Characterisation of the highly selective caesium sorption on glauconite rich sands of contrasting geological formations

Y. Bruneel^{1,2}, L. Van Laer¹, S. Brassinnes³, E. Smolders²

¹ Belgian Nuclear Research Centre (SCK CEN), Expert Group Waste & Disposal, Boeretang 200, 2400 Mol, Belgium

² Department of Earth and Environmental Sciences, Division of Soil and Water Management, KU Leuven, Kasteelpark Arenberg 20, 3001 Leuven, Belgium

³ ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and Fissile Materials, Kunstlaan 14, 1210 Brussel, Belgium

Corresponding Author. Contact: yaana.bruneel@sckcen.be

Three-site model for glauconite

Highlights

- NH_4/K selectivity coefficient on the FES corresponds with values for illite
- Three-site model has been successfully optimised to the sorption isotherm data
- Selective sites on glauconite bind ^{137}Cs with similar properties as illite
- Fraction of FES to total CEC is about a factor 5 lower than in illite

Abstract

The Neogene-Paleogene glauconite sands are investigated in the framework of the Belgian radioactive waste disposal as material for an additional sorption sink. Glauconite is an Fe-rich phyllosilicate that is mainly present as 125-250 μm sized pellets in the sand. Recent studies have shown a surprisingly strong sorption of radiocaesium (^{137}Cs) on these sands, despite the coarse sized pellet structure. This study was set up to characterise the selective $^{137}\text{Cs}^+$ sorption sites on glauconite that are likely Frayed Edge Sites (*FES*) as in illite. First, the NH_4/K selectivity on the *FES* was determined as a fingerprint for the highly selective *FES*. The NH_4/K selectivity coefficient on the *FES* for three different sand formation ranged between 3.8-5.0, well in line with the range (4-7) that has been reported for illite clay and clay formations. Second, the Cs^+ sorption isotherms were determined on three sand formations in a background solution of 0.5 mM K^+ , 100 mM Ca^+ and 10^{-8} - 10^{-4} M Cs^+ ; isotherms were fitted with an optimised three-site model adapted after the illite model of Bradbury & Baeyens (2000). The optimised model fitted the data adequately. The *FES* capacities of the sands ranged from 0.04-0.06 % of the CEC which is significantly below that of illite (0.25 %). Similarly, a strong decrease in the *FES-type II* site capacities was observed (1.7-2.2 % of the CEC vs 20 % for illite). The lower fractions of *FES-type I* and *FES-type II* sites detected in glauconite sand are related to higher fractions of smectites (XRD confirmed) that do not have specific Cs sites. Taken together, this study suggests that the glauconite sands have highly selective sites that bind $^{137}\text{Cs}^+$ with similar properties as in illite, however the fractions of these sites in the total CEC pool are about a factor five lower than in pure illite.

Keywords

Glauconite, radiocaesium, sorption isotherm, selective sorption sites, three site model

1 Introduction

Radiocaesium (^{137}Cs) is a major component of high-level nuclear waste. The combination of a long half-life ($t_{1/2}$ 30 years) and the high solubility of the Cs^+ cation under all redox (E_h) and pH conditions makes it an element of concern in radioactive waste repositories. The mobility of Cs^+ in the environment is mainly controlled by the sorption onto mineral surfaces (Fuller et al., 2015; Sawhney, 1972; Takeno, 2005). Especially the illitic type of clay minerals retain Cs^+ due to the selective sorption at the frayed edge sites (*FES*) (Sawhney, 1972; Valcke, 1993).

The $^{137}\text{Cs}^+$ sorption of the Neogene glauconite sands is being investigated in the framework of the Belgian radioactive waste disposal program. The glauconite sands are not considered to be a suitable host formation for the geological disposal of high-level and/or long-lived radioactive because of its high permeability. However, depending on the choice of primary host formation, the sands might become part of the natural barrier surrounding the host. Glauconite sands are enclosing both the Boom Clay and Ypresian clays. A secondary purpose for the glauconite sands could be as an extra embankment below a surface disposal for short-lived and low-level waste. In the Neogene and Paleogene glauconite sands (Diest, Berchem and Voort Fm), a surprisingly strong $^{137}\text{Cs}^+$ sorption has been observed. The radiocaesium (^{137}Cs) distribution coefficients ($\log K_D$, K_D in L kg^{-1}) range between 3.4 and 4.3 after 30 days of reaction with 0.5 mM K^+ as competing cation (Bruneel et al., 2020), these K_D values are very close to those of Boom Clay samples under the same conditions (3.5 log units). The main sorbent in the sands is the glauconite fraction. The $^{137}\text{Cs}^+$ K_D values on pure glauconite fractions (4.0-4.3 log units at 0.5 mM potassium (K^+)) are within the range of corresponding values on illite (4.1-4.3). The difference in $^{137}\text{Cs}^+$ K_D of glauconite fractions among the different formations remain below a factor 2.

The Diest and Berchem Formation are classified as sands based on grain size, containing 35-40 weight percent (wt %) glauconite pellets. Locally the sand can consist of > 80 wt% glauconite pellets (Adriaens, 2015; Adriaens et al., 2014). The glauconite pellets are coarse sized (125-250 μm) but consist nearly entirely out of clay minerals. The mineral glauconite shows close resemblance to an iron (Fe) rich illite. Glauconite $(\text{K},\text{Na})(\text{Fe}^{3+}\text{Fe}^{2+},\text{Al},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$ has two end-members, an illitic or micaceous form, and a more smectitic form. The form present in the sediment depends on the weathering state. In the illitic form, potassium (K^+) is the main interlayer cation (Meunier and El Albani, 2007; Odin, 1988), while in the smectitic form part of the interlayer cations were leached out and replaced by hydrated exchangeable cations. Glauconite mostly occurs as a mixed form between the illitic and smectitic end-member (Courbe et al., 1981; Meunier and El Albani, 2007; Van Ranst and De Coninck, 1983).

The structure of the clay minerals affects the Cs^+ sorption. Three sorption sites are distinguished in illitic clays: planar sites, *FES-type I* and *FES-type II* sites (Bradbury and Baeyens, 2000; Fuller et al., 2015; Poinssot et al., 1999a, b). The planar sites are characterized by high capacity and low selectivities for Cs^+ over the main other competing ions such as K^+ and Ca^{2+} . The sorption sites of interest for Cs^+ sorption are the *FES-type I* and, to a lower extent, the *FES-type II* sites (Bradbury and Baeyens, 2000).

The *FES (type I and type II)* are localized at the edges of the interlayers or in transition zone between the interlayer and hydrated interlayer, with a width of 1.0 to 1.4 nm (Nakao et al., 2008). The FES are only accessible to small cations with low hydration energies such as Cs^+ , K^+ and NH_4^+ (Fuller et al., 2015; Sawhney, 1972). Due to the high Cs^+ selectivities of these low capacity sorption sites, Cs^+ is strongly retained at low, but environmentally relevant concentrations. The *FES-type I* and *FES-type II* are distinguished based on experimental sorption isotherm data (Brouwer et al., 1982a). In more recent characterisation studies, no clear structural differences were observed between *type I* and *type II* sites (Nakao et al., 2008; Okumura et al., 2018). Therefore, the FES can be described as Cs selective sites with a continuum of selectivity rather than distinct types of sites. In this study the FES are described by two discretised sites, the term '*FES*' is used to refer to the *FES-type I* sites and '*type II*' to the *FES – type II* sites, in order to be able to compare to the existing model for illite.

In literature, selectivity coefficients (K_c) for Cs/K in the FES range between log 2.2 and 9.4 (Bradbury and Baeyens, 2000; Brouwer et al., 1982b; de Preter, 1990; Poinssot et al., 1999b). The NH_4^+ over K^+ selectivity coefficient in the FES is about 4-7 (de Preter, 1990) and this is often used as the fingerprint to demonstrate the consistence of FES properties across different environments, e.g. soil, sediments and suspended matter (Wauters et al., 1996b). At high Cs^+ concentrations, the sorption to the less selective planar sites becomes important. The replacement of K^+ by hydrated exchangeable cations during weathering increases the interlayer width. This leads to an increase in the fraction of planar sites and a decrease in FES capacity. Therefore, the binding strength of Cs^+ to glauconite will be related to the ratio of illitic and smectitic layers (Fuller et al., 2015; Missana et al., 2014).

