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The uptake of caesium and strontium radioisotopes onto clays

Allen Dyer,* John K. K. Chow and Ibrahim M. Umar†

Science Research Institute, Chemistry Division, Cockcroft Building, University of Salford, Salford, UK M5 4WT. E-mail: A.Dyer@salford.ac.uk

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Montmorillonite and illite clays have been examined for their ability to take up caesium and strontium radioisotopes from solution. Uptakes onto near homoionic Na, K, NH_4, Mg, Ca, and Sr clays have been assessed by the construction of ion exchange isotherms. Effects of changes in concentration (total normality) and temperature have been assessed. Where possible, thermodynamic constants have been calculated and selectivity series constructed. It is shown that both clays are suitable for uptake of Cs, but not Sr.

The presence of fission product radioisotopes in the environment as a consequence of accidents (like Chernobyl) or leakage from storage facilities at nuclear installations demands knowledge of the interactions between these isotopes and soils. Furthermore, the underground disposal of radioactive waste is based upon a multibarrier concept requiring barrier and backfill materials. Clays are preferred for these purposes and this field has been reviewed by Higgo.[1] This means that knowledge of the sorption and migration of fission isotopes in contact with clay minerals, either alone, or as components of soils, is required. Earlier work describes a preliminary study of some of the factors likely to be of significance and used two common clays that have been well characterised. These were a commercially available montmorillonite (Surrey Earth) and an illite (Silver Hills). Cs, Sr and Ru radioisotope uptakes onto these clays were described.[2–4] The competition between the isotopes and common cations for sites in the materials was assessed, including work at different pH and with varying anions. In addition, the publications describe leaching of the radioisotopes from the clays, comparisons to real and simulated soils, and uptakes from simulated ground waters. One of the major conclusions drawn from this work is the confirmation that the clay mineral component of the soils examined is an important factor in Cs and Sr radioisotope uptake. This paper describes the construction of cation exchange isotherms for the montmorillonite and illite, at various concentrations and temperatures. The cations studied are Cs and Sr, in competition with cations that are common in soils and environmental waters. Selectivity series have been deduced from thermodynamic parameters when isotherm measurements allowed.

Experimental

Materials

The radioisotopes (^{137}Cs, ^{89}Sr) were supplied by Amersham International, UK. The Surrey Earth montmorillonite was supplied by Laporte Inorganics, Widnes, Cheshire, from their Redhill, Surrey, UK deposit. The illite came from the Cambrian shale at Silver Hills, Montana, and was supplied by The Clay Mineral Society, Clay Mineral Repository, University of Missouri, Columbia, USA, and was designated Imt-1.

Treatment of the clays

The as-received clays were ground and wet-sieved through a 45 µm sieve. The fine fraction was dried and then stored at a constant humidity (in a desiccator over saturated sodium chloride, *R*H *ca.* 56% at 298 K).

Homoionic forms were prepared by first converting the natural clay to its ammonium form. To achieve this, clays were contacted with 0.1 M ammonium acetate solutions adjusted to pH 7.0 with acetic acid. They were rotated, in plastic containers, about their horizontal axis for at least 12 h. This procedure was repeated 5 times, at the end of which the ammonium clays were washed 3 times with deionised water, dispersed in ethanol, filtered, dried at 307 K overnight, ground, and then stored over saturated sodium chloride solution. Other homoionic cation forms were prepared from the ammonium form using 5 treatments with the appropriate metal chloride solution (0.1 M) followed by the same procedure.

Characterisation of the clays

X-Ray powder diffractometry was carried out on all the clays, using a Phillips PW Diffractometer with Cu-Kα radiation. All clays were analysed for their elemental composition using classical wet analytical methods coupled with flame photometry and atomic absorption spectrophotometry. Water contents were determined as the loss on drying (LOD) when constant weights had been achieved at 1273 K. Cation exchange capacities (CEC) for all clays, and their cation forms, were measured from their ammonium cation uptakes in the standard fashion. Ammonium contents were estimated by an automatic Kjeldahl analyser. The results of these characterisation experiments can be found in earlier work.[2]

Radiochemical determinations

Radioisotope activities were determined in the solution phase from their Cerenkov radiation using the tritium channel of a liquid scintillation spectrometer, or by liquid scintillation counting.

Cation exchange experiments

Isotherms were constructed by equilibrating accurately weighed samples of homoionic clays (about 0.05 g) with 10 mL of solutions containing varying proportions of the exchanging cations at constant total normality (T_N). The anion present was always the chloride ion. Samples were allowed to equilibrate, with constant agitation, for 10–15 days. This was

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†*Present address*: Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria.

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Table 1 Basal spacings, loss on drying (LOD) and cation exchange capacities (CEC) of homoionic Surrey Earth montmorillonites (M) and Silver Hill illites (I) (from ref. 2).

