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Ion exchange of caesium and strontium on a titanosilicate analogue of the mineral pharmacosiderite

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Ion exchange experiments were carried out for the removal of trace caesium (^{137}Cs) and trace strontium (^{89}Sr) by different cationic forms of a titanosilicate analogue of the mineral pharmacosiderite. Selectivity factors were estimated by determining batch distribution coefficients (K_d) as a function of sodium, potassium, magnesium and calcium ion concentration. Other effects studied were pH, increasing caesium and strontium ion concentration, hydrolysis of the sodium form exchanger, the presence of the complexing agents EDTA, citrate and borate, and the resistance of the material to radiation damage.

Introduction

Natural zeolites have for some considerable time been used as selective ion exchangers for the removal of the fission products ^{90}Sr/Y and $^{134/137}$Cs from aqueous nuclear waste streams.[1] They have the attraction of low cost in addition to high thermal and chemical stability, good resistance to α, β and γ radiation, and high capacities and selectivities for certain monovalent and divalent cations. However, the necessity to have materials capable of performing in highly basic or highly acidic waste solutions with very high salt concentrations and in the presence of other macro-components such as complexing agents has stimulated the research and development of synthetic inorganic ion exchangers.[2] This field is extremely large and new products are discovered regularly, some of which are analogues of natural minerals while others have novel structures. Their successful application in industry has been hindered by the fact they are often synthesised as fine powders unsuitable for column use. Advances in binder and peletization technologies can overcome these problems however.

Conventional zeolite-type crystalline microporous solids are based on frameworks formed by linked TO_4 tetrahedra with Si(Si, Al) or (Al, P) as the main T elements. There are also non-conventional solids that have high framework charges, analogous to aluminium-rich zeolites, but which have frameworks built up from T elements other than those above or are built up from elements in different coordination geometries. As part of a program to develop novel crystalline inorganic ion exchangers suitable for column use and radioactive waste volume minimisation, we have screened a large number of materials for their ability to remove certain radionuclides from aqueous solution. One group that seem promising for the removal of caesium and strontium are titanium silicates containing tetra-coordinated Si^{4+} and Ti^{4+}, usually in octahedral coordination.[3–10] Two examples that are attracting considerable interest are compounds with the composition $Na_2Ti_2O_3SiO_4\cdot 2H_2O$[3–5] and $M_3HTi_4O_4(SiO_4)_3\cdot 4H_2O$,[7–9] the last of which is a synthetic analogue of the mineral pharmacosiderite, $KFe_4(OH)_4(AsO_4)_3$. The structure is built up from octahedral TiO_6 units sharing faces, to form a cube-like Ti_4O_4 unit, which in turn share vertices with tetrahedral SiO_4 units forming an open framework enclosing spherical cavities, interconnected in three dimensions by 8-ring windows.[11,12] The charge-balancing extraframework ions occupy sites in the centres (K^+) or slightly displaced from the centres (Cs^+) of the 8-ring windows.

Recent reports have indicated that the titanosilicate pharmacosiderite exchanger is selective for low concentrations of Sr^{2+} and Cs^+ in the presence of ppm levels of Na^+, K^+, Mg^{2+} and Ca^{2+} cations at neutral pH.[7–9] Behrens and Clearfield[7] studied the effect of $NaNO_3$ concentration on the efficiency of Na form and K form exchangers. Puziy[9] followed up this work and studied the effect of $CaCl_2$, KOH, NaOH and HNO_3 for a K form material. The initial Cs^+ and Sr^{2+} concentrations in these studies were 10^{-3} or 10^{-4} M. In this paper we present a detailed investigation of the sorption efficiencies of trace strontium (^{89}Sr) and trace caesium (^{137}Cs) on a titanosilicate analogue of pharmacosiderite as a function of increasing macro-component concentrations (Na^+, K^+, Mg^{2+}, Ca^{2+}, H^+, EDTA, tetraborate, citrate). In the case of Na, K, Mg and Ca background electrolytes, the exchanger was converted to the appropriate cationic form thus enabling the determination of selectivity factors for the ion pairs Cs^+/M^{n+} and Sr^{2+}/M^{n+} from logarithmic plots of the distribution coefficient (K_d) against the macro-ion concentration. Other factors examined include increasing caesium and strontium ion concentrations, hydrolysis of the exchanger, and radiolytic stability.

Experimental

Materials and methods

Chemicals used were of reagent grade quality and were obtained from commercial sources without further purification. Radioisotopes were supplied by Amersham International. Powder X-ray diffraction (XRD) patterns were collected on a Siemens D5000 diffractometer with Cu-Kα radiation. Water contents in samples pre-equilibrated over saturated NaCl for 1 week were determined by thermogravimetry (TGA) using a Mettler TA3000 system at a heating rate of 5 K min^{-1} under a nitrogen atmosphere. Elemental chemical analyses for sodium, potassium and magnesium were conducted by dissolving the solid in HF followed by solution analysis by atomic absorption spectroscopy (AAS).

Distribution coefficients and ion exchange capacities were determined by the batch method using radioactive tracer ions.

Between 25 and 50 mg of exchanger was equilibrated at ambient temperature with spiked solutions in 15 mL polyethylene centrifuge tubes (Elkay) or 20 mL polyethylene vials (Zinsser) by end over end tumbling in a mineralogical roller. Contact times of 1 to 2 days were used. In the 'carrier-free' experiments, the concentration of strontium was in the range $1.5–3.1 \times 10^{-6}$ M and the concentration of caesium was in the range $2.0 \times 10^{-8}–3.7 \times 10^{-7}$ M. The solutions were separated from the solids by centrifugation (15 min at 4000 G) followed by filtration through a 0.22 μm PVDF membrane. ^{22}Na, ^{45}Ca, ^{89}Sr and ^{137}Cs in solution were measured by liquid scintillation counting carried out in a Canberra-Packard 1900 CA tri-Carb. Cerenkov determinations made use of the same instrument. Filtrates from all ion exchange experiments were measured using an Orion model 720A pH meter fitted with an Accumet semi micro calomel electrode.