In general, two types of ion-exchange models are used to describe equilibrium Cs^+ sorption on clay and clay minerals under variable conditions (De Koning et al., 2007). A first group of models aims to accurately predict the Cs^+ sorption at trace Cs^+ concentrations (Cremers et al., 1988; de Preter, 1990). In this single site approach, only the high affinity sites are assessed by the radiocaesium interception potential (*RIP*) or the $K_D \cdot m_K$. The description of the sorption of Cs^+ as the solid:liquid distribution K_D (L kg^{-1}) reads:

$$K_D \cdot m_K = K_c (\text{Cs/K}) \cdot [\text{FES}] \quad (1)$$

With m_K the K^+ concentration in solution (mmol L^{-1}); K_c (Cs/K) the Cs^+ over K^+ selectivity coefficient in the FES and $[\text{FES}]$ the capacity of the FES sites (mmol kg^{-1}). The *RIP* concept is theoretically valid in the 5-10 mmol L^{-1} K^+ concentration range; at lower K^+ concentrations the *RIP* decreases (de Preter, 1990). In the lower K^+ concentration domain the *RIP* is underestimated (Hisashi et al., 2013) (Wauters et al., 1996b). The *RIP* at trace Cs^+ loadings is the product of the high affinity site capacity and its selectivity, with the assumptions that i) the amount of intercepted Cs^+ in the FES is only representing a very small fraction of the total FES capacity, ii) K^+ is the only competing cation, present in known concentration, and iii) the Ca^{2+} background concentration prevents Cs^+ sorption on the planar sites.

The second type of models, the multi-site cation exchange models, allows the prediction of Cs^+ concentration dependent sorption for concentrations ranging between trace and high levels (Bradbury and Baeyens, 2000; Brouwer et al., 1982b; De Koning et al., 2007; Missana et al., 2014). The three-site model by (Bradbury and Baeyens, 2000) assumes that Cs^+ sorption in argillaceous systems is dominated by cation exchange reactions on the illite mineral component and that the uptake takes place on three sites, each with different site capacities and affinities. The total capacity of the sorption sites is described by the cation exchange capacity (CEC). The site capacity and affinity (K_c) for each site are linked. Table 1 summarizes the selectivity and capacity data for four different three-site models based on illite. The *FES* capacities for illitic clays range between 0.05 – 6.5 % of the *CEC* (Bradbury and Baeyens, 2000; Brouwer et al., 1982a; de Preter, 1990; Poinssot et al., 1999b). The variation mainly depends on the definition of the sorption sites. For mixed layer illite-smectite, *FES* capacities can be up to 10 times smaller (de Preter, 1990).

Table 1 Selectivity coefficients and individual sorption site capacity data for Illite du Puy in a three-site model (Bradbury and Baeyens, 2000; Brouwer et al., 1982b; Fuller et al., 2014; Missana et al., 2014).

	Selectivity log K_c (Cs/K)			Capacity % of the CEC		
	<i>FES</i>	<i>type II</i> sites	<i>Planar</i> sites	<i>FES</i>	<i>type II</i> sites	<i>Planar</i> sites
Brouwer et al. (1982)	4.1	1.4	0.65	0.25	2.5	97.25
Bradbury & Baeyens (2000)	4.6	1.5	0.50	0.25	20	80
Fuller et al. (2014)	5.5	3.0	1.1	0.05	2	97.95
Missana et al. (2014)	4.2	2.0	1.2	0.24	19.95	79.81

This study aimed to characterize the highly selective Cs^+ sorption on a range of natural glauconite sands and to relate sorption parameters with the mineralogy. Previous studies showed good sorption of Cs^+ on glauconite (Bruneel et al., 2020). It is unclear how to explain differences in ^{137}Cs sorption between a pure glauconite and a pure illite. Glauconite is described as an illite where part of the aluminium (Al^{3+}) has been replaced by Fe^{2+} and with K^+ as the dominant interlayer cation (Bailey, 1980; Meunier, 2005). The capacity and affinity for Cs^+ on the different sorption sites is unknown for glauconite. In addition, the K_D is lower for granular glauconite compared to milled glauconite. This could imply a different distribution of the site capacities among the accessible sites in granular versus milled glauconite. Here, the sorption isotherms of Cs^+ were measured in a wide range of Cs^+ concentrations to identify the sites capacities and corresponding selectivities. The isotherms were modelled to infer these sorption parameters. By combining the X-ray diffraction data with the modelled site capacities and selectivities, mineralogical indications for the variation between the sand and to illite can be found. The NH_4/K selectivity coefficient on the *FES* was measured and used as a fingerprint of the highly selective sorption sites..

2 Material and methods

2.1 Sample selection

A set of three natural glauconite sands was selected for the experiments (Figure 1). More details on these samples on the $^{137}\text{Cs}^+$ interception potential and kinetics were presented in Bruneel et al. (2020). The samples are part of the Neogene glauconite sands and are known to have high glauconite and total clay mineral content. Sample D1 and B2 originate from the excavation of the second shaft to the HADES research lab of ONDRAF/NIRAS and SCK CEN in Mol. Sample D2 is part of the ON-Dessel5 drilling core. A purified Na-conditioned Illite du Puy reference sample was included. The samples were stored in vacuum sealed bags since sampling. Before use, the samples were oven-dried at 60°C.

Figure 1 Optical microscopy images of the complete glauconite sands D1, D2 and B2

Table 2 Selected characteristics of the glauconite rich sands; the $^{137}\text{Cs}^+$ $\log K_D$ (L kg^{-1}) values were obtained after 35 days reaction with 0.5 mM K as competing ions. The properties were determined as described in Bruneel et al. (2020). The data is presented as mean $\pm$ standard deviation of two replicates.

	Formation	Depth	Glauconite content	Total clay content	Quartz content	CEC ^{\$\$}	$\log K_D$
		mTAW ^{\$}	wt%	wt%	wt%	cmol _c kg ⁻¹	L kg ⁻¹
D1	Diest Fm	72.8	34	34	29	10.7 $\pm$ 0.22	3.90 $\pm$ 0.04
D2	Diest Fm	90.7	27	31	60	8.2 $\pm$ 0.83	3.79 $\pm$ 0.08
B2	Berchem Fm	134.1	27	32	56	11.3 $\pm$ 0.01	3.73 $\pm$ 0.07
IdP	Na-Illite du Puy					20.4*	4.59 $\pm$ 0.05

^{\$}The sampling depth is expressed in mTAW, or the reference level in Belgium (Tweede Algemene Waterpassing)

^{\$\$}Cobalt hexamine method (Ciesielski et al., 1997). A value of 20 cmol_c kg⁻¹ was reported by Bradbury and Baeyens (2000).

2.2 Batch sorption studies

The sorption is described by the distribution coefficient K_D (L kg^{-1}), i.e. the ratio of adsorbed to solution $^{137}\text{Cs}^+$ concentration. Two sets of batch experiments were performed, a NH_4^+ - K^+ selectivity experiment and a sorption isotherm test. In both experiments the samples were prepared in duplicate in a solid/liquid ratio of 1 g to 30 mL. An internal reference sample (Na saturated Illite du Puy) was added to each of the batch experiments but was only used at zero NH_4^+ addition and zero stable Cs^+ addition, i.e. it allowed referencing the K_D values for one given ionic scenario. The samples were pre-equilibrated with the background solution 5 mM K^+ , 100 mM Ca^{2+} and 0-5 mM NH_4^+ for the selectivity experiment and 0.5 mM K^+ and 100 mM Ca^{2+} in the sorption isotherm experiment. To prevent sample loss during liquid

change in the pre-equilibration stage, the samples were weighed in dialysis bags (standard RC tubing, MWCO 6– 8 kDa) and filled with 5 mL of background solution. Thereafter, they were transferred in 50 mL polypropylene (PP) tubes filled with an additional 25 mL outer solution. During the pre-equilibration the supernatant was changed three times every 8-16 hours. Sorption experiments were performed at neutral pH in a non-buffered system. At trace concentration Cs^+ the K_D is not pH dependent (Poinssot et al., 1999a, b). The $^{137}\text{Cs}^+$ activity concentration in solution was measured with liquid scintillation counting (TriCarb 2100TR, Perkin Elmer Ins.). The concentration of stable $^{133}\text{Cs}^+$ in solution was measured by Inductively Coupled Plasma Mass Spectrometry (Agilent Technologies 7700 Series ICP-MS).