	Basal spacing/pm		LOD (%)		CEC/meq g^{-1}	
Cation form	M	I	M	I	M	I
Na	1.39	0.99	16.3	3.1	0.75	4.6
K	1.24		10.1		0.81	
Cs	1.20	1.01	8.3	2.5	0.83	4.7
NH_4	1.24		10.1[a]			0.81
Mg	1.56	1.00	16.8	3.0	0.75	[b]
Ca	1.58	0.99	15.9	3.1	0.75	4.6
Sr	1.67	1.00	16.8	3.1	0.75	4.6

[a] Corrected for ammonia loss from differential thermogram. [b] Not determined.

the time needed for equilibrium to be established, as shown by preliminary kinetic experiments. Solution phase analyses, radiochemically or by the methods mentioned earlier, were used to estimate the extent of cation replacement. Strictly speaking, confirmation of exchange should be gathered by analyses of the solid phase as well, but this was not carried out in this work. Isotherms were constructed at $T_N = 0.1$, 0.05 and 0.01 N, as well as at temperatures of 298, 323, 398, and 423 K. Experiments to check the reversibility of the exchanges were carried out using undried aliquots.

Results and discussion

Characterization of clays

The chemical analysis of the Surrey Earth was typical of a montmorillonite, apart from a relatively high iron content. The high cation exchange capacity (0.75 meq g^{-1}) may arise from isomorphous substitution of Fe^{2+} into octahedral sheet positions.[2]

Diffractograms of the Surrey Earth showed sharp peaks at 1.54,0.45,0.33 and 0.30 nm, and those of the illite showed peaks at 0.99,0.50,0.45 and 0.35 nm. Both sets of data corresponded to literature values.[5,6] The first peaks of each homoionic montmorillonite and illite, their basal spacings, are shown in Table 1 with their maximum water contents (LOD) and cation exchange capacities (CEC). The basal spacings of montmorillonite, coupled with the water contents, suggest that Na, Mg, Ca and Sr are present as hydrated ions in the inter-layer regions, whereas K, NH_4 and Cs are unhydrated.

Variations in basal spacings of the illites corresponded to changes in cation size created by unhydrated ions sited in the interlayer regions of the clay. The low water contents are in agreement with this.

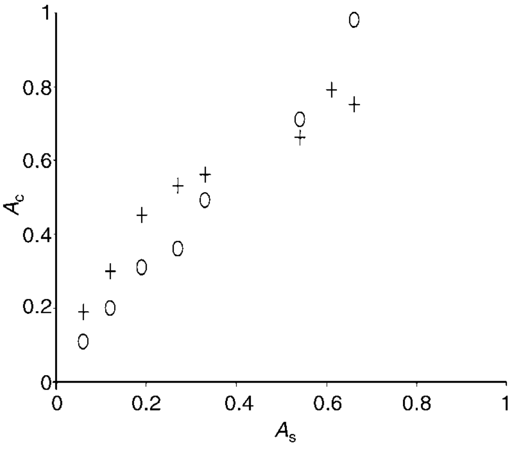

Fig. 1 ½Ca/Cs isotherms for Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K: forward +, reverse ○.

Isotherms

Binary cation exchange isotherms were plotted based upon the estimated equivalent fractions of the in-going ion in solution (A_S) and solid phases (A_C). Examples of some of the isotherms (Figs. 1–6, 8–12) with plots of ln K_C *vs.* A_C (Figs. 7 and 13) are shown. K_C is the Kielland coefficient, defined as:

$$K_C = A_C^{ZB}(m_B)_B^{ZA}\Gamma / B_C^{ZA}(m_A)_A^{ZB} \quad (1)$$

where A_C^{ZB} and B_C^{ZA} are the equivalent fractions of ions A and B in the clay, $m_{A,B}$ are the concentrations (mol dm^{-3}) of ions in solution, and Γ is the ratio of the corresponding single ion activity coefficients in solution. Kielland plots were constructed using the Kielland program from the University of Salford network.

This program made all the required adjustments for ionic activity coefficients in both clay and solution phases based on the methodology of Fletcher and Townsend.[7] Standard free energies (ΔG), for the exchange processes were generated by the same program. Enthalpy (ΔH) and entropy (ΔS) changes can also be calculated when cation exchanges have been shown to be reversible. The values obtained are given in Tables 2–4.

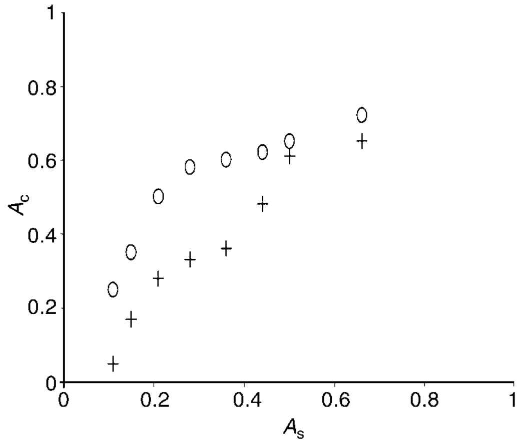

Fig. 2 ½Mg/Cs isotherms for Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K: forward +, reverse ○.

