

The use of zeolites for the treatment of radioactive waste

A. DYER AND K. Y. MIKHAIL

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

ABSTRACT. The uptake of ^{137}Cs and ^{90}Sr on to synthetic zeolite A has been studied. The use of a combined barium exchange followed by a relatively mild heat treatment has been shown to fix the isotopes within a collapsed zeolite structure. Leaching experiments using deionized and simulated sea and pond waters were carried out on zeolite compacts and zeolite/cement composites. They demonstrated the effectiveness of the calcination and cement containment. Some comments on the interpretation of leach test data are made.

KEYWORDS: radioactive waste, zeolite, cement.

THE zeolites are a class of aluminosilicate minerals with unique ion-exchange selectivities and a known resistance to radiation. These properties have encouraged extensive studies into their use in the treatment of radioactive waste.

Recently 'clean-up' investigations, concerned with zeolites, have concentrated largely on the application of natural zeolites particularly those with high Si content like clinoptilolite (Mercer and Ames, 1978), but currently synthetic zeolites have been employed successfully in, for example, the Three Mile Island aftermath (Collins *et al.*, 1982).

In some ways synthetic zeolites can be the preferred exchanger, despite a higher cost, because the supplies of natural minerals can vary in quality and more importantly a variation in geologic occurrence can cause subtle selectivity alterations (Dyer and Mikhail, unpubl.). Synthetic zeolites offer also the potential to advantageously manipulate their properties. This paper considers simple chemical ways whereby radioactive Cs and Sr species might be fixed within a zeolite matrix and the effectiveness in this treatment when isotopically loaded zeolites are contained in cement composites. The effectiveness is quantified by leach experiments on zeolites and zeolite/cement composites. The synthetic zeolite studied is zeolite A which is readily available in powder and pellet form and has been used successfully at TMI (Collins *et al.*, 1982). This zeolite is known to lose stability when exchanged with several cations, and with Ba in particular

(Dyer *et al.*, 1971), so that this property suggests a way of fixing isotopes in zeolites prior to disposal via the standard procedures of containment into cements or glasses (Matsuzuru and Ito, 1978; Siemens *et al.*, 1982) perhaps without an expensive high temperature calcination step (Goto *et al.*, 1982).

Experimental

Materials

The A zeolite used was supplied by Laporte Industries, Widnes, Cheshire. It was in its sodium form (4A), as a powder and as compacted zeolite crystals held by a clay-binder in the form of spheres (1.4-2.0 mm). The isotopes used were as supplied by Amersham International. All other chemicals were of GPR purity or better.

Characterization

As received zeolite A was characterized by X-ray powder diffraction (XRD) and by thermal analyses. These techniques were used to monitor changes in the zeolite caused by various treatments. Some elemental analyses were carried out by electron probe microanalysis.

Experiments on powdered zeolite

(i) Amounts of 4A powder were placed in contact with simulated pH 11.4 pond water (150 mg Na_2CO_3 , 200 mg NaOH in 1 l deionized water) maintaining a liquid/solid ratio of 10:1. The pond water was labelled with ^{137}Cs or ^{90}Sr (carrier free). After 24 hrs. stirring at room temperature (RT) the samples were separated from the liquid phase, dried and then treated further with BaCl_2 solution of differing concentrations at RT for 24 hrs. (with stirring) and at a liquid/solid ratio of 20:1.

(ii) A series of unlabelled NaBaCs A zeolites was prepared in a similar manner to the above (using 0.01M CsCl) and the extent of exchange monitored by the appearance of Na in solution as determined by flame photometry.

(iii) 'Back exchange' experiments were carried out on samples from (i) and (ii) which had been heated in air for 24 hrs. at different temperatures. In each case the uptake of ^{22}Na from 1.0 M NaCl was taken as a measure of 'back-exchange'. Equilibrium times were 2 days at least. Recoveries of ^{137}Cs were monitored as appropriate.