Ammonium-potassium (NH_4^+ - K^+) selectivity on the *FES*

Competing cations Cs^+ , K^+ , NH_4^+ have similar ion properties and comparable selectivity for the planar exchange sites. On the *FES*, the differences become more pronounced, due to the specific size of the selective sorption sites. By adding radiocaesium and variable concentration of NH_4^+ the selectivity of NH_4^+ to K^+ can be determined.

The $^{137}\text{Cs}^+$ sorption on glauconite sands was studied in batch sorption using the experimental procedure adapted from Wauters et al. (1996b). The method is based on masking the regular exchange sites with Ca^{2+} to ensure that only the *FES* take part in Cs^+ exchange. The experiment was performed in a background solution with 5 mM K^+ , 100 mM Ca^{2+} and NH_4^+ in five different concentrations between 0 and 5 mM (0, 1, 2, 2.5 and 5 mM). Working at lower K^+ concentrations is not relevant as the linear $K_D.mK$ relationship is not strictly valid for K^+ concentrations below 1 mM. In the lower K^+ concentration domain the RIP is underestimated (de Preter, 1990; Hisashi et al., 2013; Wauters et al., 1996b).

On day zero the supernatant was spiked with 1.5 kBq $^{137}\text{Cs}^+$ g⁻¹ sand, containing 0.0042 μgkBq^{-1} CsCl carrier. After 48 hours the $^{137}\text{Cs}^+$ activity concentration in solution was measured and the K_D determined from the difference in $^{137}\text{Cs}^+$ activity concentrations between blank (no sand) and samples, the solution volume and the sand weight. From the start of the pre-equilibration phase the tubes were shaken on an orbital bench shaker (0.42 s⁻¹). The NH_4^+ concentrations in solutions at the start, after pre-equilibration and after 48 hours were confirmed with a colorimetric method.

Comparing the two-ion system (K-Ca) with the three-ion system (K-Ca- NH_4) allows the determination of the NH_4^+ to K^+ selectivity coefficient on the *FES*. The quantitative description has been derived before (Wauters et al., 1996b). Briefly, the K_D value of $^{137}\text{Cs}^+$ in the *FES* sites in the two-ion system is termed the K_D (K-Ca) and is described by Eqn. (1) that can rearranged to

$$K_D(K - Ca) = \frac{[FES].K_c^{FES}(Cs/K)}{mK} \quad (2)$$

With K_c^{FES} (Cs/K) the selectivity to Cs^+ over K^+ on the *FES* and mK the K^+ concentration in solution (mM). It is assumed that trace levels of Cs^+ , i.e. $^{137}\text{Cs}^+$, only bind to the *FES* and not to the other sites and equations (1) and (2) assume that the *FES* sites are close to 100% occupied by K^+ . In the three-ion

system, NH_4^+ also occupies the *FES* and the K_D value of $^{137}\text{Cs}^+$ in that system is termed the $K_D(K - \text{Ca} - \text{NH}_4)$ for which it can be shown (Wauters et al., 1996b) that

$$K_D(K - \text{Ca} - \text{NH}_4) = \frac{[\text{FES}] \cdot K_c^{\text{FES}}(\text{Cs}/K)}{mK + K_c^{\text{FES}}(\text{NH}_4/K) \cdot m\text{NH}_4} \quad (3)$$

With $K_c^{\text{FES}}(\text{NH}_4/K)$ the selectivity to NH_4^+ over K^+ on the *FES* and $m\text{NH}_4$ the NH_4^+ concentration in solution (mM). The assumptions for equation 3 are similar to equation 2; valid at trace levels of $^{137}\text{Cs}^+$ and Cs^+ sorption limited to the *FES* sites. With the exception that the *FES* are nearly 100 % occupied by K^+ and NH_4^+ , with a ratio depending on the NH_4/K -selectivity coefficient in the *FES*. NH_4^+ is generally a factor 4 to 7 more competitive than K^+ in the *FES* (de Preter, 1990; Wauters et al., 1996a).

Combining equations (2) and (3) yields:

$$\frac{K_D(K - \text{Ca})}{K_D(K - \text{Ca} - \text{NH}_4)} = 1 + K_c^{\text{FES}}(\text{NH}_4/K) \cdot \frac{m\text{NH}_4}{mK} \quad (4)$$

Plotting the ratio of the K_D of $^{137}\text{Cs}^+$ with or without NH_4^+ to the concentration ratio $m\text{N}$ to $m\text{K}$ yields a linear trend and the slope of that line equals the $K_c^{\text{FES}}(\text{NH}_4/K)$. A similar concept for the determination of the $K_c(\text{K}/\text{Na})$ has been described by de Preter et al. (1991).

Sorption isotherm

Radiocaesium batch sorption experiments were performed on samples D1, D2 and B2. The experiment was performed in a 0.5 mM K^+ (KCl) and 100 mM Ca^{2+} ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) background solution. The lower background K^+ concentrations, compared to the selectivity experiment, were chosen to reproduce more realistic in-situ conditions. Freshly sampled aquifer solutions from the Diest and Berchem Formation contain 0.14-0.37 mM K^+ , Ca^{2+} concentrations range from 0.4-1.7 mM.

The procedure of the sorption isotherm experiment is similar to that of the selectivity experiment. The samples were pre-equilibrated in the background solution. At day zero the samples were spiked with $^{137}\text{Cs}^+$ (1.8 MBq g^{-1} containing 8×10^{-8} M CsCl carrier). At the same time a stable Cs^+ solution was made from a calibrated CsCl stock solution that was added in a concentration range of 10^{-8} M to 10^{-4} M. To one set of duplicates no stable CsCl was added, these samples contain the lowest dose 8×10^{-8} M Cs^+ . The supernatant was sampled and $^{137}\text{Cs}^+$ and total dissolved stable Cs^+ concentrations were measured at different time points (48 hours, 7 days, 28 days, 53 days and 90 days). The samples were placed on an end-over-end shaker (30 RPM) for the entire duration of the experiment. The adsorption K_D values of $^{137}\text{Cs}^+$ were derived from the radioactivity based concentrations, the volumes and sand weight as described above.

All samples had been pre-equilibrated with the background solution without added stable Cs^+ , however natural Cs^+ is present at trace levels in the samples. At very low added Cs^+ concentrations in solution, this natural Cs^+ can be desorbed from the sample and this increases the total stable Cs^+ concentration in solution. The Cs^+ in solution detected by ICP-MS consists of the fraction of added stable Cs^+ that is

not sorbed on the glauconite plus the desorbed natural Cs⁺. The stable Cs⁺ concentration can be measured at low concentrations by ICP-MS (limit of detection (LOD) 0.002 µg ¹³³Cs⁺ L⁻¹, equivalent to 1.5 10⁻⁸ M).

The adsorbed [Cs⁺] (mol kg⁻¹ sand) at equilibrium is preferably derived from the ¹³⁷Cs⁺ activity based K_D by the following equation.

$$C_{S_s} = [^{133}\text{Cs}]. K_D^{^{137}\text{Cs}} \quad (5)$$

with C_{S_s} the sorbed stable Cs⁺ concentration in mol kg⁻¹, [¹³³Cs⁺] the solution concentration of stable Cs⁺ in mol L⁻¹ and the K_D of ¹³⁷Cs⁺ in L kg⁻¹. The data of C_{S_s} were plotted to the measured stable ¹³³Cs⁺ concentrations to obtain the isotherms.