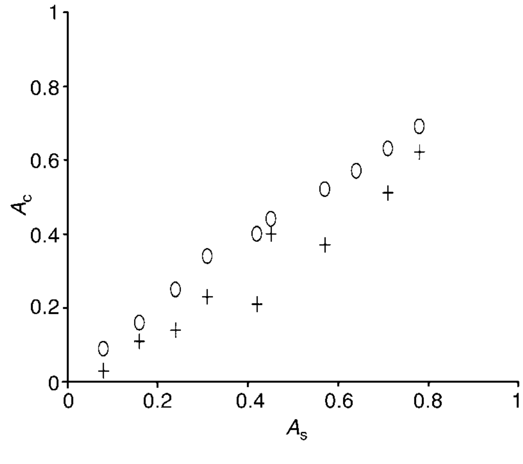

Fig. 3 ½Cs/Sr isotherms for Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K: forward +, reverse ○.

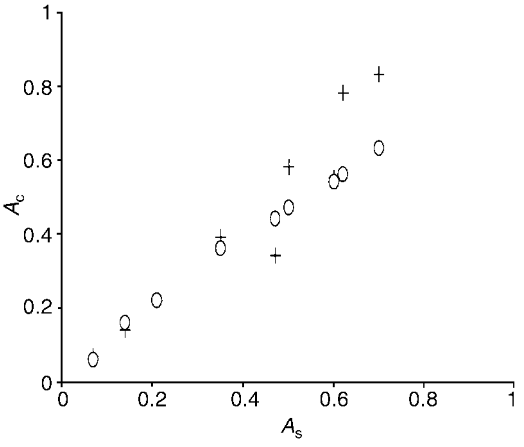

Fig. 4 Na/Cs isotherms for Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K: forward +, reverse ○.

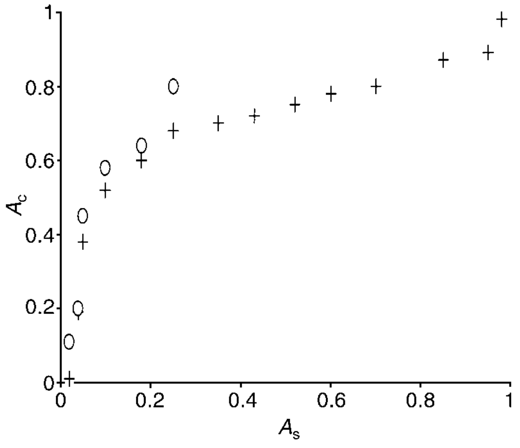

Fig. 5 Ca/Sr isotherms for Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K: forward +, reverse ○.

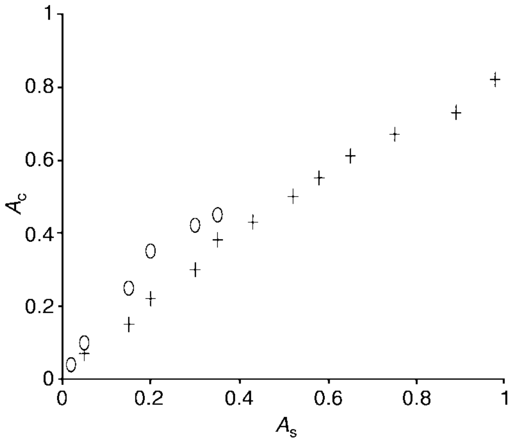

Fig. 6 Mg/Sr isotherms for Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K: forward +, reverse ○.

Binary free energies of exchange

Surrey Earth montmorillonite. *Comment on the calculation of thermodynamic parameters.* Strictly speaking, the fundamental requirement for the generation of thermodynamic data from isotherms is that the exchange must be shown to be reversible. When hysteresis occurs (as here) a thermodynamic analysis can be made on both the forward and reverse process. Such a study has been performed on montmorillonites by Fripiat *et al.*,[8] and Barrer and Munday[9] have carried out similar calculations for a zeolite. Many authors have made estimates of energies of exchange based solely on a forward isotherm, without confirming reversibility. For simplicity, the approach herein is to use the forward arm to generate "thermodynamic quantities". Comparisons can then be made to previous work in similar montmorillonites. Results shown in Tables 2 and 4 show some variance with the triangle rule (that ΔG for three conjugate binary exchange pairs should sum to zero). This almost certainly arises from the assumption of reversibility in their calculations.

