Applied Geochemistry 40 (2014) 32–42

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Ionic strength and pH dependent multi-site sorption of Cs onto a micaceous aquifer sediment ☆

Adam J. Fuller [a], Samuel Shaw [b], Caroline L. Peacock [a], Divyesh Trivedi [c], Joe S. Small [c], Liam G. Abrahamsen [c], Ian T. Burke [a,*]

[a] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
[b] School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL, UK
[c] National Nuclear Laboratories, Chadwick House, Warrington Road, Birchwood Park, Warrington WA3 6AE, UK

ARTICLE INFO

Article history:
Received 5 August 2013
Accepted 24 October 2013
Available online 1 November 2013
Editorial handling by M. Kersten

ABSTRACT

Caesium-137 ($t_{1/2}$ = 30 years) is a common contaminant at nuclear legacy sites. Often the mobility of ^{137}Cs in the environment is governed by its sorption to charged sites within the sediment. To this end it is important to understand the sorption behaviour of caesium across a wide range of environmental conditions. This work investigates the effect of varying solution composition (pH and competing ions) on the sorption of caesium to micaceous aquifer sediment across a large concentration range (1.0×10^{-11} – 1.0×10^{-1} mol L^{-1} Cs^+). Experimental results show that Cs^+ exhibits three distinct sorption behaviours at three different concentration ranges. At very low concentrations < 1.0×10^{-6} mol L^{-1} Cs^+ sorption was unaffected by competition with Na^+ or H^+ but significantly reduced in high ionic strength K^+ solution. Secondly between 1×10^{-6} and 1.0×10^{-3} mol L^{-1} Cs^+ is strongly sorbed in a neutral pH, low ionic strength background but sorption is significantly reduced in solutions with either a high concentration of Na^+ or K^+ ions or low pH. At high concentrations > 1.0×10^{-3} mol L^{-1} Cs^+ sorption is reduced in all systems due to saturation of the sediment's sorption capacity. A multi-site cation exchange model was used to interpret the sorption behaviour. From this it was determined that at low concentrations Cs^+ sorbs to the illite frayed edge sites only in competition with K^+ ions. However, once the frayed edge sites are saturated the Cs^+ sorbs to the Type II and Planar sites in competition with K^+, Na^+ and H^+ ions. Therefore sorption of Cs^+ at concentrations > 1.0×10^{-6} mol L^{-1} is significantly reduced in both high ionic strength and low pH solutions. This is a significant result with regard to predicting the migration of $^{137}Cs^+$ in acidic or high ionic strength groundwaters.

1. Introduction

Fallout from nuclear weapons testing and reactor accidents (e.g. Chernobyl, Ukraine; Fukushima, Japan and Three Mile Island, USA) have left many areas of land around the world contaminated with radionuclides (chiefly $^{137}Cs^+$) (Bandstra et al., 2012; Beresford, 2006). Additionally, legacy wastes from civil power generation are held in storage ponds at a number of nuclear facilities internationally, e.g. Sellafield, UK and Hanford, USA (Babad et al., 1993; McKenzie and Armstrong-Pope, 2010). Accidental and approved releases from these storage facilities have led to contamination of the subsurface (e.g. soils and sediments) and groundwater environments (Chorover et al., 2008; McKenzie and Armstrong-Pope, 2010; Reeve and Eilbeck, 2009). Particular focus has been on the isotopes of caesium, notably ^{137}Cs ($t_{1/2}$ = 30 years), which occurs as $^{137}Cs^+$ in all environmental situations (Söderlund et al., 2011). As a high yield fission product $^{137}Cs^+$ is relatively abundant in nuclear waste (NDA, 2010). It is a high energy gamma emitter, which is not easily shielded by soils and structures (Hill et al., 2001). This makes it one of the main sources of external radiation dose at contaminated sites. Predicting the transport and remediation of Cs^+ contamination at these sites is a major environmental challenge and many studies have reported its environmental behaviour (Beresford, 2006; Livens and Baxter, 1988; Shand et al., 1994). However, developing detailed models of Cs^+ transport requires site specific knowledge of its sorption behaviour, including the effect of changing geochemical conditions (e.g. pH and ionic strength).

It is well established that sorption to clay minerals governs the mobility of Cs^+ in the subsurface environment (Aldaba et al., 2010; Shenber and Eriksson, 1993). Studies into the sorption behaviour of Cs^+ in soils and sediments have traditionally used solution based experimental approaches (mainly batch experiments) to probe these processes (Eberl, 1980; Sawhney, 1972). In soils Cs^+ chiefly sorbs to the surfaces of clay minerals in the fine (<2 μm) fraction

* Corresponding author. Tel.: +44 113 3437532; fax: +44 113 3435259.
E-mail address: I.T.Burke@leeds.ac.uk (I.T. Burke).

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http://dx.doi.org/10.1016/j.apgeochem.2013.10.017

(He and Walling, 1996). This is due to their large surface area and high density of charged surface sites (Langmuir, 1997). Like other monovalent cations, Cs^+ sorbs principally on clay minerals by charge compensating cation exchange (Beresford, 2006; Bouzidi et al., 2010; Cornell, 1993; Hird et al., 1995). Although Cs^+ will interact with all the charged surfaces in a soil or sediment, it has been shown repeatedly that Cs^+ sorbs preferentially to some sites before others (de Koning et al., 2007; Francis and Brinkley, 1976; Livens and Loveland, 1988).

Cs^+ selectively sorbs to 2:1 aluminosilicate clays of the mica group, specifically illite $(K,Ca,Mg)\ (Al,Mg,Fe)_2\ (Si,Al)_4O_{10}[(OH)_2, (H_2O)]$, through charge compensating cation exchange (Chorover et al., 2008; Cremers et al., 1988; Sawhney, 1972). Illite is a common constituent of many temperate mineral soils (Meunier and Velde, 2004) such as those found at contaminated nuclear sites. Grutter et al. (1986) also noted that Cs can selectively sorb to (illite like) collapsed vermiculate interlayer defects in chlorite. Therefore many studies have focused on the sorption of Cs^+ to illite or illitic soils and sediments (de Koning et al., 2007; Poinssot et al., 1999; Sawhney, 1972). It is important to be able to accurately predict the likely behaviour of contaminants under all potential circumstances. As sorption of cations is known to be controlled by the ionic strength and pH of the system (Krauskopf and Bird, 1995; Sposito, 1984, 1989) it is important to understand the sorption behaviour of Cs^+ under a range of geochemical conditions.

Isotherm investigations of Cs^+ sorption have shown that its uptake onto illitic sediments changes non-linearly with concentration (Campbell and Davies, 1995). Jacobs and Tamura (1960) were the first to propose a multi-site sorption process to account for this non-linearity. They suggested a small number of high affinity sites where Cs^+ preferentially sorbs, and a large number of non-specific exchange sites. Subsequent authors have used competitive sorption and retention studies to develop this theory. Currently the high affinity sorption sites are thought to be Frayed Edge Sites (FES), which sorb and retain Cs^+ in preference to other cations (Chorover et al., 2008; Davies and Shaw, 1993; Dyer et al., 2000; Hird et al., 1996). As sorption of Cs^+ to iron oxides and organic matter is known to be negligible (Campbell and Davies, 1995; Hou et al., 2003), the low affinity sites are commonly assigned to the basal plane of clay minerals. The FES are defined by Nakao et al. (2008) as a partially expanded wedge zone at the edge of the clay interlayer with a basal spacing of 10–14 Å. The FES forms as the mica–illite undergoes weathering of the interlayer which expands from the edge inwards (Jackson, 1968; Jackson et al., 1952). Cs^+ ions are thought to sorb in this wedge through cation exchange with structural interlayer K^+ ions at the edge of the particle (Chorover et al., 1999; Kim et al., 1996; Sawhney, 1965). As Cs^+ is a weakly hydrated cation it is able to readily shed its hydration shell and form inner-sphere complexes with oxygen atoms from the illite tetrahedral layers (Cornell, 1993; Kim et al., 1996; Sawhney, 1972). These sites are inaccessible to more strongly hydrated monovalent and divalent cations (e.g. Na and Ca) so they selectively sorb Cs^+ from solution (Cremers et al., 1988; de Koning and Comans, 2004; Francis and Brinkley, 1976; Staunton, 1994).