Preparation of titanosilicate samples for sorption studies

The potassium titanosilicate $K_3HTi_4O_4(SiO_4)_3{\cdot}4H_2O$ (KTS, ideal formula based on X-ray refinement[11]) was synthesised as described previously.[11,13] Fumed silica (4.65 g), titanium isopropoxide (11.07 g) and double distilled (DD) water (61 g) were mixed overnight in a plastic container. The gel was centrifuged and the solid washed twice with DD water. DD water (11.1 g) and 5.1 M KOH (22.3 g) were then added to the washed solid (35.5 g) with vigorous stirring. The mixture was transferred to a 100 mL capacity Teflon-lined autoclave and heated at 200 °C for 64 h. The colourless microcrystalline product was separated from the clear colourless supernatant solution by filtration, rinsed with DD water, and air-dried at 55 °C (yield 7.75 g). The powder XRD pattern (not shown) conformed with that reported for the crystalline potassium titanosilicate pharmacosiderite analogue.[7,11] Found: K, 16.9%; H_2O, 14.9% (TGA to 500 °C). Calc. for $K_3HTi_4O_4(SiO_4)_3{\cdot}4H_2O$: K, 16.24%; $4H_2O$, 9.97%; $6H_2O$, 14.2%. A somewhat lower water content of 12.7% was reported by Behrens *et al.*[11] for the same synthesis.

KTS (1 g) was converted to the sodium form (NaTS) by three successive equilibrations in 1 M NaCl (100 mL) at 55 °C, centrifuging and discarding the supernatant between each treatment.[7] The product was washed once with 0.01 M NaOH (100 mL), once with 0.001 M NaOH (100 mL), air-dried at 55 °C and rehydrated over saturated NaCl. Found: Na, 8.9% (3.9 mequiv. g^{-1}); H_2O, 20.0% to 500 °C. Calc. for $Na_3HTi_4O_4(SiO_4)_3{\cdot}8H_2O$: Na, 9.25%; H_2O, 19.31%. The sodium ion exchange capacity was also determined by isotope dilution analysis as follows. NaTS was equilibrated at ambient temperature for 1 day with ^{22}Na-labelled 0.1 M $NaNO_3$. The exchangeable sodium content (Q, mequiv. g^{-1}) was calculated from eqn. (1)

$$Q = [\mathrm{Na^+}]\left(\frac{A_i - A}{A}\right)\frac{V}{m} \tag{1}$$

where $[\mathrm{Na^+}]$ is the concentration of sodium in solution (0.1 M), A_i and A are the initial and final ^{22}Na tracer activities in solution respectively, and V/m is the solution volume to exchanger mass ratio used (100 mL g^{-1}, based on the hydrated mass of NaTS. All V/m ratios quoted in this paper are for the hydrated mass of the exchanger). A value of 4.0 mequiv. g^{-1} was obtained (9.2% Na), or 5.0 mequiv. g^{-1} based on the dehydrated mass of the exchanger.

NaTS was converted to the magnesium and calcium forms (MgTS and CaTS) by three successive treatments in 1 M $M(NO_3)_2$ ($V/m = 75$ mL g^{-1}) at 55 °C, centrifuging and discarding the supernatant between each step. The solids were washed two times with DD water, air-dried at 55 °C and rehydrated over saturated NaCl. Found (MgTS): Mg, 4.2% (3.46 mequiv. g^{-1}); H_2O, 23.4% to 500 °C. Calc. for $Mg_{1.25}H_{1.5}Ti_4O_4(SiO_4)_3{\cdot}9.5H_2O$: Mg, 4.14%; H_2O, 23.3%. The calcium ion exchange capacity in CaTS was determined by isotope dilution analysis as described above for ^{22}Na except using ^{45}Ca-labelled 0.0075 M $Ca(NO_3)_2$, $V/m = 2000$ mL g^{-1}, and a contact time of 2 days. Found: Ca, 6.7% (3.34 mequiv. g^{-1}); H_2O, 22.3% to 500 °C. Calc. for $Ca_{1.25}H_{1.5}Ti_4O_4(SiO_4)_3{\cdot}9.3H_2O$: Ca, 6.7%; H_2O, 22.3%.

Hydrolysis studies

^{22}Na-labelled sodium titanosilicate (^{22}NaTS) was prepared by equilibrating NaTS (1.9 g) with ^{22}Na-labelled 0.05 M NaOH–0.05 M $NaNO_3$ (100 mL). After mixing for 1 day, the solid was recovered by centrifugation and washed once with 0.01 M NaOH (30 mL), once with 0.001 M NaOH (30 mL), air-dried at 55 °C and rehydrated over saturated NaCl. Samples were equilibrated in $NaNO_3$ solutions ($V/m = 200$ mL g^{-1}, concentration range 0.001–1 M). The final sodium ion concentrations in solution were calculated from the measurement of the final ^{22}Na activity in solution and a knowledge of the activity per gram in ^{22}NaTS ($\overline{A}$), which was calculated from eqn. (2)

$$\overline{A} = \frac{A}{m}\left(\frac{Q}{[\mathrm{Na^+}]}\,\frac{1}{V/m} + 1\right) \tag{2}$$

where A is the activity in solution after equilibrating ^{22}NaTS with 1 M $NaNO_3$ ($V/m = 200$ mL g^{-1}), Q is the sodium ion exchange capacity (4.0 mequiv. g^{-1}) and $[\mathrm{Na^+}]$ is the final sodium ion concentration in solution (1.0 M). This assumes that in 1 M $NaNO_3$ the degree of hydrolysis of the sodium-form exchanger is negligible, *i.e.*, that the equilibrium sodium ion concentration in solution equals the initial one.

