The CaCO_3 concentration was measured following the Bernard calcimeter method (AFNOR NF ISO 10693) and the pH_{water} and pH_{KCl} measurements were performed following the NF ISO 10390.

Table IV. 2. Organic matter (OM), organic carbon (C_{org}), nitrogen, pH_{water} , pH_{KCl} and CaCO_3 composition of soil samples (< 2 mm).

	OM $\text{g}\cdot100\text{g}^{-1}$	C_{org} $\text{g}\cdot\text{kg}^{-1}$	N $\text{g}\cdot\text{kg}^{-1}$	C/N	pH_{water}	pH_{KCl}	CaCO_3 $\text{g}\cdot100\text{g}^{-1}$
Pusignan	4.39	25.4	2.14	11.8	6.9	7.1	3.5
Etoile-sur-Rhône	2.03	11.7	1.1	10.7	7.5	7.4	4.9
Herqueville	4.94	28.5	2.64	10.8	5.5	4.7	1.4

Pusignan is a neutral soil ($\text{pH}_{\text{water}} = 6.9$) with a moderate concentration of limestone and organic matter. In solution the dissolution of limestone could interfere in the adsorption of strontium through carbonate complexation. Nevertheless, at the value of pH_{water} , and with the proportion of CaCO_3 of soils in Table IV. 2, only a minor amount of SrHCO_3^+ (4%) complex is calculated using thermodynamic data from Busenberg et al. (1984). Etoile-sur-Rhône is also a neutral soil with the biggest concentration of limestone but with the lowest concentration of natural organic matter. Herqueville is an acidic soil ($\text{pH}_{\text{water}} = 5.5$), which contains low limestone content (value at the limit of quantification by the method) but with the highest proportion of organic matter (OM). OM is known to interfere in the adsorption of Cs^+ (Dumat and Staunton, 1999).

3.2.1.2 Chemicals reagents

The chemicals reagents used were at least of analytical grade. Stable Sr solutions were prepared from a $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ salt (99.995% Suprapure, Merck).

3.2.2 Experimental protocols

All experiments were made by batch method and conducted at room temperature ($22 \pm 2^\circ\text{C}$). They were performed in 10 mL polycarbonate Nalgene centrifuge tube (3138-0010, Thermo Scientific). All solutions and suspensions were made by weighing.

3.2.2.1 Sample preparation

To avoid both coarse sand and gravels, and to optimize the soil aliquots homogeneity, the < 2 mm dry soil was dry sieved at 150 μm . First, experiments were made with these untreated materials. For experiments on soils without NOM, soils samples were placed in H_2O_2 15% and heated at 80°C under agitation until the mixtures stop bubbling. Samples were washed first with milli-Q water (Millipore, $18.2 \text{ M}\Omega \cdot \text{cm}^{-2}$), then with ethanol. This operation was repeated twice, then the organic carbon and nitrogen contents were analysed in an automatic CHNS analyser (Thermofisher) after acidification of samples with

8% H₃PO₄. The removing of dissolved Al³⁺ in Herqueville was made with several washings with 1 mol.kg_w⁻¹ KCl solution at pH ca. 4. The extraction of dissolved Al³⁺ was followed measuring the concentrations of Al and Si in supernatants in inductive-coupled plasma by atomic emission spectroscopy (ICP-AES). The final step was washing the soils with 0.1 mol.kg_w⁻¹ CaCl₂, then with ethanol.

3.2.2.2 Characterization of samples

The cation exchange capacities (CEC) and the exchangeable cations (Ca²⁺, Na⁺, K⁺, and Mg²⁺) concentrations were determined on the three < 2 mm soils by using the Metson method (NF X31-130) and on the < 150 µm soil sample. Then the CEC was measured by extracting all exchangeable cations with a 0.1 mol.kg_w⁻¹ KCl solution at pH ca. 10 (KOH) during one day to replace them by K⁺. Supernatant was removed and the soil was washed with milli-Q water, then with ethanol. The adsorbed K⁺ was extracted with a 0.1 mol.kg_w⁻¹ CsCl solution, and analysed by inductive-coupled plasma in ICP-AES. To determine the exchangeable cations concentrations, soil samples were put in contact with a 0.1 mol.kg_w⁻¹ CsCl solution during 3 days, then supernatants were removed and analysed in ICP-AES.

The CEC of fractions < 150 µm and < 2 mm are similar (cf. Table IV. 4 and Table IV. 5). It shows that the reactive composition of soil samples has not been affected by the dry sieve. The < 150 µm fractions can be considered as representative of untreated soil fractions.

The mineralogical composition and the CEC of soil samples were also determined on < 2 µm soil fractions obtained by grain-size fraction of the bulk soil (< 2 mm). Results are summarized in Table IV. 3 and Table IV. 4. After a H₂O₂ treatment, CEC were measured with the MgCl₂ method (Righi et al., 1993). It consists to saturate samples with MgCl₂, the excess of which is removed with ethanol. Finally, Mg²⁺ are exchanged with NH₄⁺ and dosed by atomic adsorption spectroscopy. The mineralogical composition was estimated by XRD of air dried deposits, and deposits saturated with ethylene glycol. Two other treatments were analysed by XRD: heating to 105°C and heating to 500°C. These treatments were made in order to refine the mineralogical analysis. Identification of crystallized phases used the ClayXR software (Bouchet, 1992) and NEWMOD© software (Reynolds, 1985) for quantification. Quantification of the clay minerals in soils is based on the quantification of clay minerals contained in the clay size-fraction (< 2 µm) of soils.

Table IV. 3. Average of the mineralogical proportion (in %) of the fraction < 2 µm of Pusignan, Etoile-sur-Rhône and Herqueville.

Sample	mica, illite, glauconite	I/S R=1, G/S R=1	I/S R=0, G/S R=0	kaol.	chlorite ± C/S	quartz	feldsp. K	plagio-clases	goeth./Fe-mx	gypse	TiO ₂
Pusignan	8.6	25.6	-	22.8	4.5	30	0.2	0.5	7.1	-	0.7
Etoile-sur-Rhône	17.9	45.7		10.3	1.8	3.1	0.3	0.4	20.2	<0.1	0.3
Herqueville	14.5	50.5	-	20	2.1	5.3	0.2	0.4	6.2	<0.1	0.8

Abbreviations: **mica, illite, glauconite:** mica, illite and mixed layer (<20 % of smectite); **I/S R=1:** ordered mixed layer illite/smectite; **I/S R=0:** disordered mixed layer illite/smectite; **G/S R=1:** ordered mixed layer glauconite/smectite; **I/S R=0:** disordered mixed layer glauconite /smectite; **kaol.:** kaolinite; **C/S:** mixed layer chlorite/smectite; **feldsp.K:** potassium feldspar; **goeth./Fe-mx:** iron minerals (goethite, hematite, siderite, etc.); **TiO₂:** titanium oxide.

Pusignan soil presents an important proportion of quartz (30 %) but in this study, quartz is considered as a non-adsorbing phase with regards to Cs⁺ and Sr²⁺. The ratio I/S was estimated following the position of the peak compared to the positions of peaks from a pure illite and a pure smectite on the XRD diffractogram at the position (001). For Pusignan, the mixed layer ratio was estimated at I/S (40/60). To simplify simulations and because it was not possible to distinguish mica and glauconite from illite, all these phases were considered as illite in a first approximation. Pusignan was also described in terms of clay mineral phases—illite, smectite, kaolinite and chlorite. Its clay mineral proportions are shown in Table IV. 4. Considering also the goethite with a CEC of 100 meq.100g⁻¹ (Langmuir, 1997) and by applying general CEC of 24.9 meq.100g⁻¹ for illite (Wissocq, 2017; Wissocq et al., submitted), 88.7 meq.100g⁻¹ for smectite (Siroux et al., submitted), 5.6 meq.100g⁻¹ for kaolinite (Reinoso-Maset and Ly, 2014), 10 meq.100g⁻¹ for chlorite, the clay mineral quantification from Pusignan gives a CEC of 26.3 meq.100g⁻¹, close to the measured value of 22.9 meq.100 g⁻¹.

Mixed layer I/S represents the major part of the reactive minerals in the < 2 µm fraction of Etoile-sur-Rhône. Moreover, more than 20% of goethite was quantified. Thought goethite may slightly contribute to the CEC value in the < 2 µm and raw soil at pH ca. 7.5, it was neglected in simulations of batch experiments in a first approximation. In light of the XRD diffractograms, three mixed layers can be distinguished in a mixture of 6% I/S (10/90),

30% I/S (50/50) and 9.7% C/S (50/50). The dedicated clay fraction proportions are resumed in Table IV. 4. These proportions allow calculating a CEC of 52.2 meq.100g⁻¹.

The XRD of Herqueville soil shows the presence of pure mica. As explained before, XRD analysis does not permit differentiating mica from illite, thus micaceous minerals were considered as illite. The 50.5% of mixed layers were interpreted as a mixture of 18.5% I/S (40/60) and 32% M/C (50/50). At this pH (pH_{water} = 5.5), the goethite surface is supposed to be positively charged—pzc varies from 7.5 to 9.3 (Lyklema, 1995) depending on carbonate content (Villalobos and Leckie, 2000)—and does not interfere in the CEC measurement. Thus these proportions represent a CEC of 22.6 meq.100g⁻¹, close to the measured CEC (i.e. 20 meq.100g⁻¹).

The obtained clay mineral proportions illite/smectite/kaolinite/chlorite and the CEC calculated from these clay mineral proportions are summarized in Table IV. 4. As shown previously, the calculated CEC are akin to those measured for each soil samples.

Table IV. 4. Calculated illite, smectite, kaolinite and chlorite proportions for each samples (<2 μm) and their associated calculated CEC.

Sample	% illite	% smectite	% kaolinite	% chlorite	Calculated CEC (meq.100g ⁻¹)	Measured CEC on < 2 μm fraction (meq.100g ⁻¹)	Measured CEC on < 2 mm fraction (meq.100g ⁻¹)
Pusignan	18.8	14.4	22.8	4.5	26.3	22.9	12.2
Etoile-sur-Rhône	33.5	25.25	10.5	6.65	52.2	49.7	9.9
Herqueville	37.9	11.1	20	18.1	22.6	20.0	7.6

In this study, the < 150 μm fractions were used for the experiments. The CEC and the exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) of these untreated fractions were measured in order to determine the clay minerals proportions in agreement with the CEC of the samples (Table IV. 5).

Table IV. 5. Exchangeable cations concentrations and CEC measurement of soil samples (< 150 μm).

Exchangeable cations

Sample	Na	Ca	Mg	K	Al	Sum of exchangeable cations	CEC
	(meq.100g ⁻¹)	(meq.100g ⁻¹)	(meq.100g ⁻¹)	(meq.100g ⁻¹)	(meq.100g ⁻¹)	(meq.100g ⁻¹)	
Pusignan	0.08	8.09	0.40	0.70	-	9.27	12.41
Etoile-sur-Rhône	0.08	9.25	0.22	0.40	-	9.95	9.78
Herqueville	0.24	2.44	0.52	0.36	1.43 ^a	4.99	7.53

^aAl concentration obtained on < 2 mm, extracted by KCl 1M

The CEC measured with < 150 μm material are lower than those obtained with 2 μm (cf. Table IV. 4). This is logical given that clay minerals fraction < 150 μm is lower than those from 2 μm . The sum of exchangeable cations is fairly similar with the CEC, except for Herqueville in which the exchangeable H⁺ are greatly present—as awaited for an acidic soil.

As illite and smectite were supposed to be the most reactive phases for the adsorption of Cs⁺ and Sr²⁺, the compositions of soil samples were next simplified to illite/smectite mixtures. In order to attain the measured CEC on < 150 μm fractions (Table IV. 6), illite and smectite proportions were calculated by keeping the illite/smectite ratio constant.

Table IV. 6. Calculated proportions of illite/smectite proportions for each samples (<150 μm).

Sample		Measured CEC (meq.100g ⁻¹)	% illite	% smectite
Unreated material	Pusignan	12.4	13.0	10.3
	Etoile	9.8	10.7	8.1
	Herqueville	7.5	15.2	4.2
After removal of NOM	Pusignan	10.4	10.9	8.7
	Etoile	9.6	10.4	7.9
	Herqueville	7.1	14.3	4.0
After removal of Al ³⁺	Herqueville	10.1	20.4	5.7

The removal of NOM does not change significantly the CEC of soil samples except for Pusignan. Nonetheless, the adequacy between the CEC before and after the treatment tends to prove that the treatment has not damaged samples. The removal of Al³⁺ leads to an increase of the Herqueville CEC. It seems that the CEC measurement protocol used in this study was not sufficient to remove Al coatings from untreated samples. Thus measured CEC on untreated Herqueville sample and after removal of NOM are probably underestimated.

3.2.2.3 Isotherms protocol

Experiments were made with < 150 μm fractions of soil samples. A mass of 0.35 g of soils was placed in centrifuge tubes with 7 mL of electrolyte to obtain a 50 g.L⁻¹ S/L ratio. As soils were mostly composed of exchangeable calcium ions, the electrolyte solutions were made with CaCl₂ to work in a calcic environment. First, the ionic strength was set at I = 0.1 mol.kg_w⁻¹—a 0.033 mol.kg_w⁻¹ CaCl₂ solution was used as background electrolyte. Soils were equilibrated under agitation with the CaCl₂ solution for 24 h. The pH values were not adjusted at this step to preserve the natural environment of soils. A stable SrCl₂ (or CsCl) was added in batches to reach an initial Sr concentration span from 10⁻² to 10⁻⁶ mol.kg_w⁻¹, and from 10⁻² to 10⁻¹⁰ mol.kg_w⁻¹ for Cs. Then mixtures were spiked with ⁸⁵Sr or ¹³⁷Cs, and left under agitation for two or five days for Sr and Cs, respectively. Finally, suspensions

were ultracentrifuged (20.000 g during 45 min, 70.1 Ti Rotor, Optima LE-80R, Beckman) and 1 mL of the supernatant was collected and counted in gamma spectrometry.

The initial activities in the spiked experiments were determined using a blank procedure—same protocol but without soil samples in batches. The partition coefficients R_D (L.kg^{-1}) were calculated using:

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

where C_i and C_{eq} are respectively the initial and equilibrium activities of either Cs or Sr, V is the total volume of solution, and m is the total dry mass of solid phase.

3.2.2.4 Analytical methods

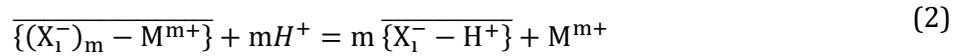
The measurement of the aqueous concentrations of stable Sr, Na, Ca, K, Mg, Al and Si were made by ICP-AES (Activa, Horiba Jobin Yvon). Aliquots were diluted with 2% sub-boiling HNO_3 (DuoPur, Milestone) and measurements were made at 407.771 nm for strontium, 589.592 nm for sodium, 317.933 nm for calcium, 766.490 nm for potassium, 273.553 nm for magnesium, 167.02 and 396.152 nm for aluminium and 212.412 nm for silicon. The aqueous concentrations of Cs were measured by ICP-MS (Element 2, Thermo Fisher Scientific). The activities of supernatant were determined after sampling a 1 mL aliquot using a gamma counter (1480 Wizard 3, Perkin Elmer). The pH values were determined with a combined microelectrode (pH InLab, Mettler Toledo) through a 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 pH-units.