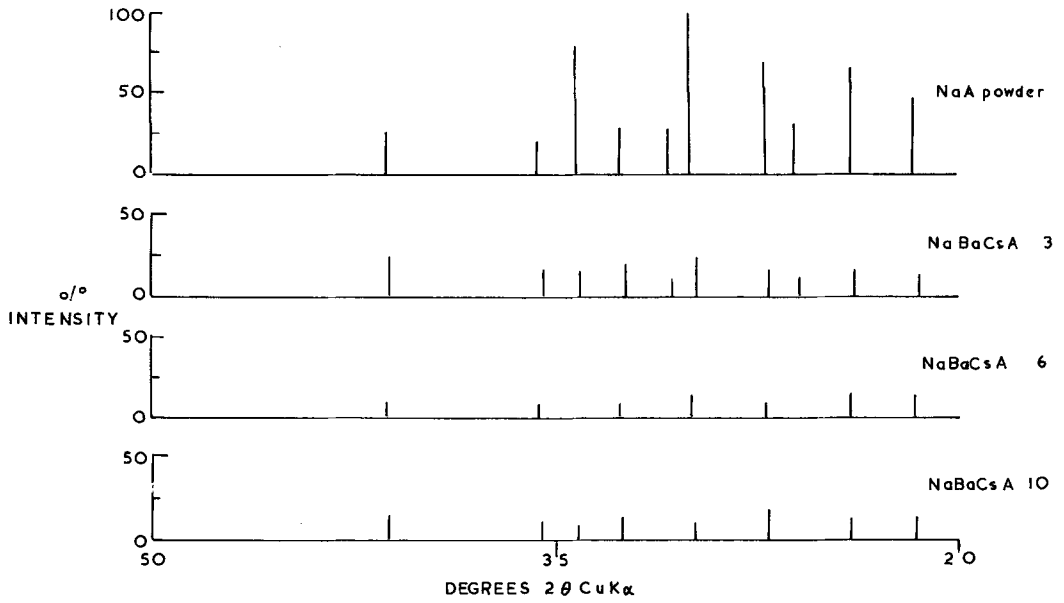


FIG. 1. XRD patterns of Na Ba Cs A powder prepared by using 3, 6, and 10 ml of 0.5 M BaCl_2 per gram zeolite (referred to as 3, 6, and 10 in subsequent diagrams).

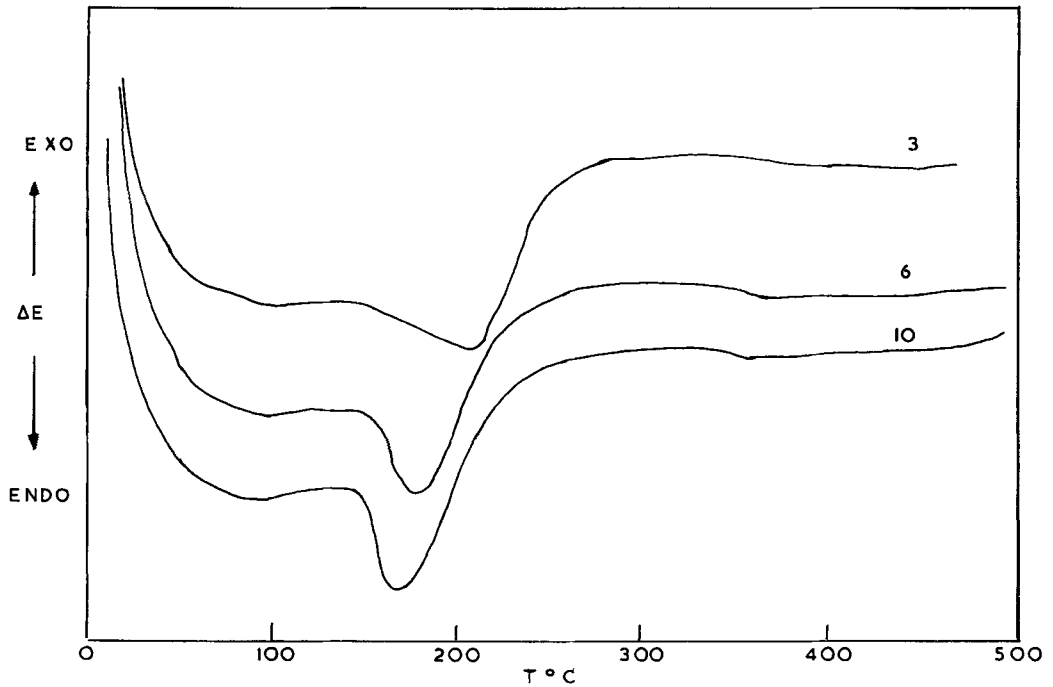


FIG. 2. DSC traces of samples prepared as fig. 1.

Experiments on zeolite spheres

(i) Breakthrough curves were constructed to measure the uptake of 137-Cs and 90-Sr on to spheres from simulated pond water. The columns contained 3 g of spheres in a glass column (6.75 mm i.d.) and the flow rate was 24 ml hr⁻¹.