Many authors have tried to use isotherms to elucidate the properties of the FES but the value of this approach is limited because they offer no direct mechanistic explanation for the site or Cs sorption behaviour. However, the introduction of geochemical modelling codes has allowed the complexities of the sorption process to be more effectively explained. A number of different geochemical speciation codes exist including Geochemists workbench (Bethke and Yeakel, 2013), MINSORB (Bradbury and Baeyens, 1997) and PHREEQC (Parkhurst and Appelo, 1999). These vary in both their mathematical formulation of activity coefficients and their programming language and structure. Most investigators have modelled Cs^+ sorption isotherms for either pure illite systems (Poinssot et al., 1999) or bulk sediments containing mica/illite (Liu et al., 2004; Steefel et al., 2003; Zachara et al., 2002). The sorption of Cs^+ in these systems is modelled as a multi-site cation exchange process. Selectivity coefficients (K_c values) are used to assign one site with high Cs^+ affinity and one generic site. More recently authors have proposed splitting the high affinity site in two to give a FES and "Type II" sorption site (Bradbury and Baeyens, 2000; Steefel et al., 2003). Experimental evidence for this was obtained by Brouwer et al. (1983) who showed the high affinity site could be divided into a Cs^+ selective site and a Cs^+/Rb^+ selective site. The FES are thought to be located right at the edge of the interlayer, with the Type II site further out in the wedge where the interlayer is slightly expanded (Bradbury and Baeyens, 2000; Brouwer et al., 1983). Although much work has been done on competitive sorption of Cs^+ in the presence of a variety of other cations (de Koning et al., 2007; Sawhney, 1970) there is limited knowledge of the effect of pH on Cs^+ uptake by sediments. All previous investigations where pH was varied have been done at trace Cs^+ concentrations where H^+ is not expected to compete for the specific FES, and Cs^+ will be selectively sorbed (Chorover et al., 1999; de Koning et al., 2007; Giannakopoulou et al., 2007). Although it is likely that on the non-specific sites H^+ will compete with Cs^+, this effect has not previously been investigated experimentally. Poinssot et al. (1999) observed some pH dependence at low Cs^+ concentrations, where sorption to the FES dominates, and they explained this as either mineral dissolution or H^+ cation exchange.

This study focuses on the Sellafield site, located in West Cumbria, UK on the Irish Sea coast and to the west of the Lake District National Park. The facility is located on heterogeneous glacial drift deposits which overlie a complex succession of Triassic sandstone, Carboniferous limestone and Ordovician volcanics (Chaplow, 1996). The deposits themselves are course sediments, with the sand or gravel fraction comprising 90% by weight, and around 1–5% clay sized particles (Randall et al., 2004). The mineralogy is dominated by quartz (65%) and K-feldspar (12%), with the remaining comprised of iron oxides and aluminosilicate clay minerals, dominantly illite (around 70% of the <2 μm fraction) (Dutton et al., 2009; Randall et al., 2004). The site has a complex mix of radioactive and non-radioactive contaminants present as a result of its long history of civil and military nuclear development and waste reprocessing (McKenzie and Armstrong-Pope, 2010). It is reported to be one of the most radioactively contaminated sites in Europe (McKie, 2009) and provides a good test case for understanding the behaviour of radionuclides in the subsurface environment.

This paper presents a study of the sorption behaviour of Cs^+ at a range of concentrations on a micaceous sediment representative of that underlying the Sellafield site. The first objective of the work was to experimentally describe Cs^+ sorption across a wide range of Cs^+ solution concentrations. Batch sorption experiments were used to determine the effect of varying pH and competing ions on the concentration dependent sorption process. This data was then interpreted using a fitted multi-site cation exchange model. The implications of these results for the management of contaminated land at Sellafield are then discussed in detail. However, the results are likely to be broadly applicable to sites with similar mineralogy to Sellafield (especially if illite is present).

2. Materials and methods

2.1. Sediment collection and storage

Experiments reported here were performed on sediment collected in August 2009 from the Calder Valley, Cumbria. This is close to the Sellafield site, on the same glacial till geological unit as that

underlying the site. After collection, the sediment was oven dried at 40 °C and stored in a HDPE plastic container (Law et al., 2010; Wallace et al., 2012).

2.2. Sorption experiments

In this work two types of experiments were performed: concentration variable isotherm experiments where the pH was kept constant and the concentration of Cs^+ varied across a range from 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1} and pH sorption edge experiments where a fixed Cs^+ concentration was used, and the pH varied across the range 2–10. Both sets of experiments were conducted using three background solution matrices, namely starting solutions of deionised water (DIW), 1.0 mol L^{-1} NaCl and 1.0 mol L^{-1} KCl to probe the effect of cationic competition. An initial set of competing ion experiments were performed to determine the most appropriate concentrations of K^+ and Na^+ to use as a background matrix to maximise any competing ion effect. It was determined that both Na^+ and K^+ should be included in the background matrix at a concentration of 1.0 mol L^{-1} to ensure an easily measurable competing ion effect was observed (see Supporting information Fig. S1).

The full range of experimental conditions is shown in Table 1, and the specific procedure for setting up each experiment is described below. All experiments were performed in triplicate with a sediment-free control sample to determine if any sorption to the tubes was occurring. Results from the blank experiments showed that there was no sorption of Cs^+ to the tubes under any of the experimental conditions (data not shown). Therefore all Cs^+ sorption was attributed to the sediment.

The solution composition of the system was varied depending on the requirements of the experiment. For all experiments samples of <1.0 mm sieved sediment were pre-wetted with deionised water. Samples were then suspended in the particular experimental solution, containing the desired amount of inactive CsCl, in 50 mL polypropylene Oak Ridge tubes at a solid solution ratio of 100 g L^{-1}. Following suspension the samples were spiked with a radiotracer of $^{137}Cs^+$ at a specific activity of 30 Bq mL^{-1} (equivalent to 7.0×10^{-11} mol L^{-1}). Samples were then agitated for 48 h on an orbital shaker at 140 rpm at room temperature (20 ± 1 °C). Comans et al. (1991) and Poinssot et al. (1999) showed that Cs^+ sorption is kinetically moderated, involving a rapid initial cation exchange process, followed by a period of slow incorporation into the clay structure (Comans and Hockley, 1992). This work focuses solely on the cation exchange process so a 48 h sorption period was chosen to allow pseudo-equilibrium to be reached and for cation exchange processes to reach completion. The pH of the solution was measured before and immediately after addition to the sediment and adjusted with 1.0 mol L^{-1} HCl and NaOH to overcome the sediments buffering capacity and ensure minimal pH drift during the 48 h equilibration period (when pH was not monitored). Final experimental pH was recorded after 48 h and this value was reported in the results. The pH was recorded using an Orion model 420A bench top pH meter and glass bulb electrode calibrated to pH 4, 7 and 10 using standard buffer solutions. Following the sorption period tubes were centrifuged for 10 min at 6000*g*. A 1 mL representative sample of the supernatant was then transferred to a liquid scintillation vial containing 10 mL of Ecoscint A solution. Final solution activity (Bq mL^{-1}) was then measured by liquid scintillation counting on a Packard Tri-Carb 2100TR liquid scintillation counter with a counting window of 0–280 keV and 10 min counting period. Percentage Cs^+ sorption and distribution coefficient, K_d, values were then calculated using the methodology of Khan et al. (1995) shown in Wallace et al. (2012). The final concentration of other ions (i.e. non-Cs^+) in the system was not measured.