Sorption experiments

The purification of nuclear waste effluents using inorganic ion exchangers always involves column exchange. The batch distribution coefficient (K_d) of a given radionuclide is a useful quantity in this respect since it represents the maximum processing capacity, that is, the saturation value of the capacity of the ion exchanger in terms of solution volume (V, L or mL) that can be treated with a given amount (m, kg or g) of ion exchanger.[14] K_d was calculated from eqn. (3) where A_i and A are the initial and final ^{137}Cs or ^{89}Sr tracer activities respectively, measured by liquid scintillation, and V/m is the batch factor (b.f.).

$$K_d = \frac{(A_i - A)}{A}\,\frac{V}{m} = \frac{\text{Concentration of ion in exchanger}}{\text{Concentration of ion in solution}} \tag{3}$$

The K_d calculations were based on the dry weight of the exchanger. In determining K_d as a function of pH, the pH was adjusted by adding concentrated HNO_3 to the solution/exchanger mixture. Prior to the experiments to study the effect of complexants on trace strontium ion sorption efficiencies, freshly prepared solutions of trisodium citrate, sodium tetraborate and disodium dihydrogenethylenediaminetetraacetate were spiked with the radioactive tracer and left standing at room temperature for 3 days to allow the complexation of strontium with the agent.

Radiolytic stability

XRD patterns and K_d values of ^{137}Cs in 0.1 M KNO_3 ($V/m = 100$ mL g^{-1}) were measured under identical conditions for a sample of KTS before and after irradiation in the ^{60}Co source located at the Department of Chemistry and Applied Chemistry, University of Salford (total dose = 6.1 MGy).

Theory

A binary ion exchange reaction between ion A (charge z_A) and ion B (charge z_B) may be written in terms of eqn. (4)

$$z_B A^{z_A+} + z_A \overline{B}^{z_B+} \leftrightarrow z_A B^{z_B+} + z_B \overline{A}^{z_A+} \tag{4}$$

where over-bars refer to the ions in the ion exchanger. The selectivity coefficient is then given by eqn. (5)

$$K_{A/B} = \frac{\overline{C}_A^{z_B} C_B^{z_A}}{\overline{C}_B^{z_A} C_A^{z_B}} \tag{5}$$

where the $\overline{C}$ values are the concentrations of the ions in the exchanger and C values those in the solution. From eqn. (3) ($K_d = \overline{C}_A/C_A$) and eqn. (5) one obtains eqn. (6).

$$K_d = K_{A/B}^{1/z_B} \left(\frac{\overline{C}_B}{C_B}\right)^{z_A/z_B} \tag{6}$$

Under the special condition that A is present in solution and in the exchanger at much lower concentration than B ($\overline{C}_A \ll \overline{C}_B$, $C_A \ll C_B$, *e.g.*, when A is trace caesium ion and B is a macro-ion such as sodium),[14] $K_{A/B}$ and $\overline{C}_B$ are practically constant ($\overline{C}_B \approx Q$, the ion exchange capacity) and one obtains eqn. (7) which indicates that a plot of $\log K_d$ against $\log C_B$ should give a straight line with slope $-z_A/z_B$.

$$\log K_d = \frac{1}{z_B}\log(K_{A/B}Q^{z_A}) - \frac{z_A}{z_B}\log C_B \tag{7}$$

However, the overriding condition for linear dependence becomes apparent if, for simplicity, we consider a binary uni–univalent exchange ($z_A = z_B = 1$).[14] Inserting $\overline{C}_B = Q - \overline{C}_A$ into eqn. (5) and combining with $K_d = \overline{C}_A/C_A$ gives eqn. (8).

$$K_d = \frac{Q}{(C_B/K_{A/B}) + C_A} \tag{8}$$

This shows that the condition for linear dependence is in fact $C_B/K_{A/B} \gg C_A$.

Results and discussion

The distribution coefficient of ^{137}Cs and ^{89}Sr on NaTS is shown as a function of sodium ion concentration in Fig. 1. Up to a sodium ion concentration of 0.1 M, K_d of ^{137}Cs is approximately constant at 65 000 mL g^{-1} (99.62% sorption). At higher concentrations K_d decreases linearly on a logarithmic scale with a slope of -1.11. This is close to the theoretical value of -1 for exchange of a univalent ion for a univalent ion. The sorption behaviour of ^{89}Sr is strikingly different in that in the sodium concentration range 0.001–0.03 M K_d increases by nearly two orders of magnitude, from 60 000 to $>10^6$ mL g^{-1} (99.98% sorption). At higher concentrations it decreases linearly with a slope of -1.61. This value diverges slightly from the expected value of -2 for exchange of a divalent ion for a univalent ion.