3.2.3 Modelling

3.2.3.1 Multi-sites ion-exchanger formalism

The detailed formalism was already fully described (Motellier et al., 2003; Reinoso-Maset and Ly, 2014; Siroux et al., submitted). A simple case will be presented here. Considering a

negatively charge type of site X_i^- -at the surface of the exchanger-occupied by a cation H^+ . The exchange equilibrium reaction between H^+ and a cation M^{m+} is described as followed:



This reaction is described by the mass-action law and the corresponding equilibrium constant can be written as:

$$K_{M^{m+}/mH^+}^i = \frac{[\overline{X_i^- - H^+}]^m \cdot [M^{m+}]}{[\overline{(X_i^-)_m - M^{m+}}] \cdot [H^+]^m} \cdot \frac{(f_{X_i^- - H^+})^m}{(f_{(X_i^-)_m - M^{m+}})} \cdot \frac{\gamma_{M^{m+}}}{\gamma_{H^+}^m} \quad (3)$$

where $[]$ is the solution (mol.kg⁻¹ of water) concentration, $\overline{[]}$ is the adsorbed concentration (mol.kg⁻¹ of solid) of species, f are the activity coefficients of adsorbed species and γ are the activity coefficient of aqueous species—calculated here using Davies (1962) equation. As the activity coefficients of the adsorbed species are not known, it is assumed in this modelling that the ratio between these coefficients is constant. Thus, the apparent constants (called corrected selectivity coefficients) are described as follows:

$$K_{M^{m+}/mH^+}^{*i} = \frac{[\overline{X_i^- - H^+}]^m \cdot [M^{m+}]}{[\overline{(X_i^-)_m - M^{m+}}] \cdot [H^+]^m} \cdot \frac{\gamma_{M^{m+}}}{\gamma_{H^+}^m} \quad (4)$$

Each type of site X_i^- is also described by its site concentration SC_i in mol.kg⁻¹ of solid. These sites are typically determined studying the adsorption of a major cation in saturation under homo-ionic exchanger at different pH values—See Motellier et al. (2003) and Reinoso-Maset and Ly (2014) for details. The site concentration is equal to the sum of all the adsorbed species concentrations.

$$SC_i = \overline{X_i^- - H^+} + m \overline{(X_i^-)_m - M^{m+}} \quad (5)$$

Combining the questions (3) and (4) allows calculating $\overline{(X_i^-)_m - M^{m+}}$ then the partition coefficients with:

$$R_D = \frac{[\overline{M}]}{[M]} = \frac{\sum_i \overline{(X_i^-)_m - M^{m+}}}{[M]} \quad (6)$$

In this study, soils were considered as saturated with calcium. The addition of trace elements involves that the site concentrations can be re-expressed as follows:

$$SC_i = \overline{X_i^- - H^+} + m \overline{(X_i^-)_m - M^{m+}} + 2 \overline{(X_i^-)_2 - Ca^{2+}} \quad (7)$$

Combining (3) and (6) allows determining $[\overline{X_I^- - H^+}]$ then $[\overline{(X_I^-)_m - M^{m+}}]$ in order to calculate the partition coefficient.

3.2.3.2 K⁺ illite-smectite database

As a substantial amount of potassium will be added in one of the following experiments (vide post, § 3.3.4), K⁺ exchange parameters have to be added to the database for Cs⁺ and Sr²⁺ for smectite and illite.

3.2.3.2.1 General presentation of the strategy

The construction follows the principal steps presented in Siroux et al. (submitted): (i) compilation of experimental results from the literature made on homo-ionic exchanger (saturation curve by K⁺, adsorption isotherms made on K-exchanger); (ii) applying the modelling to these experimental results and simultaneous fitting of the modelling with the experimental data using the MS Excel Solver; and (iii) determination of the uncertainties of the fitted parameters using the SolverAid macro from De Levie (2005).

3.2.3.2.2 Adsorption behaviour of K⁺ onto smectite

In the case of smectite, only one paper on the literature allows determining the selectivity coefficients K⁺/H⁺. Gaucher (1998) has studied the saturation of a purified K-bentonite at I = 0.02 M (KCl) and S/L = 8 g.L⁻¹. The saturation curve by K⁺ of the purified bentonite is presented in Figure IV. 1 with the modelling and the contribution of the different sites.

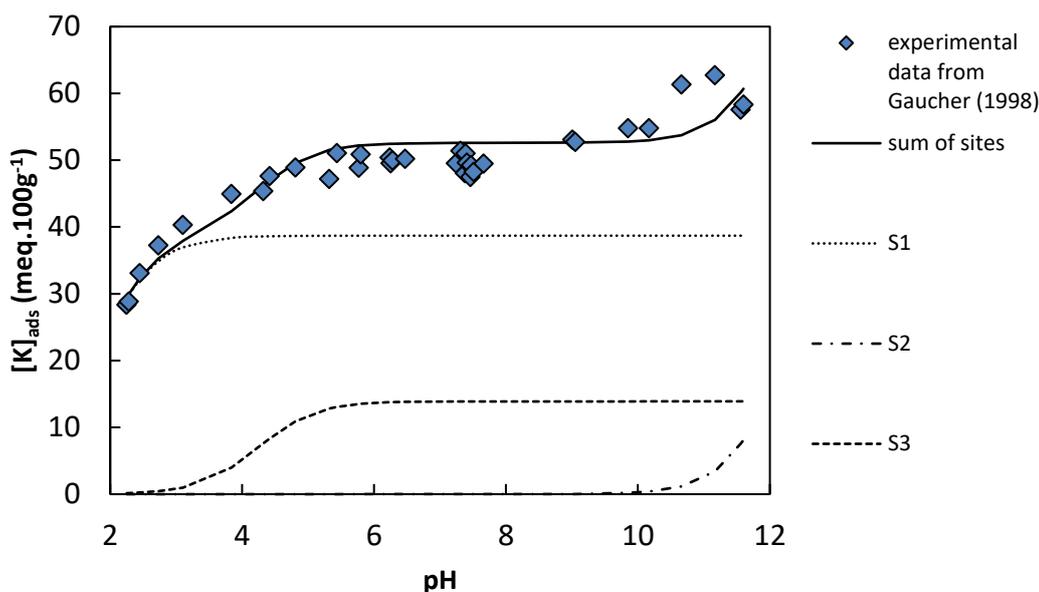


Figure IV. 1. Saturation of a bentonite with K^+ vs. pH at constant $I = 0.02 \text{ M}$ (KCl) and solid/liquid ratio (S/L) of 8 g.L^{-1} from Gaucher (1998).

For the sake of consistency, the site concentrations presented in Table IV. 7 of the main text—from our previous work Siroux et al. (submitted)—has been preserved. Gaucher (1998) proposed a CEC of $92.4 \text{ meq.100g}^{-1}$ for his purified bentonite, but it appears on this saturation curve that K^+ did not saturate the CEC. The adsorbed K^+ reached a maximum of 63 meq.100g^{-1} . Nevertheless, the simulation follows well the experimental data. The obtained selectivity coefficients are resumed in Table IV. 7.

Even though obtained selectivity coefficients have relatively low uncertainties, they could be questioned. The saturation curve does not reach the announced CEC ($92.4 \text{ meq.100g}^{-1}$) and is underestimated probably caused by an incomplete conditioning of the bentonite or difficulties in the experiment. Thus, the obtained corrected selectivity coefficient from this saturation curve must be considered with caution. Despite this problems, these selectivity coefficients will be used in § 3.3.4 in order to test the predictive capacities of the modelling.

3.2.3.2.3 Adsorption behaviour of K^+ onto illite

Two studies were particularly used in order to build the database of the adsorption of K^+ onto illite. As for smectite, Gaucher (1998) has studied the saturation of an illite by K^+ . This study was also made at $I = 0.02 \text{ M}$ (KCl) but the S:L ratio was increased to 20 g.L^{-1} . Missana et al. (2014) have studied the adsorption at trace level of Cs onto K-illite. This study is

particularly interesting because it permits determining the behaviour of K^+ in the low concentration site S_0 .

The saturation curve of illite by K^+ is showed in Figure IV. 2. The experimental data from Gaucher (1998) are represented together with the modelling and the contribution of the different sites. The S_0 site is not represented in this saturation curve as its concentration is very low ($0.11 \text{ meq.}100\text{g}^{-1}$), and does not influence the saturation of the exchanger.

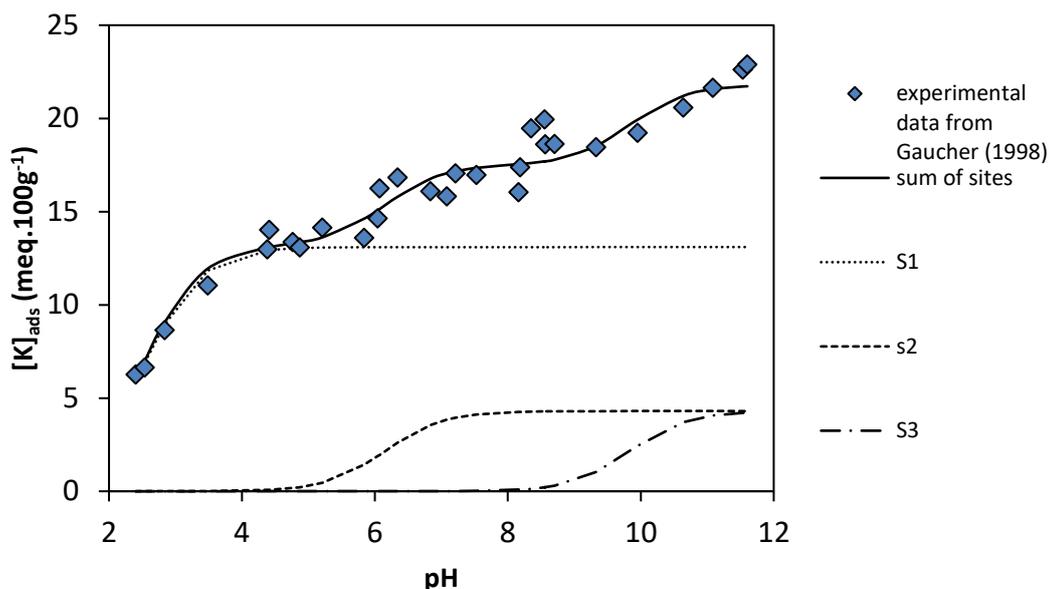


Figure IV. 2. Saturation of an illite with K^+ vs. pH at constant $I = 0.02 \text{ M (KCl)}$ and solid/liquid ratio (S/L) of 20 g.L^{-1} from Gaucher (1998)

The adsorption isotherm of Cs onto K-illite is presented in Figure IV. 3. The simulation satisfactorily represents experimental points. Moreover, the simulation seems rather similar to the one from Gaucher (1998). The differences can come from the illite itself. In our database, the CEC of illite is at $24.9 \text{ meq.}100 \text{ g}^{-1}$ while Missana et al. (2014) proposed a CEC of $19 \text{ meq.}100 \text{ g}^{-1}$.

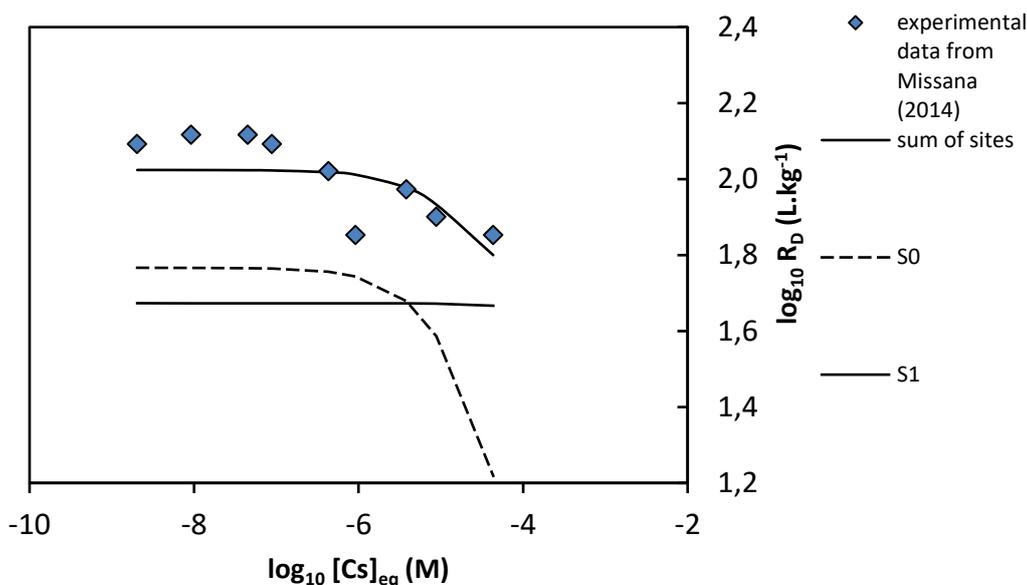


Figure IV. 3. Adsorption isotherm of Cs onto K-illite at $I = 0.1 \text{ M (KCl)}$, $\text{pH} = 7$ and $\text{S:L} = 2 \text{ g.L}^{-1}$ from Missana et al. (2014)

Both experiments were fitted simultaneously in order to obtain a coherent database. The site concentrations were set as the selectivity coefficients Cs^+/H^+ . The selectivity coefficients obtained from these experiments are shown in Table IV. 7.

From the Cs^+/H^+ selectivity coefficients in Table IV. 7, and in order to compare with the literature, it is possible to calculate a $\log_{10} K_{\text{K}^+/\text{Cs}^+}^{\text{S0}} = 3.77 \pm 1.01$ comparable to those obtained by Missana et al. (2014).

3.2.3.3 Database used

Initial parameters (SC_i and $\log_{10} K_{\text{M}^+/\text{N}^+}^i$) were needed to realize simulations. These parameters were taken from Wissocq et al. (Wissocq, 2017; Wissocq et al., submitted) that treat the adsorption behaviour of Cs^+ and Sr^{2+} onto Ca-conditioned smectite and illite in the multi-sites ion-exchanger formalism. As Ca^{2+} is the major exchangeable cation in all soil samples, it seems preferable to use the Ca-database than the Na- one. All parameters used for simulations are summarized in Table IV. 7.

Chapitre IV. On the use the multi-site ion exchange model to predictively simulate the adsorption behaviour of cesium and strontium onto French agricultural soil

Table IV. 7. Summary of the site concentrations and selectivity coefficients used in this study.