For the isotherm experiments, the effect of Cs^+ solution concentration on sorption was investigated using CsCl solutions at a range of concentrations between 1.0×10^{-9} mol L^{-1} and 1.0×10^{-1} mol L^{-1}. Isotherms were performed at circumneutral pH (6.8 ± 0.2); achieved by adjustment with HCl or NaOH (as described above). The sorption behaviour was analysed using a tracer spike of $^{137}Cs^+$ (30 Bq mL^{-1} or 7.0×10^{-11} mol L^{-1}) and the aqueous activity measured by liquid scintillation counting.

For the pH sorption edge experiments, the effect of pH upon the sorption of Cs^+ was determined by adjusting the initial experimental suspensions with 1.0 mol L^{-1} HCl and 1.0 mol L^{-1} NaOH to give a pH range from 2 to 10. Samples were pH checked at the beginning of the analysis, and after adjustment to overcome the sediments buffering capacity. The final pH values at the end of a 48 h sorption period are then reported. For the pH experiments three concentrations of Cs^+ were chosen. These were selected based on the different regimes of Cs^+ sorption behaviour displayed in the isotherm experiments and were 7.0×10^{-11} mol L^{-1} added as a 30 Bq mL^{-1} tracer spike of $^{137}Cs^+$ and 1.0×10^{-4} mol L^{-1} and 1.0×10^{-1} mol L^{-1} added as CsCl (with a radioactive tracer spike to allow analysis by liquid scintillation counting).

Table 1
Experimental parameters.

Experiment	pH	Initial Cs concentration (mol L^{-1})	Background solution
Isotherms	6.8 ± 0.2	1×10^{-9} mol L^{-1}; 1×10^{-4} mol L^{-1}; 1×10^{-1} mol L^{-1}	Deionised water
			1 mol L^{-1} NaCl
			1 mol L^{-1} KCl
pH sorption edges	2.0–10.0	1×10^{-11} mol L^{-1}	Deionised water
			1 mol L^{-1} NaCl
			1 mol L^{-1} KCl
		1×10^{-4} mol L^{-1}	Deionised water
			1 mol L^{-1} NaCl
			1 mol L^{-1} KCl
		1×10^{-1} mol L^{-1}	Deionised water
			1 mol L^{-1} NaCl
			1 mol L^{-1} KCl

2.3. Modelling

A multi-site cation exchange model was constructed in PHREEQCv2 Parkhurst and Appelo (1999) to perform geochemical modelling of Cs^+ sorption to the micaceous sediment. The full PHREEQC modelling input is provided in the Supporting information. The model was based initially on the model of Bradbury and Baeyens (2000). The modelling aim was twofold: Firstly to test the validity of the generic Bradbury and Baeyens (2000) model under scenarios of Cs^+ contamination relevant to Sellafield, and secondly to refine the model in light of our experimental results to provide a specific description and prediction of Cs^+ sorption at Sellafield. The generic K_c values (selectivity coefficients) proposed by Bradbury and Baeyens (2000) for Cs^+ sorption to argillaceous rocks in the presence of competing Na^+ and K^+ ions have been used in previous models of Cs^+ sorption at Sellafield (Randall et al., 2004). These models are used to predict likely sorption and migration of Cs^+ in the subsurface as part of safety case evaluations. Therefore it is extremely important to assess whether the generic Bradbury and Baeyens (2000) model accurately predicts Cs^+ sorption onto Sellafield-like sediments, and to refine the model in light of our experimental investigation to improve the accuracy of future predictive modelling. As experiments were performed across a large ionic strength range the aqueous activity coefficients, γ, were calculated accordingly. At ionic strengths $\leqslant$ 0.1 mol L^{-1} the extended Debye–Hückel equation was used, with the wateq4f.dat

thermodynamic database (Ball and Nordstrom, 1991). However, in the systems with a total ionic strength > 0.1 mol L^{-1} the Pitzer equations were used, with the Pitzer.dat database (Plummer et al., 1988). A detailed discussion of these calculations is provided in the Supporting information.

2.4. Binary cation exchange

The following section is heavily indebted to Bradbury and Baeyens (2000) whose model this work is based on, and refined from. All the sorption processes within the PHREEQC model are presented as binary cation exchange reactions, according to the Gains–Thomas convention. In the Gains–Thomas approach cation exchange is generically represented as $m_1\text{-site} + m_2 \leftrightarrow m_2\text{-site} + m_1$, where m_1 and m_2 are two distinct species (e.g. Na^+ and Cs^+, respectively) and the site is a specific cation exchange site in the sediment. Chemical species exchange in thermodynamic equilibrium with the sorption site, determined by a Gaines and Thomas (1953) mass action equation with an associated equilibrium constant, K_c. Taking the example of Cs^+ for Na^+ exchange this gives ${}^{Cs}_{Na}K_c = N_{Cs}/N_{Na} \cdot \alpha_{Na}/\alpha_{Cs}$ where α_i is the aqueous activity of the solution species i and N_m is the occupancy of the site with the given species, m, defined by $N_m = \Gamma_m/Q$ where Γ is the concentration of the sorbed species (mol L^{-1}) on the site and Q is the total site capacity (mol L^{-1}).

In the model there are several specific sites available for cation exchange and a cation's affinity for each type of site is described by the relevant K_c value. In the above example, a higher K_c for any given site indicates that this site has a higher affinity for Cs and would sorb it more readily from solution compared to a site with a lower K_c. All the K_c values are normalised against Na (with ${}^{Na}_{Na}K_c$ being 1), thus they describe the selectivity of each site for the sorbing ion relative to Na. The ${}^{Cs}_{K}K_c$ can be determined from ${}^{Cs}_{Na}K_c$ and ${}^{K}_{Na}K_c$ using the relationship ${}^{Cs}_{K}K_c = {}^{Cs}_{Na}K_c / {}^{K}_{Na}K_c$. In the model, K_c values are entered as $\log K_c$, and are referred to as such throughout.

3. Results and discussion

3.1. Sediment characterisation

The sediment was previously characterised by Wallace et al. (2012) and Law et al. (2010), a brief summary is given here. It had a sandy texture containing 94% sand, 5% silt and 1% clay sized particles. Quartz dominated the bulk with minor muscovite, chlorite, albite and microcline also identified by XRD. XRD analysis of the separated clay sized fraction showed it contained quartz, K- feldspar, iron oxides and aluminosilicate clays, namely illite and chlorite (clinochlore). Additionally, SEM observations by Wallace et al. (2012) showed that many of the quartz grains were coated with aluminosilicate clay minerals, suggesting that the surfaces available for reaction within the sediment are likely to be dominated by clay minerals, including illite. Also, Dutton et al. (2009) showed that the same coatings were present on quartz grains in sediment taken from below the Sellafield site. The total cation exchange capacity (CEC) of the sediment, as determined by sorption of copper triethylenetetramine, was 8.2 ± 5.1 meq 100 g^{-1} and it had a BET surface area of 3.4 ± 0.6 m^2 g^{-1}.

3.2. Cs concentration dependence

To allow maximum clarity for interpretation, the experimental and modelling results are presented in this work in terms of percentage sorption of the initial solution concentration. However, the isotherms (presented in Fig. 1) are also presented in terms of equilibrium solution and solid concentrations in the Supporting information (Fig. S2).