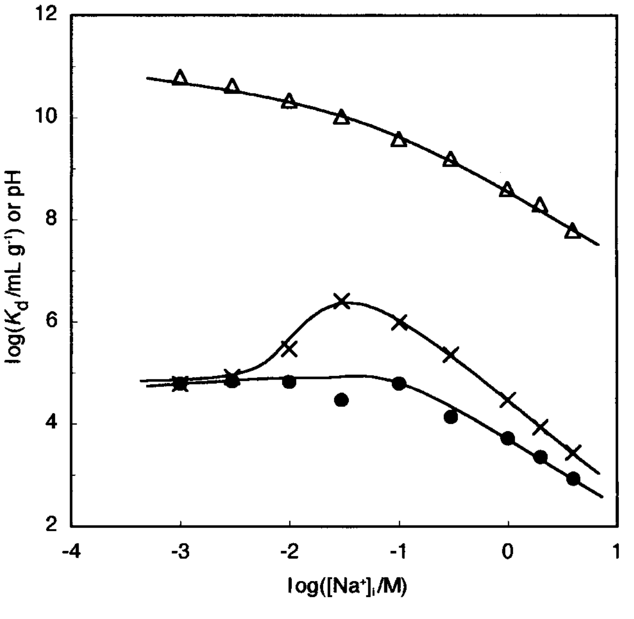

Fig. 1 Distribution coefficient of ^{137}Cs (●) and ^{89}Sr (×) on NaTS, and the corresponding equilibrium pH (△) as a function of sodium ion (NaNO$_3$) concentration ($V/m = 200$ mL g^{-1}).

Selectivity factors were determined by fitting a straight line to the linearly declining parts of the curves in Fig. 1 and using eqn. (7) (Table 1). Values of *ca.* 740 and 2050 were obtained for the ion pairs Cs/Na and Sr/Na respectively. The former value is comparable to or slightly higher than that reported for caesium selective conventional zeolites such as Na-mordenite.[15]

Caesium exchange by $Na_3HTi_4O_4(SiO_4)_3{\cdot}xH_2O$ involves two processes [eqn. (9) and (10)].

$$Na_3HTi_4O_4(SiO_4)_3 + 3Cs^+ \rightleftharpoons Cs_3HTi_4O_4(SiO_4)_3 + 3Na^+ \tag{9}$$

$$H_4Ti_4O_4(SiO_4)_3 + 3Cs^+ \rightleftharpoons Cs_3HTi_4O_4(SiO_4)_3 + 3H^+ \tag{10}$$

The lower the pH, the greater is the proportion of the exchanger in the hydrogen form and the higher the proportion of reaction (10). The proportion of reaction (9) increases with pH. It has been reported that only three of the four protons of $H_4Ti_4O_4(SiO_4)_3$ are exchangeable by sodium, potassium and caesium ions.[7,11] There is no room for a fourth metal ion to occupy the void in the centre of the cubic unit cell and instead this space is occupied with water molecules. The proton is probably bonded to a titanium octahedron. Similar reactions can be conceived for Sr^{2+} exchange by NaTS except that in alkaline solution (especially at pH > 10) exchange of the hydrolysed species of strontium [$Sr(OH)^+$] must also be considered. A contribution from this species to the trace strontium exchange by NaTS in sodium nitrate solutions obviously distorts the ideal picture and probably accounts for why a slope of -1.61 is obtained from $\log K_d$ against $\log [Na^+]$. This behaviour is similar to that observed for strontium exchange by the layered sodium titanate $Na_4Ti_9O_{20}{\cdot}xH_2O$.[16]

There are at least three factors to consider in explaining the peculiar behaviour of K_d in dilute solutions: (1) hydrolysis of the exchanger; (2) suspended particles in solution; (3) loss of linear dependence due to a high selectivity factor.[14–17] The first two factors are probably the most important. For example, Harjula *et al.*[15] showed that the levelling off of the K_d of trace caesium on Na-mordenite was caused by hydrolysis and peptisation of the exchanger. The alkaline sodium titanosilicate studied here is a weak acid exchanger and reaction (9) above will be accompanied by partial hydrolysis [eqn. (11)].[7]

$$Na_3HTi_4O_4(SiO_4)_3 + 3H_2O \rightleftharpoons H_4Ti_4O_4(SiO_4)_3 + 3Na^+ + 3OH^- \tag{11}$$

The result for NaTS in sodium nitrate solutions is that equilibrium sodium ion concentrations become significantly higher than initial ones, below initial concentrations of 0.01 M, and the equilibrium pH is alkaline (Fig. 2). In the extreme, with an initial sodium concentration of 0.001 M, the equilibrium concentration was 0.003 M. It follows that *ca.* 10% of the sodium ions in the exchanger were exchanged with hydronium ions during contact with the solution. In other words the equivalent fraction of hydrogen ions in the exchanger increased from 0.25 to 0.33. The levelling off of equilibrium sodium ion concentrations in dilute solutions partly explains the constant ^{137}Cs K_d values obtained at low concentrations. Moreover, increasing amounts of sodium ions in solution will cause a shift to the left in reaction (11) and a decrease in the proportion of the hydrogen form, as evidenced by a decrease in the equilibrium pH from 10.3 to 7.8 in the concentration range

Table 1 Selectivity coefficients ($K_{A/B}$) of trace caesium and strontium exchanges in the titanosilicate pharmacosiderite exchanger

Ion pair	CEC[a]	C^b/M	Linear regression equation	$K_{A/B}$
Cs/Na	5.00	0.1–4.0	$y=-1.11x+3.65$	740
Sr/Na	5.00	0.1–4.0	$y=-1.61x+4.44$	2050
Cs/K	4.62	0.1–2.0	$y=-1.03x+2.46$	60
Sr/K	4.62	0.1–2.0	$y=-1.05x+4.75$	11120
Cs/Mg	4.52	0.01–1.0	$y=-0.37x+5.30$	$>10^6$
Sr/Mg	4.52	0.01–1.0	$y=-1.08x+3.42$	260 000
Cs/Ca	4.29	0.01–1.0	$y=-0.61x+4.23$	$>10^6$
Sr/Ca	4.29	0.01–1.0	$y=-1.05x+1.93$	340

[a]Sodium, potassium, magnesium and calcium cation exchange capacities (mequiv. g^{-1}), based on the dehydrated mass of the exchanger. [b]Concentration range for linear regression fit to log K_d against log C.