Mineral	Site	Site concentration (mmol.100g ⁻¹)	Selectivity coefficient	Selectivity coefficient value	References
Illite	S ₀	0.1	$\log_{10}K_{Ca^{2+}/2H^+}^{+0}$	0.40 ± 1.98	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+0}$	-1.70 ± 1.82	
			$\log_{10}K_{Cs^+}/H^+$	-5.68 ± 1.00	
			$\log_{10}K_{K^+}/H^+$	-1.91 ± 0.12	
	S ₁	13.1	$\log_{10}K_{Ca^{2+}/2H^+}^{+1}$	2.17 ± 0.07	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+1}$	2,43 ± 0.64	
			$\log_{10}K_{Cs^+}/H^+$	-0.85 ± 0.51	
			$\log_{10}K_{K^+}/H^+$	0.70 ± 0.12	
	S ₂	4.3	$\log_{10}K_{Ca^{2+}/2H^+}^{+2}$	4.31 ± 0.22	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+2}$	3.68 ± 0.37	
			$\log_{10}K_{Cs^+}/H^+$	4.91 ± ∞ ^b	
			$\log_{10}K_{K^+}/H^+$	4.32 ± 0.18	
	S ₃	7.4	$\log_{10}K_{Ca^{2+}/2H^+}^{+3}$	11.74 ± 0.20	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+3}$	11.25 ± 0.71	
			$\log_{10}K_{Cs^+}/H^+$	13.85 ± ∞ ^b	
			$\log_{10}K_{K^+}/H^+$	7.98 ± 0.27	
Smectite	S ₀	0.01	$\log_{10}K_{Ca^{2+}/2H^+}^{+0}$	-1.46 ± 0.58	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+0}$	-	
			$\log_{10}K_{Cs^+}/H^+$	-3.85 ± 0.27	
			$\log_{10}K_{K^+}/H^+$	-	
	S ₁	38.7	$\log_{10}K_{Ca^{2+}/2H^+}^{+1}$	0.49 ± 0.49	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+1}$	0.31 ± 0.03	
			$\log_{10}K_{Cs^+}/H^+$	-0.65 ± 0.08	
			$\log_{10}K_{K^+}/H^+$	-0.06 ± 0.12	
	S ₂	36.1	$\log_{10}K_{Ca^{2+}/2H^+}^{+2}$	4.35 ± 0.03	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+2}$	4.47 ± 0.09	
			$\log_{10}K_{Cs^+}/H^+$	7.80 ± ∞ ^b	
			$\log_{10}K_{K^+}/H^+$	10.26 ± 0.14	
	S ₃	13.9	$\log_{10}K_{Ca^{2+}/2H^+}^{+3}$	14.84 ± 0.06	Wissocq (2017); Wissocq et al. (submitted)
			$\log_{10}K_{Sr^{2+}/2H^+}^{+3}$	14.78 ± 0.22	
			$\log_{10}K_{Cs^+}/H^+$	13.50 ± ∞ ^b	
			$\log_{10}K_{K^+}/H^+$	2.39 ± 0.22	

Table IV. 7. Summary of the site concentrations and selectivity coefficients used in this study.

Mineral	Site	Site concentration (mmol.100g ⁻¹)	Selectivity coefficient	Selectivity coefficient value	References
Kaolinite	X _s	8.2.10 ⁻³	$\log_{10}K_{Ca^{2+}/2H^+}^{*S}$	<0 ^a	Reinoso-Maset and Ly (2014)
			$\log_{10}K_{Cs^+}/H^+$	-2.90	
	Y ₁ O H	1.1	$\log_{10}K_{Ca^{2+}/2H^+}^{*1}$	0.33	
			$\log_{10}K_{Cs^+}/H^+$	-0.10	
	Y ₂ O H	1.9	$\log_{10}K_{Ca^{2+}/2H^+}^{*2}$	2.71	
			$\log_{10}K_{Cs^+}/H^+$	3.62	

^a Gussed value. See text for details

^b Infinite uncertainties were attributed to several selectivity coefficients of cesium. These uncertainties are explainable by the absence of constraint during the acquisition of these selectivity coefficients (Wissocq, 2017; Wissocq et al., submitted)—these fixation sites were not useful to model the experimental isotherms. Nonetheless, as the adsorption of Cs onto soils is generally driven by FES of illite, these fixation sites should have a minimal influence on the adsorption behaviours of Cs.

The parameters of the adsorption onto kaolinite were directly taken from Reinoso-Maset and Ly (2014) where the adsorption behaviour of major cations was studied according to the multi-sites ion-exchanger formalism. The adsorption of Cs⁺ at trace level has also been studied on a Na-kaolinite. It shows specific adsorption behaviour of Cs⁺ at the lowest concentrations site X_s. The $\log_{10}K_{Cs^+}/H^+^{*iX_s}$ was determined in the paper, but not the behaviour of Ca²⁺ on this site. We have made the hypothesis that this binding site would be also saturated by Ca²⁺ at any pH. Thus the maximal value of $\log_{10}K_{Ca^{2+}/2H^+}^{*iS}$ was supposed to be 0.

3.3 Results & Discussion

3.3.1 Adsorption of Cs⁺ and Sr²⁺ onto soils, and simulations in the framework of the multi-site ion-exchange model

Sorption isotherms of cesium and strontium were done onto untreated soil samples (< 150 μm). To simplify the simulations, only clay minerals were considered as possible adsorbent of Cs⁺ and Sr²⁺, and the clay minerals proportion was approximated to an illite/smectite mixture as explained in § 3.2.2.2. Another simplification was as Ca²⁺ is the most

concentrated major exchangeable cation in all soils—except for Herqueville –, soils were considered as initially saturated with calcium and Ca^{2+} was the only major cation considered for simulations. Thus, adsorption isotherm in concentration of Cs^+ and Sr^{2+} were made on soil samples at pH_{water} and $I = 0.1 \text{ mol.kg}_w^{-1}$ in CaCl_2 . Accounting for kaolinite in the simulation was also considered.

High and low limits represent simulations considering $\log_{10}K_{\text{Ca}^{2+}/2\text{H}^+}^{*i} + \sigma$ and $\log_{10}K_{\text{Cs}^+/\text{H}^+}^{*i} - \sigma$ (low limit) and inversely (high limit).

3.3.1.1 Adsorption of Cs^+

The adsorption isotherms of Cs^+ onto Pusignan, Etoile-sur-Rhône, and Herqueville at $I = 0.1 \text{ mol.kg}_w^{-1}$ (CaCl_2) is shown in Figure IV. 4. Simulations (plain line) and extremum limits of simulations—dashed line, calculated using the maximum uncertainty on $K_{\text{Ca}^{2+}/2\text{H}^+}^{*is}$ and $K_{\text{Cs}^+/\text{H}^+}^{*iXs}$, which might overestimate the actual uncertainty—of these adsorptions are also represented. For each soil, isotherms remind the shape of Cs^+ isotherms in concentration onto illite (Poinssot et al., 1999a, b; Missana et al., 2014) with the specific and strong adsorption of Cs^+ at low concentrations generally attributed to the FES. In view of isotherms shape, it is possible to claim that illite drives adsorption of Cs^+ onto soils—especially for Pusignan and Etoile-sur-Rhône. This assessment is verified by looking at the clay mineral repartition for the adsorption of Cs^+ (Figure IV. 12) in which the adsorption is widely dominated by illite.

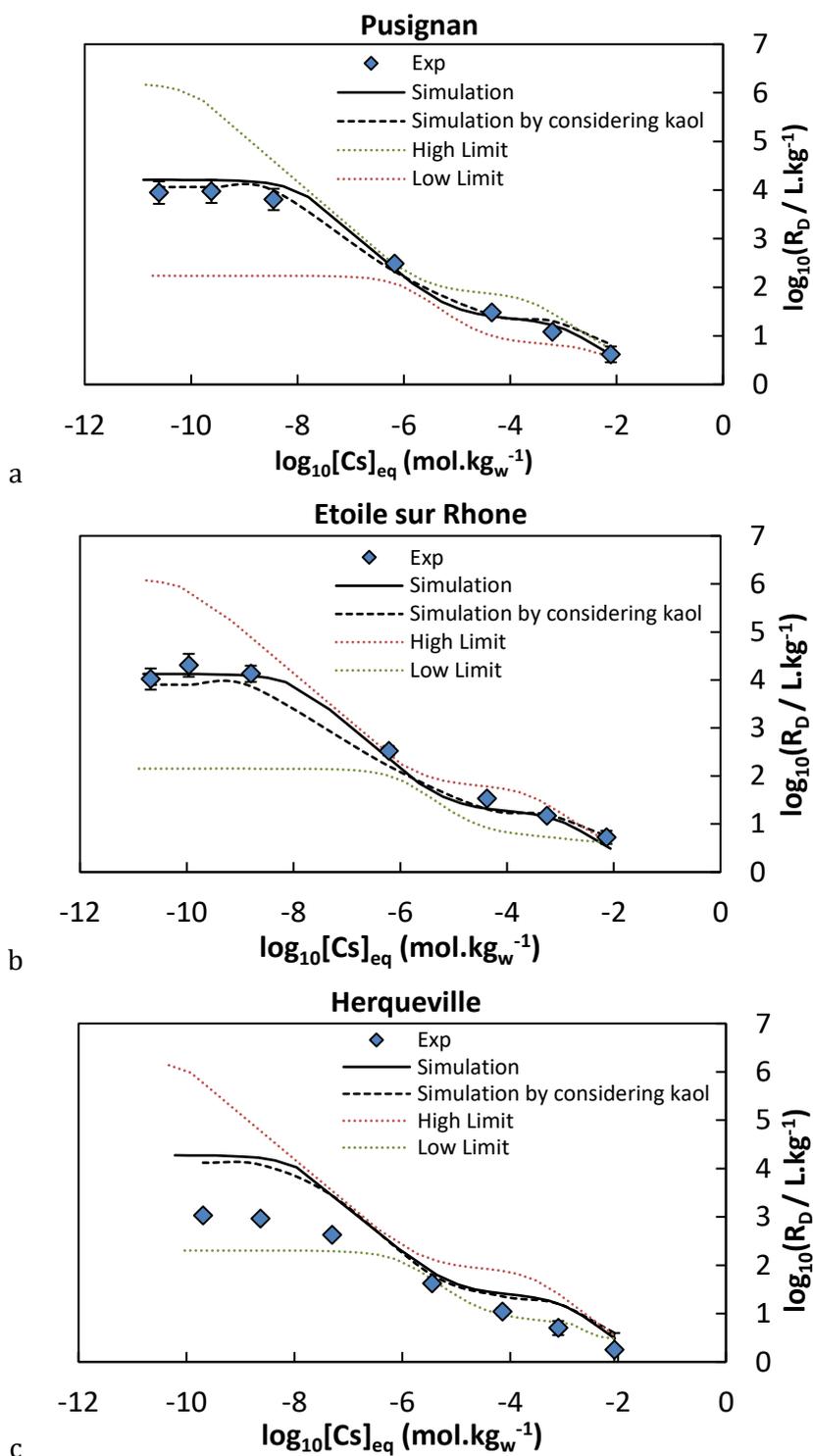


Figure IV. 4. Adsorption isotherms of Cs⁺ onto soil samples at pH_{water}—6.4, 6.5 and 4.6 for Pusignan (a), Etoile-sur-Rhône (b) and Herqueville (c) respectively –, S/L = 0.05 kg.L⁻¹ and I = 0.1 mol.kg_w⁻¹ (CaCl₂) with the associated simulations (plain lines) and the simulation extrema. Representation in dotted line of obtained simulations if kaolinite is taken into account.

3.3.1.2 Adsorption of Sr²⁺

Figure IV. 5 presents adsorption isotherms in concentration of Sr onto soils at pH_{water} and I = 0.1 mol.kg_w⁻¹ (CaCl₂). As for Cs, the simulation and the extremum values of simulation are also represented. In the Supplementary data is presented the adsorption percentage of Sr²⁺ onto soil samples and the repartition of this adsorption following the different clay minerals. Illite and smectite have comparable affinities for Sr. Nevertheless, as smectite presents a higher CEC than illite; smectite tends to drive the adsorption of Sr onto soils. Sr experimental adsorption results are slightly underestimated by simulations in the cases of Pusignan and Etoile-sur-Rhône—in terms of percentage of adsorption, the highest overestimation is at 3.4% for Pusignan and 4.4% for Etoile-sur-Rhône –, while it is slightly overestimated for Herqueville—the adsorption is lowered to 3.7%. Assuming that the contribution of S₀ site of illite is minor, we only consider the uncertainties relative to other sites and principally to the high uncertainty associated to log₁₀K_{Ca²⁺/2H⁺}^{*1} for smectite (i.e. 0.49±0.49). This site has a minor role in the adsorption of Cs but a major one for Sr.

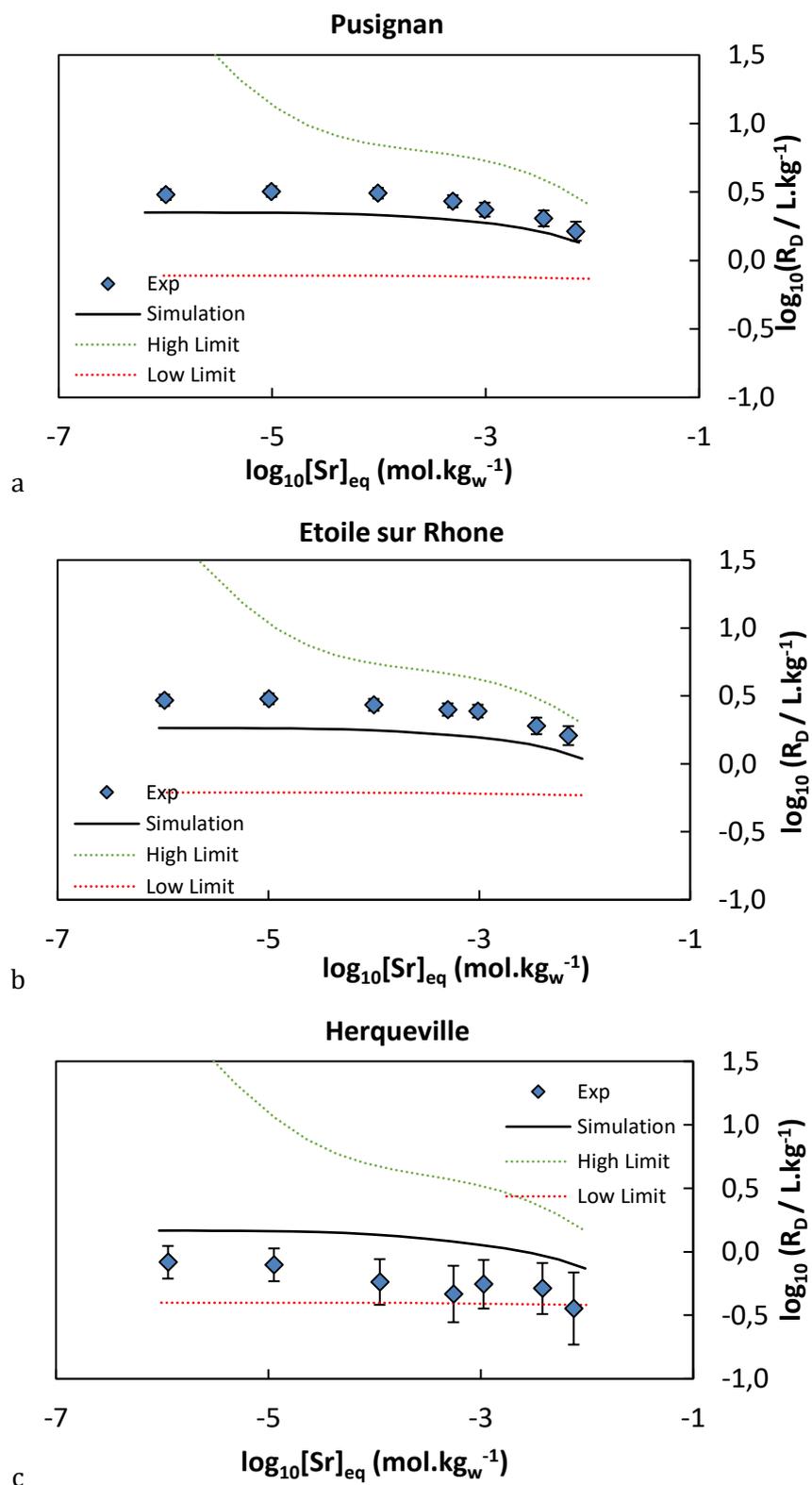


Figure IV. 5. Adsorption isotherms of Sr onto soil samples at $\text{pH}_{\text{water}} = 6.8, 7.1$ and 4.8 for Pusignan (a), Etoile-sur-Rhône (b), and Herqueville (c), respectively, $S/L = 0.05 \text{ kg.L}^{-1}$ and $I = 0.1 \text{ mol.kg}_w^{-1}(\text{CaCl}_2)$ with the associated simulations (plain lines) and the simulation extrema.