For those experiments with no competing ion (Fig. 1a) near total sorption of Cs^+ (99.4 ± 0.2%) was observed at very low Cs^+ concentrations (1.0×10^{-7} mol L^{-1}). This translates to a K_d of 1471 ± 268 L kg^{-1}. A slight decrease in sorption was determined above this concentration. At 1×10^{-5} mol L^{-1} Cs^+, sorption was reduced by ~1% to 98.4 ± 0.9% which gives a K_d of 695 ± 373 L kg^{-1}, a reduction of around 800 K_d units. There was no further significant change in Cs^+ sorption until 1.0×10^{-3} mol L^{-1} where % sorption was reduced to 93.7 ± 1.9% with a corresponding K_d of 159 ± 45 L kg^{-1}. Further reduction in sorption was seen above this Cs^+ concentration with values of 46.2 ± 1.2% at 1.0×10^{-2} mol L^{-1} and 8.3 ± 6.6% at 1×10^{-1} mol L^{-1}. This reflected a reduction in

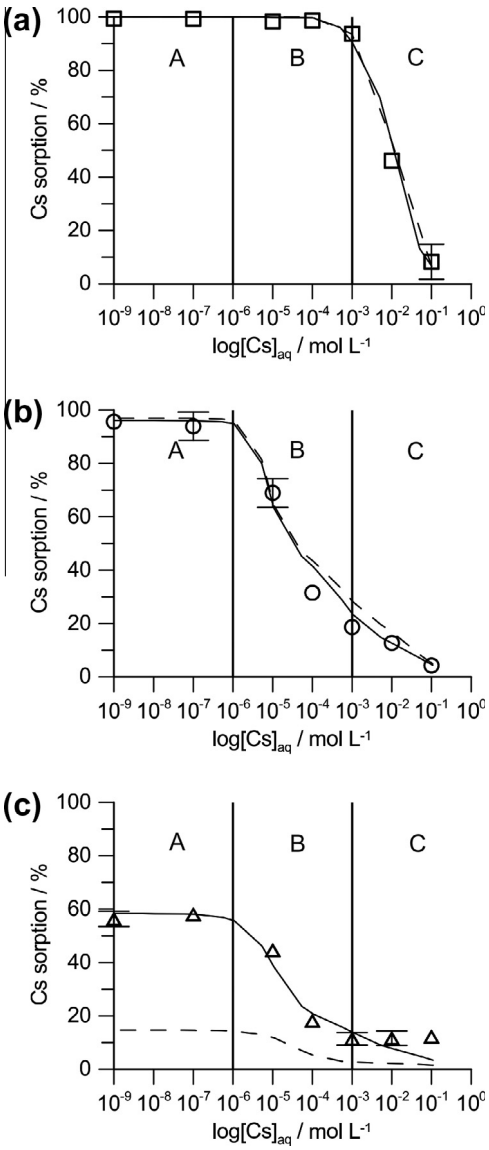

Fig. 1. Sorption isotherm showing sorption of ^{137}Cs ions from a solution of CsCl at a range of concentrations; from 1×10^{-9} to 1 mol L^{-1} and at a solid solution ratio of 100 g L^{-1}. Cs was present in a background of (a) deionised water (b) 1 mol L^{-1} Na (as NaCl) and (c) 1 mol L^{-1} K (as KCl). Solid line represents modelling results using the new fitted values. Dotted line represents modelling prediction using generic values from Bradbury and Baeyens (2000). Vertical bars and reigons labelled A, B and C differentiate the concentration ranges with different Cs sorption behaviours, see Section 3.2 main text. All data was collected at circumneutral pH. Data points represent the average of a triplicate sample. Error bars are shown on those points where the error (standard deviation) was greater than or equel to the size of the symbol.

sorption of 85.4% over two orders of magnitude of change in Cs^+ aqueous concentration.

When the concentration dependent sorption experiments were repeated in a background of 1.0 mol L^{-1} Na, markedly different results were observed (Fig. 1b). Again at the very low concentrations (1.0×10^{-7} mol L^{-1}) near total Cs sorption occurred (95.9 ± 2.3%, with a K_d of 256 ± 156 L kg^{-1}). However, above this concentration there was a reduction in sorption. At 10^{-5} mol L^{-1} Cs^+ only 71.1 ± 5.0% (K_d: 25 ± 5 L kg^{-1}) of the Cs^+ is sorbed. This was a reduction of ~25%, compared to the same concentration of Cs^+ with no competing ion. There was a steady reduction in percentage sorption as Cs^+ concentration was increased reaching a minimum value of 10.8 ± 1.0% at a Cs^+ concentration of 1.0×10^{-1} mol L^{-1}.

In a background of 1.0 mol L^{-1} K^+ (Fig. 1c) the Cs^+ sorption behaviour showed a similar trend with maximum sorption between 1.0×10^{-9} and 1.0×10^{-7} mol L^{-1}. At 1.0×10^{-7} mol L^{-1} 57.3 ± 1.0% of the Cs^+ sorbed with a K_d of 13 ± 1 L kg^{-1}. This then decreased to 43.7 ± 0.1% at 1.0×10^{-5} mol L^{-1} (K_d 8 ± 0 L kg^{-1}). A further reduction was then observed at 1.0×10^{-3} mol L^{-1} where 10.0 ± 2.4% of the Cs^+ was sorbed. Above an aqueous Cs^+ concentration of 1.0×10^{-3} mol L^{-1} there was no significant reduction in sorption.

Three clear regions are visible within the results (differentiated by solid vertical lines in Fig. 1). At aqueous Cs^+ concentrations < 1.0×10^{-6} mol L^{-1} (region A) there is near total sorption in the DIW system, and the system with competing Na^+ ions. However, in the K^+ competitive system only around 60% of the Cs^+ sorbs. This is followed by a region (B) of slightly reduced sorption between 1.0×10^{-6} and 1×10^{-3} mol L^{-1} in the DIW system. There is a more significant reduction in Cs^+ sorption in the Na^+ and in the K^+ systems. Finally, in the DIW system there is a region (C) of rapidly reduced sorption percentages between 1.0×10^{-3} and 1.0×10^{-1} mol L^{-1} above which the sediment reaches sorption saturation. This region of rapidly reducing sorption is also seen in the Na^+ system, although the total percentage reduction is lower than the DIW system. However, in the K^+ system the sediment had already reached a minimum sorption by 1.0×10^{-3} mol L^{-1} and no further change in sorption was determined at higher Cs^+ concentrations.

3.3. pH dependency

The effect of pH on the sorption of Cs^+ was investigated at three concentrations of Cs^+, chosen to access each of the dominant sorption regions identified from the isotherms. At each of these concentrations 3 distinct pH sorption behaviours were observed as shown in Fig. 2(a–c). At the trace concentrations (1.0×10^{-11} mol L^{-1}) near total (99 ± 1%) sorption of Cs^+ was seen at all pH values. Here the pH had no discernible effect upon the sorption of Cs^+. As Cs^+ concentration was increased, however, to 1.0×10^{-4} mol L^{-1} a strong amphoteric effect emerged. A clear sorption edge occurred between pH 2 and 5. At pH 2, 7.0 ± 1.5% of the Cs^+ was sorbed. This increases to 61.6 ± 2.9% at pH 3.4 and 99.3 ± 0.3% at pH 5.2. Sorption then remained constant as pH was increased before dropping slightly to 96.9 ± 1.5% sorption at pH 8.8. Finally, at the saturating concentration of 1×10^{-1} mol L^{-1} around 10–15% of the Cs^+ was sorbed at all pH values and any amphoteric behaviour was masked. Although Poinssot et al. (1999) suggested illite dissolution as a potential cause of reduced Cs^+ sorption at low pH, they also noted that the rate of dissolution meant that only 0.1% of the illite had dissolved over a 7 day period at pH 3, which is insignificant. The experiments presented here were only run for 48 h so dissolution is likely to be much less than 0.1% of the total illite/clay fraction. Therefore H^+ competition is most likely the dominant process.