(ii) Experiments were carried out to discover the optimal conditions for Ba treatment of the spheres beyond breakthrough to minimize 137-Cs loss. These were column experiments and the pH was varied as well.

(iii) Spheres containing isotopes were heated in air and vacuum, after various treatments, to check the validity of the powder experiments.

Containment experiments

(i) Zeolites from column experiments were calcined at 300 °C and then mixed with cement (OPC) to a ratio of water/cement at 0.4 (see Table I). After sufficient mixing the cement paste was poured into a polythene container and left for 24 hrs. at room temperature (RT). It was then taken from the container and air cured for 24 days. Compressive strengths and density measurements were made in triplicate.

Table I. Properties of zeolite/cement composites (water/cement ratio = 0.4) cured in air for 28 days

Zeolite/zeolite + cement ratio	Density g cm ⁻³	Compressive strength kg m ⁻² 10 ¹
0.10	1.88 ± 0.02	321 ± 15
0.15	1.87 ± 0.02	308 ± 17
0.20	1.86 ± 0.02	235 ± 17
Cement control	1.90 ± 0.03	440 ± 8

(ii) Leach tests were carried out, by a modified IAEA method (Hespe, 1971), on composites containing a 0.15 zeolite/zeolite and cement weight ratio. Cured samples were immersed in 100–200 ml leachant in plastic vessels held, with frequent agitation, at 25 °C in a water bath. The leachants were renewed daily for 3 days, weekly for 3 weeks, and then once per month for 3 months. The leachants were deionized water, synthetic sea water (Taylor and Kuwairi, 1978), see Table II, and simulated

Table II. Composition of synthetic sea water

Component	Content (wt. %)
NaCl	2.3480
MgCl ₂	0.4981
Na ₂ SO ₄	0.3917
CaCl ₂	0.1102
KCl	0.0664
NaHCO ₃	0.0192
KBr	0.0096

pond water. Tests were also made on zeolite spheres loaded with 137-Cs without cement. Some electron probe microanalyses on leached samples were carried out.

(iii) *Measurement of radioactivity.* All measurements were carried out by determining Cerenkov radiation from aqueous solution in the tritium channel of a Nuclear Chicago Mark II liquid scintillation counter. Polythene vials were used throughout.

Results and Discussion

Zeolite powder experiments

The preliminary experiments described showed that 0.5 M BaCl₂ solution was suitable for treating 137-Cs-containing zeolites in that a minimum of isotope was displaced even when the initial Cs exchange was 0.01 M. Test experiments demonstrated that sodium was also exchanged from the zeolite by the Ba²⁺ treatment.

Table III. Effect of replacement of Na from Na Cs A by Ba

ml g ⁻¹ of 0.5M BaCl ₂ used	% Na replaced	% Wt. loss to 500°C (TG)	Endotherm T °C from DSC
1.99	44.2	17.9	208
2.99	54.3	17.0	205
3.98	64.9	16.8	192
5.98	72.7	16.5	175
7.98	73.4	16.0	170
9.95	74.4	15.5	165

The effect of treatment was monitored by XRD (fig. 1) and thermal analysis (see fig. 2 for DSC and Table III for TG results). The loss of intensity in the XRD photographs was an artefact of the presence of Ba (a high X-ray absorber) and not a consequence of lattice collapse. This phenomenon has been discussed in detail elsewhere (Dyer *et al.*, 1970) and the ‘back-exchange’ experiments carried out here confirmed that Na could replace Ba from the treated powders.

Fig. 3 shows XRD patterns after heat treatments. These results, and further characterization by DSC (fig. 4), showed that lattice collapse had occurred. This was confirmed by ‘back-exchange’ experiments as can be seen from figs. 5(a) and (b).

These experiments demonstrated that 137-Cs could be fixed into A zeolite by barium exchange followed by heat treatment. They were used to predetermine the conditions in which zeolite spheres were used to take up both 137-Cs and 90-Sr.