3.3.1.3 Influence of adding kaolinite properties in the simulations

The database for kaolinite in Table IV. 7 is included in the simulation. The clay minerals proportions have been recalculated following § 3.2.2.2, and calculated proportions of illite, smectite and kaolinite used for these new simulations are given in Table IV. 8. The influence of the addition of the kaolinite database on simulation of Cs onto soil samples is also shown in Figure IV. 4 (dotted lines).

Table IV. 8. Calculated proportions of illite, smectite and kaolinite for soil samples

	Measured CEC (mmol.100g ⁻¹)	% Illite	% smectite	% kaolinite
Pusignan	12.4	12.3	9.8	12.1
Etoile-sur-Rhône	9.8	10.5	7.9	3.2
Herqueville	7.5	14.3	4.0	7.2

3.3.2 Removal of the natural organic matter

Natural organic matter is known to be able to affect the adsorption of cesium in clay minerals by blocking the access of fixation sites (Staunton et al., 2002). To study the effects of natural organic matter on the adsorption of Cs and Sr onto soils, NOM was removed from the soil samples (cf. Table IV. 9). After two destructions steps, the removal was not total but sufficient to appreciate an evolution in the adsorption behaviour of Cs and Sr. Moreover, the highest removal is observed on the most problematic soil, i.e. Herqueville.

Table IV. 9. Concentration of natural organic matter in untreated soils and after removal of the fraction < 150 µm

Sample	Raw material	After 2 destructions	% removal
	NOM (g.100g ⁻¹)	NOM (g.100g ⁻¹)	
Pusignan	4.30	0.80	81
Etoile-sur-Rhône	2.91	0.95	67
Herqueville	4.21	0.31	93

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The CEC and the exchangeable cation concentrations were checked in order to know the basic properties of the treated materials (cf. Table IV. 10). The treatment has barely modified the CEC of soil samples that appears slightly lower, especially for Pusignan soil. For Herqueville, the exchangeable Al^{3+} and H^+ has not been measured. It could explain the large difference between the sum of exchangeable cations and the measured CEC. The sum of exchangeable cations is comparable to the measured CEC except for Herqueville soil, the difference of which could be explained by the non-measurement of H^+ and exchangeable Al^{3+} .

The adsorption isotherms of Cs and Sr onto soil samples after removing NOM are represented in Figure IV. 6 and Figure IV. 7. Adsorption isotherms of untreated materials are also represented for the sake of comparison. For Cs, as the S_0 for illite drives simulations, and as illite/smectite ratio stays constant, the CEC drop does not change significantly simulations.

The adsorption onto Etoile-sur-Rhône and Herqueville is slightly increased but not significantly in view of experimental uncertainties—at $[\text{Sr}]_{\text{eq}} = 1 \mu\text{mol.kg}_w^{-1}$, the adsorption percentage increases at 3% for Etoile-sur-Rhône and 1% for Herqueville. In the case of Pusignan, the adsorption of Sr is slightly lowered but the simulation is also lowered. This diminution can be explained by the slight decrease of the CEC of Pusignan after the removal of NOM, which implies a slight decrease of the simulated $\log_{10}R_D$.

Table IV. 10. Exchangeable cations concentrations and CEC measurement of < 150 μm soil samples after removal of NOM.

Sample	Exchangeable cations				Sum of exchangeable cations (meq.100g ⁻¹)	CEC (meq.100g ⁻¹)
	Na (meq.100g ⁻¹)	Ca (meq.100g ⁻¹)	Mg (meq.100g ⁻¹)	K (meq.100g ⁻¹)		
Pusignan	0.05	10.26	0.35	0.35	11.01	10.40
Etoile-sur-Rhône	0.08	8.90	0.16	0.74	9.86	9.58
Herqueville	0.05	2.24	0.34	0.21	2.85	7.08

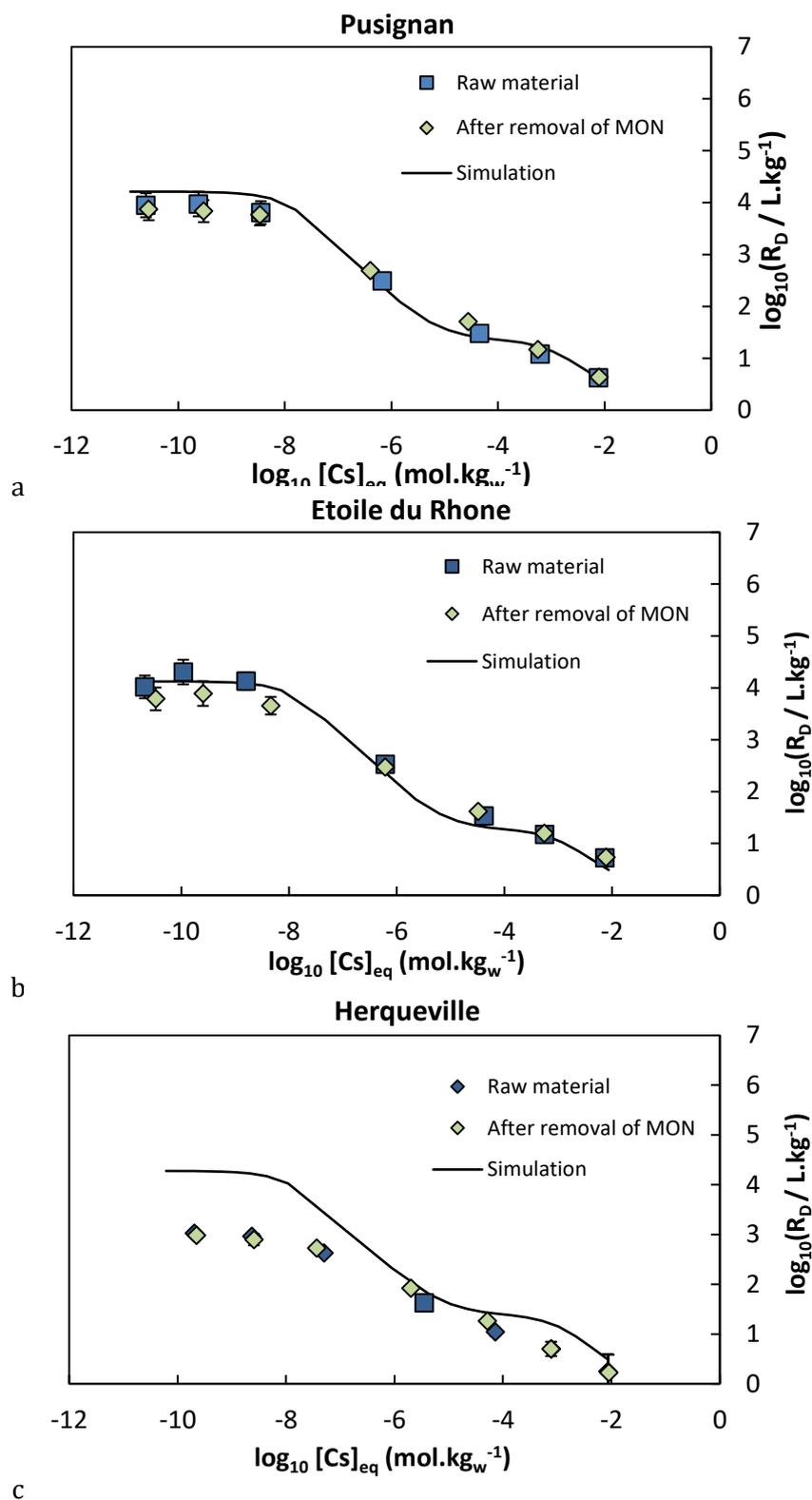


Figure IV. 6. Adsorption isotherms of Cs onto raw soil samples (squares) and after the removal of NOM (diamonds) at $\text{pH}_{\text{water}} = 6.5, 6.8$ and 5.2 for Pusignan (a), Etoile-sur-Rhône (b), and Herqueville (c), respectively $-, S/L = 0.05 \text{ kg.L}^{-1}$ and $I = 0.1 \text{ mol.kg}_w^{-1}$ (CaCl_2).

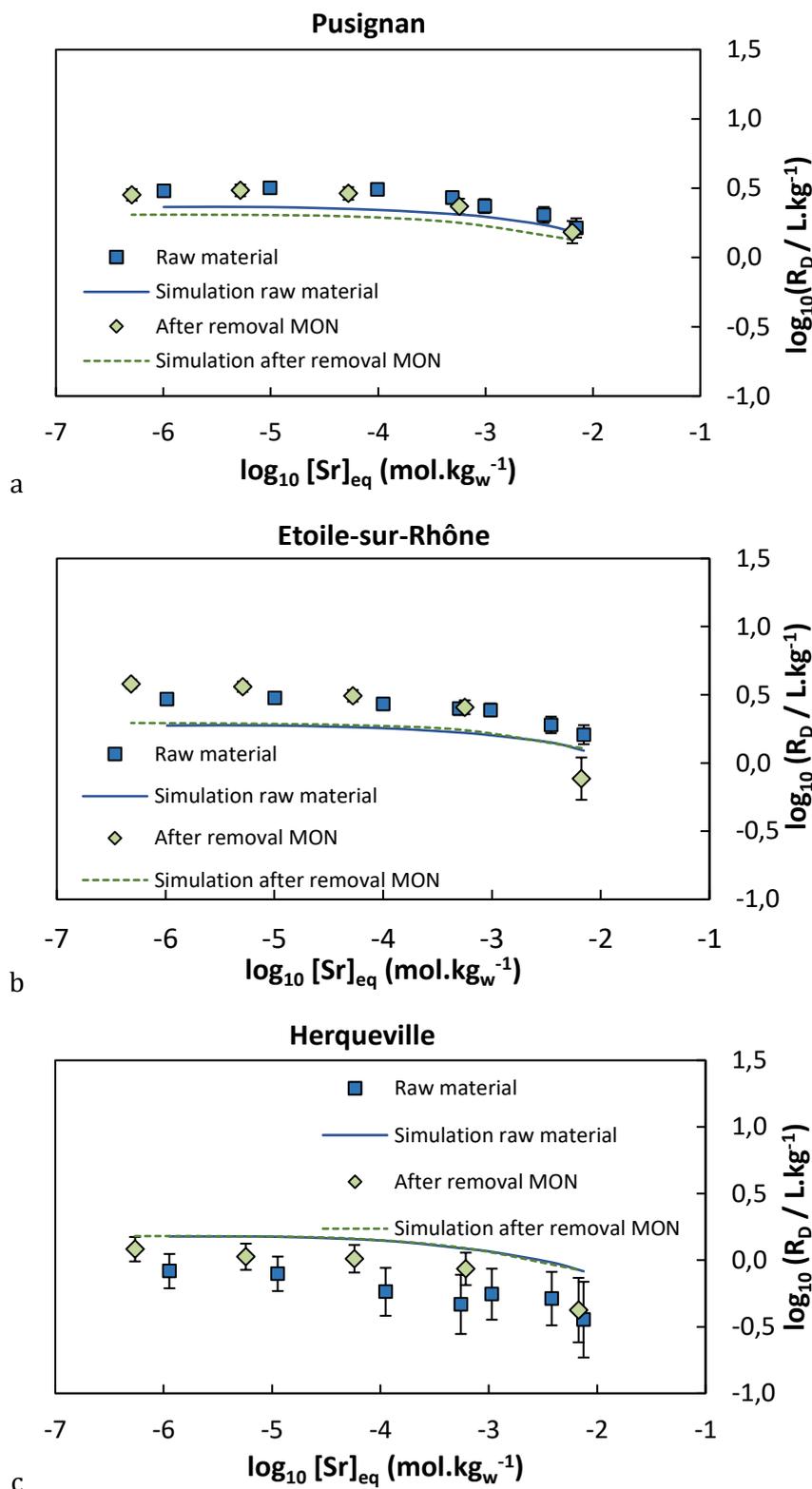


Figure IV. 7. Adsorption isotherms of Sr onto untreated soil samples (squares) and after the removal of NOM (diamonds) at $\text{pH}_{\text{water}}=6.7, 7.2,$ and 5.2 for Pusignan (a), Etoile-sur-Rhône (b), and Herqueville (c), respectively-, $S/L = 0.05 \text{ kg.L}^{-1}$ and $I = 0.1 \text{ mol.kg}_w^{-1}$ (CaCl_2) and the associated simulations.

3.3.3 Adsorption onto Herqueville soil after removing the exchangeable aluminium

An important amount of exchangeable Al^{3+} was found in Herqueville soil. As trivalent cations, Al^{3+} could be particularly difficult to be exchanged by Cs^+ and Sr^{2+} . Thus, the exchangeable aluminium removal procedure was applied on Herqueville soil. Next the soil sample was Ca-conditioned then the CEC and the exchangeable cations were determined (Table IV. 11).

This treatment has enhanced the CEC of Herqueville soil. It tends to prove that the CEC and the exchangeable cations measuring protocols (cf. § 3.2.2.2) were not sufficient to exchange Al^{3+} from the soil. Thus, this information also tends to prove the difficulty of Cs^+ to remove all the adsorbed Al^{3+} . Given the CEC change, this also implies a readjustment of the illite/smectite proportions (cf. Table IV. 6).

Table IV. 11. Exchangeable cations concentrations and CEC measurement of Herqueville soils after removal of Al^{3+}

Sample	Exchangeable cations				Sum of exchangeable cations (meq.100g ⁻¹)	CEC (meq.100g ⁻¹)
	Na (meq.100g ⁻¹)	Ca (meq.100g ⁻¹)	Mg (meq.100g ⁻¹)	K (meq.100g ⁻¹)		
Herqueville	0.05	9.20	0	0.32	9.61	10.1

The adsorption isotherms of Sr and Cs onto Herqueville after the removal of Al^{3+} , and the new simulations are represented in Figure IV. 8 and Figure IV. 9. In the case of Sr, the removal Al^{3+} allows a better simulation of experiments. The adsorption and simulation of Sr (Figure IV. 8) and Cs (Figure IV. 9) are enhanced due to the CEC increase. The experimental results are satisfactorily represented by the simulation for Sr but still not for Cs.