To investigate the interplay between H^+, Na^+ and K^+ competition with Cs, pH dependent sorption experiments were also performed in a background of 1.0 mol L^{-1} Na^+ and K^+. Results from pH dependent sorption experiments performed in 1.0 mol L^{-1} Na^+ are shown in Fig. 2d–f. At low concentrations of Cs^+ (1.0×10^{-11} mol L^{-1} of measured $^{137}Cs^+$, Fig. 2d) near total sorption (95 ± 2%) of Cs^+ was determined across the entire pH range with no pH dependency. This is the same as the result for experiments with no competing ions (Fig. 2a). At an elevated concentration (1.0×10^{-4} mol L^{-1}, Fig. 2e) the sorption mainly occurred independently of pH, although a reduction in the sorbed Cs^+ was measured at pH 2, to 12.6 ± 1.1% compared to an average of 33.0 ± 7.0% of the Cs^+ being sorbed across the rest of the pH range (3–10). At highly elevated concentrations of Cs^+ (10^{-1} mol L^{-1}) an average of 17.0 ± 6.0% of the Cs^+ was sorbed by the sediment and this process occurred independently of pH, likely due to the higher ratio of Cs^+ to H^+ ions.

In the K^+ dominated system (with 1.0 mol L^{-1} K, Fig. 2g–i) Cs^+ sorbed independently of pH at all concentrations. Here at the lowest concentration of Cs^+ (1.0×10^{-11} mol L^{-1} Fig. 2g) an average of 37.0 ± 3.0% of the Cs^+ was sorbed across the pH range. As the concentration of Cs^+ was increased to 1.0×10^{-4} mol L^{-1} (Fig. 2h) the percentage of Cs^+ sorbed was reduced to an average of 11.0 ± 1.0% across the pH range. Here pH had no effect on Cs^+ sorption. At the highest Cs^+ concentration (1.0×10^{-1} mol L^{-1}) an average of 19.0 ± 6.0% of the Cs^+ was sorbed across the pH range, with no pH effect. This was higher than at 1.0×10^{-4} mol L^{-1}; however, there are large errors on a number of the data points. This is likely due to heterogeneity of the sediment and the extremely high salinity of the system (1.0 mol L^{-1} K^+ and 1.0×10^{-1} mol L^{-1} Cs^+). Again at this high Cs^+ concentration there was no apparent pH dependency.

3.4. Cation exchange modelling

To interpret the sorption behaviour of the Cs^+ in this system a three site cation exchange model was employed. The model was based on the generic model of Bradbury and Baeyens (2000) and refined as discussed below. In both the Bradbury and Baeyens (2000) model and this refinement of it there are three specific site types for the Cs sorption: Frayed Edge Sites (FES, located right at the edge of the interlayer), Type II sites (located on the edges of the clay particles) and Planar sites (located on the basal plane). Each site is assigned a site concentration (termed site capacity) in mol L^{-1} and for each site there is a $\log K_c$ for the exchange onto the site of K^+ for Na^+ ($\log {}^{K}_{Na}K_c$) and Cs^+ for Na^+ ($\log {}^{Cs}_{Na}K_c$) (where $\log {}^{Na}_{Na}K_c$ is 0). Another selectivity constant describing H^+ exchange for Na^+ ($\log {}^{H}_{Na}K_c$) was also used in the model. All H^+ selectivity coefficients (FES, Type II and Planar sites) were initially set to equal 1. In the modelling, site capacities and $\log K_c$ values were the adjustable parameters used to fit the model to the data.

Initially all the experimental data sets were individually modelled using the generic site capacities for the three sites and K_c values for K^+ and Cs^+ exchange provided by Bradbury and Baeyens (2000). These are listed in Table 2. On inspection of the initial unrefined fits it was determined that both the total estimated CEC and the site ratios were incorrect. Initially the modelling was done using the average CEC value given by Wallace et al. (2012) and the site ratios determined by Bradbury and Baeyens (2000). These were 0.25% FES (2.05×10^{-5} mol L^{-1}), 20% Type II (1.64×10^{-3} mol L^{-1}) and 79.75% Planar (6.48×10^{-3} mol L^{-1}), with a total given CEC of 8.2×10^{-3} mol kg^{-1}. The CEC was converted from meq 100 g^{-1} as measured to mol L^{-1}; as experiments were performed with a solid:solution ratio of 1:10 and Cs is a monovalent ion, this gave a direct conversion of 1 meq 100 g^{-1} = 1×10^{-3} mol L^{-1}. When these site capacities were used it was seen that the Na-competitive isotherm overestimated Cs sorption at all concentrations, but especially at low concentrations (where sorption to the FES and Type II sites dominated). To correct this, the