2.3 Modelling

The three-site model (Bradbury and Baeyens, 2000) was described for Illite du Puy in the PHREEQC geochemical code (Parkhurst and Appelo, 1999). PhreeqC allows the adjustment of the model parameters and constants, however, direct optimisation of the parameters is not possible. We used the PHREEQC version embedded in HP1 that allows for a straightforward optimisation of the parameters by coupling to the UCODE_2014 code (Poeter, Hill et al. 2014). The parameters can be iteratively optimised using least squares fitting to improve the fit between the experimental and modelled data points. Each of the parameters is defined by upper and lower constraints in a realistic range, based on known illite parameters from literature. UCODE makes it possible to calculate parameter statistics.

2.4 X-ray diffraction (XRD) analysis

The glauconite content of the complete glauconite sands 'bulk' was determined by quantitative powder X-ray diffraction (XRD) measurements. The complete sample was milled to produce a fine random powder (using the McCrone micronizing mill). Zincite was used as internal standard in a 10 wt% ratio. The samples were loaded using the side loading technique. In addition to the bulk measurement oriented clay slides were made for detailed clay analysis. The samples were subjected to the Jackson treatment (modified after (Jackson, 1975), (Zeelmaekers, 2011)) before XRD analysis. In several steps the aggregates were broken up, the carbonates, organic matter (OM) and Fe-(oxy)hydroxides were removed. The carbonates were removed by a acetic acid-sodium acetate (CH₃COOH-CH₃COONa) buffer with a pH of 5. Hydrogen peroxide (H₂O₂) was used to remove the OM. And the Fe-(oxy)hydroxides are removed by small amounts of sodium dithionite (Na₂S₂O₄). To ensure homogeneous swelling of the smectite phases the clay was Ca-saturated and oven-dried at 60°C.

The X-ray diffraction scans were measured using a Phillips PW1830 diffractometer with CuKα radiation at 30 mA and 45 kV using a graphite monochromator and a scintillation detector. The diffractometer scans were recorded in Bragg-Brentano geometry, 5 to 65 ° for bulk measurements and 2 to 47 ° for clay measurements, each time with a step size of 0.02 ° and 2 s counting time per step. The oriented clay slides were measured under air-dry and glycolated conditions.

3 Results and discussion

3.1 The K_D of $^{137}\text{Cs}^+$ at trace levels of glauconite sand relative to that in illite

At the lowest Cs^+ concentration, i.e. no carrier Cs^+ added except for that added through the $^{137}\text{Cs}^+$ spike, the sorption strength of $^{137}\text{Cs}^+$ is largest, corresponding to a log K_D value of 3.64 (D1), 3.56 (D2) and 3.78 (B2) in the presence of 0.5 mM K^+ as the only competing cation (Table 3). The illite Cs^+ K_D values are a factor 7.5 to 5.2 higher than those glauconite sands. The difference in K_D can only partially be explained by the glauconite content: the $^{137}\text{Cs}^+$ K_d is still a factor 1.8 to 2.0 higher for illite has than for pure glauconite. The difference in K_D is also only partially explained by the CEC (Table 3). This is the first indication that the glauconite sands contain a smaller fraction of *FES* than the pure illite.

Table 3 The K_D of $^{137}\text{Cs}^+$ at 0.5 mM K and at trace levels of stable Cs^+ for the glauconite sands and for illite as a reference.

Sample	K_D L kg^{-1}	CEC $\text{cmol}_c \text{ kg}^{-1}$	$K_D.m_K$ per unit of CEC (mol cmol_c^{-1})
D1	4340	10.7	0.26
D2	3530	8.2	0.16
B2	5350	11.3	0.25
Illite du Puy	38 900	20.4	0.95

3.2 The NH_4^+ to K^+ selectivity coefficients in the *FES*

The selectivity of NH_4^+ ions for the *FES* was tested in a batch experiment. The K^+ and NH_4^+ ions have similar ion properties and comparable selectivity for planar exchange sites (Bruggenwert and Kamphorst, 1979). The dependence of the ratio $K_D(\text{K}^+)$ to $K_D(\text{NH}_4^+ + \text{K}^+)$ versus the NH_4/K plots for all three samples are shown in Figure 2. The resulting selectivity coefficients are summarized in Table 4.

Figure 2 Dependence of the $K_D(K)/K_D(NH_4+K)$ on the molar NH_4^+/K^+ ratio, in the liquid phase for sample D1, D2 and B2. The K^+ and Ca^{2+} concentrations are kept constant at respectively 5 and 10 mM.

Table 4 Selectivity coefficients for NH_4/K on the *FES* obtained from the batch experiments with glauconite sand samples (D1, D2 and B2) performed in duplicate. The slope of the linear fit of the experimental data (Figure 2) gives the selectivity coefficient. The error on the selectivity coefficients of NH_4/K represent the error on linear fit.

	$K_c^{FES}(NH_4/K)$
D1	4.96 ± 0.31
D2	3.84 ± 0.31
B2	4.96 ± 0.25

The $K_c^{FES}(NH_4/K)$ values on the *FES* (Table 4) are in good correspondence to results reported by de Preter (1990) and Wauters et al. (1994) showing that NH_4^+ ions bind 4 to 7 times more selective than K^+ ions on the *FES*. More specifically, de Preter (1990) reported K_c values for the *FES* on clay minerals (illite 5.85, Boom Clay 5.50 and illite-smectite 7.50), while Wauters et al. (1994) reported data for different soil types (sandy 3.5, sandy loam 5.7, loam, 6.5 and clay 6.4). The consistency of these data indicate that the *FES* sites in the glauconite rich sands are structurally not different from those in illite clays. This will be taken forward for isotherm fitting where we will assume that $K_c(Cs/K)$ is identical to that in illite as a starting point in the non-linear curve fitting procedure. The implication of the NH_4/K selectivity coefficient is that $^{137}Cs^+$ can be remobilized by ammonium in anoxic sediments.

3.3 Sorption isotherm: effect of the Cs^+ concentration in solution on sorption

The experimental sorption isotherm data of the natural glauconite sands are similar for all three samples (Figure 3). A strong decrease in K_D is observed at increasing Cs^+ concentration. The shape of the log-log plot of the isotherm indicates non-linear sorption due to the site heterogeneity.

Figure 3 Experimental sorption isotherm data for three complete glauconite sands in a Cs^+ concentration range of 10^{-8} M to 10^{-4} M set against a background solution of 0.5 mM K^+ and 100 mM Ca^{2+} .

To fit the experimental data of the sorption isotherm, the three-site illite model of Bradbury & Baeyens (2000) was chosen as the starting point. That model has six adjustable parameters: three site capacities and three selectivity coefficients of Cs-K for each type of sorption site. The capacities of the different sites are linked through the known cation exchange capacity.

$$[\text{planar sites}] = \text{CEC} - [\text{FES}] - [\text{type II}] \quad (6)$$

with $[\text{planar sites}]$ the capacity of the *planar* sites (cmolc/kg)
 $[\text{FES}]$ the capacity of the *FES*-(type I) sites (cmolc/kg)
 $[\text{type II}]$ the capacity of the *FES*-type II sites (cmolc/kg)

This leaves five parameters to be optimised because the *CEC* is the experimentally determined value (Table 1). The illite model was plotted on the experimental data of sample D1, using the experimentally determined *CEC* value for sample D1, i.e. assuming equal selectivity coefficients and assuming that the fractions of *FES*, *type II* and *planar* sites in the total *CEC* are identical as in illite. The illite model in PHREEQC uses sorption constants between free sites and occupied sites, a value for each ion separately. The selectivity coefficients between two ions is, by definition, the ratio of sorption constants and it is that ratio which was used as a starting point in the isotherm fitting. For example, the sorption constants of K^+ on the *FES* is $10^{2.4}$, that for Cs^+ is $10^{7.0}$ and, hence, the $K_c (\text{Cs/K}) = 10^{(7.0-2.4)} = 10^{4.6}$.