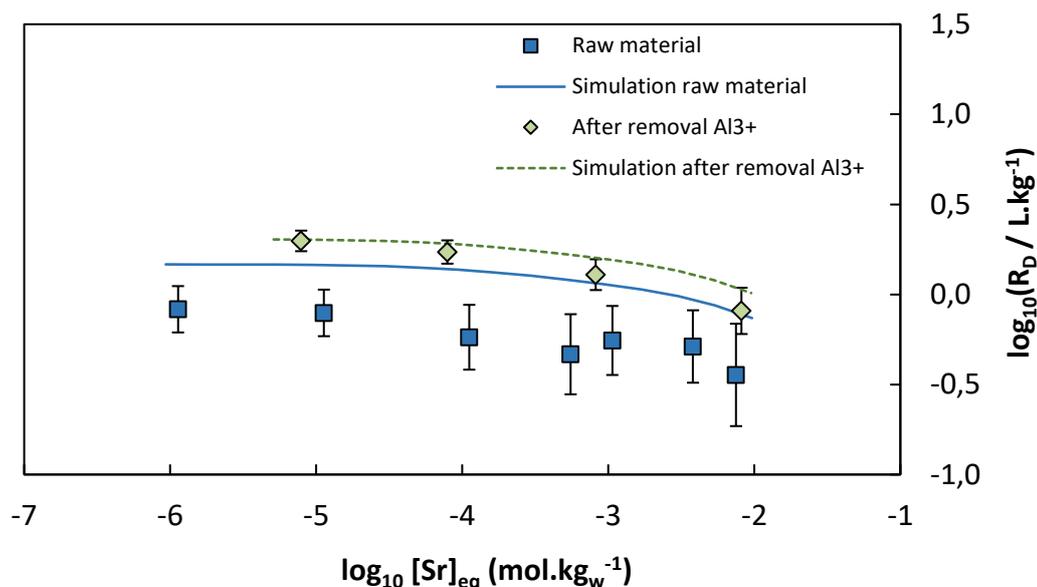


Figure IV. 8. Adsorption isotherms of Sr onto raw Herqueville sample (square, simulation plain line) and after the removal of Al³⁺ (triangles, simulation dashed line) at $\text{pH}_{\text{water}} = 6$, $S/L = 0.05 \text{ kg.L}^{-1}$ and $I = 0.1 \text{ mol.kg}_w^{-1}$ (CaCl₂).

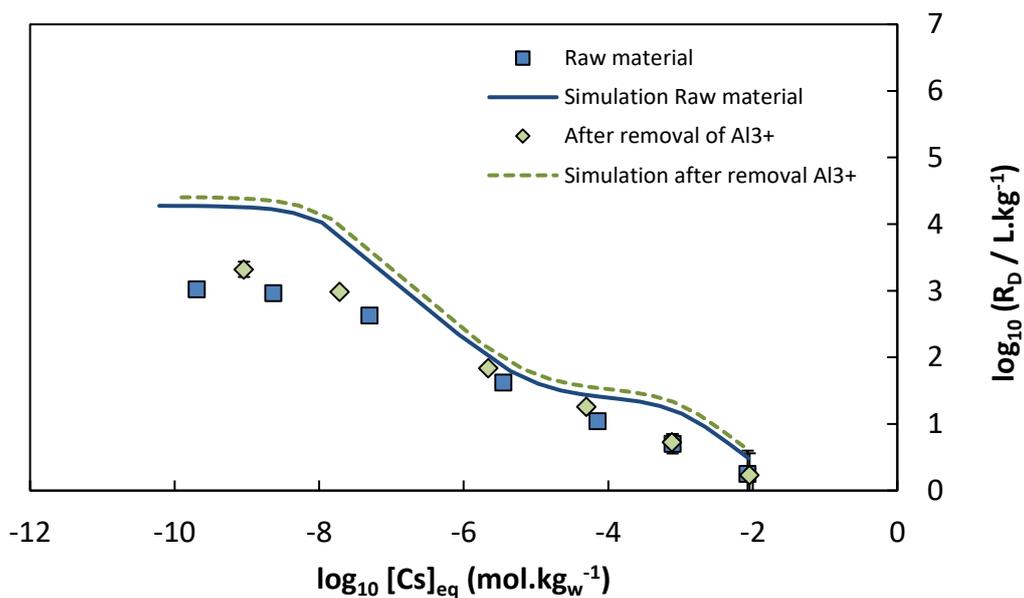


Figure IV. 9. Adsorption isotherms of Cs onto untreated Herqueville sample (square, simulation plain line) and after the removal of Al³⁺ (triangles, simulation dashed line) at $\text{pH}_{\text{water}} = 6.4$, $S/L = 0.05 \text{ kg.L}^{-1}$ and $I = 0.1 \text{ mol.kg}_w^{-1}$ (CaCl₂).

3.3.4 Adsorption on Etoile-sur-Rhône with a simplified synthetic pore water

The modelling and the associated database were applied in order to simulate the adsorption behaviour of Cs and Sr on Etoile-sur-Rhône soil with experimental conditions closer to environmental ones. Thus, the solid/liquid ratio was increased to 0.25 kg.L^{-1} . The CaCl_2 concentration was decreased to $1.5 \text{ mmol.kg}_w^{-1}$ for Sr, and $2.5 \text{ mmol.kg}_w^{-1}$ for Cs. To simulate the effects of a possible amendment of agricultural soil with potassium, electrolytes were implemented with the addition of 1 and 2 mmol.kg_w^{-1} of KNO_3 . Under these conditions, K^+ is another competitor for the access to fixation sites. Adsorption isotherms of Sr^{2+} and Cs^+ , and simulations are shown in Figure IV. 10 and Figure IV. 11, respectively. In both cases, the addition of KNO_3 lowers the adsorption, as well as simulations. Contrary to § 3.3.1.2, the simulation of the adsorption of Sr in $1.5 \text{ mmol.kg}_w^{-1}$ CaCl_2 is slightly overestimated (Figure IV. 10).

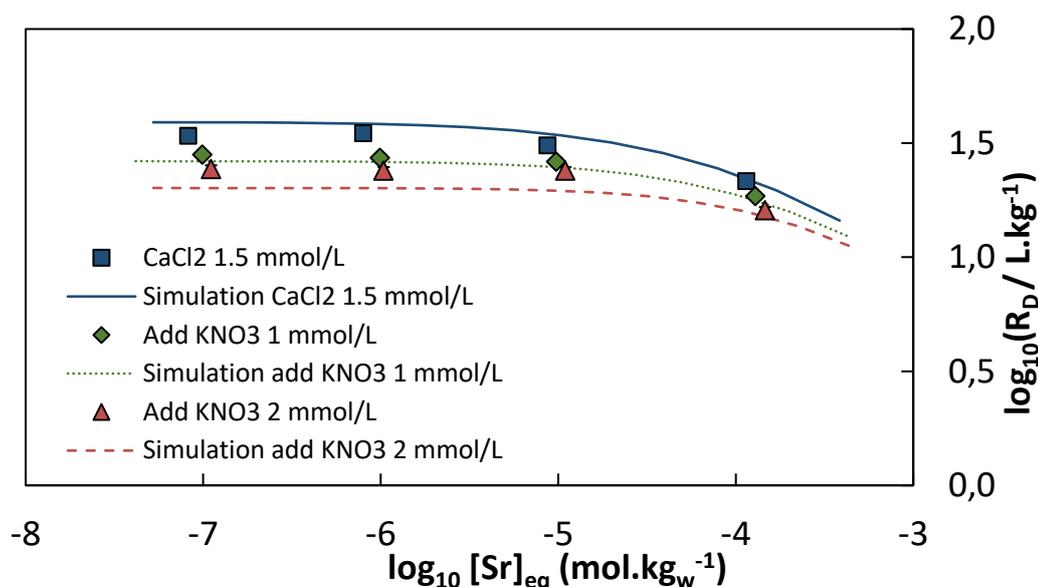


Figure IV. 10. Adsorption isotherm of Sr onto Etoile-sur-Rhône at $\text{pH}_{\text{water}} = 7.2$, $S/L = 0.25 \text{ kg.L}^{-1}$ and $[\text{CaCl}_2] = 1.5 \text{ mmol.kg}_w^{-1}$ (squares, simulation plain line), addition of $[\text{KNO}_3] = 1 \text{ mmol.kg}_w^{-1}$ (diamonds, simulation dotted line) and addition of $[\text{KNO}_3] = 2 \text{ mmol.kg}_w^{-1}$ (triangles, simulation dashed line).

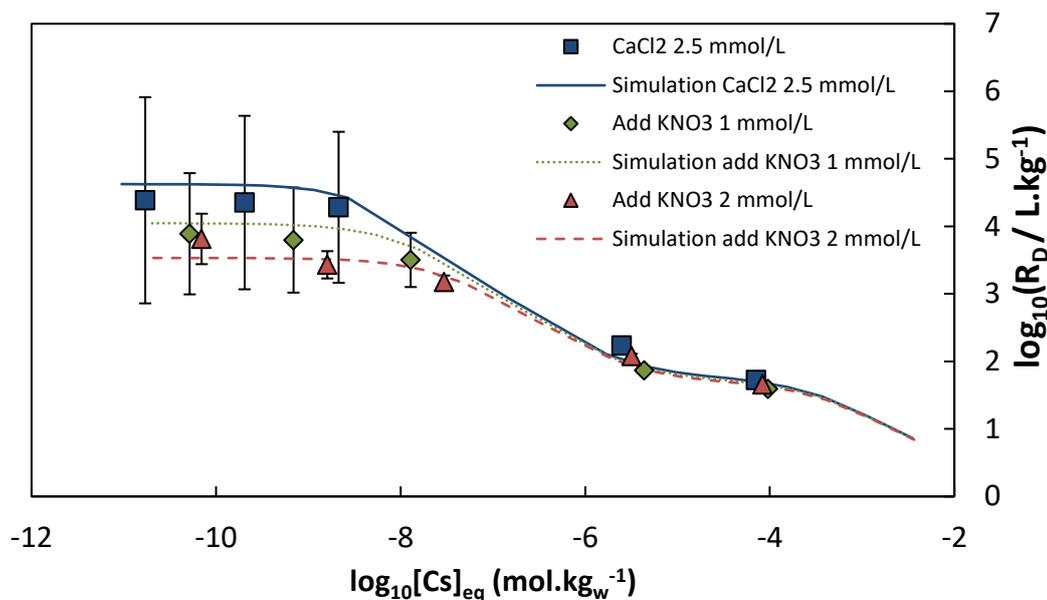


Figure IV. 11. Adsorption isotherm of Cs onto Etoile-sur-Rhône at $\text{pH}_{\text{water}} = 6.9$, $\text{S/L} = 0.25 \text{ kg.L}^{-1}$ and $[\text{CaCl}_2] = 2.5 \text{ mmol.kg}_w^{-1}$ (square, simulation plain line), addition of $[\text{KNO}_3] = 1 \text{ mmol.kg}_w^{-1}$ (diamonds, simulation dotted line), and addition of $[\text{KNO}_3] = 2 \text{ mmol.kg}_w^{-1}$ (triangles, simulation dashed line).

3.4 Discussions

3.4.1 Simulation of Cs^+ adsorption onto soils

Regarding the agreement between experiments and simulations, it seems that simulations also follow satisfactorily the experimental results for Pusignan and Etoile-sur-Rhône—in terms of percentage of adsorption (see Supplementary data), highest overestimation of 9% for Pusignan and 11% for Etoile-sur-Rhône. The presence of goethite in Etoile-sur-Rhône soil has been neglected. Goethite does not present any strong affinity for Cs^+ (Jacquier et al., 2001; Peynet, 2003; Ararem et al., 2011) under these pH conditions. In the case of Herqueville soil, the $\log_{10}R_D$ values of cesium are largely overestimated—this comment could be mitigated in term of percentage of adsorption onto which the overestimation is lower than 2% at low concentration (20% for the highest overestimation).

Concerning uncertainties of simulations, they appear particularly important at low concentrations of Cs. They are caused by the high uncertainties on selectivity coefficients of the S_0 site of illite (cf. Table IV. 7). The selectivity coefficient of Ca^{2+} on S_1 sites for smectite

has also a high uncertainty but smectite seems having a weak contribution in the adsorption of Cs^+ and varying the value from this site does not significantly influence the simulations. Nevertheless, the agreement between experiments and simulations for Pusignan and Etoile-sur-Rhône indicates that the selectivity coefficients used for simulation are efficient. It also tends to confirm that the simulation problem with Herqueville soil does not come from the selectivity coefficients uncertainties.

This issue can arise from several approximations made in the Herqueville case. Experiments were made on untreated materials, but Herqueville soil presents the highest amount of NOM, which is known to obstruct the adsorption of Cs^+ in soils (Dumat and Staunton, 1999; Staunton et al., 2002). Moreover soils were considered as Ca-saturated, which is not really the case for Herqueville soil (cf. Table IV. 5). Herqueville soil also presents a large amount of exchangeable aluminium that could be particularly difficult to exchange by mono-valent cations as Cs^+ .

Concerning the account of kaolinite in the simulations, the principal variations are that simulations are slightly lower at low concentration and higher at high concentrations. Kaolinite is a strong adsorbent for Cs but not strong enough to prevent the illite and smectite to drive the adsorption. Thus, considering kaolinite in the adsorption of Cs does not change the simulations significantly.

3.4.2 Simulation of Sr^{2+} adsorption onto soils

Especially for Etoile-sur-Rhône soil, goethite could be a good candidate to explain the difference between experimental results and simulation. Goethite seems to be a strong adsorbent for Sr. Hofmann et al. (2005) have studied the adsorption of Sr on a synthetic goethite and have observed a pH-edge in the pH span 6-8 at $[\text{NaNO}_3] = 0.01$ and 0.1 mol.L^{-1} . Nevertheless the role of goethite was neglected in this study due to the lack of exploitable previous studies within our formalism. A reinterpretation of available data—e.g., recent data from Hofmann et al. (2005) and Nie et al. (2017) –, whenever possible should be done as done in Siroux et al. (submitted) and § 3.2.3.2.

Contrary to the other soils, adsorption of Sr onto Herqueville is slightly overestimated. This difference could be attributable to the reasons exposed in § 3.2.2.2. Despite NOM does not

strongly prevent the adsorption of Sr in clay minerals (Samadfam et al., 2000; Anjolaiya, 2015), as for Cs, the presence of dissolved Al^{3+} can reduce the adsorption of Sr in soils.

The adsorption of Sr onto kaolinite is particularly scarce in the literature. Samadfam et al. (2000) worked with unconditioned kaolinite and did not specify its purity. Rafferty et al. (1981) studied the adsorption of Sr onto Na-kaolinite at different ionic strength. Neglecting the possible difference in behaviour of Sr onto Na or Ca-kaolinite, the $\log_{10}R_D$ is low enough—at $I = 0.1 \text{ M}$, $\log_{10}R_D$ around 1.6 at pH 7 compared to 2.1 for smectite at $I = 0.1 \text{ mol.kg}_w^{-1}$ (Siroux et al., submitted) and 1.8 for illite (Poinssot et al., 1999a)—that the adsorption of Sr onto soils should not be significantly influenced by kaolinite.

3.4.3 Removal of natural organic matter

In Figure IV. 4 at low Cs concentration, the adsorption results onto Pusignan and Etoile-sur-Rhône are barely lower. This concentration domain corresponds to the zone with the higher uncertainties for the experimental points. These uncertainties are due to the relatively high error on the activity counting—ranging from 10% at the lowest concentrations to 1% at the highest concentrations. Despite this slight reduction of $\log_{10}R_D$, the adsorption was assumed to be unchanged. For Herqueville, the adsorption is exactly the same with or without removal of the NOM. Thus, the influence of NOM does not permit to explain why the simulation does not follow the experimental points for this soil in the case of cesium.