Table 2 Free energies of exchanges in Surrey Earth montmorillonite ($T_N = 0.01$)

Cation pair	T/K	ΔG/kJ mol^{-1}	Cation pair	T/K	ΔG/kJ mol^{-1}
Mg/Sr	298	−0.18	Ca/Sr	298	0.90
	333	−0.32		333	−0.12
	353	0.59		353	0.84
½Mg/Cs	298	−5.95	½Ca/Cs	298	−7.32
	333	−7.34		333	−7.43
	353	−7.96		353	−8.32
Na/Cs	298	−4.33	½Ca/Na	298	2.05
	333	−6.78		333	−1.01
	373	−3.62		373	2.36
	423	−3.38		423	2.10
½Sr/Cs	298	−5.34	½Sr/Cs	373	−4.67
	333	−5.79		423	−5.90

Table 3 Enthalpies and entropies, measured at 298 K, for the exchanges listed in Table 2

Cation pair	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Mg/Sr	−6.56	−21
Ca/Sr	4.45	12
Mg/Cs	5.60	39
Ca/Cs	1.39	29
Na/Cs	−3.27	4
Sr/Cs	1.60	23
Ca/Na	0.35	−0.8

Table 4 Free energies of exchange in Surrey Earth montmorillonite with $T_N = 0.01$ at 298 K

Cation pair	ΔG/kJ mol^{-1}	Cation pair	ΔG/kJ mol^{-1}
K/Cs	−3.83	Na/NH_4	10.36
NH_4/Cs	−3.61	K/NH_4	5.3
K/Na	9.75	Cs/NH_4	10.98
Mg/Na	1.45	Ca/NH_4	−0.49
Sr/Na	0.11	Sr/NH_4	1.07

Effect of changes in concentration. The exchanges Ca/Cs, and Sr/Cs showed little change in free energy in the range T_N 1→0.01. Replacement of Ca by Sr from the clay was less

Table 5 Other literature values for the free energies observed from similar studies

Cation pair	ΔG/kJ mol^{-1}	Reference
Na/Cs	−9.5	12
	−4.5→−9.5	13 (4 different montmorillonites)
	−9.0	14
Sr/Na	1.4	12
Sr/Cs	−16.8	12
	−14.6	15
K/Na	4.1	16

Table 6 Variation of free energies of exchange (ΔG) with concentration at 298 K for Silver Hills illite

T_N	Cation pair	ΔG/kJ mol^{-1}	Cation pair	ΔG/kJ mol^{-1}
0.1	Na/Cs	3.57	Na/½Sr	9.61
0.05		8.80		9.50
0.01		9.60		15.14
0.1	½Ca/Cs	0.77	Ca/Sr	4.90
0.05		0.50		3.32
0.01		0.54		4.75
0.1	Ca/½Na	1.85	Sr/½Cs	2.02
0.05		4.95		1.18
0.01		2.67		0.06

Table 7 Variation in the limits of exchange (max A_C) with temperature in Silver Hills illite

Cation pair	T/K	Max A_C	Cation pair	T/K	Max A_C
Mg/Sr	298	0.7	Ca/Sr	298	0.7
	333	0.6		333	0.6
½Mg/Cs	298	0.6	½Ca/Cs	298	0.6
	333	0.2		333	0.2
	353	0.2		353	0.4

favoured at $T_N = 0.1$ ($\Delta G = 3.74$ kJ mol^{-1}) than at lower concentrations ($\Delta G \rightarrow 0$ when $T_N = 0.01$, 0.05). Ca was slightly more readily displaced for the clay by Na at $T_N = 0.1$ ($\Delta G = 1.65$ kJ mol^{-1}) than at $T_N = 0.01, 0.05$ ($\Delta G = 2.05$ and 3.13 kJ mol^{-1}, respectively).

ΔG should be independent of T_N, so it may be that other mechanisms made contributions at the higher T_N values.

Reversibility. All the systems examined showed some degree of hysteresis when the forward path of exchange was compared to that of the return. Hysteresis is well known in clays and has been reviewed by Verburg and Baveye.[10]

These authors emphasise the complex nature of any explanation for this phenomenon and cite the following possible mechanisms: charge or site heterogeneity at the surface, differential hydration of cations, dehydration of the exchanger, crystalline swelling hysteresis, and inaccessibility of sites caused by domain or quasi-crystal formation. In the work carried out here, dehydration of the clay has been excluded as a factor by the non-drying of the exchanger prior to checking the reversibility. Site heterogeneity did not seem to be a major contribution. The forward isotherm for the replacement of Mg by Cs had a tendency to the 's' shape characteristic of sites of different energy, but experimental error could have caused this.

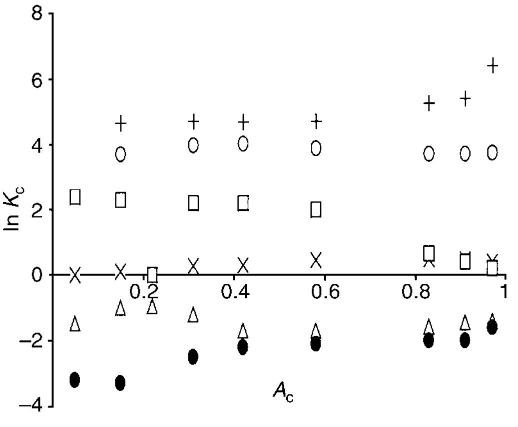

Fig. 7 Kielland plots for the exchanges listed in Table 2: ½Ca/Cs +, ½Mg/Cs ○, Ca/Sr □, Mg/Sr ×, Na/Cs Δ, Na/½Ca ● ($T_N = 0.01$ at 298 K).

