Ion exchange of strontium and caesium into amorphous zirconium phosphates

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The ion exchange of the radioisotopes ^{89}Sr and ^{137}Cs onto various ionic forms of amorphous zirconium phosphate has been studied. Ion exchange isotherms have been constructed at three temperatures (298, 313 and 333 K) and evaluated to give the thermodynamic parameters ΔG°, ΔH° and ΔS° for the exchange processes. Discussions of ion exchange selectivities, with comparisons to past work on similar materials, have been made.

Amorphous zirconium phosphate (ZrP) was amongst the first inorganic ion exchange materials used to process aqueous nuclear waste for the purpose of removing the fission products ^{90}Sr and ^{137}Cs.[1] The ZrP used in this early work was in a granular form specially prepared for column use. Similar materials were available commercially for a more general utility in smaller scale analytical separations of cations. More recently studies have been made on a wider range of radioisotopes likely to arise in wastes from nuclear fuel production, reprocessing and decommissioning. This work considers the use of powdered materials, including ZrP, in a process for aqueous nuclear waste treatment based on ultrafiltration.[2]

This work describes work on a powdered ZrP from a commercial source providing the material for cartridge use in haemodialysis machines.[3] Earlier publications described the measurement of distribution coefficients for Cs and Sr radioisotopes on several ion-exchanged forms of the ZrP, as well as column, and cement encapsulation experiments.[4–6] Herein experiments designed to provide information of a more fundamental nature relating to cation exchanges performed on the ion-exchanged forms of ZrP are described.

Experimental

Materials

Amorphous zirconium phosphate was from Magnesium Elektron Ltd., Clifton Junction, Swinton, Manchester UK. It was a white powder of average particle size 50 µm, and had a mass% composition: Zr, 26.0; HPO_4, 52.0; H_2O, 15.0; Na, 7.2.[7]

Strontium-89 was used in preference to ^{90}Sr/^{90}Y and this, with the ^{137}Cs isotope, was supplied by Amersham International, UK. All other reagents were of AnalR grade.

Cation-exchanged forms of ZrP were obtained by treating the semi-sodium material, as supplied, with excess aqueous metal salts at room temperature. Full details of this, with their characterization, are given in ref. 4.

Ion exchange isotherms

The method of isotope dilution was used to construct isotherms. Aliquots (0.1 g) of homoionic forms of ZrP were contacted with 20 dm^3 of isonormal ($T_N = 0.01$) chloride solutions containing ^{89}Sr or ^{137}Cs, and varying amounts of ingoing cations (H_3O, Li, Na, K, NH_4, Cs/Sr, Ca). Each exchange was stirred continuously in a separate polythene vial, and equilibration times were one week based on previous preliminary kinetic experiments. At equilibrium the supernatant solutions were examined for radioisotope content by estimation of Cerenkov radiation using the tritium setting of a liquid scintillation counter.

Ion exchange was carried out at 298, 313 and 333 K for each ion pair and periodic checks for reversibility were made.

Results

Ion exchange isotherms were plotted based upon the measured equivalent fractions of the ingoing ion in the solution (A_s) and solid (A_c) phases. The isotherms are shown in Fig. 1–12. Plots of A_c *vs.* ln K_c, where K_c is the Kielland coefficient, were constructed using the Kielland Program available on the University of Salford network. This program made all the required adjustments for ionic activity coefficients in both solution and ZrP phases.

The free energies (ΔG°), enthalpies (ΔH°) and entropies (ΔS°) of the exchange process for each ion pair were generated by the same program. The values acquired are in Tables 1 and 2.