For Sr, as illite and smectite are showing similar behaviours for adsorption of Sr, simulations are mostly driven by the CEC. Contrary to Pusignan, The CEC values of Etoile-sur-Rhône and Herqueville have not significantly changed. Thus, as for Cs^+ , the removal of NOM does not seem to influence the adsorption of Sr^{2+} in these soils.

Contrary to literature, Cs-adsorption does not seem to be affected by the removal of NOM for these soils. It is generally reported that the NOM avoid the adsorption of Cs^+ onto clay mineral, especially illite, by blocking the access of frayed edge site (Dumat and Staunton, 1999; Staunton et al., 2002). In our case, the removal of NOM has not changed significantly the adsorption behaviour of Cs^+ . The adsorption of Sr^{2+} does not seems to be affected either, but it is more in agreement with the literature (Samadfam et al., 2000).

3.4.4 Influence of exchangeable aluminium on Herqueville soil

For Sr the account for exchangeable aluminium in the simulations and experiments are in good agreement (Figure IV. 8). For Cs, as shown in Figure IV. 9, the adsorption is slightly increased by the removal of Al^{3+} but simulations still do not follow the experimental results, even if they are also increased—this is caused by the increase of the CEC. In Table IV. 11, the consistency between the sum of the exchangeable cations and the measured CEC allows assuming that exchangeable Al was well removed. But it is possible that a very low concentration of aluminium still remained in soil and particularly in the FES of illite. Thus, the adsorption of Cs^+ onto these sites could remain disadvantaged.

3.4.5 Case of the synthetic pore water of Etoile-sur-Rhône soil

Concerning Sr adsorption onto Etoile-sur-Rhône in synthetic pore water (Figure IV. 10), one must remind that compared to the adsorption of Sr onto the soils (§ 3.3.1.2), the ionic strength is lowered from 100 to 4.5 mmol.kg_w^{-1} . The selectivity coefficients used for these simulations were obtained at $I = 0.03 \text{ M}$ (Wissocq, 2017; Wissocq et al., submitted). Thus, the simulation efficiency of the selectivity coefficients could be lowered at different ionic strengths. It can explain the underestimation at $I = 100 \text{ mmol.kg}_w^{-1}$ and the overestimation at 4.5 mmol.kg_w^{-1} . Moreover, simulations slightly overestimate the decrease of the adsorption of Sr after the addition of KNO_3 . Nevertheless simulations represent satisfactorily the experimental results, but these simulations could be further refined by improving the selectivity coefficients of potassium.

In the case of Cs (Figure IV. 11), the addition of KNO_3 also imposes an adsorption decrease. Due to the high affinity of K^+ for FES, K^+ competes with Cs^+ onto these sites and the decrease is more important at low than at high Cs concentrations. The high uncertainties on the experimental points at low concentration show that the experiment was probably not properly dimensioned. By increasing the S/L ratio and by lowering the ionic strength, the adsorption of Cs was supposed to be enhanced but the spike's activity of radioactive tracers has not been changed. Thus the activities of equilibrium solutions were too low to obtain a count with a good accuracy. Nonetheless simulations represents well the adsorption of Cs^+ at low ionic strength and the addition of K^+ is also well reproduced.

Accounting for all the uncertainties generated by the calculated proportions on clay minerals and the selectivity coefficients used, the modelling seems able to predict the adsorption behaviour of Sr and Cs onto Etoile-sur-Rhône under environmental relevant conditions. Based on highest addition of KNO_3 —the more relevant condition for an agricultural soil –, it seems possible to simulate the adsorption of Cs with an accuracy of 97%—this accuracy is lower at low concentrations of Cs—and 95% concerning the adsorption of Sr.

3.4.6 Comments on modelling and simulations accuracy

The modelling using the additivity principle allows representing satisfactorily the adsorption behaviour of Cs^+ and Sr^{2+} onto these soil samples. Some parameters still limit the simulations. First, the clay mineral repartitions in soils are submitted to analyses uncertainties. The repartition was made from the average percentages, but changes in these percentages can influence the simulation results (cf. Supplementary data).

Moreover, the difficulty to differentiate micaceous minerals from illite by XRD seems inducing a problem in simulations—especially for the adsorption of Cs^+ . In our case, these minerals were combined because weathered micaceous minerals, as biotite or muscovite, are known to strongly adsorb cesium due to the presence of FES (Zaunbrecher et al., 2015). Nevertheless, this adsorption is not necessarily as strong as for illite. Cornell (1993) has reviewed the adsorption in different clay minerals including illite, biotite, and muscovite. He has reported lower adsorption of Cs onto biotite than onto illite. The reported partition coefficient of Cs^+ onto muscovite is also lower than those for illite. Henceforth, to improve the simulation in the case of Herqueville, differentiate mica to illite seems necessary.

Considering these soils as saturated with calcium is a limiting element of simulations but taking into account all the exchangeable cations (Na^+ , Mg^{2+} , K^+ , etc.) would require a complete database for each of these exchangeable cations. Nonetheless, the good representation of the experimental results by simulation tends to confirm the choice of considering these exchangers as saturated in Ca –except for Herqueville.

In this study, the secondary minerals (quartz, feldspar, goethite, etc.) were neglected. This choice was made in view of their low CEC and their absence of specific adsorption behaviour for Cs^+ and Sr^{2+} . In his review, Cornell (1993) reported weak adsorption of Cs

onto quartz, chlorite, and albite (feldspar). Quartz is also reported as a weak adsorbent of strontium (Nordén et al., 1994). The case of goethite, and others iron oxi-hydroxides, has already been discussed in § 3.3.1. It does not represent a particularly strong adsorbent for cesium, but it seems to correctly retain strontium (Hofmann et al., 2005; Fuller et al., 2016; Nie et al., 2017). Having neglected its contribution may explain part of the differences between the experimental results and the simulations for the adsorption of Sr onto soils, especially for Etoile-sur-Rhône.

As shown in § 3.3.1, the uncertainties from the used selectivity coefficients cause high uncertainties on simulations. Nevertheless, simulations represent fairly well the experimental results in most cases. Thus it seems that used selectivity coefficients are correct and that uncertainties are overestimated.

Finally, we saw in § 3.3.3 that dissolved exchangeable Al^{3+} plays a role in adsorption process of Sr^{2+} . The removal of Al^{3+} allowed us to simulate well the adsorption behaviour of strontium. Adding the selectivity coefficient of the aluminium system— $\text{Al}(\text{OH})_n^{(3-n)+}/(3-n)\text{H}^+$ —would permit to improve the database and the prediction capacities of the model, but these studies are missing in the literature and difficult to obtain on phyllosilicate phases. In our case, the lack of information on these exchanges is impeding a good representation of the adsorption behaviour on acidic soils-rich in dissolved Al^{3+} .

3.5 Conclusions

The adsorption of cesium and strontium were studied on French soil samples. These samples were approximated to illite/smectite or illite/smectite/kaolinite mixtures in order to simulate their adsorptions behaviours and compare these simulations with experimental results. The databases used for the simulations were taken from literature for illite and smectite (Reinoso-Maset and Ly, 2014; Wissocq, 2017; Siroux et al., submitted; Wissocq et al., submitted) or were exposed in this study for kaolinite.

Simulations were made considering the additivity principle between several phases. The agreement between simulations and experimental results, mainly for Etoile-sur-Rhône and Pusignan, tends to confirm the efficiency of the database and the modelling to predict and represent the adsorption behaviour of Cs and Sr onto soils. In the case of Herqueville soil, simulations were not totally satisfactory from a $\log_{10}R_D$ point of view and the problem

stays unresolved for the Cs⁺ adsorption—nevertheless, it can be mitigated in view of the adsorption percentage. For Sr²⁺, it has been shown that the simulation difficulties came from the presence of exchangeable aluminium in Herqueville. For Cs⁺, simulation difficulties can also come from remaining exchangeable aluminium in the FES of illite or it could also come from the initial calculation of the clay minerals proportions and the absence of differentiation between mica and illite.

If first results made on more relevant environmental conditions made on Etoile-sur-Rhône are promising, it seems that the database could be further improved adding the adsorption behaviour of other principal and secondary mineral phases (chlorite, goethite, quartz, etc.). Nevertheless, this study confirms that the multi-site ion-exchanger modelling—with a more complete and detailed database—could allow predicting the adsorption of cations onto various soils.

Acknowledgments

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3.7 Supplemental informations

3.7.1 Soil samples characterization

Table IV. 12. Range of the mineralogical proportion (in %) of the fraction < 2 µm of Pusignan, Etoile-sur-Rhône and Herqueville

	mica, illite, glauconite	I/S R=1, G/S R=1	I/S R=0, G/S R=0	kaol.	chlorite ± C/S	quartz	feldsp. K	plagio- clases	goeth/ Fe-mx	gypse	TiO ₂
Pusignan	8-11	21-31	-	18-23	>0-7	26-31	0-<1	0-1	3-8	-	0-0.7
Etoile-sur- Rhône	14-25	40-50		9-12	>0-4	2-6	0-2	0-1	15-22	0-1	0-0.4
Herqueville	11-22	43-56	-	14-23	>0-7	3-9	>0-1	0-1	3-7	0-1	0-0.9

Abbreviations: **mica, illite, glauconite:** mica, illite and mixed layer (<20 % of smectite); **I/S R=1:** ordered mixed layer illite/smectite; **I/S R=0:** disordered mixed layer illite/smectite; **G/S R=1:** ordered mixed layer glauconite/smectite; **I/S R=0:** disordered mixed layer glauconite /smectite; **kaol.:** kaolinite; **C/S:** mixed layer chlorite/smectite; **feldsp.K:** potassium feldspar; **goeth./Fe-mx:** iron minerals (goethite, hematite, siderite, etc.); **TiO₂:** titanium oxide.

3.7.2 Adsorption curves in percentage of adsorption

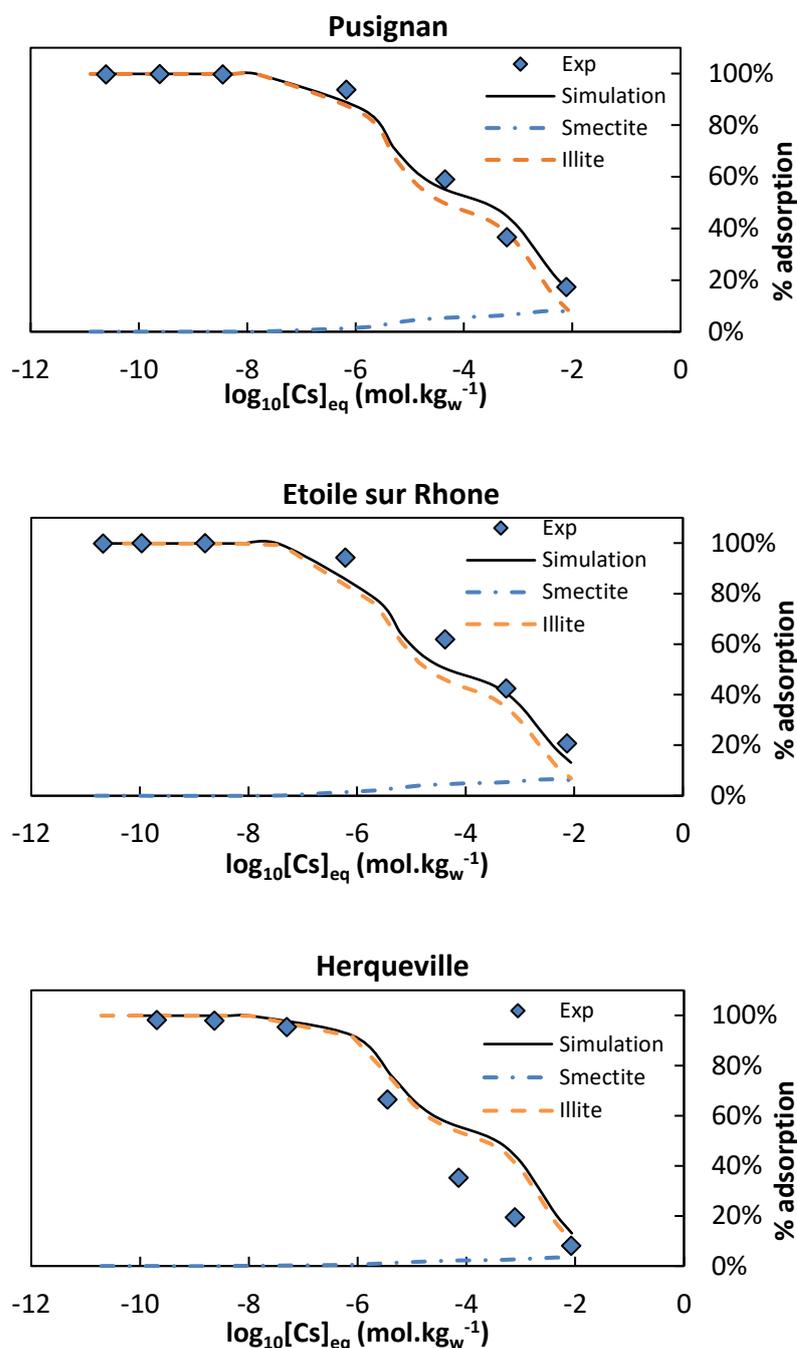


Figure IV. 12. Adsorption curves in percentage of adsorption of Cs⁺ onto soil samples at pH_{water} = 6.4, 6.5 and 4.6 for Pusignan (a), Etoile-sur-Rhône (b) and Herqueville (c) respectively, S/L = 0.05 kg.L⁻¹ and I = 0.1 mol.kg_w⁻¹ (CaCl₂) with the associated simulations (plain lines) and the clay minerals repartition (illite dash line and smectite dash dot line).