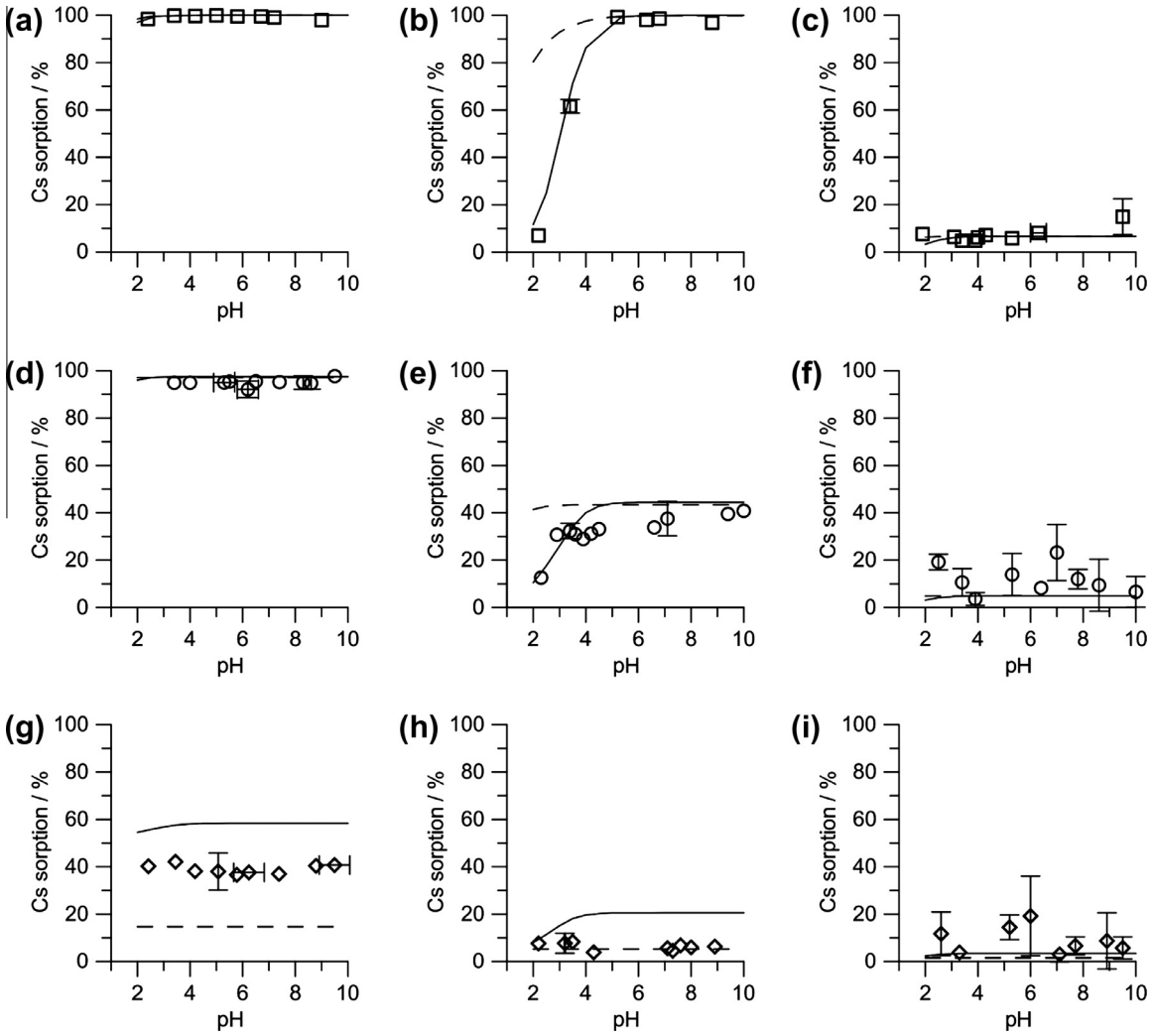

Fig. 2. Concentration dependent Cs sorption across a pH range in a background of competing K and Na. Each figure shows a different solution condition: (a) 10^{-11} mol L^{-1} Cs in deionised water; (b) 10^{-4} mol L^{-1} Cs in deionised water; (c) 10^{-1} mol L^{-1} Cs in deionised water; (d) 10^{-11} mol L^{-1} Cs in 1 mol L^{-1} Na; (e)10^{-4} mol L^{-1} Cs in 1 mol L^{-1} Na; (f) 10^{-1} mol L^{-1} Cs in 1 mol L^{-1} Na; (g) 10^{-11} mol L^{-1} Cs in 1 mol L^{-1} K; (h) 10^{-4} mol L^{-1} Cs in 1 mol L^{-1} K and (i) 10^{-1} mol L^{-1} Cs in 1 mol L^{-1} K. All data points represent averages of triplicate samples. For clarity error bars are not shown where they were smaller than the size of the symbol. Results of modelling using fitted parameters (solid line) and generic parameters from Bradbury and Baeyens (2000) (dashed line) are also shown.

Table 2
Modelling exchange $\log K_c$ values normalised against Na^+.

Source	Exchange species	FES	Type II	Planar
Bradbury and Baeyens (2000)	K^+	2.4	2.1	1.1
	Cs^+	7.0	3.6	1.6
This paper	K^+	1.5	0.6	0.5
	H^+	1.8[a]	3.6	2.5
	Cs^+	7.0	3.6	1.6

[a] From Poinssot et al. (1999)

CEC of each site was iteratively adjusted, when keeping all other values constant. This gave new site concentrations of 0.05% FES (4.0×10^{-6} mol L^{-1}), 2% Type II (1.6×10^{-4} mol L^{-1}) and 97.95% Planar (6.5×10^{-3} mol L^{-1}), giving a total CEC of 6.66×10^{-3} mol L^{-1} (which is still within error of the original measured CEC of $8.2 \pm 5.1 \times 10^{-3}$ mol L^{-1}). Bradbury and Baeyens (2000) determined their site capacity ratios based on Opalinus clay, which contains around 10% illite. As the sediments used in this study contain a far lower percentage of clay minerals (and therefore less illite), this likely explains the lower concentration of the FES and Type II sites, which are located on the clay minerals. The sediments also contain comparatively more minerals with planar sites which accounts for the relatively higher percentage of these sites in our system. It should be noted that these new site ratios were close to those used by Steefel et al. (2003) when modelling mixed sediments (rather than a clay rock). The model was then re-run with the new CEC values and the $\log K_c$ values of Bradbury and Baeyens (2000) and these fits are shown in all figures as dashed lines. From the modelling above it was determined that at all concentrations Cs^+ sorption was significantly underestimated in the 1 mol L^{-1} K^+ background (dashed line, Fig. 1c). To correct this, the K^+ affinity was reduced by iterating the $\log {}^{K}_{Na}K_c$ values while maintaining all other values as constant, until a good fit was obtained (solid line Fig. 1c). These new values are shown in Table 2.

From the pH matrix results (Fig. 2), it was found that the model was significantly underestimating the effect of pH at intermediate Cs^+ concentrations (dashed lines Fig. 2b and e). Therefore the competitive effect of H^+ with Cs^+ (represented by $\log {}^{H}_{Cs}K_c$ values) was deemed to be too low. The $\log {}^{H}_{Cs}K_c$ values were determined by the relationship between the $\log {}^{H}_{Na}K_c$ and the $\log {}^{Cs}_{Na}K_c$ values as described in Section 2.4. As the $\log {}^{Cs}_{Na}K_c$ had previously been fixed in the model adjustment of the $\log {}^{H}_{Na}K_c$ was used to increase the

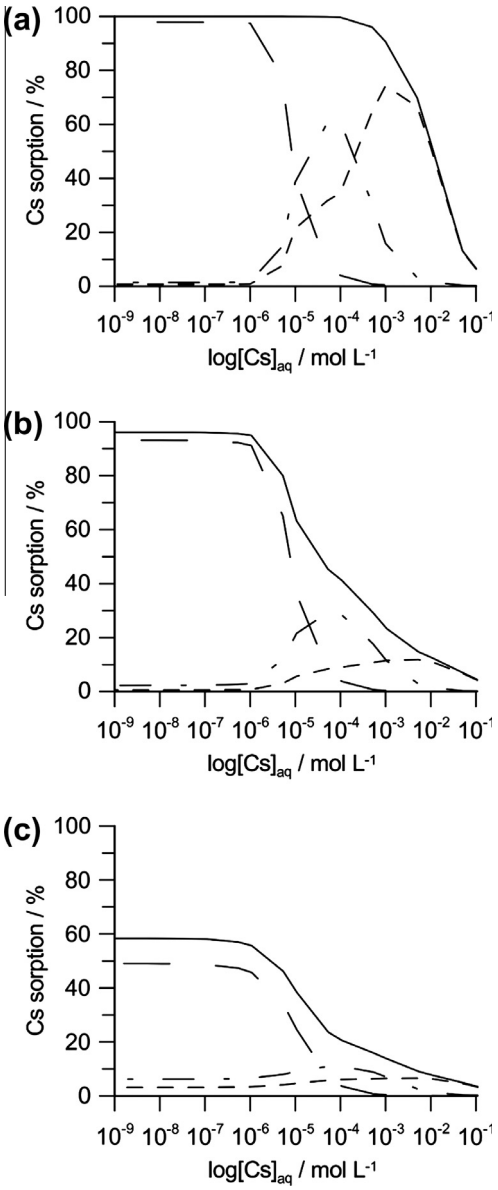

Fig. 3. Modelled sorption isotherms showing relative contributions of the three sorption sites (see main text Section 3.4). The long dashed line represents the FES, the dotted and dashed line represents the Type II site and the short dashed line indicates the contributions from the Planar sites. The solid line represents the cumulative total sorption.