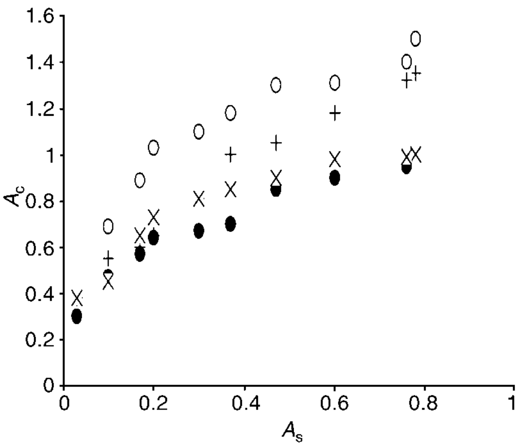

Fig. 8 ½Sr/Na isotherms for Surrey Earth montmorillonite with $T_N = 0.01$: 298 K ○, 323 K +, 398 K ×, 432K ●.

Verburg and Baveye[10] quote examples from other work which claim that hysteresis in cation exchange on clay minerals did not occur with cations taken from the same group of the periodic table. This was not true in the results for montmorillonite reported here (Figs. 4–6). Inaccessibility of sites may well be a factor, as the isotherms did not always reach the maximum level of exchange. However, consideration of the relative cation affinities for water also creates a possible framework to follow the pattern of hysteresis seen here—whether it be a simple consequence of individual cation water environments or the source of changes in crystal swelling.

Hysteresis was small when cations had similar heats of hydration, as can be seen for the cation pairs Mg/Sr (Fig. 6), Ca/Sr (Fig. 5) and Na/Cs (Fig. 4). The most evident hysteresis arose in the Mg/Cs (Fig. 2) and Ca/Cs (Fig. 1) systems where large differences in hydration properties existed between the ions, probably enhanced by the "fixing" of the large monovalent Cs cation (see comment below).

The case of the Cs/Sr exchange was less clear-cut (Fig. 3). It can be noted that the conclusions drawn did not completely follow the trends of changing basal spacing with the nature of the cation present in the dried samples used to produce the results in Table 1.

Selectivity of Surrey Earth at $T_N = 0.01$ in reversible systems. The figures in Table 2 are based on exchanges carried out over a wide temperature range to mimic possible conditions in waste storage, as well as less demanding environmental cases. The montmorillonite had very similar affinities for the divalent ions studied, in line with uptake of the cations from solution as hydrated species into the clay interlayer sites, as suggested above. When caesium was the in-going ion, it was preferred to all the divalent species and to sodium.

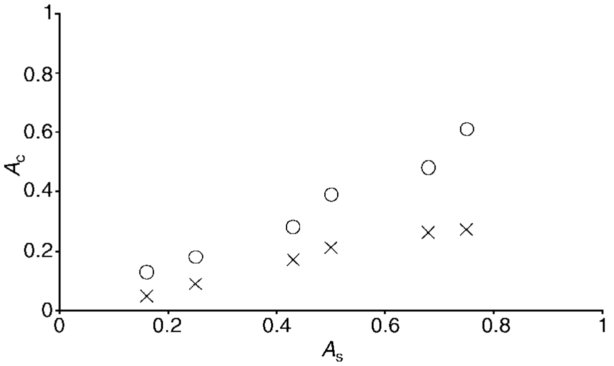

Fig. 9 ½Ca/Cs exchange isotherms on Silver Hills illite with $T_N = 0.01$ at 298 K: forward ○, reverse ×.

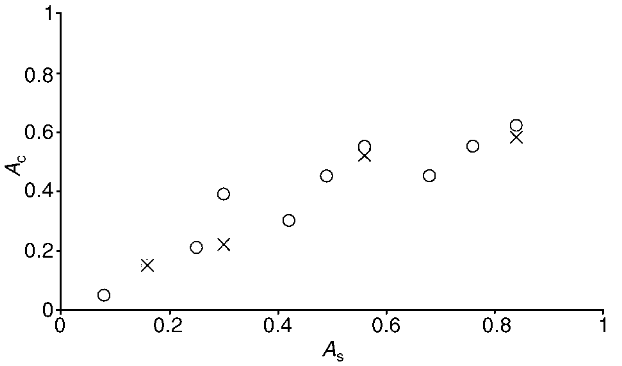

Fig. 10 ½Mg/Cs exchange isotherms on Silver Hills illite with $T_N = 0.01$ at 298 K: forward ○, reverse ×.

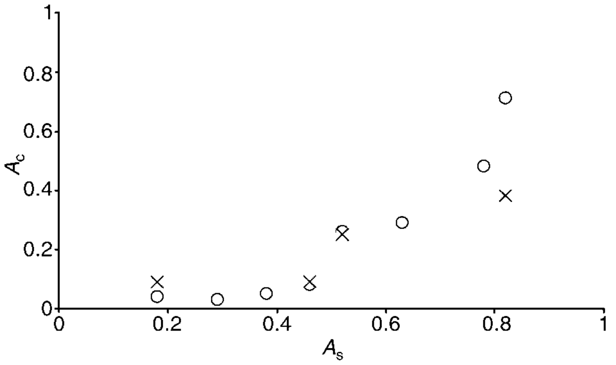

Fig. 11 Ca/Sr exchange isotherms on Silver Hills illite with $T_N = 0.01$ at 298 K: forward ○, reverse ×.