Discussion

Isotherms

All checks of the exchange processes showed them to be reversible. No inconsistencies such as might have arisen from hydrolytic degradation of the amorphous ZrP were seen. This was in line with the absence of heat content changes in the temperature range associated with hydrolysis when differential scanning calorimetry was used in the characterisation of each homoionic form of ZrP.[8]

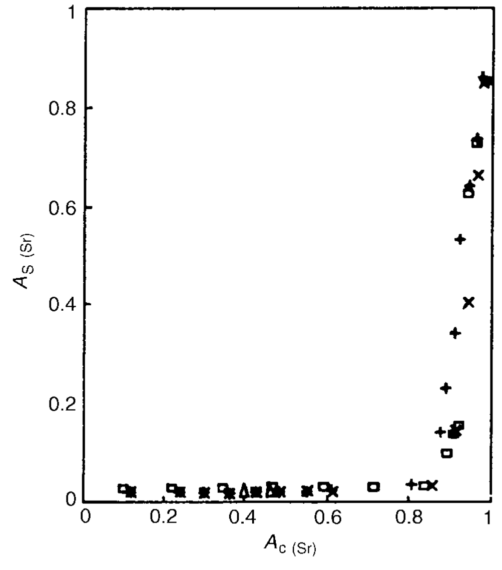

Fig. 1 Ion exchange isotherm for the Li/Sr ions on ZrP (+, 298 K; □, 313 K; ×, 333 K; △, reverse 298 K)

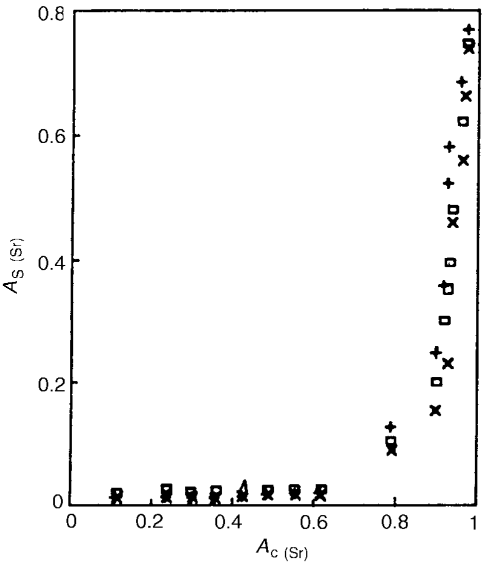

Fig. 2 Ion exchange isotherm for the Na/Sr ions on ZrP (symbols as in Fig. 1)

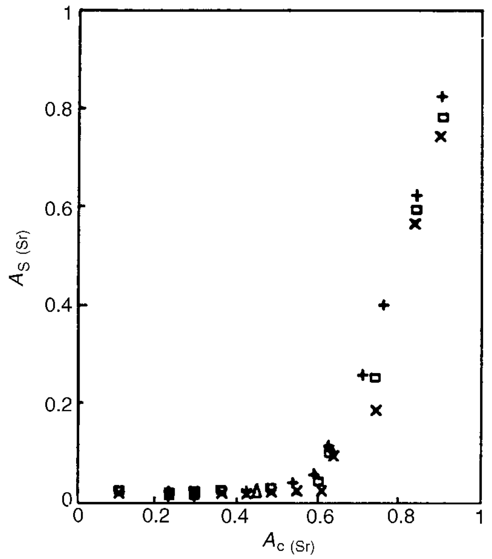

Fig. 3 Ion exchange isotherm for the K/Sr ions on ZrP (symbols as in Fig. 1)

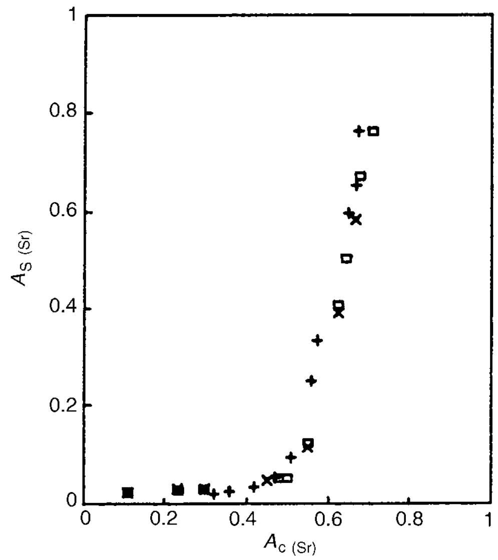

Fig. 4 Ion exchange isotherm for the Cs/Sr ions on ZrP (symbols as in Fig. 1)