Zeolite sphere experiments

Fig. 6 shows the effect of (i) volume of 0.01 M CsCl passed through a column (ii) volume of 0.5 M

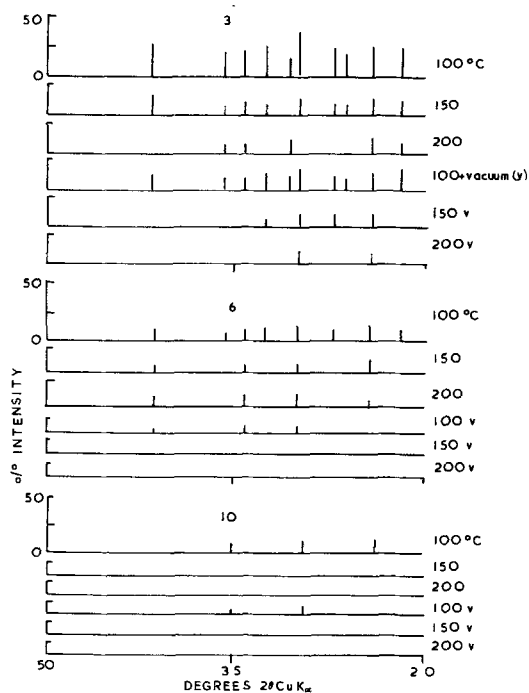


Fig. 3. Effect of heat and vacuum treatment on Na Ba Cs A powders as shown by XRD patterns.

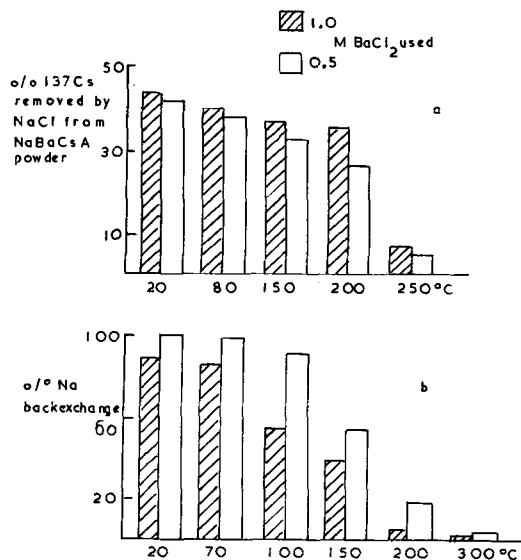


Fig. 5. (a) Percentage 137-Cs removed from Na Ba Cs A powders prepared with both 1.0 M and 0.5 M BaCl₂ solution and preheated to various temperatures. (b) Percentage Na back exchanged from the same samples.

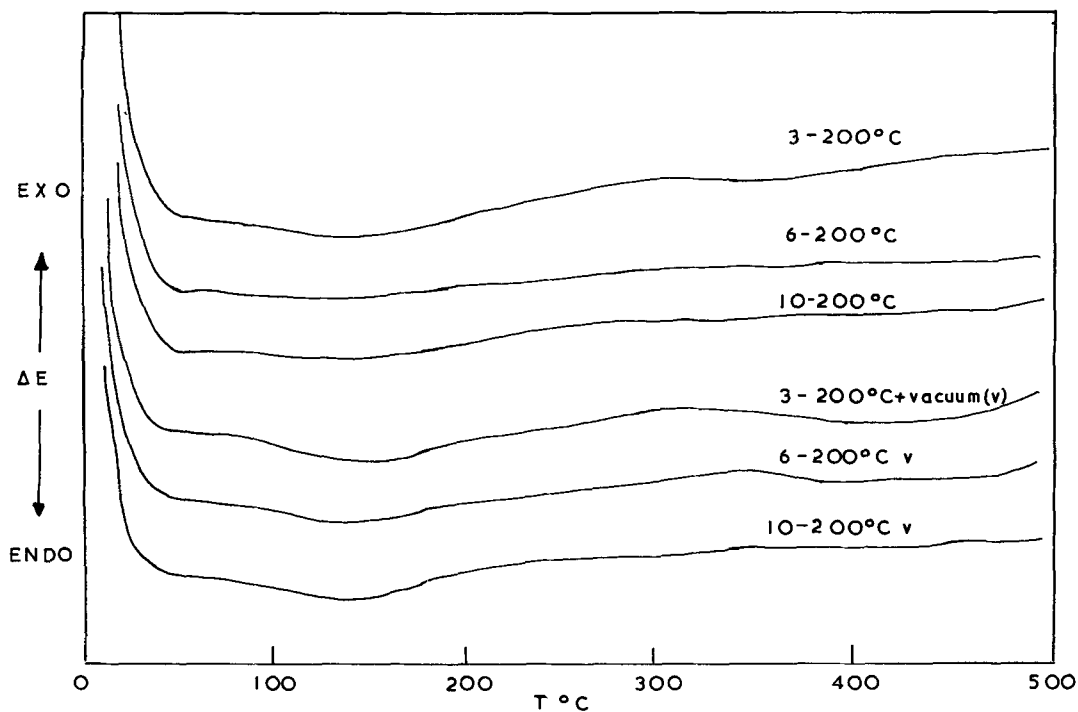


Fig. 4. DSC traces of Na Ba Cs A powders after heat and vacuum treatments.