This arose from the ability of the large caesium ion to occupy "fixed" unhydrated positions in the clay layers, so that the cation charge was unshielded from the negatively charged aluminosilicate framework.

The hydrated divalent calcium cation was preferred in competition to the hydrated monovalent sodium cation.

When the data in Table 3 is considered, it can be seen that the replacement of magnesium by Sr was aided by a large change in entropy which presumably arose from the high heat of hydration of the magnesium cation in solution when compared to that of strontium. Changes in ion hydration state were seen to have adverse effects on all the other exchanges listed, particularly when divalent ions were moving to the solution phase and being replaced by unhydrated monovalent species. The Ca/Na cation pair was an exception to this, with the cation charge overriding the favourable change in hydration. Clearly the effect of hydration was small when the monovalent ions, Na and Cs, were exchanging so that the favourable energetics of this process again reflected the "fixing" of the larger caesium ion into lattice positions.

Cation preferences in cation pairs studied with $T_N = 0.01$ at 298 K. Although reverse isotherms have not been carried out for the cation pairs listed in Table 4 the free energy values calculated were again a convenient way of comparing cation access to the montmorillonite exchange sites.

Ready uptake of caesium occurred in the presence of both sodium and potassium; K, Mg and Sr were selected in preference to sodium. Ammonium cation exchange was difficult in competition with Na, K, Cs, and Sr; the exchange of ammonium by calcium was slightly favoured under the conditions examined. This observation necessitates a comment on the current wide-spread practice of using the ammonium ion to measure cation exchange capacities of clays. The method[11] uses 1 M ammonium acetate, which is above the concentration range studied here, and pH adjustment. The changes in selectivity as a function of concentration have been noted above and further evidence of similar changes can be found in earlier work.[2]

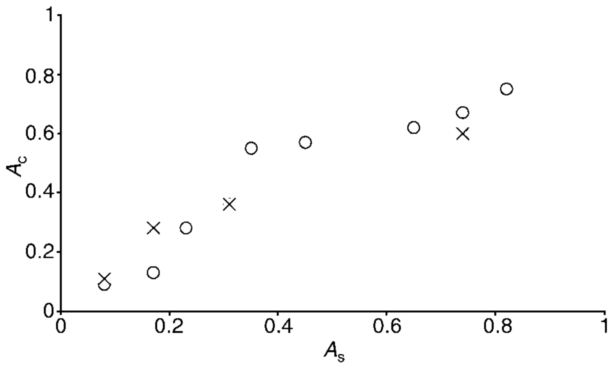

Fig. 12 Mg/Sr exchange isotherms on Silver Hills illite with $T_N = 0.01$ at 298 K: forward ○, reverse ×.

Comparison to other work. Table 5 lists the free energy values obtained by other workers for similar cation exchanges in other montmorillonites. It shows that the ΔG values measured in this work are in general agreement with past determinations. Existing differences can be ascribed to temperature of measurement, and cation composition of the initial clay.

Selectivity Series. The results in Tables 2–4 were used to construct a cation selectivity series for Surrey Earth montmorillonite, *viz.* $Cs > K > Na >> NH_4 > Ca > Sr > Mg$. This is similar to that reported by Carroll.[17]

Exchange between strontium and sodium (Fig. 8.). When the isotherms for the exchanges in which the strontium ion was attempting to replace the sodium ion from the clay were constructed, large over-capacities were measured in some cases. Strontium uptakes of the order of 40–50% larger than the expected capacity were noted when T_N was 0.01→0.1 and $T = 298$–323 K. These were absent at $T = 398$, 432 K and $T_N = 0.01$.

Sposito *et al.*[18] have suggested that calcium and magnesium chloride solutions may contain the $[MCl]^+$ ions. Strontium radioisotope solutions are of very low strontium concentration (pg) and it may be that $[SrCl]^+$ ions exist at these low levels. It seems that, if present, the ions disassociated in the temperature range 323–398 K. The other isotherm data did not show excess strontium exchange, which suggests that $[SrCl]^+$ was absent in the presence of other cations, and no evidence for the existence of similar calcium and magnesium species was noted. Because of this, only estimates of free energy for the Sr/Na exchange could be made from the isotherms at 398 and 423 K. Values of $\Delta G = -1.50$ and -1.69 kJ mol^{-1}, respectively, were obtained.

Alternative views of the over-exchange can be suggested, in which a strontium species had precipitated out on the clay surface, or that selective exchange had occurred at defect or edge sites. It might be expected that, if either of these reasons for the excess were correct, it should be present in all the strontium cation exchanges studied.