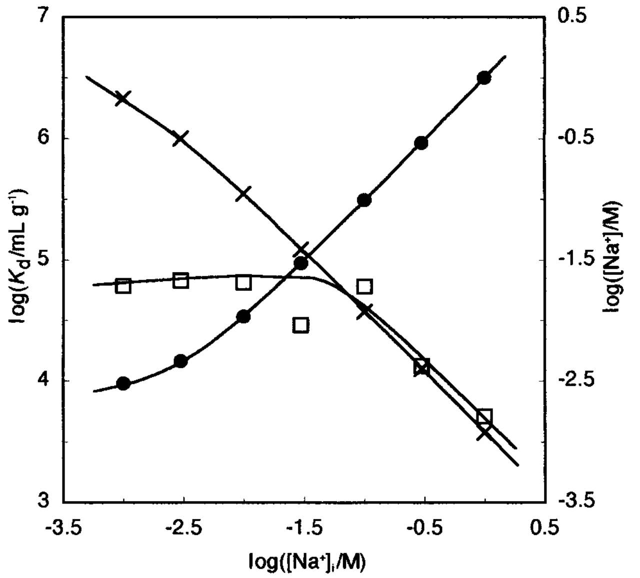

Fig. 2 Observed distribution coefficient of ^{137}Cs (□), calculated distribution coefficient of trace caesium (×) and equilibrium [Na$^+$] (●) as a function of [Na$^+$]$_i$ in equilibrations of NaTS with NaNO$_3$. Calculated K_d values were obtained using eqn. (8) with $Q=5.0$ mequiv. g^{-1}, $C_A=10^{-6}$ M and $K_{A/B}=750$.

0.01–4 M. The sodium titanosilicate prefers hydrogen ions to sodium ions and therefore sorption of caesium or strontium on the sodium form is more favourable. This may account for the very large initial increase of the ^{89}Sr K_d values.

The second important factor to consider is that very fine colloidal particles may be released from the exchanger and left in solution after centrifugation at 4000 G and filtration through a 0.22 µm membrane. These particles could retain exchanging ions in the same manner as the bulk of the exchanger material. Hence determination of the solution concentration of the ion will not be correct. Finally, it has been noted by Harjula *et al.* that levelling off of logarithmic plots of K_d for a trace ion A against concentration for a macro-ion B will be inevitable especially at lower concentrations of B if the selectivity coefficient is very large, *i.e.*, if the condition $C_B/K_{A/B} \gg C_A$ is not met [eqn. (8)].[14] Ultimately, K_d becomes independent of [Na$^+$] and tends towards Q/C_A if the selectivity is very large. To check whether this could be a factor in the results presented here, K_d values were calculated using eqn. (8) with $Q=5.0$ mequiv. g^{-1}, $C_A=10^{-6}$ M and $K_{A/B}=750$ (Fig. 2). The dependence is linear above a concentration of 0.01 M. Below this concentration K_d starts to level off but only very slightly.

The distribution coefficient of ^{137}Cs and ^{89}Sr on KTS as a function of potassium ion concentration follows a similar pattern to that described above for sodium (Fig. 3). However, there are some notable differences. Once again there is a linear dependence in the concentration range 0.1–2.0 M but, while the slope for caesium (−1.03) is very close to the expected value of −1, the slope for strontium is −1.05 which is a large deviation from the expected value of −2. Furthermore, in the same concentration range, the K_d of ^{89}Sr is about 200 times higher than that of ^{137}Cs. Sorption of trace strontium was still 99.53% even in 2.0 M KNO$_3$ ($K_d=25\,000$ mL g^{-1}). The situation changes drastically at lower potassium ion concentrations. Thus, the K_d of strontium decreases from *ca.* 600 000 mL g^{-1} in 0.1 M KNO$_3$ to about 14 000 mL g^{-1} in 0.001 M KNO$_3$, probably for similar reasons to those discussed above. In this range the K_d of caesium starts to level off but only slightly. The result is that below 0.008 M, the sorption efficiency of trace caesium on the exchanger is actually higher than that of strontium. Overall the discouraging performance of the material for the removal of caesium in the presence of potassium is reflected in the modest selectivity factor ($K_{Cs/K} \approx 60$, Table 1). The value for strontium was about 200 times higher, although this must be treated with caution due to the peculiar value of the slope obtained, noted above.

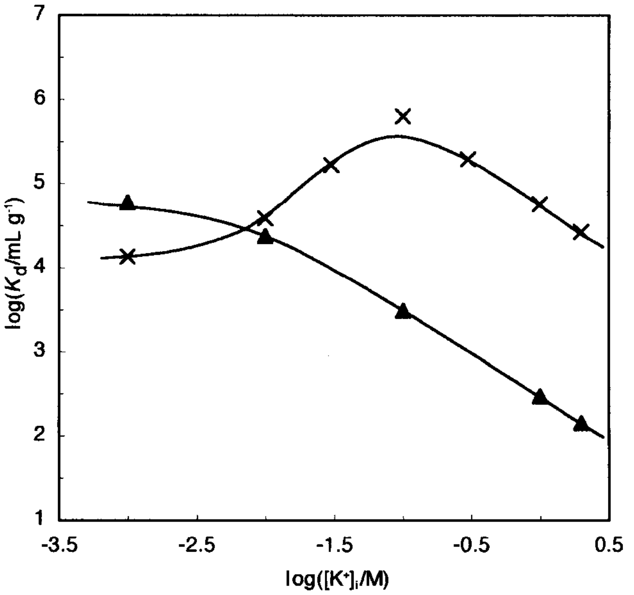

Fig. 3 Distribution coefficient of ^{137}Cs (▲) and ^{89}Sr (×) on KTS as a function of potassium ion (KNO$_3$) concentration ($V/m=100$ mL g^{-1}).