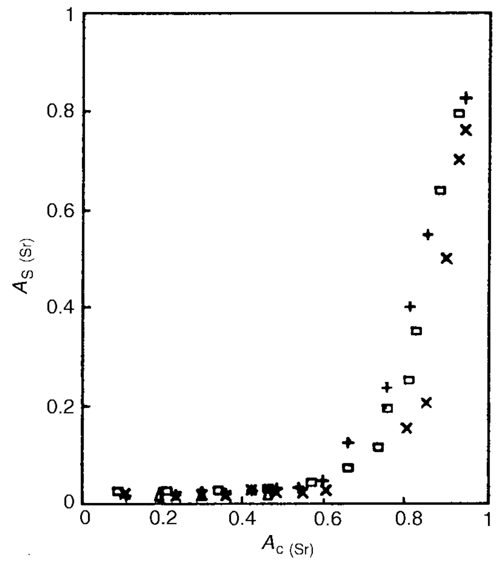

Fig. 5 Ion exchange isotherm for the NH_4/Sr ions on ZrP (symbols as in Fig. 1)

Strontium exchanges

Strontium was taken up extremely selectively on both lithium and sodium forms of ZrP, and was independent of temperature to within experimental error (Fig. 1 and 2). Full capacity was essentially attained in both cases. In the presence of potassium, strontium was still clearly preferred by the exchanger, but to a lesser extent (Fig. 3). The process was still essentially temperature insensitive and full capacity was not quite reached. When caesium was present, temperature still had little effect and strontium was selected preferentially, but now only about 65% of the total available exchange capacity was in use (Fig. 4).

When the outgoing ion was ammonium, (Fig. 5) the behaviour was close to that of potassium which reflected the similarity in bare cation radius between K^+ and NH_4^+. Both hydronium and calcium ion exchange for strontium were different (Fig. 6 and 7). Calcium/strontium exchange had the highest dependence on temperature observed in this series, with little strontium being taken into the ZrP phase at 298 K but, at 333 K, signs of strontium preference were clear and a reasonable use of capacity achieved. Hydronium ion presence negated strontium exchange and the isotherm shapes were little changed by temperature.

Caesium exchanges

The ability of ZrP to take up caesium was not as good as that shown for strontium. A slight preference was shown over lithium and sodium at lower solution concentrations of caesium (Fig. 8 and 9), but caesium/potassium and caesium/ammonium exchanges showed no selectivity (Fig. 10 and 11). Perhaps the caesium ion could be claimed to be preferred to the hydronium ion at higher solution concentrations but this was not convincing (Fig. 12).

The isotherms for ammonium and lithium were temperature dependent to a small extent, but all other exchanges were temperature insensitive. The limits to exchange generally followed the same patterns as those exhibited by strontium. The caesium/calcium exchange was not carried out.

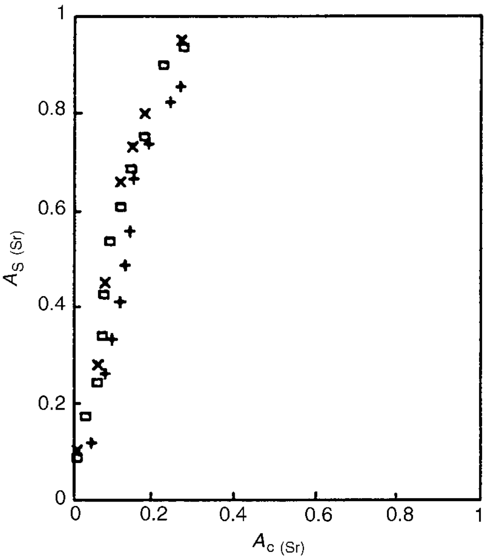

Fig. 6 Ion exchange isotherm for the H_3O/Sr ions on ZrP (symbols as in Fig. 1)