Silver Hills illite

Effect of concentration. Earlier work has shown that Cs and Sr uptake onto Mg illite is relatively independent of solution cation concentration,[2] in line with the theoretical expectation.

In the work carried out here, there were some indications

Table 8 Free energies of exchanges in Silver Hills illite ($T_N = 0.01$)

Cation pair	T/K	ΔG/kJ mol^{-1}	Cation pair	T/K	ΔG/kJ mol^{-1}
Mg/Sr	298	−0.10	Ca/Sr	298	1.32
	333	0.63		333	0.69
	353	1.47		353	0.33
½Mg/Cs	298	−4.94	½Ca/Cs	298	−5.11
	333	−6.37		333	−7.28
	353	−7.19		353	−8.52
Na/NH$_4$	298	10.03	Cs/NH$_4$	298	9.36
½Ca/NH$_4$	298	0.05	½Sr/NH$_4$	298	−0.85

Table 9 Enthalpies and entropies measured at 298 K for some exchanges listed in Table 8

Cation pair	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Mg/Sr	−7.36	−25
Ca/Sr	6.68	18
½Mg/Cs	7.28	41
½Ca/Cs	13.37	62

that replacement of sodium by both caesium and strontium was favoured at the higher concentrations of the in-going ions (Table 6).

This can be taken as an indication of different mechanisms operating at higher concentrations, in contrast to the replacement of calcium by the same ions, which was virtually independent of concentration. Other ion pairs also showed mild anomalies. Broadly similar conclusions were drawn earlier for exchanges in montmorillonites.

Nature of the isotherms. The isotherms in Fig. 9–12 show the maximum replacement of the cation originally present in the clay to reach a maximum of $A_C \approx 0.6$–0.7 at 298 K. Kielland plots are given in Fig. 13.

At higher temperatures, the extent of exchange was reduced, as shown in Table 7. This unusual observation may arise from subtle changes in the hydration state of the cations initially residing in the clay. Loss of water molecules linked to the divalent ions, as temperatures rise, may encourage a stronger bond between the cation and the aluminosilicate layer, so making replacement more difficult. As in all cation exchange processes, this tenet must be viewed in the context of the energy gains in the system caused by hydration effects in the solution phase.

When replacements of magnesium and calcium by strontium are compared, the larger heat of hydration of the magnesium cation promotes the larger extent of exchange.

In the cases where caesium is endeavoring to replace the more highly hydrated cations from interlayer sites, the drop in amount of exchange seen as the temperature rises comes about as the divalent cations adopt more tightly bound sites. The consequent restriction in interlayer spacing makes it difficult for the large, little hydrated, monovalent caesium cation to enter occupy interlayer sites.

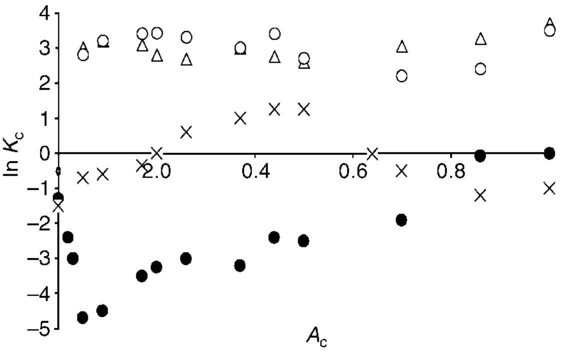

Fig. 13 Kielland plots for ion exchange in Silver Hills illite: ½Mg/Cs ○, ½Ca/Cs Δ, Mg/Sr ×, Ca/Sr ● ($T_N = 0.01$ at 298 K).

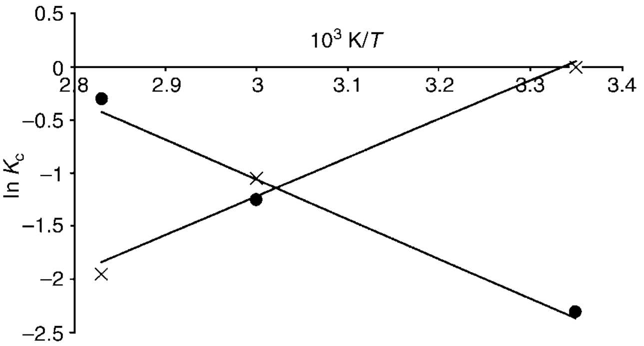

Fig. 14 Plot of ln K_a as a function of 1/T for Ca/Sr(●) and Mg/Sr(×) exchanges (298 K, $T_N = 0.01$) in Silver Hills illite.

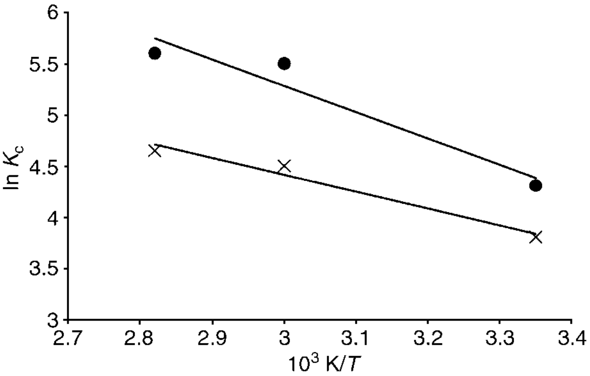

Fig. 15 Plot of ln K_a as a function of 1/T for ½Ca/Cs(●) and ½Mg/Cs(×) exchanges (298 K, $T_N = 0.01$) in Silver Hills illite.