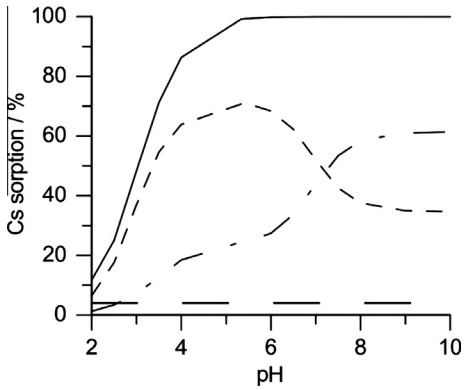

Fig. 4. Modelling of 10^{-4} mol L^{-1} Cs in a DIW background (see Fig. 3b). Showing relative contribution of the three sorption sites (see Section 3.4 of main text). The long dashed line represents the FES, the dotted and dashed line represents the Type II site and the short dashed line indicates the contributions from the Planar sites. The sum of these three sites, the total sorption, is shown by the solid line.

modelled pH dependency of Cs sorption in the system and improve the models fit to the experimental data. To do this the log ${}^{H}_{Na}K_c$ value for the FES (1.8) was taken from Poinssot et al. (1999). For the Type II and Planar sites no literature values were available. As the focus was on determining the Cs^+/H^+ competition of the system the log ${}^{H}_{Na}K_c$ values were initially set as equal to log ${}^{Cs}_{Na}K_c$ values. As previously, the values were then sequentially iterated until the best fit to the experimental data was obtained. From this it was determined that further refinement of only the planar sites value was required to give a good fit for the pH behaviour seen in the experimental data (Fig. 3). The initial Bradbury and Baeyens (2000) and final adjusted values for all parameters are shown in Table 2 and the final fits are shown as solid lines in all figures. The final model overestimated Cs sorption in the pH varied system with a high K background (Fig. 2g and h). This is an artefact of the fact that ${}^{K}_{Na}K_c$ was refined from the isotherm experiments (Fig. 1c). In that system 60% of the Cs^+ was sorbed at low concentrations to the FES, at neutral pH. Therefore the model predicts 60% sorption of Cs^+ across the pH range at low concentrations (Fig. 2g). However, the experimental results presented in Fig. 2g show that only 40% of the Cs^+ was sorbed at pH 7 (and across the pH range). Therefore the model overestimates Cs^+ sorption in this system, when compared to the experiment. The difference between % sorption reported from the two experiments is likely due to variation in the illite concentration between the two sub-samples of sediment. At these low concentrations the Cs^+ would be sorbing to the FES and Type II sites with strong competition from the background K^+ ions. The relative concentration of these sites in the sediment is extremely low and they are exclusively located on the clay minerals. Therefore a small variation in the total mass of clay minerals (especially illite) between the two sub-samples could give a large variation in the total concentration of FES and Type II sites. In the K rich system a large fraction of these sites would also be occupied by K^+ rather than Cs^+ ions. Therefore the effect on total Cs^+ sorption percentage would be very sensitive to small changes in clay content. This variability between sediment sub-samples is therefore the most likely explanation for the models overestimation of Cs^+ sorption in Fig. 2g and h. This also presents a major constraint on the accuracy of modelling predictions in environmental scenarios.

It was previously identified from the experimental results (Fig. 1) that there are three regions of distinct Cs^+ sorption behaviour, governed by the solution concentration. The cation exchange modelling shows that these three sorption regions related to the dominance of the three separate cation exchange sites within the sediment. Fig. 3 shows that at low concentrations, where sorption was only reduced by K^+ competition, Cs^+ was sorbed almost exclusively onto the FES. However, when Cs^+ was present at concentrations above 10^{-6} mol L^{-1}, Na effectively reduced Cs^+ sorption. The model shows that this was due to saturation of the FES and that sorption to the Type II sites dominated, where both Na^+ and K^+ could effectively compete with Cs^+. Finally above 10^{-3} mol L^{-1} Cs, the Planar sites dominated sorption before becoming quickly saturated, which accounts for the reduction in sorption in the DIW system.

Finally, the relative contribution of the different sites to the pH dependent sorption is shown in Fig. 4. This represents the relative contribution of each site for sorption of 1.0×10^{-4} mol L^{-1} Cs^+ in a DIW background, which was the system with the strongest pH dependency (experimental data Fig. 2b). Due to the relatively high concentration of Cs^+ in this system the FES are saturated and contribute to <5% of total sorption. Therefore the Type II and Planar sites control sorption in this system. It can be seen from the results

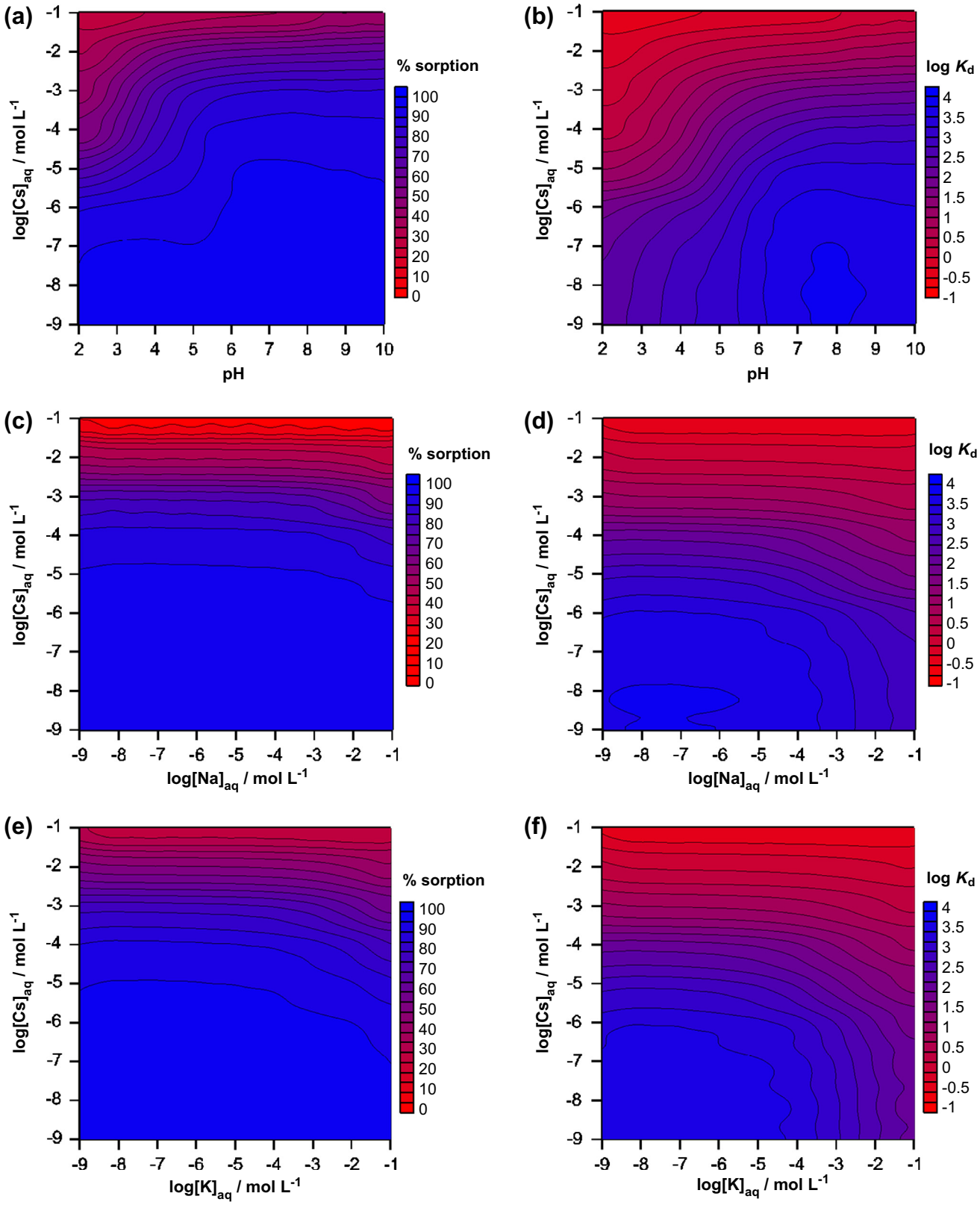

Fig. 5. Modelled dependency of Cs sorption on concentrations of H^+, Na^+ and K^+. All figures are plotted on log/log axis for clarity. Results are shown in both % sorption and log K_d space for ease of reference with blue representing high sorption and red low. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that at low pH the Planar sites dominated the total sorption, however, once the sorption edge reaches its maximum the Type II sites dominate at >pH 7. This was due to the relative balance of the H^+ and Cs^+ K_c values of each site (see Table 2). The Type II sites have a higher Cs affinity than the Planar sites, but are far more amphoteric. Therefore at low pH the H^+ out-competed Cs^+ on the Type II

sites and instead the Cs^+ sorbed to the planar sites, which although they have a lower Cs^+ affinity also have a low H^+ affinity. However, at neutral pH and above H^+ ions cease to affect Cs^+ sorption and therefore the larger ${}^{Cs}_{Na}K_c$ of the Type II sites relative to the Planar sites, means that more Cs^+ ions sorbed to the Type II sites and it became the dominant control on Cs^+ sorption, as was seen in the DIW isotherm experiments conducted at neutral pH (Fig. 3a).