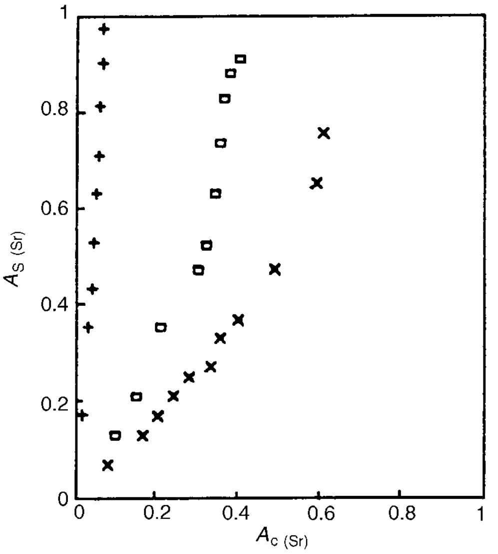

Fig. 7 Ion exchange isotherm for the Ca/Sr ions on ZrP (symbols as in Fig. 1)

Thermodynamics of the exchanges

The results obtained in this work for the values of the free energies (ΔG°), enthalpies (ΔH°) and entropies (ΔS°) of each ion pair studied are listed in Tables 1 and 2. Table 3 contains the values of other workers for similar systems. The first column in each Table lists the ion pairs as the outgoing ion followed by the ingoing ion.

Table 3 shows that no previous work of this nature has been carried out on strontium exchange so the results involving the caesium ion will be considered first.

Exchanges with caesium on ZrP

The ΔG° values measured in this work give a selectivity series for caesium uptake, at 298 K, as $Li^+ < Na^+ < H_3O^+ < NH_4^+ < K^+$.

Alberti[3] quoted a similar sequence, at high loading of ions in the exchanger phase, as one that follows the sizes of the hydrated ions, with caesium, the least hydrated ion, being the most preferred by amorphous ZrP. Alberti did not include the hydronium and ammonium ions in his sequence. The allocation of a definitive hydrated ion radius to these ions is complicated by their ability to create hydrogen bonds with their immediate environment. Horvath[14] states that hydrated ammonium and potassium ions are identical in size (33.1 nm), so the position of ammonium in the selectivity series quoted above is sensible. Similar data on the hydronium ion are lacking but, if the hydration number in the appropriate shell is similar to that of sodium, then it is not unreasonable to anticipate that the size of the hydrated hydronium ion resembles the hydrated sodium ion. This estimate would be justifiable on the basis that the radius of the water molecule is close to that of the sodium ion, although it must also be pointed out that the bare ion radius of the hydronium ion is 14.1 nm, and so lies between K^+ and Cs^+.

The ΔS° values reflect an involvement of waters of hydration in the cation exchange process. The drop in negative entropy seen from Li to K presumably relates to the diminishing difference in hydration shell when the two exchanging ions are compared. The replacement of the more structured hydrated

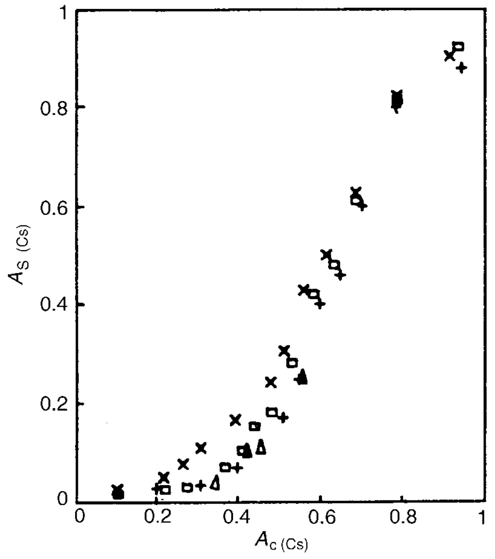

Fig. 8 Ion exchange isotherm for the Li/Cs ions on ZrP (symbols as in Fig. 1)