The model fit sensitivity was analysed for all five parameters. First, the isotherm fitting is insensitive to the parameter K_c (Cs/K) on the planar sites (supplementary information). The effect of the planar K_c is beyond the investigated concentration range and only at high Cs^+ loadings, the planar sites and divalent competing cations will become relevant. Therefore, this parameter was fixed to the illite reference value in all other further optimisation. A refinement of the selectivity coefficients only or the capacities can both lead to a good optimisation of the model to the experimental data. Hence, fitting all parameters simultaneously in an optimisation will most probably give several optimised error minima and there is a covariance in optimised site capacities and selectivities (Bradbury and Baeyens, 2000). Therefore, a choice need to be made. The selectivity can be determined in batch sorption with the competing cations as done in 3.1. The similarities of the *FES* of glauconite with those of illite was described above, hence it was selected to use the *Cs-K* selectivities of illite on *FES*, *type II* and *planar* sites as the starting point.

The unadjusted illite model overestimated the sorption isotherms of glauconite by factors 4.5 – 5.9 at the lower Cs^+ concentration range, i.e. the environmentally relevant range. The fractions of the *type II* and *FES* were optimised within boundaries, respectively 5 - 30 % and 0.02 - 0.30 % of the *CEC*. The optimised model fitted the data of all three glauconite sands fairly well in a wide range of Cs^+ concentrations (Figure 4). The results of the optimisation are given in Table 5. The model predicts the experimental data quite well. In the trace Cs^+ concentration domain the model differs from the experimental data within factors 0.9 - 1.1, i.e. an excellent fit. The main difference between the illite model and the optimised model are the much lower *FES* capacities (D1 0.042 ± 0.009 , D2 0.055 ± 0.005 , B2 0.049 ± 0.016 % of the *CEC*), the error on the *FES* capacities refer to the 95 % confidence interval of the parameter.

*Table 5 Results of the optimisation of the three-site model. The selectivity coefficients values were taken from the illite model (Bradbury and Baeyens, 2000) ($\log K_c$ (Cs/K) *FES* 4.6, $\log K_c$ (Cs/K) *type II* 1.5, $\log K_c$ (Cs/K) *planar* sites 0.5). The represented capacities are the optimised values with the error on the site capacities representing the 95% confidence interval and the RMSE (residual mean squared error) of the $\log [Cs_s]$.*

		D1	D2	B2	Illite du Puy B&B model
Capacity <i>FES</i>	%CEC	0.042 ± 0.009	0.055 ± 0.005	0.049 ± 0.016	0.25
Capacity <i>type II</i>	%CEC	1.70 ± 0.93	2.22 ± 0.56	1.87 ± 1.38	20
RMSE		0.15	0.030	0.31

Figure 4 Optimisation results for each of the three samples (A sample D1, B sample D2, C sample B2). The selectivity coefficients values were taken from the illite model (Bradbury and Baeyens, 2000). The plots contain the model to the experimental data using the original illite parameters (with CEC values of the glauconite sands) (dashed line) and the optimised model (full line) including the 95% confidence interval on the optimisation (dotted line).

Compared to the original illite model, the capacity of the *type II* is markedly smaller. The *type II* sites have much lower selectivity for Cs^+ than the *FES*. At trace concentration Cs^+ the lower capacities of the *type II* sites have no importance. However, there will be an impact on the sorption isotherm in the concentration range $10^{-7.5}$ to 10^{-4} M $[\text{Cs}^+]$ in solution.

3.4 Alternative determinations of the *FES* capacity

Direct measurement of *FES* capacity is rarely correct, due to very small capacity of the sites (De Koning et al., 2007; de Preter, 1990). Often the corrections for non-specific Cs^+ sorption are larger than the *FES* capacity. The determination of the *FES* capacity through the isotherm fitting is likely most correct, however several other approximate methods exist. A first method was applied by Wauters et al. (1996b): in a system with known ionic composition, the *FES* capacity can be calculated based on the sorption potential and the selectivity of the ions in the system. At trace concentration Cs^+ (no carrier Cs^+ added

except with the radiotracer), the fraction K^+ on the FES (Z_K) is ~ 1 (equation 1). The illite K_c (Cs/K) (log 4.6) is used to calculate the FES capacity for the glauconite sands. The sorption potential values are based on the equilibrium K_D (48 hours). The FES capacities determined by the method of Wauters range between 4.43 and $6.71 \cdot 10^{-8} \text{ eq g}^{-1}$ for the glauconite sands, about one order of magnitude below estimates for Illite du Puy ($4.89 \cdot 10^{-7} \text{ eq g}^{-1}$) (Table 6).

Table 6 Estimated FES capacity for all three samples (complete sand) calculated with the method of Wauters (Wauters et al., 1996b) with a log K_c Cs/K of 4.6 and with the method of Bradbury & Baeyens (Bradbury and Baeyens, 2000) using equilibrium K_D values measured in batch sorption (after 48 hours).

Sample	FES capacity – RIP, Method of Wauters (1996b)		FES capacity – break in the isotherm, Method of Bradbury and Baeyens (2000)	
	% CEC	eq g ⁻¹	% CEC	eq g ⁻¹
D1	0.05	5.45 E-8	0.06 ± 0.02	6.53 ± 2.03 E-8
D2	0.05	4.43 E-8	0.12 ± 0.01	9.42 ± 0.96 E-8
B2	0.06	6.71 E-8	0.07 ± 0.01	7.34 ± 1.22 E-8
Illite Du Puy	0.24	4.89 E-7		

A second method for FES capacity approximation is based on the break in the sorption isotherm (Bradbury and Baeyens, 2000). The break indicates the saturation of the FES and the transition to sorption on the less selective *type II* sites. The intersection of the two linear fits on the two sections of the sorption isotherm represents the FES capacity. With this dataset the position of the break cannot be determined with good accuracy due to the limited amount of data points in the log 10^{-9} to $10^{-7.5} \text{ M } [Cs^+]$ in solution. Instead, the two outermost breakpoints were determined to give a FES capacity range (Table 6).

Figure 5 FES capacity estimate based on the break in the sorption isotherm for sample D1. The limited number of data points in the log 10^{-9} to $10^{-7.5} \text{ M } [Cs^+]$ in solution does not allow an exact determination of the break point. Based on the linear fit of separate sections of the sorption isotherm two break points were determined.

The three different models to determine the *FES* capacities denote similar trends that its fraction of the CEC is a factor 5 lower than that of illite. The average *FES* fractions among the three glauconite samples are 0.05 % (isotherm method), 0.05 % (Wauters et al. (1996) method) and 0.08 % (Bradbury and Baeyens (2000) 'break in the isotherm' - method).

Variations in mineralogy, induced by weathering for example, are expected to have a strong effect on the capacity of the *FES*. Weathering of glauconite is described by K^+ leaching from the interlayer, isomorphic substitutions in the octahedral (Fe^{2+} and Mg^{2+} for Al^{3+}) and tetrahedral sheet (Si^{4+} for Al^{3+}) and is associated with a decrease in layer charge (Meunier, 2013; Pugliese Andrade et al., 2014). The glauconite evolves smectite via a I/S type mixed layer. K content is inversely correlated with the smectite content (Meunier, 2005). Removal of the K^+ ions from the interlayer will cause an increase of the interlayer width, what has on its turn an effect on the sorption site capacities. During smectitisation the fraction of *FES* of the total CEC will decrease, while the total CEC can increase. Although the *FES* are only representing an extremely small fraction of the CEC, its capacity will determine the sorption potential at trace Cs^+ concentration. A secondary effect of the mineralogical variations concerns the selectivity coefficients. The strength of the selectivity for a certain cation depends on the size and charge of the cation and on the size and charge of the site. Isomorphic substitutions in the structure changing the layer charge will therefore have an effect on the K_c values. However, the effect on the K_c values is estimated to be smaller than the effect on the capacity of the *FES*.