In a recent paper devoted to the kinetics of caesium uptake on to calcium and potassium exchanged illites, Brouwer *et al.*[19] describe the identification of three possible exchange sites, as conjectured by earlier workers. The most selective for caesium were in two "frayed edge" locations, which represented about only 3–4% of the total cation exchange capacity. Access to these sites has been shown to be fast, whereas access to the less selective sites (96–97%) in the interlayer space was much slower.[20,21] The experimental conditions used in this work clearly encouraged access to the bulk interlayer sites and it seems unlikely that other cation sites play any major role in the observed changes in the availability of cations for exchange.

Hysteresis (at 298 K) was noted only for the ½Ca/Cs exchange (Fig. 9) This is in contrast to the isotherms for similar ion pairs in montmorillonite, which all had some hysteresis, as commented on earlier.

Selectivity and thermodynamic quantities. Tables 8 and 9 list the thermodynamic data obtained from the illite isotherms. Table 8 suggests that Silver Hills illite has the following selectivity series for the cations studied: Cs > Sr > Ca > Mg, at $T_N = 0.01$ and 298 K, which is the same as that recorded earlier for montmorillonite.

At this stage, it needs to be pointed out that the thermodynamic data was obtained from normalised isotherms, following the suggestions of Fletcher and Townsend.[22] It seems that the processes being quantified are those of equilibrium cation exchanges in the interlayer spacings, like those in montmorillonite. This conclusion is supported by the clear similarities between the observed ΔG values for all the cation pairs studied in the two clays, bearing in mind that those for montmorillonite follow patterns expected from cations moving within the layered clay structure. Further support for the assumption that similar processes were being measured comes from the good linearity of the ln K_a *versus* $1/T$ plots constructed to estimate enthalpies (see Figs. 14 and 15).

Finally, the value of ΔG estimated for the ½Ca/Cs exchange is close to that quoted for planar sites by Brouwer *et al.*[19] for the same cation pair (-7.5 kJ equiv.$^{-1}$). The same authors showed that exchanges at edge sites are exclusively enthalpic. Perusal of the figures in Tables 8 and 9 shows that entropy effects have a major role in the cation exchanges studied. The Mg/Sr pair has a relatively large negative ΔS contribution to the free energy of exchange, which arises from the release of waters of hydration from a well-defined environment of water surrounding the magnesium cation in the interlayer space. On the other hand, the replacement of calcium by strontium probably reflects the more ordered location of the larger, less hydrated, strontium cations in the clay.

When caesium was the cation replacing divalent ions (Ca, Mg), the favourable free energies came from the entropic contributions as caesium cations attained "fixed" sites in the clay layers, in which they were unshielded by water molecules. The entropy values were high, reflecting the replacement of one divalent ion by two monovalent ions.

Consideration of the ½Ca/Cs exchange shows that both changes in enthalpy and entropy were the highest recorded in the cation pairs studied and it may be that this accounted for the observed hysteresis, which could have arisen from site hetrogeneity, as proposed by Goulding and Talibudeen.[23]

Finally, the approximate ΔG values measured for the non-reversible exchanges demonstrate the difficulty that the ammonium cation experiences in replacing either sodium or caesium cations at $T_N = 0.01$ and 298 K. Replacement of divalent cations under these conditions was much easier.

Conclusions

The calculations of thermodynamic values for the forward arm of systems, even though they show hysteresis, has enabled the data produced to be discussed in a way that can provide useful information.

Surrey Earth montmorillonite showed excellent selectivity for caesium and can be expected to scavenge, and fix, caesium radioisotopes in the presence of cations commonly present in ground waters or as part of the cation composition of the original clay. Use of montmorillonite as a buffer/barrier material to contain environmental releases of this fission product can be encouraged.

Containment of strontium radioisotopes in montmorillonite was less assured and some workers have suggested that clinoptilolite, a natural zeolite, will be more effective in retarding strontium ion migration in the environment of nuclear waste storage facilities.[24]

Exchange of cations into an illite shows that the incorporation of caesium into "fixed" interlayer sites is a selective process like that shown for low concentration occupancy of "frayed edge" sites. Caesium was unlikely to be easily displaced from these planar sites by ions commonly present under environmental conditions. Strontium was much less selectively retained by the illite and was likely to be eluted by magnesium, calcium and ammonium cations from any illites present in soils. The soil on the Sellafield (Cumbria, UK) site of BNF plc has an approximate clay fraction composition of; illite 40%, kaolinite 10%, chlorite 5–10%, with quartz/felspar 10–20%.[25]

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