From the selectivity factors discussed so far for trace caesium and strontium exchange, one can infer that the sodium form material should be more efficient than the potassium form for removal of caesium, whereas in the case of strontium removal the potassium form material should be more efficient than the sodium form. This was what Behrens and Clearfield[7] found when they determined caesium and strontium distribution coefficients on a pharmacosiderite titanosilicate, prepared as in this work, as a function of increasing NaNO$_3$ concentrations (initial Cs$^+$ and Sr^{2+} concentrations were 10^{-3} M). Thus, the Sr^{2+} K_d values for the potassium phase were approximately five times greater than those of the sodium phase for all NaNO$_3$ concentrations up to 5 M. The situation was reversed in the case of caesium distribution coefficients. In contrast, it was also found that the sodium form material gave the highest K_d values (*ca.* 10 000 mL g^{-1}) for both caesium and strontium removal from a groundwater simulant containing ppm levels of Ca^{2+}, Mg^{2+}, K$^+$ and Na$^+$ (8.0 ppm Cs$^+$, 6.1 ppm Sr^{2+}, equilibrium pH 7.2). The reduced efficiency of the potassium phase for Sr^{2+} is probably due to partial hydrolysis in dilute solution as discussed above.

In contrast to potassium, the exchanger is highly selective for trace caesium in the presence of magnesium and calcium

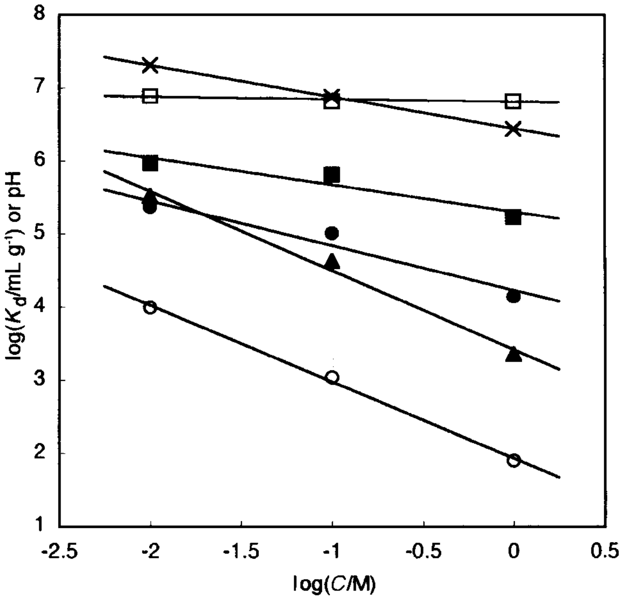

Fig. 4 Distribution coefficient of ^{137}Cs (■) and ^{89}Sr (▲) on MgTS, and the corresponding equilibrium pH (×) as a function of magnesium ion [Mg(NO$_3$)$_2$] concentration; distribution coefficient of ^{137}Cs (●) and ^{89}Sr (○) on CaTS, and the corresponding equilibrium pH (□) as a function of calcium ion [Ca(NO$_3$)$_2$] concentration (V/m = 200 mL g^{-1}).

($K_{Cs/Mg} > 10^6$, $K_{Cs/Ca} > 10^6$, Table 1, Fig. 4). Even more encouraging is the performance for strontium ($K_{Sr/Mg} \approx 260\,000$, $K_{Sr/Ca} \approx 340$). The pH in the experiments was in the range 6.4–7.3 indicating that only very minor hydrolysis of the magnesium and calcium forms took place. The slopes for the linear regression fits to log K_d against log [M^{2+}] were close to the expected values of -0.5 for pure Cs$^+$–M^{2+} exchange and -1.0 for pure Sr^{2+}–M^{2+} exchange. Calcium ions usually interfere very strongly in the sorption efficiency of strontium on cation exchangers. Bengtsson *et al.*[18] tested a wide range of inorganic adsorbents for strontium removal from calcium bearing solutions. The materials investigated included manganese oxides, mixed titanium–manganese oxides, modified carbons, synthetic and natural zeolites. The K_d values of ^{85}Sr were measured in 0.01 M CaCl$_2$ (pH $\approx$ 7, V/m = 200 mL g^{-1}). One antimony-based adsorbent gave a K_d of 4280 mL g^{-1}. Otherwise the K_d values were at or below *ca.* 1000 mL g^{-1}. The best synthetic zeolite was Na-zeolite P (K_d = 1400 mL g^{-1}). The calcium-form pharmacosiderite analogue studied here gave a K_d of 10 000 mL g^{-1} in 0.01 M Ca(NO$_3$)$_2$ (97.5% sorption).

Distribution coefficients of ^{137}Cs and ^{89}Sr were determined on KTS as a function of pH in 0.1 M NaNO$_3$ (Fig. 5). The behaviour is very different. The sorption efficiency of caesium is a maximum at about neutral pH ($K_d \approx 3500$ mL g^{-1}, 96.75% sorption). K_d then decreases smoothly by about one order of magnitude either to pH 1 or 13. The K_d of ^{89}Sr is constant at *ca.* 5×10^5 mL g^{-1} in the pH range 10–13. Below pH 10 the K_d decreases sharply, approximately linearly on a logarithmic scale. At pH 1 practically no strontium is taken up by the exchanger.