3.5 Lower *FES* capacity of glauconite evidenced by the mineralogy

The implication of the lower *FES* and *type II* capacity on the structure has to be found in the mineralogical analysis. In Table 7 the mineralogical composition of the samples is given. The quantification of the glauconite content in QUANTA is based on the 060 peak positions. Due to the proximity of the d_{060} values the minerals glauconite, nontronite, illite, illite-smectite and Fe-smectite are grouped together. The position of the d_{060} peak depends on the size of the cations and isomorphic substitutions in the octahedral layer. The strong differences in Fe content between illite and glauconite allow clear identification based on the d_{060} value (illite 1.499 Å versus glauconite >1,510 Å (Bailey, 1979)). The samples have a broad d_{060} reflection and can be identified as glauconite. The d_{060} values shift slightly towards lower values from D1 to B2 (Figure 6), indicating a change in the composition of the octahedral layer. Isomorphic substitutions in the octahedral (Fe^{2+} and Mg^{2+} for Al^{3+}) and tetrahedral sheet (Si^{4+} by Al^{3+}) increase the interlayer width (Meunier, 2013; Pugliese Andrade et al., 2014). Small increases in the width of the *FES* can decrease the selectivity of the *FES*.

Smectite has in general higher CEC values than illite due to the accessible interlayer (e.g. ferruginous smectite ref. SWa-1 90 $cmol_c\ kg^{-1}$ (Favre et al., 2006) vs 20 $cmol_c\ kg^{-1}$ for Illite du Puy). Illite is defined as pure endmember with a smectite content < 10 wt % (Clay Mineral Society). Glauconite sands have smectite contents of 20-27 wt%, corresponding to higher CEC values for the glauconite fraction (24.2 to 33.3 $cmol_c\ kg^{-1}$). In the smectite component, the *FES* and *type II* site capacity is ~ 0. The combination

of these two effects decreases the *FES* fraction of the total CEC drastically. In the case of a mixture of 80-20 illite-smectite, the CEC of the mixture is expected to be 34 cmol_c kg⁻¹. Assuming that the *FES* and *type II* capacity in the illite component are resp. 0.25 and 20% of the CEC, the capacities of the fractions in the mixture will be resp. 0.12 and 9.4%. The calculated *FES* capacity of the CEC slightly overestimates the optimised values. The *FES* capacity is the most important value as this fraction will determine the *K_D* at trace Cs⁺ loadings.

Table 7 Mineralogical composition of the complete sample in wt%. The category 'other' groups the carbonate and feldspar mineral phases (n.p. not present). Other parameters given are the CEC of the glauconite fraction, the K⁺ content of the glauconite fraction as determined by major element analysis, the smectite content (S%) in the clay fraction (e.g. for D1 20% of 34%, or 6.8% of the complete sample) and the position of the d₀₆₀ peak for the glauconite samples. The CEC was measured using the cobalthexamine method.

composition	Quartz	Glauconite	Other clays	Fe- oxide	other	CEC	K ⁺	Smectite	d ₀₆₀
	wt%	wt%	wt%	wt%	wt%	cmol _c kg ⁻¹	mg g ⁻¹	wt%	Å
D1	59	34	< 0.1	0.6	6.4	26.9	54.1	20	1,5166
D2	60	27	4.0	0.9	8.2	24.2	47.9	27	1,5162
B2	56	27	5.0	n.p.	12	33.3	69.7	25	1,5153

Figure 6 The d₀₆₀ peak position in the 60.5 to 62.5 2θ region for samples D1, D2 and B2 in comparison to illite (1.499 Å), theoretical glauconite (>1.511 Å) and nontronite (1.521 Å). The broadened shoulder indicates the presence of illite.

4 Conclusion

The sorption of caesium in a range of 10^{-8} to 10^{-4} M CsCl on natural glauconite sands is non-linear and requires a multi-site ion exchange model to fit the experimental data. The sorption isotherms denote lower Cs^+ sorption for the *FES* and *type II* sites than Illite du Puy. However, glauconite sands have a uniquely larger radiocaesium interception potential than most sand substrates due to the larger fraction of clay minerals present in the glauconite pellets. The sorption per unit CEC is lower than for illite because of a lower capacity of the *FES* compared to illite (0.04-0.06 % of the CEC vs 0.25% for Illite du Puy) combined with a lower *type II* site capacity (1.6-2.2 % vs 20%). The presence of mixed layer illite-smectite and smectite in the glauconite pellets can account for part of this observation. The NH_4^+ to K^+ selectivity studies in the glauconite indicate that the ion binding characteristics are highly similar as in illite. Hence, lower sorption of Cs^+ on glauconite than in illite is likely reflecting the lower *FES* site capacities. Glauconites contain smectite that increase the CEC, however, the fraction of *FES* to the total CEC decreases. The K_D at trace Cs^+ occupation is the product of the *FES* selectivity and its capacity. If the capacity is significantly lower, the K_D will also be lower. The optimised model for glauconite is able to represent Cs^+ sorption data qualitatively and quantitatively in a wide range of Cs^+ concentrations. Determining the selectivity coefficients for additional competing cations (e.g. Na^+ and Rb^+) can fine-tune the model for more complex chemical conditions.

5 Acknowledgements

This PhD is performed in close cooperation with, and with financial support of ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and Fissile Materials.

6 Appendix

6.1 Model fit sensitivity

The model parameters each affect different parts of the sorption isotherm. To assess the sensitivity of the univariate parameters sensitivity an analysis was performed in Phreeqc (Figure 7). The modelled Cs^+ concentration in solution (equilibrium) is affected by the K_c (Cs/K) in the *FES* in the region $< 10^{-6.5} \text{ mol L}^{-1}$, K_c (Cs/K) in the *type II* between $10^{-8} - 10^{-3} \text{ mol L}^{-1}$ and K_c (Cs/K) in the planar sites $> 10^{-3.5} \text{ mol L}^{-1}$. The selectivity of the planar sites is not relevant in the investigated concentration domain ($10^{-8} - 10^{-4} \text{ mol L}^{-1}$). Testing the effect of the individual sorption site capacity is more complicated due to the correlation of the fractions by the CEC (Eqn. 6). Five different runs were executed varying the *FES* between 0.05-0.25 % of the CEC, the *type II* sites 10-20% of the CEC.

Figure 7 Univariate parameter sensitivity analyses of the three-site Cs^+ sorption model (Bradbury and Baeyens, 2000) on sample D1 for A) the effect of the Cs - K selectivity coefficient in the *FES*; (B) the effect of the Cs - K selectivity coefficient in the *type II* sites; (C) the effect of the Cs - K selectivity coefficient in the planar sites; (D) the effect of site capacities, i.e. as fractions of the CEC (%) for the *FES* and for the *type II* sites.

6.2 Determination of the FES capacity (method Bradbury & Baeyens, 2000).

Figure 8 FES capacity estimate based on the break in the sorption isotherm for sample B2(A) and D2(B). The limited number of data points in the log 10⁻⁹ to 10^{-7.5} M [Cs⁺] in solution don't allow an exact determination of the break point. Based on the linear fit of separate sections of the sorption isotherm two break points were determined.

6.3 ¹³³Cs versus ¹³⁷Cs data

The Cs⁺ concentration in solution can be measured by solution concentration - here done by ICP-MS (¹³³Cs & ¹³⁷Cs) and solution activity – here by beta counter (¹³⁷Cs). The Cs⁺ concentration calculated by the activity in solution uses one measurement of the CsCl stock solution (¹³³Cs) and the initial activity (¹³⁷Cs) in solution. Most of the existing Cs⁺ sorption isotherm data on clay minerals is based on the activity in solution. Often an AAS (atomic absorption spectrometry) measurement was used to determine the ¹³³Cs⁺ concentration in the CsCl stock solution. With these values the activity per unit of concentration can be calculated, and the concentration of Cs⁺ in solution can be calculated based on the activity measurement. With the current detection limits of the ICP-MS very low Cs⁺ concentrations can be measured and even active samples can be measured. The total Cs⁺ concentration in solution was measured initially (before adding sorbent) and after 48 hours.