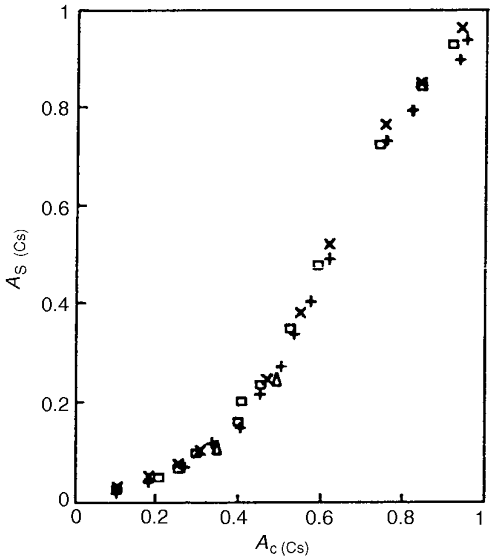

Fig. 9 Ion exchange isotherm for the Na/Cs ions on ZrP (symbols as in Fig. 1)

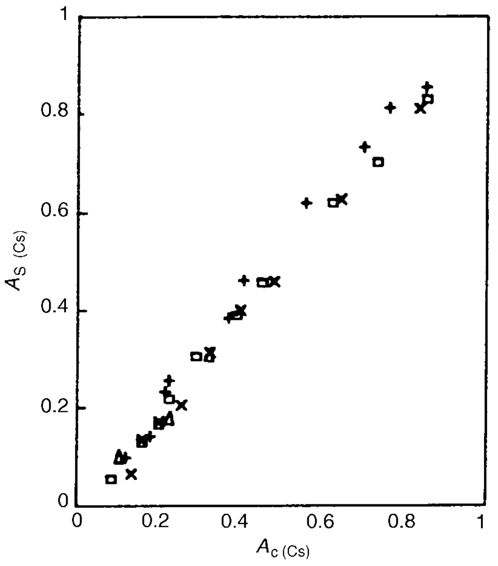

Fig. 10 Ion exchange isotherm for the K/Cs ions on ZrP (symbols as in Fig. 1)

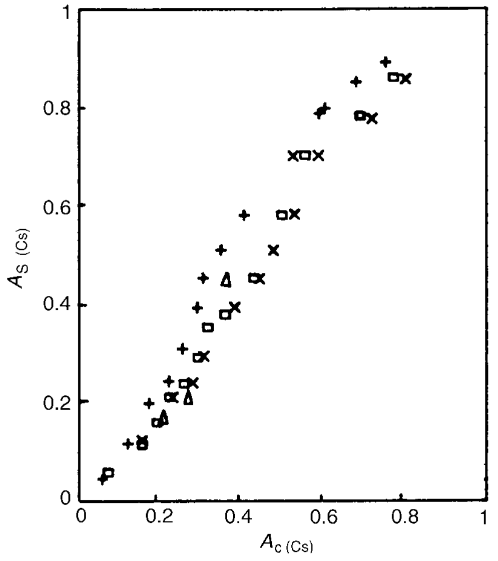

Fig. 11 Ion exchange isotherm for the NH_4/Cs ions on ZrP (symbols as in Fig. 1)

lithium ion by the less hydrated caesium ion, thus creates the highest entropy change. The high negative values seen for hydronium and ammonium ions can be linked to their ability to form hydrogen bonds that must be disrupted for exchange with the caesium to occur.

Comparisons to thermodynamic parameters cited in existing literature (Table 3) are not easy for a variety of reasons. Some data is at lower temperatures, and not all investigators have demonstrated reversible exchange. In addition there are compositional differences between the amorphous ZrPs studied, and in some instances the ZrP is described as 'semi-crystalline'. Furthermore it can be seen that nearly all the results are for systems with the hydronium ion being the ion initially present in the ZrP phase. However the data of Baetsle,[13] which included the ammonium and hydronium ions, gave a very similar selectivity series to that noted herein. This was based on the distribution coefficients measured for the uptake of carrier free tracer solutions of the ingoing ions, rather than isotherm data.