3.5. Implications for $^{137}Cs^+$ mobility

The experimental results and modelling outlined in this study have important implications for the potential mobility of $^{137}Cs^+$ at contaminated nuclear sites such as Sellafield. It has long been known that a trace amount of Cs^+ will selectively and irreversibly sorb to the illitic FES (Comans et al., 1991; Cornell, 1993; Hird et al., 1996). However, results presented here show that once the FES are saturated Cs^+ sorption to the Type II and Planar sites occurs in competition with other cations and is strongly controlled by pH and ionic strength. The current models (e.g. Bradbury and Baeyens (2000)) do not predict the likely impact of H^+ competition on the sorption of Cs^+ and greatly overestimate Cs^+ uptake. The experimental results show during a leak of acidic liquor with high Cs^+ concentration, Cs^+ sorption to the sediment will be lower than previously predicted by existing models. Therefore it is recommended that future modelling of this type of scenario at Sellafield use the new selectivity values presented here (Table 2), as they more accurately describe a leak of this nature and may give a more realistic description of likely Cs^+ migration in acidic liquors. It should be noted however that the modelling results here are calibrated for the experimental conditions, specifically the sediment particle size and experiment solid: solution ratio. In applying the new model to site specific reactive transport scenarios it is important to account for variation in these parameters. Hydrological parameters such as sediment density and porosity should also be considered. This paper presents a simple cation exchange model, rather than a reactive transport model so these hydrological factors are not considered.

The fact that H^+ competes with Cs^+ for the Type II and Planar sites is an important new finding with implications for management and modelling of Cs^+ sorption and migration from acidic leaks. However, the results also show that in alkaline leaks, which are much more common at Sellafield (Wallace et al., 2012; Thorpe et al., 2012), all the Cs^+ present will sorb to the clay fraction, even if the FES are saturated. It should also be noted that the ability of K^+ and Na^+ to compete with Cs^+ is an important controlling factor on Cs^+ sorption potential. These results have shown that at high concentrations (1.0 mol L^{-1}) K^+ can significantly reduce sorption of Cs^+ to the FES. Where the FES is saturated both Na^+ and K^+ can also significantly reduce the sorption of Cs^+ to the less specific Planar and Type II sites. This is especially noticeable in the high ionic strength solutions tested here. Therefore in highly alkaline liquors, rich in NaOH and KOH (such as young cement leachates), or salty solutions, rich in NaCl and KCl (such as seawater), Cs^+ sorption may be significantly reduced by cationic competition.

To summarise all of the findings of this work the refined cation exchange model was used to predict the sorption of Cs^+ under a wide range of solution conditions and contour plots were constructed (Fig. 5). The concentration of Cs^+ is the most important parameter controlling its sorption behaviour. Therefore the effect of pH, Na^+ and K^+ concentrations were modelled with relation to increasing Cs^+ concentration. These results are expressed in both K_d and % sorption terms for ease of reference. The results of this modelling clearly show that Cs^+ sorption is governed by the concentration of different ions in solution, as previously described. The system where pH was varied (Fig. 5a and b) shows two regions where pH has little effect on sorption. More than 90% of the Cs^+ sorbs across the whole pH range at very low Cs^+ concentrations (<1.0×10^{-7} mol L^{-1}). Sorption is also pH independent at very high Cs^+ concentrations (>1.0×10^{-2} mol L^{-1}), however <10% of the Cs^+ sorbs. The pH of the system has the greatest effect at intermediate Cs^+ concentrations, with a clear sorption edge between pH 3 and 5 most visible at Cs^+ concentrations between 1.0×10^{-2} and 1.0×10^{-6} mol L^{-1}. Na^+ has a less clear impact of Cs^+ sorption than pH. Fig. 5c and d shows that Cs^+ sorption in the Na^+ background system is largely governed by the Cs^+ concentration (and therefore saturation of the sediments CEC). When expressed in K_d terms (Fig. 5d) it is clearer that when Na^+ is present at concentrations > 1.0×10^{-3} mol L^{-1} it competes with Cs^+ and reduces total sorption. This is most noticeable at Cs^+ concentration between 1.0×10^{-6} and 1.0×10^{-3} mol L^{-1}. Finally K^+ effectively competes with Cs^+ at all concentrations when present at concentrations > 1.0×10^{-4} mol L^{-1} (Fig. 5e and f). This competition effect is masked above Cs^+ concentration of 10^{-2} mol L^{-1} where the sediments sorption capacity is saturated and <10% of the total Cs^+ sorbs. These modelling outputs give a strong prediction of likely Cs^+ sorption under a wide range of measureable conditions. Therefore it is essential when predicting the potential mobility of Cs^+ from leaks at Sellafield, and other nuclear sites, with similar near surface mineralogy (illite present), that the groundwater conditions and the chemistry of the leak solution are known.

The Nuclear Decommissioning Authority's inventory of waste at Sellafield (NDA, 2007; SellafieldLtd, 2009) shows that Cs^+ is present at high concentrations in a number of wastes on the sites. Notably at around 1×10^{-5} mol L^{-1} in both the Magnox cladding waste and Magnox fuel pond sludge, which are known to have leaked to ground (McKenzie et al., 2011; Wallace et al., 2012). Other high level liquid wastes contain up to 2×10^{-2} mol L^{-1} of Cs^+ (NDA, 2007; leaks from this source are currently not reported or suspected), which is in the sorption regime where both the FES and Type II sites would be saturated. Therefore this new modelling predicts that if the wastes containing Cs^+ at these very high concentrations were to leak then sorption is likely to be significantly reduced in groundwater with either low pH (e.g. an acid leak) or high ionic strength (e.g. seawater intrusion). However, they also show that the Cs^+ could be effectively immobilised by either buffering the pH of the system to >pH 5 or reducing the ionic strength. Therefore it is important that any Cs^+ bearing solutions are treated to neutralise their pH and reduce their ionic strength.

4. Conclusion

Here it has been shown through experimentation and cation exchange modelling that Cs^+ sorption to a micaceous aquifer sediment representative of those at the Sellafield site was predominantly controlled by Cs^+ solution concentration. At intermediate and high Cs^+ solution concentrations (>10^{-6} mol L^{-1}) the pH and ionic strength of the system are of great importance due to the multi-site nature of the Cs^+ sorption to these sediments. The Frayed Edge Sites (FES) selectively sorb Cs^+ in preference to other solution cations, but are quickly saturated. Once they become saturated, excess Cs^+ sorbs to the non-specific Type II and Planar sites where other cations can effectively compete and reduce total Cs^+ sorption. Under most leak scenario conditions Cs^+ concentrations would be low enough that the FES are far from saturation. Therefore in these circumstances most of the Cs^+ will sorb to the FES regardless of solution conditions. However, under the scenario of an acidic leak with high Cs^+ concentrations present, a significant amount of the Cs^+ may migrate further than predicted by existing models because these do not account for H^+ competition.

Acknowledgements

Thanks are offered to Sarah Wallace for sharing knowledge of the sediment and advice on experimental procedures. This work was funded by the UK Engineering and Physical Sciences Research Council industrial CASE Studentship #10000173 in partnership with National Nuclear Laboratory Ltd. awarded to AJF.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2013.10.017.

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