Figure 9 Experimental data (after 48 hours) plotted as [Cs⁺] in solution (log mol L⁻¹) versus the [Cs⁺] sorbed (mol kg⁻¹) with the concentrations plotted for the ICP-MS data (¹³³Cs) and for the beta counter (BC) data (¹³⁷Cs). Figure B a gives a more detailed section of the low concentration domain.

The Cs⁺ solution concentrations measured by ICP-MS have a large spread (between the replicates) and are higher than the concentrations calculated from the activity in solution (Figure 9). The samples had to be diluted 100 times because of the matrix effect of Ca²⁺ (100 mM). This implies that the samples with the lowest Cs⁺ concentrations contained a concentration between 10⁻¹¹ and 10⁻¹². This range is still

measurable though the error is higher. The relatively small differences between the two datasets lead to large differences in K_D (Table 8).

Table 8 Cs⁺ concentrations in solution after 48 hours measured by ICP-MS and beta counter (calculated based on activity) and the related distribution coefficients.

K_D	Initial [Cs ⁺] mol L ⁻¹	¹³³ Cs	¹³⁷ Cs	¹³³ Cs	¹³⁷ Cs	¹³³ Cs	¹³⁷ Cs
		mol L ⁻¹	mol L ⁻¹	L kg ⁻¹	L kg ⁻¹	log (L kg ⁻¹)	log (L kg ⁻¹)
B2	8 E-8	1.33 E-9	5.28 E-10	2300	4930	3.36	3.69
	9 E-8	6.99 E-10	4.80 E-10	3950	5770	3.60	3.76
	2 E-7	1.23 E-9	1.56 E-9	4450	3930	3.65	3.59
	1 E-6	1.24 E-8	1.23 E-8	2640	2610	3.42	3.42
	1 E-5	1.54 E-6	1.50 E-6	166	172	2.22	2.24
	1 E-4	4.95 E-5	4.57 E-5	31	36	1.49	1.55
D1	8 E-8	8.24 E-10	5.60 E-10	3060	4410	3.49	3.64
	9 E-8	1.22 E-9	6.47 E-10	2720	4270	3.43	3.63
	2 E-7	1.44 E-9	1.44 E-9	3780	3790	3.58	3.58
	1 E-6	2.12 E-8	2.12 E-8	1500	1500	3.18	3.18
	1 E-5	1.81 E-6	1.77 E-6	137	141	2.14	2.15
	1 E-4	5.23 E-5	5.01 E-5	27	30	1.44	1.48
D2	8 E-8	8.74 E-10	6.50 E-10	2830	3790	3.45	3.58
	9 E-8	9.42 E-10	9.16 E-10	2930	3260	3.47	3.51
	2 E-7	1.87 E-9	1.73 E-9	2900	3160	3.46	3.50
	1 E-6	2.16 E-8	2.52 E-8	1480	1300	3.17	3.11
	1 E-5	1.91 E-6	1.93 E-6	128	127	2.11	2.10
	1 E-4	5.47 E-5	5.31 E-5	25	27	1.40	1.42

6.4 Evaluation of the model in the lower concentration domain

The model provides a good fit with the experimental data. The modelled data differ a factor 0.89 to 1.1 from the experimental data (Table 9). The most relevant part of the sorption isotherm is in the Cs⁺ trace concentration range, i.e. the environmentally relevant range. At trace concentration Cs⁺ it can be assumed that only the *FES* take part in the Cs⁺ sorption reaction (Eqn. 1). The K_D was calculated based on the selectivity coefficients of illite and the modelled results. The original illite model (Bradbury and Baeyens, 2000) has much higher *FES* capacity (0.25 vs 0.05 % of the CEC) leading to an overestimate of the K_D by a factor 4.5 to 5.1. Even though the *type II* sites are assumed not to take part in the sorption at trace concentration Cs⁺, the carrier CsCl in the spike contributed to a 8×10^{-8} M initial Cs⁺ concentration in solution. However, even if the *type II* sites take part in the sorption reaction, the effect is rather limited due to the much lower selectivity coefficients (1-1.1% difference). The optimised model predicted significantly lower capacities for the *type II* sites (1.7-2.2 vs 20 % of the CEC). Though, even at ten times higher *type II* site capacities the difference in K_D remains limited (8-11 %).

Table 9 Testing of the model in the trace Cs^+ concentration domain with the assumption that at trace concentration the K_D depends solely on the K_C (Cs/K) and the FES capacity. Comparison of the calculated K_D for the modelled and experimental values for the FES sites. To simulate the effect of both the FES and type II sites taking part the combined K_D was calculated.

	D1		D2		B2	
	% CEC	K_D (L kg ⁻¹)	% CEC	K_D (L kg ⁻¹)	% CEC	K_D (L kg ⁻¹)
Modelled FES	0.04	6180	0.06	6010	0.05	7400
Modelled FES + type II	1.7	6250	2.3	6080	1.9	7480
Modelled FES + 10 times type II	17	6880	22	6560	19	8200
Illite FES	0.25	36800	0.25	27200	0.25	37500
Experimental		7940		6170		5370
Ratio illite FES to modelled FES		5.1		5.9		4.5
Ratio experimental to modelled FES		1.1		1.0		0.89

6.5 Evolution of the sorption site availability over time

The Cs^+ sorption potential increases with a factor 6-8 between 2 and 30 days (Bruneel et al., 2020). The total site capacity does not necessarily increase, more likely the site availability increases over time. The initial sorption occurring at the edges of the layers, both at *type II* and *FES* sites, and slowly migrating to deeper sorption sites (Figure 10). In addition to the microscale changes the density and size of the pores in the pellet limit the migration of Cs^+ . The sorption isotherm was optimised for the experimental results at four different time points (2, 7, 28 and 94 days) (Table 10). The capacity of the *FES* increases with a factor 1.6-2.1, the *type II* sites with a factor 1.4-1.7.

Figure 10 Evolution of the site capacity over time at grain level and at the clay platelet. At the level of the grain Cs^+ migrates through the pores, limited by diffusion. At the clay layers itself, most of the sorption occurs at the *FES* sites at first (2 days). Cs^+ sorption at the *type II* sites can block the access to deeper sites. At this time no sorption occurs at the interlayer sites. After 90 days the Cs^+ occupancy in both *FES* and *type II* sites increases. And a small fraction of the Cs^+ can exchange the interlayer K^+ .

Table 10 Results of the optimisation of the three-site model at four different time points (2, 94, 28 and 94 days). The selectivity coefficients values were taken from the illite model (Bradbury and Baeyens, 2000) ($\log K_c$ (Cs/K) FES 4.6, $\log K_c$ (Cs/K) type II 1.5, $\log K_c$ (Cs/K) planar sites 0.5). The represented capacities are the optimised values with the error on the site capacities representing the 95% confidence interval and the RMSE (residual mean squared error) of the $\log [Cs_s]$.