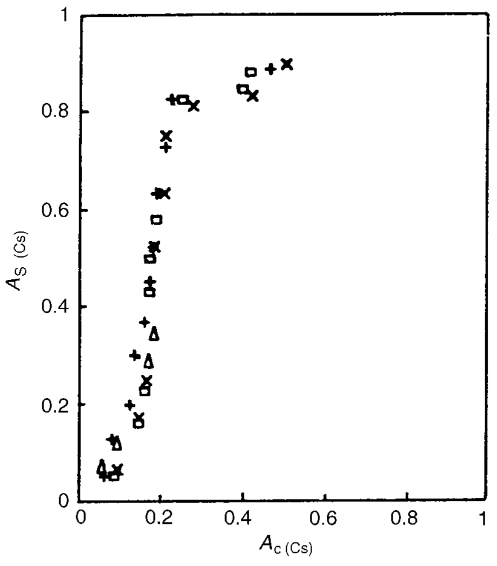

Fig. 12 Ion exchange isotherm for the H_3O/Cs ions on ZrP (symbols as in Fig. 1)

Table 1 Thermodynamic parameters for the exchange of caesium onto homoionic forms of ZrP

exchange	T/K	ΔG°/ kJ mol^{-1}	ΔH°/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}
Li/Cs	298	−6.7		−21
	313	−7.1	−13	−19
	333	−7.3		−17
Na/Cs	298	−5.9		−17
	313	−6.3	−10	−15
	333	−6.8		−13
K/Cs	298	−3.8		−14
	313	−3.6	−8	−14
	333	−3.3		−14
H[a]/Cs	298	−5.6		−25
	313	−5.8	−13	−23
	333	−6.3		−20
NH_4/Cs	298	−4.9		−24
	313	−5.1	−12	−22
	333	−5.7		−19

[a] H = H_3O^+.

Broadly the values in Tables 1 and 3 are appropriate for cation exchange processes taking place in open porous solids controlled by the exchange of hydrated ions, in contrast to those in less open, more structured, exchangers like the zeolite minerals. In these minerals exchange is frequently controlled by the movement of bare, or partially hydrated, cations through the exchanger phase.[15]

Exchanges with strontium on ZrP

The ΔG° values in Table 2 suggest the following selectivity series for strontium uptake at 298 K; $Li^+ < Na^+ < K^+ < Cs^+ < Ca^{2+} < NH_4^+ < H_3O^+$.

The ΔH° and ΔS° values clearly show the increased influence of water in the exchange process in comparison to the caesium systems. The monovalent/divalent exchanges of strontium for Li, Na, K and Cs show how the replacement of the monovalent ion becomes progressively less favourable as the monovalent ion decreases in hydrated cation radius. This follows the expected effect that, in an open exchanger, cations with larger hydrated radii will be preferred. Entropy contributions to the free energies of exchange are unfavourable to the ingress of the smaller hydrated cation, in line with the previous conclusions summarised by Alberti.[3]

In the Ca/Sr exchange, both ions have the same hydrated

Table 2 Thermodynamic parameters for the exchange of strontium onto homoionic forms of ZrP

exchange	T/K	ΔG°/ kJ mol^{-1}	ΔH°/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}
Li/Sr	298	−4.6		−55
	313	−3.5	21	−56
	333	−2.5		−56
Na/Sr	298	−4.5		−52
	313	−3.2	−20	−53
	333	−2.5		−53
K/Sr	298	−4.0		−37
	313	−3.7	−15	−36
	333	−3.3		−35
Cs/Sr	298	−3.6		−35
	313	−3.4	−14	−34
	333	−3.3		−32
H[a]/Sr	298	18.6		35
	313	18.0	29	35
	333	17.3		35
NH_4/Sr	298	13.5		52
	313	12.7	29	52
	333	12.4		52
Ca/Sr	298	−3.5		−52
	313	−3.0	−19	−51
	333	−2.7		−49

[a] $H = H_3O^+$.