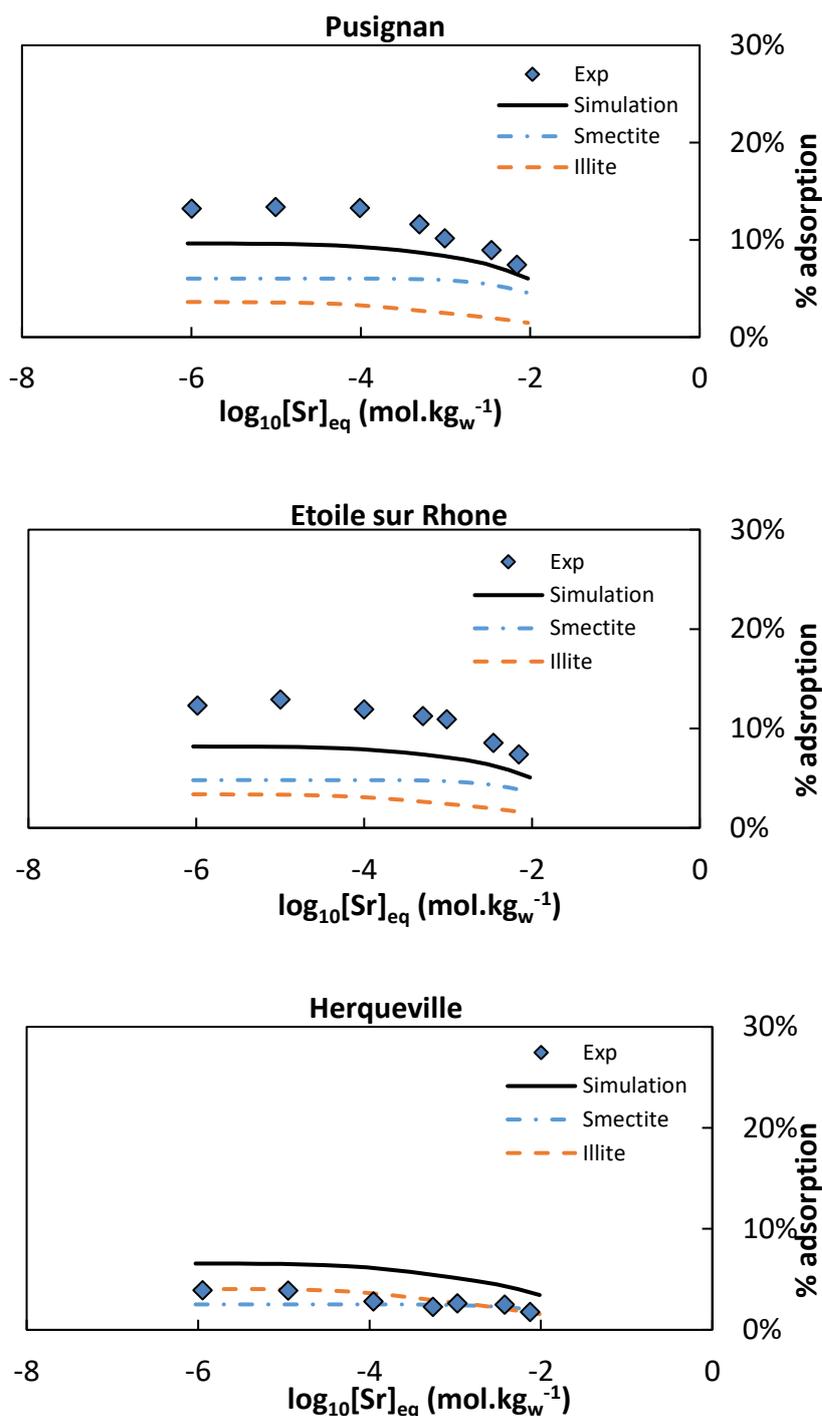


Figure IV. 13. Adsorption curves in percentage of adsorption of Sr onto soil samples at $\text{pH}_{\text{water}} = 6.8, 7.1$ and 4.8 for Pusignan (a), Etoile-sur-Rhône (b), and Herqueville (c), respectively, $S/L = 0.05 \text{ kg.L}^{-1}$ and $I = 0.1 \text{ mol.kg}_w^{-1}(\text{CaCl}_2)$ with the associated simulations (plain lines) and the clay minerals repartition (illite dash line and smectite dash dot line).

CONCLUSION GENERALE ET PERSPECTIVES

1 Mise en place de la base de données Cs⁺, Sr²⁺ sur smectite et illite

Au cours de cette thèse, une base de données de l'adsorption des ions Cs⁺ et Sr²⁺ a été mise en place sur la smectite et l'illite, deux des principaux minéraux argileux environnementaux, et vis-à-vis des ions Na⁺ et Ca²⁺, deux des cations majeurs environnementaux. Cette base de données a été réalisée en collaboration avec la thèse d'Aubéry Wissocq (2017) qui a étudié plus particulièrement les comportements d'adsorption de ces 2 cations dans des minéraux argileux calciques. Cette base de données a été construite selon le formalisme des échangeurs d'ions multi-sites. Elle s'est appuyée sur la modélisation de différentes isothermes d'adsorption compilées de la littérature, mais également sur des isothermes d'adsorption effectuées directement au laboratoire : ce fut notamment le cas pour l'adsorption du strontium sur smectite sodique. Cette base de données a notamment été testée par le biais d'expériences d'adsorption sur des mélanges de phases minérales pures illite/smectite, et par comparaison avec les simulations réalisées.

Le fait d'avoir construit cette base de données à partir d'expériences tirées de la littérature, et donc réalisées sur des échangeurs qui ne sont pas tout à fait identiques (en termes d'origine géologique, de pureté ou de conditionnement), entraîne des contraintes et des incertitudes sur les constantes obtenues par ces modélisations. La base de données pourrait alors être potentiellement améliorée, en essayant de diminuer ces incertitudes grâce à l'acquisition contrôlée de toutes les courbes et isothermes nécessaires sur un même matériau. Plus spécifiquement, on observe une forte incertitude sur la première constante du calcium sur la smectite ($\log_{10}K_{Ca^{2+}/2H^+}^* = 0.49 \pm 0.49$). Réaliser à nouveau une courbe de saturation du calcium sur la smectite ainsi que des isothermes d'adsorption des ions Cs⁺ ou Sr²⁺ sur une smectite calcique à pH acide, devrait permettre de consolider la valeur de constante associée à ce premier site.

Une forte incertitude sur toutes les constantes associées au site S_0 (pouvant être assimilé aux FES) de l'illite est également observée. Ces incertitudes sont notamment dues au fait que la concentration même du site S_0 est peu ou mal connue. Elle est majoritairement estimée à partir d'isothermes d'adsorption (généralement du césium) représentant la concentration du cation adsorbé en fonction de la concentration libre du cation à l'équilibre, à partir de la rupture de pente, caractéristique d'une saturation d'un site d'adsorption. Néanmoins, lors de ce type d'étude, la concentration de ce site de forte affinité ne peut qu'être estimée avec une forte incertitude (généralement aux alentours de 50%). A titre d'exemple, POINSSOT *et al.* (1999) estiment la concentration des FES des illites entre 0.02 et 0.05 meq.100g⁻¹ à l'aide d'une étude de l'adsorption de l'ion Cs⁺. Ils ont décidé néanmoins de fixer cette valeur à 0.05 meq.100g⁻¹ pour effectuer leurs simulations. Cette valeur a notamment été reprise par ALTMANN *et al.* (2015). MISSANA *et al.* (2014) estiment, quant à eux, la concentration de site des FES à 0.046 meq.100g⁻¹. COMANS *et al.* (1991) ont évalué la concentration entre 0.25 et 0.55% de la CEC totale de l'illite (soit entre 0.06 et 0.13 meq.100g⁻¹ pour une CEC de 24.9 meq.100g⁻¹). On observe ainsi une relative dispersion entre les différentes valeurs de la littérature. Lors de cette étude, la concentration du site S_0 a été fixée à partir de différentes isothermes d'adsorption du césium, afin de modéliser au mieux ces isothermes. Malgré l'apport extrêmement fort de ce site dans les processus de rétention de l'ion Cs⁺, sa très faible concentration par rapport aux autres sites de fixation rend difficile la détermination d'une concentration précise. Il serait donc intéressant d'essayer de minimiser cette incertitude. Cependant, la très faible concentration de ce site limite les possibilités de la déterminer par étude de saturation. Il semblerait tout de même possible d'atteindre cette concentration en travaillant avec de grandes quantités d'illite (afin d'augmenter la concentration en FES dans le milieu) et en saturant ces sites avec du césium. Il faudrait ensuite laver l'illite avec un cation moins spécifique des FES pour éliminer le césium qui se serait fixé sur d'autres sites. La bonne saturation de ces sites pourrait être vérifiée par microscopie électronique en transmission (FULLER *et al.*, 2015), puis de désorber et quantifier le césium. Les difficultés de cette expérience viendraient alors de cette dernière étape, tant l'ion Cs⁺ semble lent et difficile à désorber au niveau des FES (TURNER *et al.*, 2006).

Afin d'améliorer encore la base de données et permettre ainsi une meilleure représentativité des processus d'adsorption du césium et du strontium, il serait utile

d'implémenter la base de données avec d'autres cations majeurs de l'environnement comme l'ion Mg^{2+} ou K^+ , mais aussi NH_4^+ , fréquemment utilisé pour réguler le pH dans les sols alcalins et compétiteur naturel de l'adsorption de l'ion Cs^+ dans les sols (SAWHNEY, 1972 ; SÖDERLUND *et al.*, 2016).

Enfin, on a vu au cours de ce manuscrit que les différents minéraux argileux présentait des comportements d'adsorption pouvant différer selon le cation majeur en présence. Ce phénomène mériterait d'être exploré. Pour cela, il est possible d'imaginer le couplage d'expérience d'adsorption avec des études DRX ou microscopiques afin de cibler les modifications comportementales des phases minérales selon le cation majoritairement présent et le degré de saturation. Par exemple, il faudrait faire varier le ratio de saturation Ca^{2+}/Na^+ du minéral argileux. La difficulté principale se trouverait alors dans le fait de vérifier que la saturation est effectuée de manière homogène. Sinon, il serait également intéressant d'étudier les comportements d'adsorption des différents cations majeurs vis-à-vis non pas uniquement de l'ion H^+ , comme lors des expériences menées au cours de cette thèse, mais par rapport au cation majoritairement présent. Par exemple, il serait utile de modéliser des isothermes d'adsorption de l'ion K^+ sur un minéral argileux sodique ou alors, d'étudier l'adsorption de l'ion Na^+ sur une argile calcique.

Malgré tout, la base de données mise en place permet de modéliser efficacement les différentes isothermes d'adsorption étudiées. Elle a également été utilisée avec succès pour simuler le comportement d'adsorption de Cs^+ et Sr^{2+} sur des mélanges de phases pures illite/smectite.

2 Application pour la prédiction des comportements d'adsorption sur échantillons réels de sol

La base de données a ensuite été mise en application afin de prédire le comportement d'adsorption des ions Cs^+ et Sr^{2+} sur différents échantillons de sols. Trois sols ont été utilisés pour effectuer ces expériences, prélevés respectivement à Pusignan, Étoile-sur-Rhône et Herqueville. Les simulations effectuées ont permis de bien représenter le comportement d'adsorption de l'ion Cs^+ sur deux de ces trois sols (Pusignan et Étoile-sur-Rhône). Le strontium a, quant à lui, été correctement représenté par les simulations malgré

quelques surestimations ou sous-estimations. Afin d'essayer de comprendre les difficultés de simulation rencontrées sur le sol de Herqueville, la matière organique naturelle, originellement présente dans ces sols, a été éliminée puis des isothermes d'adsorption des ions Cs^+ et Sr^{2+} ont été à nouveau réalisées. Cependant, l'élimination de la matière organique n'a que très faiblement modifié ces isothermes. Ensuite, sur le sol d'Herqueville, les cations échangeables aluminium ont été également éliminés afin de déterminer leur influence. Cette élimination a permis de mieux simuler le comportement d'adsorption de l'ion Sr^{2+} mais pas celui de l'ion Cs^+ .

Il apparaît donc utile d'implémenter la base de données avec le comportement d'adsorption de l'aluminium dans les minéraux argileux. Cependant, ce type d'étude est particulièrement difficile à réaliser. En effet, les minéraux argileux étudiés étant des phyllosilicates, l'aluminium libre peut aisément s'équilibrer avec le minéral argileux et entraîner des restructurations du minéral. La mesure des Al^{3+} échangeables est également compliquée à acquérir étant donné les réactions potentielles de dissolution/restructuration des minéraux argileux pouvant entraîner un relargage ou un repiégeage d'aluminium.

Concernant le césium, il semblerait que le problème de simulation rencontré puisse provenir d'aluminium restant fixé sur les sols. Mais ce problème peut également provenir des hypothèses initialement faites. Lors du calcul des proportions en minéraux argileux du sol d'Herqueville, les micas (dont une partie a été observée à l'état pur) ont été assimilés aux illites du fait de la complexité pour les différencier par DRX. Ce choix a été fait car les micas, comme les illites, possèdent un comportement d'adsorption fort et spécifique pour le césium (ZAUNBRECHER *et al.*, 2015). Néanmoins, ce comportement d'adsorption n'est pas nécessairement aussi fort dans les micas que dans les illites (CORNELL, 1993). Ainsi, pour permettre de simuler le comportement d'adsorption du césium dans des sols comprenant de l'illite, ainsi que d'autres minéraux micacés, il est nécessaire de les différencier. De plus, il faudrait également implémenter la base de données avec les comportements d'adsorption de l'ion Cs^+ avec les différents minéraux micacés (phlogopite, muscovite, glauconite, etc.).

L'étude a été réalisée en décrivant chaque sol en tant que mélanges illite/smectite. Pour affiner les résultats des simulations, il serait souhaitable de considérer plus de phases

minérales qui pourraient influencer les comportements d'adsorption. Ainsi, la base de données pourrait être implémentée avec les comportements d'adsorption des ions Cs^+ et Sr^{2+} sur la kaolinite – dont l'étude a déjà été partiellement menée par REINOSO-MASET & LY (2014) dans le formalisme des échangeurs d'ions multi-sites, mais sans étudier le comportement de l'ion Sr^{2+} vis-à-vis de cette phase réactive –, les chlorites – dont les études sont rares dans la littérature – ou encore les goethites – malgré une adsorption quasi nulle du césium (PEYNET, 2003), les goethites présentent une capacité de rétention du strontium non négligeable (HOFMANN *et al.*, 2005 ; NIE *et al.*, 2017).

Cependant, au cours de cette étude, des expériences d'adsorption des ions Cs^+ et Sr^{2+} ont été menées sur le sol d'Étoile-sur-Rhône dans des conditions plus proches des conditions environnementales - augmentation de rapport solide/ratio, baisse de la force ionique, ajout d'un cation compétiteur, K^+ . Le bon accord entre les résultats de simulation avec les isothermes d'adsorption prouvent l'efficacité du modèle et de la base de données pour prédire l'adsorption des ions Cs^+ et de Sr^{2+} dans un sol. De plus, concernant le sol d'Herqueville, si les simulations sont assez éloignées des mesures en termes de K_D , si cette adsorption est étudiée selon son pourcentage d'adsorption (cf. Chapitre IV), l'écart semble plus acceptable aux faibles concentrations (l'écart entre la valeur mesurée et celle simulée est de 0.2%). La représentation en K_D ayant tendance à dilater les parties extrêmes des isothermes, d'où son intérêt pour une description exhaustive des comportements d'adsorption. La base de données ainsi mise en place au cours de ce projet de thèse représente donc un outil d'aide à la décision efficace pour prédire le comportement d'adsorption de Cs^+ et Sr^{2+} dans un sol selon ses caractéristiques physicochimiques (pH, concentration en cations échangeables, force ionique, etc.) et minéralogiques (composition en minéraux argileux).

3 Pour aller plus loin

Dans le cadre de ce projet de thèse, l'accent a été particulièrement placé sur les interactions césium/strontium avec les différents minéraux argileux des sols, en s'articulant sur des sols agricoles pouvant supporter différentes cultures. Afin d'améliorer la capacité prédictive, il serait intéressant de prendre en compte également le transfert des contaminants dans les plantes. Le facteur de transfert sol/plante (TF) est défini par le rapport entre l'activité au

niveau des plantes, racines sur celle au niveau du sol (GASTBERGER *et al.*, 2000). Il est généralement considéré que lorsque ce facteur est supérieur à 1, il y a bioaccumulation du contaminant dans les plantes. A l'inverse, le contaminant est considéré comme fortement affilié au sol. Ce rapport dépend d'une multitude de paramètres :

- le type de sol (concentration en minéraux argileux, en matière organique, etc.) ;
- le type de culture sur le sol ou les amendements pratiqués sur le sol, par effet de compétition entre les cations amendés et les contaminants (TWINING *et al.*, 2004).