Fig. 6 presents the distribution coefficient of strontium and caesium on KTS as a function of strontium and caesium ion concentration respectively. In the concentration range 10^{-5}–10^{-3} M hydrolysis of the potassium form exchanger results in a high equilibrium pH (11.0). In this concentration range, the K_d of caesium is high and almost constant at *ca.* 60 000 mL g^{-1}. By contrast, the K_d of strontium is initially *ca.* 20 000 mL g^{-1} but increases by nearly one order of magnitude to 180 000 mL g^{-1} when the initial strontium concentration is 0.001 M. The explanation given above can be applied again in this case, *i.e.*, an increasing amount of potassium ions in solution as they exchange with Sr^{2+}, which then causes a shift to the left in reaction (11), and a decrease in the proportion of the exchanger in the hydrogen form. At higher concentrations of caesium and strontium, the distribution coefficients decrease smoothly as the saturation capacities are approached. However, there is one notable difference in that the equilibrium pH for caesium remains high and is almost constant at 10.8 while that for strontium decreases sharply and is neutral with an initial strontium concentration of 0.1 M. This indicates that hydrolysis of the caesium form of the exchanger is much more significant compared to the strontium form, for which only very minor hydrolysis takes place, as observed for the calcium and magnesium forms.

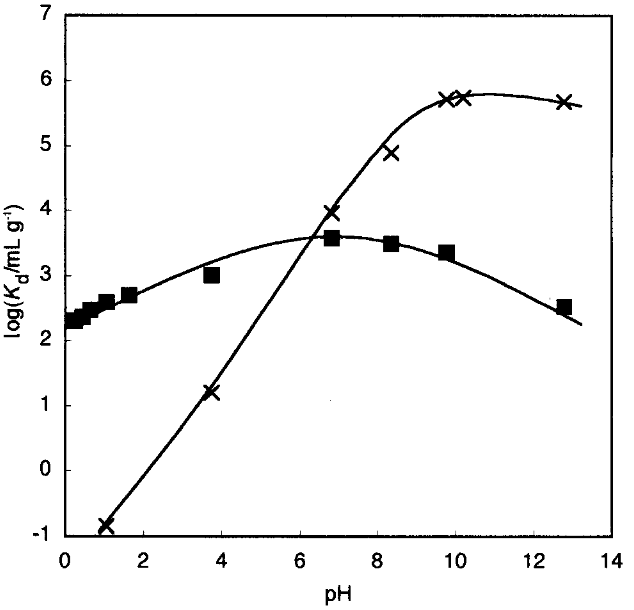

Fig. 5 Distribution coefficient of ^{137}Cs (■) and ^{89}Sr (×) on KTS as a function of pH in 0.1 M NaNO$_3$ (V/m = 100 mL g^{-1}).

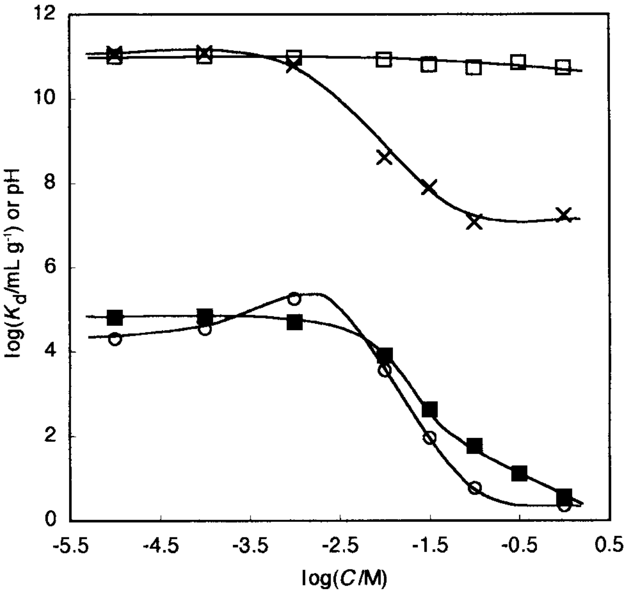

Fig. 6 Distribution coefficient of caesium (■) and strontium (○) on KTS, and the corresponding equilibrium pH [caesium (□), strontium (×)] as a function of initial caesium ion (CsNO$_3$) and strontium ion [Sr(NO$_3$)$_2$] concentration respectively (V/m = 100 mL g^{-1}).

The distribution coefficient of ^{89}Sr on NaTS was measured as a function of pH in 0.001 M sodium tetraborate (Na$_2$B$_4$O$_7$), sodium citrate [HOC(CO$_2$Na)(CH$_2$CO$_2$Na)$_2$] and the disodium salt of EDTA [–CH$_2$N(CH$_2$CO$_2$Na)CH$_2$CO$_2$H]$_2$ (Fig. 7). In acidic solution (pH < 5) the complexing agents have no obvious

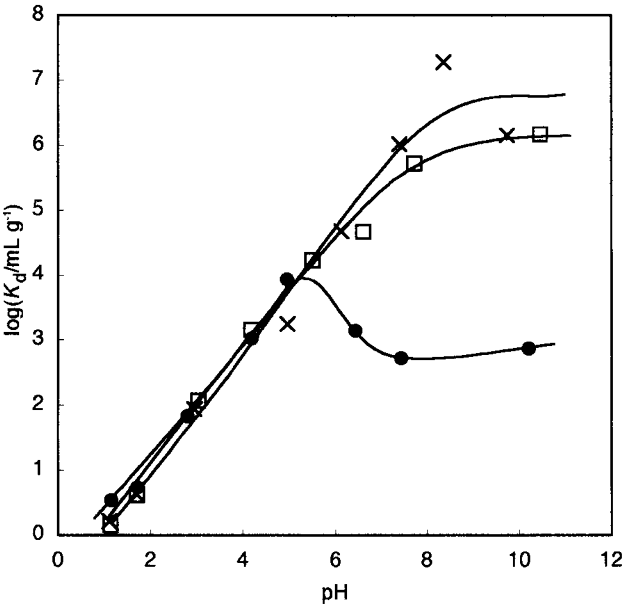

Fig. 7 Distribution coefficient of ^{89}Sr on NaTS as a function of pH in 0.001 M sodium tetraborate (×), trisodium citrate (□) and disodium EDTA (●) ($V/m = 200$ mL g^{-1}).