Table 3 Thermodynamic parameters for ion exchanges in amorphous ZrP, taken from past work

exchange	T/K	ΔG°/ kJ mol^{-1}	ΔH°/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}	ref.
H/Rb[a]	298	−0.34	−10.6	−34.3	9
	313	0			
H/Cs	298	−0.93	−9.1	−27.4	9
	313	−0.53			
Cs/K	293	1.35			9
Cs/Rb	293	0.34			9
H/Li	287	2.0	0	−6.07	10
H/Na	287	1.1	−2.70	−13.0	10
H/K	287	0.56	−5.70	−21.0	10
H/Cs	298	~0	−0.03		11
H/Li	298	1.87	−1.13	−12.4	12
H/K	298	0.90	−4.40	−4.2	12
H/Cs	298	−0.38	−4.47	−3.5	12
H/NH_4	287	−1.92	—	−24.0	13
H/Rb	287	−2.26	−9.74	−25.2	13
H/Cs	287	−2.86	−10.96	−28.3	13

[a] $H = H_3O^+$.

cation radius so their thermodynamic parameters are seen to be very similar.[14] When ammonium or hydronium ions are initially in the ZrP phase strontium uptake is relatively highly unfavoured. The ΔS° values recorded are in compliance with a hydrogen-bonding controlled process which in this case aids the release of H_3O^+ and NH_4^+ ions. It should be noted that the size of the hydrated ammonium ion is the same as that of potassium so differences in exchange parameters cannot be solely due to size considerations.

The observation of incomplete exchange in the Sr/Cs and Sr/Ca ion pairs is unusual and no simple explanation presents itself for this phenomenon.

Conclusions

The ability of the powdered ZrP used in this work to take in the caesium ion from aqueous solution has been demonstrated and confirms earlier studies on different forms of this material.[3] It would be expected to usefully scavenge Cs fission isotopes from waste solutions arising from storage pond water (high pH), and reprocessing (acid or ammonium ion containing). The presence of lithium ions, as in many nuclear reactor circuits, would not be deleterious to Cs exchange.

The removal of strontium radioisotopes from similar aqueous environments could be expected to be much less successful when acid or alkaline ammonium conditions are encountered. The presence of sodium or lithium ions would be much less critical. It would seem that potassium would interfere with caesium exchange more than strontium, and that calcium ions could be tolerated in strontium solutions. As a final comment, this material would not be expected to be used in columns. It should be compatible for use in ultrafiltration and fluidised bed systems or, perhaps, in a batch mode as a 'precipitant'.

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References

1 C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
2 J. E. Cross and E. W. Hooper, in *Ion Exchange for Industry*, ed. M. Streat, Ellis Horwood, Chichester, 1988, p. 457.
3 G. Alberti, in *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press Inc., Boca Raton, FL, 1982, p. 1.
4 M. Zamin, T. Shaheen and A. Dyer, *J. Radioanal. Nucl. Chem.*, 1994, **182**, 323.
5 M. Zamin, T. Shaheen and A. Dyer, *J. Radioanal. Nucl. Chem.*, 1994, **182**, 335.
6 M. Zamin, T. Shaheen and A. Dyer, *J. Radioanal. Nucl. Chem.*, 1994, **182**, 345.
7 Data Sheet, Magnesium Elektron Ltd., Clifton Junction, Swinton, Manchester.
8 M. Zamin, PhD Thesis, University of Salford, 1991.
9 C. B. Amphlett, P. Eaton, L. A. McDonald and A. J. Miller, *J. Inorg. Nucl. Chem.*, 1964, **26**, 297.
10 G. H. Nancollas and B. V. K. R. A. Tilak, *J. Inorg. Nucl. Chem.*, 1968, **31**, 3643.
11 J. P. Harkin, G. H. Nancollas and R. Paterson, *J. Inorg. Nucl. Chem.*, 1964, **26**, 305.
12 E. M. Larsen and D. R. Vissers, *J. Phys. Chem.*, 1960, **64**, 1732.
13 L. H. Baetsle, *J. Inorg. Nucl. Chem.*, 1963, **25**, 271.
14 A. L. Horvath, *Handbook of Aqueous Electrolyte Solutions*, Ellis Horwood, Chichester, 1985.
15 A. Dyer, in *Inorganic Ion Exchangers in Chemical Analysis*, ed. M. Qureshi and K. G. Varshney, CRC Press Inc., Boca Raton, FL, 1991, p. 33.

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