En guise d'exemple, SARAP *et al.* (2015) ont étudié les facteurs de transfert de ^{90}Sr et ^{137}Cs sur différentes parties d'un blé d'hiver et selon 6 traitements des terrains agricoles. Ils ont observé que les TF du strontium varient entre 4 et 11 au niveau des racines, et entre 0.2 et 1.8 au niveau des tiges. Le césium, lui, semble fortement fixé au sol avec des facteurs de transfert inférieurs à 0.4. Dès lors, si la prise en compte des transferts du césium dans les plantes ne semble pas influencer de façon importante la prédiction du devenir du césium dans les sols, considérer les transferts sol-plante dans le cas du strontium peut influencer plus fortement les résultats de rétention.

L'activité microbienne est également un facteur non pris en compte par notre modélisation mais qui peut impacter le devenir des contaminants radioactifs par biotransformation et biodégradation. Les précipités de carbonates microbiens sont un sous-produit de l'activité microbienne. Ces processus de précipitation peuvent s'appliquer à différents cations et métaux (ZHU & DITTRICH, 2016), et sont à la base de nombreuses recherches en bio-remédiation. HORIIKE *et al.* (2017) travaillent sur la remédiation du strontium à l'aide d'un microorganisme halophile adapté au milieu fortement salin. Ce microorganisme permettrait de précipiter le strontium sous forme de strontianite (SrCO_3) afin de faciliter son élimination. Cependant, contrairement au strontium, le césium semble, lui, peu impacté par ces processus (WOLFRAM *et al.*, 1997).

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ANNEXES

1 Protocole expérimentaux

1.1 Protocole de purification des minéraux argileux

Lors de l'étude de l'additivité sur mélanges de phases minérales brutes, une smectite Swy-2 et une illite du Puy ont été utilisées. Ces phases minérales sont naturellement composées de différentes phases accessoires telles que le quartz ou la calcite. Afin de travailler sur une phase minérale pure, un protocole purification a été appliqué sur ces deux argiles.

Tout premièrement, les argiles ont été dispersées dans de l'eau milli-Q (avec des rapports de 1:20 pour la smectite et 1:10 pour l'illite) en présence de H₂O₂ 15%. Le mélange a été agité pendant 24 h puis centrifugé et le surnageant a été éliminé. Cette étape permet de supprimer la matière organique naturelle potentiellement présente dans l'argile.

Le culot a ensuite été dispersé dans de l'eau milli-Q (mêmes rapports). Le mélange a été ensuite agité puis tamisé à 63 µm pour la smectite et 25 µm pour l'illite. Cette étape permet d'éliminer par tamisage une partie des phases accessoires.

Ensuite, quelques gouttes de HCl 0.1 M ont été ajoutées au mélange sous agitation. L'ajout de HCl s'arrête lorsque que l'effervescence s'arrête et que le pH chute, cela signifie que la calcite a bien été dissoute. Le mélange a ensuite été centrifugé et le surnageant éliminé.

Les minéraux argileux ainsi purifiés ont ensuite été conditionnés sous forme sodique à l'aide de plusieurs dispersions/agitations/suppressions du surnageant dans du NaCl 1 M puis 0.1 M. Lors de la dernière dispersion, le pH est ajusté à 9.5 avec du NaOH afin de garantir l'adsorption du sodium sur toute la surface du minéral argileux.

L'excès salin est ensuite supprimé à l'aide d'un rinçage à l'éthanol. Une fois l'éthanol éliminé, les minéraux argileux sont laissés à sécher à l'air libre puis dans une étuve à 50°C.

La bonne élimination de la calcite a été vérifiée par calcimétrie Bernard (LAMAS *et al.*, 2005), la pureté des minéraux argileux a été estimée à l'aide d'analyse DRX des échantillons et le bon conditionnement des minéraux argileux a pu être mesuré par analyse des cations échangeables.

1.2 Analyse CEC et cations échangeables

Les différents échantillons de minéraux argileux et de sols ont été constamment étudiés selon leurs capacités d'échange cationiques (CEC) et leurs concentrations en cations échangeables.

Cette étude s'effectue également par batch. La masse de solide à ajouter dans le tube est calculée afin d'avoir dans le batch, une concentration suffisante pour être mesuré par ICP-AES (cf. Tableau 1).

Tableau 1. Résumé des différentes limites de quantification utilisées lors des analyses ICP-AES

	Na	Ca	K	Mg
LOQ (ppm)	0.1	0.5	0.5	0.05

Lors de la détermination des CEC, une fois la masse de solide calculée, celle-ci est ajoutée dans un tube de centrifugation avec une solution de KCl. La concentration de la solution de KCl est également calculée pour s'assurer une saturation complète du solide. Connaissant, de manière approximative, la CEC des échantillons, il est possible de déterminer la concentration de sites à saturer et donc de déterminer la concentration minimale nécessaire en KCl. Il a été choisi pour ces expériences de multiplier par 10 cette concentration minimale afin de s'assurer de la saturation de l'échangeur. Le pH du mélange est ensuite augmenté à pH 10 à l'aide de KOH afin d'augmenter l'adsorption du potassium. Le mélange est ensuite agité pendant 1 jour puis ultra-centrifugé. Le surnageant est éliminé puis remplacé par l'eau Milli-Q pour éliminer l'excès salin (1 jour d'agitation) puis par de l'éthanol pour éliminer l'excès d'eau (1 jour d'agitation). Une fois l'éthanol enlevé,

l'échantillon solide est laissé sous hotte pour séchage pendant 2 jours. Une fois le séchage terminé, le solide est à nouveau pesé, pour vérifier l'absence de perte lors des différents lavages, puis une solution de CsCl (à la même concentration que KCl) est ajoutée au tube puis l'ensemble est mis à agiter pendant 2 jours. Une fois cette dernière étape passée, le mélange est mis à centrifuger puis le surnageant est récupéré, filtré à 0.45 μm (Filtre seringue 25 mm en polypropylène, VWR) puis analysé par ICP- AES. La CEC est alors déterminée à partir de la concentration en solution du potassium.

Le protocole d'analyse des concentrations en cations échangeables reprend la dernière étape du protocole précédent. Une masse de solide est mis en contact avec une solution de CsCl. Le mélange est agité 2 jours puis le surnageant est prélevé, filtré puis analysé par ICP- AES.

2 Calcul des erreurs expérimentales

2.1 Théorie de la propagation des erreurs

A partir de la théorie de la propagation des erreurs, il est possible d'évaluer la variance d'une grandeur G , dépendante de plusieurs variables x_i , à partir des variances respectives de chacune des variables :

$$\sigma_G^2 = \sum_{i=1}^n \left(\frac{\partial G}{\partial x_i} \right)^2 \cdot \sigma_{x_i}^2 + 2 \sum_i \sum_j \frac{\partial G}{\partial x_i} \frac{\partial G}{\partial x_j} \sigma_{x_{ij}}$$

Avec $\sigma_{x_i}^2$ la variance de la variable x_i et $\sigma_{x_{ij}}$ la covariance des variables x_i et x_j .

La covariance $\sigma_{x_{ij}}$ est une mesure relatant le degré de corrélation des erreurs relatives associées aux variables x_i et x_j . Si les erreurs relatives des variables sont indépendantes, alors la covariance est égale à zéros.

2.2 Calculs de l'erreur associée à la mesure de R_D

Expérimentalement, le coefficient de partage R_D a été déterminée à l'aide de l'expression suivante :

$$R_D = \frac{A_0 - A}{A} \cdot \frac{V}{m}$$

Avec :

A_0 : Activité initiale de la solution

A : Activité à l'équilibre de la solution

V : Volume de solution (en mL)

m : Masse d'échangeur (en g)

Les différentes activités des solutions ont été déterminées à partir du comptage gamma de 1 mL de ces solutions. L'activité totale a donc été calculée selon la formule :

$$A = \frac{Cpm \cdot V}{m_p}$$

Avec :

Cpm : Coups par minute, activité de comptage

m_p : Masse de prélèvement pour comptage (en mL)

Ainsi, le coefficient de partage peut-être développé de la façon suivante :

$$R_D = \left(\frac{\frac{Cpm_0 \cdot V_0}{m_{p,0}}}{\frac{Cpm \cdot V}{m_p}} - 1 \right) \cdot \frac{V}{m}$$

La variance associée à R_D dépend donc de 7 variables :

$$\begin{aligned} \sigma_{R_D}^2 = & \left(\frac{\partial R_D}{\partial Cpm_0} \right)^2 \cdot \sigma_{Cpm_0}^2 + \left(\frac{\partial R_D}{\partial Cpm} \right)^2 \cdot \sigma_{Cpm}^2 + \left(\frac{\partial R_D}{\partial m_{p,0}} \right)^2 \cdot \sigma_{m_{p,0}}^2 + \left(\frac{\partial R_D}{\partial m_p} \right)^2 \cdot \sigma_{m_p}^2 \\ & + \left(\frac{\partial R_D}{\partial V_0} \right)^2 \cdot \sigma_{V_0}^2 + \left(\frac{\partial R_D}{\partial V} \right)^2 \cdot \sigma_V^2 + \left(\frac{\partial R_D}{\partial m} \right)^2 \cdot \sigma_m^2 \end{aligned}$$

Sans détailler les différentes étapes de calculs, nous obtenons la formule suivant pour estimer les incertitudes expérimentales :

$$\begin{aligned} \sigma_{R_D}^2 = & \left(\frac{V_0}{m_{p,0} \cdot A} \cdot \frac{V}{m} \right)^2 \cdot \sigma_{Cpm_0}^2 + \left(\frac{A_0}{A \cdot Cpm} \cdot \frac{V}{m} \right)^2 \cdot \sigma_{Cpm}^2 + \left(\frac{Cpm_0 \cdot V_0}{m_{p,0}^2 \cdot A} \cdot \frac{V}{m} \right)^2 \cdot \sigma_{m_{p,0}}^2 \\ & + \left(\frac{A_0}{Cpm} \cdot \frac{1}{m} \right)^2 \cdot \sigma_{m_p}^2 + \left(\frac{Cpm_0}{m_{p,0} \cdot A} \cdot \frac{V}{m} \right)^2 \cdot \sigma_{V_0}^2 + \left(\frac{1}{m} \right)^2 \cdot \sigma_V^2 + \left(R_D \cdot \frac{1}{m} \right)^2 \cdot \sigma_m^2 \end{aligned}$$

Les variances associées au comptage par spectrométrie gamma sont directement fournies dans les rapports de comptage. Les variances de pesées $\sigma_{m_{p,0}}^2$, $\sigma_{m_p}^2$ et σ_m^2 correspondent à la variance des mesures sur balance électronique de précisions (0.0005 g). Quant aux volumes de solution, ils ont été pesés puis déterminés par calcul en suivant les relations proposées par NOVOTNY & SOHNEL (1988) :

$$p = p_w + Ac + Bct + Cct^2 + Dc^{1.5} + Ec^{1.5}t + Fc^{1.5}t^2$$

Avec :

p : la masse volumique de la solution en kg.m^{-3}

p_w : la densité de l'eau, calculée à l'aide de

$$p_w = 999.65 + 2.0438 \cdot 10^{-1}t - 6.1774 \cdot 10^{-2}t^{-1.5}$$

t : la température en °C

c : la concentration en solution mol.dm^{-3}

A, B, C, D, E, F : constantes de NOVOTNY & SOHNEL (1988) répertoriée dans Tableau 2.

Tableau 2. Coefficients de la relation de NOVOTNY & SOHNEL (1988)

	A.10 ⁻²	-B.10	C.10 ³	-D	E.10 ²	-F.10 ⁴
NaCl	0.4485	0.9634	0.6136	2.71	1.009	0
CaCl ₂	1.012	61.56	1.028	9.749	96.94	3.165

Étant donné l'impossibilité d'accéder à l'incertitude liée à ce calcul de masse volumique, il a été choisi de la négliger. Ainsi, la variance liée aux volumes de solution a été choisi comme égale à la variance d'une pesée σ_p^2 fois le nombre (n) de pesées réalisées pour produire la solution :

$$\sigma_n^2 = n \cdot \sigma_p^2$$

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Interactions dans un système césium, strontium/matière organique naturelle/argiles des sols : de la décontamination à la remédiation

par
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Résumé

Le projet de thèse s'inscrit dans le Projet Investissement d'Avenir (PIA) DEMETERRES, dont l'objectif est le développement de méthodes et de technologies pour la décontamination et la remédiation des sols et effluents contaminés après un accident nucléaire. L'objectif de cette thèse est de mieux appréhender les interactions de ^{137}Cs et ^{90}Sr avec les différentes composantes des terres agricoles et ainsi être capable de prédire l'état chimique dans lequel ces éléments se trouveraient dans les sols en cas d'accident nucléaire. Une base de données dans le formalisme des échangeurs d'ions multi-sites a été mise en place, représentant les comportements d'adsorption de Cs^+ et Sr^{2+} dans les illites et smectites (deux des principaux minéraux argileux) vis-à-vis des cations majeurs environnementaux H^+ , Na^+ et Ca^{2+} . Cette base de données a par la suite été utilisée pour tenter de prédire le comportement d'adsorption de Cs^+ et Sr^{2+} dans des échantillons de sols agricoles français (Pusignan, Etoile-sur-Rhône et Herqueville). De bonnes simulations du comportement d'adsorption de Cs^+ et Sr^{2+} ont été obtenues sur Pusignan et Etoile-sur-Rhône. Dans le cas d'Herqueville, la suppression de la MON n'a pas amélioré l'accord entre les simulations et les expériences, tandis que l'élimination de l'aluminium échangeable a lui permis une meilleure simulation de l'adsorption de Sr^{2+} , mais pas de Cs^+ . Ces travaux permettent de simuler efficacement le comportement d'adsorption de Cs et Sr dans des sols et ainsi d'appuyer les stratégies de décontamination et remédiation après un d'accident nucléaire.

Mot-clés : césium, strontium, modélisation échangeur d'ions multi-sites, minéraux argileux, sols agricoles

Abstract

This study is part of the DEMETERRES project, which aims to develop new methods and technologies in the field of decontamination and remediation of contaminated soils and effluents after a nuclear accident. The objective of this PhD is to obtain a better knowledge of ^{137}Cs and ^{90}Sr interactions onto agricultural soils and to better predict the chemical state of these elements in soils after a nuclear accident. A database in the multi-sites ion exchanger formalism has been built, reflecting the adsorption behaviours of Cs^+ and Sr^{2+} onto illite and smectite (two major clay minerals) with regards to major environmental cations: i.e. H^+ , Na^+ , and Ca^{2+} . It was used to predict the adsorption of Cs^+ and Sr^{2+} onto French agricultural soil samples (Pusignan, Etoile-sur-Rhône and Herqueville). Good simulations of the adsorption of Cs^+ and Sr^{2+} onto Pusignan and Etoile-sur-Rhône are obtained. In the case of Herqueville, the removal of NOM does not improve the agreement between experimental results and simulations, but the removal of exchangeable aluminum allows a better representation of the adsorption results of Sr^{2+} onto Herqueville, but not for Cs^+ . This work allows efficiently simulating the adsorption of Cs and Sr onto soils and support decontamination and remediation strategies after a nuclear accident.

Key-words: cesium, strontium, multi-sites ion exchanger model, clay minerals, agricultural soils