discriminating effect on strontium removal and the K_d values in all three solutions decrease from *ca.* 1000 mL g^{-1} (80% sorption) at pH 4 to 1 mL g^{-1} (0.4% sorption) at pH 1. Above pH 5 and in the presence of citrate and tetraborate, K_d continues to increase and the situation is very favourable in the alkaline pH region. The lack of interference from citrate is not unexpected since it forms relatively weak monocomplexes with Sr^{2+}, as evidenced by the low stability constant, log $K = 2.7$.[19] The behaviour in the presence of EDTA is very different. It also forms 1 : 1 complexes with Sr^{2+} but the stability constant is much higher (8.63).[20] Maximum uptake is at pH 5 ($K_d \approx 7400$ mL g^{-1}, 96.7% sorption) and then K_d decreases with increasing pH, levelling off or passing through a minimum at pH 8–9 ($K_d \approx 300$ mL g^{-1}, 55% sorption). This trend appears to be linked to the relative amounts of EDTA species present in solution.[20] Thus, in aqueous solution at pH 3–5, EDTA exists mainly as H_2L^{2-} (maximum at pH 4.5). Proton dissociation from one of the nitrogens becomes significant above pH 5 and at pH 8 EDTA exists mainly as HL^{3-}. The reaction of HL^{3-} with Sr^{2+} may be written as $Sr^{2+} + HL^{3-} \rightleftharpoons SrL^{2-} + H^+$.

The effects of the complexing agents on the distribution coefficient of ^{89}Sr were also studied in the concentration range 10^{-6}–0.05 M (Fig. 8). One can immediately see that even at a concentration of 10^{-5} M, EDTA starts to have a suppressing effect. Citrate concentration has a stronger effect than tetraborate concentration on the uptake of strontium, especially at concentrations higher than 0.01 M.

As a final note, the radiation stability of the material was tested. A sample of KTS was exposed to 6.1 MGy in the ^{60}Co source at the University of Salford. The powder XRD pattern of the irradiated sample was very similar to that before irradiation and indicated no loss of crystallinity or phase change. As a further test of the material's resistance to radiation damage, the distribution coefficient of ^{137}Cs in 0.1 M KNO_3 was measured on the sample before and after irradiation. Again, there was no significant change (3090 mL g^{-1} before exposure, 3270 mL g^{-1} after exposure).

Conclusions

The titanosilicate pharmacosiderite studied here is a promising ion exchanger for the separation of both caesium and strontium radionuclides in aqueous solution. Selectivity factors ranging from high to very high were found for trace strontium exchange against the macro-ions sodium, potassium, magnesium and calcium. In particular the material compares very favourably against other inorganic ion exchangers for the removal of strontium in the presence of calcium ($K_{Sr/Ca} = 340$). However, the efficiency of the material for strontium decreases sharply once the pH is below neutral. Selectivity decreases were also observed in dilute sodium and potassium ion solutions, presumably as a result of hydrolysis which partially converts the exchanger to the hydrogen form with a concomitant levelling off of sodium and potassium ion concentrations. The complexants citrate and borate did not significantly suppress trace strontium sorption efficiencies in the pH range 1–12. In contrast, EDTA in the absence of other macro-ions had a very large effect above pH 6, even when very dilute ($>10^{-5}$ M). The overall efficiency for trace caesium in the presence of sodium and potassium was lower than for strontium, at least for concentrations higher than 0.1 M. However, selectivity in the presence of magnesium and calcium was very high.

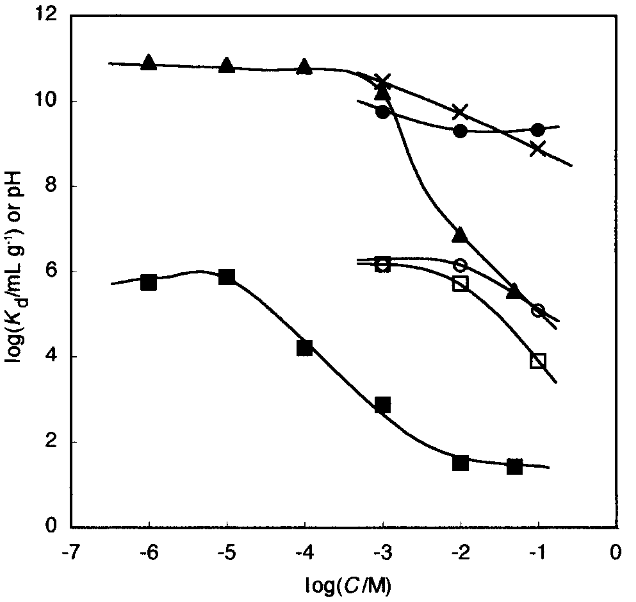

Fig. 8 Distribution coefficient of ^{89}Sr on NaTS as a function of sodium tetraborate (○), trisodium citrate (□) and disodium EDTA concentrations (■), and the corresponding equilibrium pH [tetraborate (●), citrate (×), EDTA (▲)] ($V/m = 200$ mL g^{-1}).

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