			2 d	7 d	28 d	94 d
D1	FES	CEC %	0.042 ± 0.009	0.059 ± 0.004	0.074 ± 0.006	0.087 ± 0.008
	Type II	CEC %	1.7 ± 0.9	1.9 ± 0.3	2.1 ± 0.4	2.3 ± 0.4
	RMSE		0.15	0.059	0.11	0.11
D2	FES	CEC %	0.055 ± 0.005	0.073 ± 0.004	0.087 ± 0.006	0.10 ± 0.01
	Type II	CEC %	2.2 ± 0.6	2.6 ± 0.3	3.2 ± 0.5	3.7 ± 0.5
	RMSE		0.030	0.055	0.080	0.095
B2	FES	CEC %	0.049 ± 0.016	0.071 ± 0.003	0.064 ± 0.003	0.079 ± 0.007
	Type II	CEC %	1.9 ± 1.4	2.0 ± 0.2	2.1 ± 0.209	2.7 ± 0.4
	RMSE		0.31	0.025	0.036	0.12

7 References

- Adriaens, R., 2015. Neogene and Quaternary clay minerals in the southern North Sea. Leuven : KU Leuven. Science, engineering & Technologie.
- Adriaens, R., Vandenberghe, N., Elsen, J., 2014. Natural Clay-Sized Glauconite in the Neogene Deposits of the Campine Basin (Belgium). *Clays and Clay Minerals* 62, 35-52.
- Bailey, S.W., 1979. Summary of recommendations of AIPEA nomenclature committee. *Clay science* 5, 209-220.
- Bailey, S.W., 1980. Summary of recommendations of AIPEA Nomenclature Committee on clay minerals. *American Mineralogist* 65, 1-7.
- Bradbury, M.H., Baeyens, B., 2000. A generalised sorption model for the concentration dependent uptake of caesium by argillaceous rocks. *Journal of Contaminant Hydrology* 42, 141-163.
- Brouwer, E., Baeyens, B., Maes, A., Cremers, A., 1982a. Cesium and rubidium ion equilibria in illite clay. *The Journal of Physical Chemistry* 87, 1213-1219.
- Brouwer, E., Baeyens, B., Maes, A., Cremers, A., 1982b. Cesium Ion Equilibria Illite Clay Abstr. Pap. Am. Chem. Soc. 183, 97-COLL.
- Bruggenwert, M., Kamphorst, A., 1979. Survey of experimental information on cation exchange in soil systems, *Developments in Soil Science*. Elsevier, pp. 141-203.
- Bruneel, Y., Van Laer, L., Brassinnes, S., Smolders, E., 2020. Radiocaesium sorption on natural glauconite sands is unexpectedly as strong as on Boom Clay. *Science of the Total Environment* 720, 137392.
- Ciesielski, H., Sterckeman, T., Santerne, M., Willery, J.P., 1997. Determination of cation exchange capacity and exchangeable cations in soils by means of cobalt hexamine trichloride. Effects of experimental conditions. *Agronomie* 17, 1-7.
- Courbe, C., Velde, B., Meunier, A., 1981. Weathering of glauconites: reversal of the glauconitization process in a soil profile in western France. *Clay Minerals* 16, 231-243.
- Cremers, A., Elsen, A., Preter, P.D., Maes, A., 1988. Quantitative analysis of radiocaesium retention in soils. *Nature* 335, 247.
- De Koning, A., Konoplev, A., Comans, R., 2007. Measuring the specific caesium sorption capacity of soils, sediments and clay minerals. *Applied geochemistry* 22, 219-229.
- de Preter, P., 1990. Radiocesium retention in the aquatic, terrestrial and urban environment: a quantitative and unifying analysis, *Faculteit Landbouwwetenschappen. KULeuven, Leuven*, p. 93.
- de Preter, P., Vanloon, L., Maes, A., Cremers, A., 1991. Solid Liquid Distribution of Radiocesium in Boom Clay - A Quantitative Interpretation. *Radiochimica Acta* 52-3, 299-302.
- Favre, F., Bogdal, C., Gavillet, S., Stucki, J.W., 2006. Changes in the CEC of a soil smectite-kaolinite clay fraction as induced by structural iron reduction and iron coatings dissolution. *Applied Clay Science* 34, 95-104.
- Fuller, A.J., Shaw, S., Peacock, C.L., Trivedi, D., Small, J.S., Abrahamsen, L.G., Burke, I.T., 2014. Ionic strength and pH dependent multi-site sorption of Cs onto a micaceous aquifer sediment. *Applied Geochemistry* 40, 32-42.
- Fuller, A.J., Shaw, S., Ward, M.B., Haigh, S.J., Mosselmans, J.F.W., Peacock, C.L., Stackhouse, S., Dent, A.J., Trivedi, D., Burke, I.T., 2015. Caesium incorporation and retention in illite interlayers. *Applied Clay Science* 108, 128-134.
- Hisashi, M., Kohei, S., Masato, I., Daigo, Y., Kazuki, I., 2013. Characterization of radiocaesium retention in Japanese soils. *SCK-CEN; KULeuven*, p. 17.
- Jackson, M.L., 1975. *Soil chemical analysis: Advanced course*. UW-Madison Libraries Parallel Press.
- Meunier, A., 2005. *Clays*. Springer Science & Business Media.
- Meunier, A., and Bruce D. Velde, 2013. *Illite: Origins, evolution and metamorphism*. Springer Science & Business Media.
- Meunier, A., El Albani, A., 2007. The glauconite?Fe-illite?Fe-smectite problem: a critical review. *Terra Nova* 19, 95-104.

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

Nakao, A., Thiry, Y., Funakawa, S., Kosaki, T., 2008. Characterization of the frayed edge site of micaceous minerals in soil clays influenced by different pedogenetic conditions in Japan and northern Thailand. *Soil Science and Plant Nutrition* 54, 479-489.

Odin, G., 1988. Green marine clays. *Developments in Sedimentology* 45, 1-444.

Okumura, M., Kerisit, S., Bourg, I.C., Lammers, L.N., Ikeda, T., Sassi, M., Rosso, K.M., Machida, M., 2018. Radiocesium interaction with clay minerals: Theory and simulation advances Post-Fukushima. *Journal of Environmental Radioactivity* 189, 135-145.

Parkhurst, D.L., Appelo, C., 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water-resources investigations report* 99, 312.

Poinssot, C., Baeyens, B., Bradbury, M.H., 1999a. Experimental and modelling studies of caesium sorption on illite. *Geochimica Et Cosmochimica Acta* 63, 3217-3227.

Poinssot, C., Baeyens, B., Bradbury, M.H., 1999b. Experimental Studies of Cs, Sr, Ni and Eu Sorption on Na-illite and the Modelling of Cs Sorption. Paul Scherrer Institut (PSI), Villigen.

Pugliese Andrade, G.R., de Azevedo, A.C., Cuadros, J., Souza Jr., V.S., Correia Furquim, S.A., Kiyohara, P.K., Vidal-Torrado, P., 2014. Transformation of Kaolinite into Smectite and Iron-Illite in Brazilian Mangrove Soils. *Soil Science Society of America Journal* 78, 655-672.

Sawhney, B., 1972. Selective sorption and fixation of cations by clay minerals: a review. *Clays and Clay Minerals* 20.

Takeno, N., 2005. Atlas of Eh-pH diagrams. Geological survey of Japan open file report 419, 102.

Valcke, E., 1993. the behaviour dynamics of radiocesium and radiostrontium in soils rich in organic matter, *Faculteit landbouwkundige en toegepaste biologische wetenschappen*. KULeuven, Leuven, p. 135.

Van Ranst, E., De Coninck, F., 1983. Evolution of glauconite in imperfectly drained sandy soils of the Belgian Campine. *Journal of Plant Nutrition and Soil Science* 146, 415-426.

Wauters, J., Elsen, A., Cremers, A., Konoplev, A., Bulgakov, A., Comans, R., 1996a. Prediction of solid/liquid distribution coefficients of radiocaesium in soils and sediments. Part one: a simplified procedure for the solid phase characterisation. *Applied Geochemistry* 11, 589-594.

Wauters, J., Sweeck, L., Valcke, E., Elsen, A., Cremers, A., 1994. Availability of radiocaesium in soils: a new methodology. *Science of the Total Environment* 157, 239-248.

Wauters, J., Vidal, M., Elsen, A., Cremers, A., 1996b. Prediction of solid/liquid distribution coefficients of radiocaesium in soils and sediments. Part two: a new procedure for solid phase speciation of radiocaesium. *Applied geochemistry* 11, 595-599.

Zeelmaekers, E., 2011. Computerized qualitative and quantitative clay mineralogy: introduction and application to known geological cases. Leuven : K.U.Leuven. Faculteit Wetenschappen.