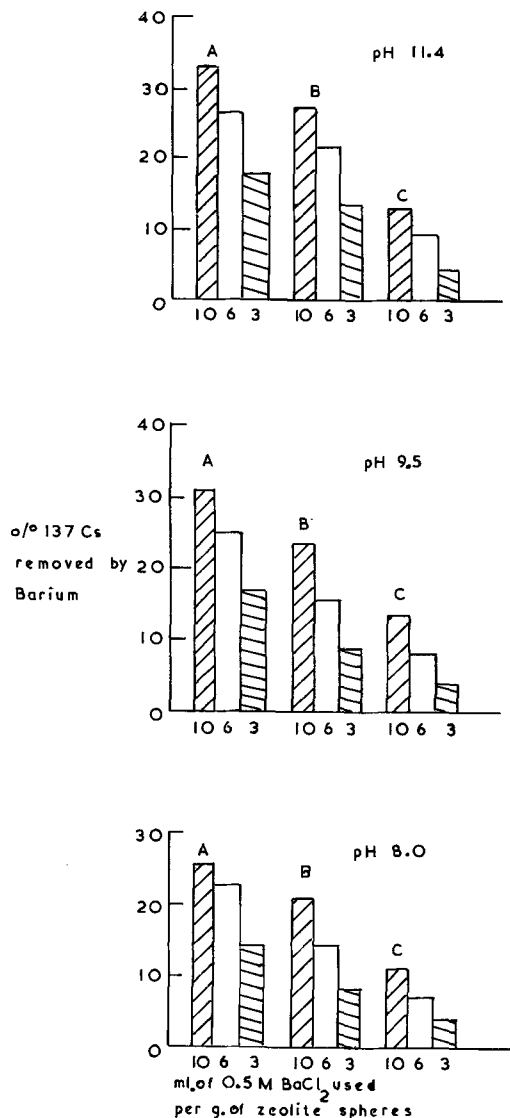


FIG. 6. Effect of various parameters on ¹³⁷-Cs removal from Na Ba Cs A spheres (A = 150, B = 75, and C = 15 mls of 0.01 M CsCl passed through the bed of zeolite).

BaCl₂ solution subsequently passed (iii) variation in pH of 0.01 M CsCl.

It can be seen that pH variation has little effect and that the replacement of ¹³⁷-Cs is a function of BaCl₂ treatment as anticipated. The conditions used to prepare samples for leach testing are summarized in Table IV.

Heat and vacuum treatments of the spheres monitored by DSC showed that again vacuum had

Table IV. Typical column operating conditions

Influent solutions -	
(a) labelled 0.01M CsCl, or carrier free ¹³⁷ -Cs	
or carrier free ⁹⁰ -Sr	
(b) deionized water wash	
(c) 30 ml of 0.5M BaCl ₂	
Influent pH	11.4
Influent flow rate	24 ml hr ⁻¹ (12 ml hr ⁻¹ for BaCl ₂)
Temperature	ambient
Wt. of zeolite spheres	3 g
Column dimension (i.d.)	6.75 mm
Free column volume	1.5 ml

little effect and that treatment at 200 °C caused lattice collapse. It was decided to use 300 °C without vacuum to treat zeolites from the column experiments prior to containment (fig. 7).

The breakthrough curves observed are shown in fig. 8. The free column volumes were the void space observed in the bed of 3.0 g of zeolite pellets packed into the column of internal diameter quoted. That of ¹³⁷-Cs is satisfactory but those for ⁹⁰-Sr not so. In fact most of the activity detected in the effluent was later shown to be ⁹⁰-Y and further work is in progress on this system.

Leach experiments

(i) Analyses of leached samples showed that leaching with pond and sea waters had little effect on the samples (Table V) as judged by the SiO₂/Al₂O₃ ratio. The calcined sample seemed to show

Table V. Composition of the Zeolites after Pond Water and Sea Water Treatment

Content, %	NaBaCs A		Calcined NaBaCs A	
	a	b	c	d
Al ₂ O ₃	21.5	23.2	22.8	21.7
SiO ₂	33.6	36.2	35.2	33.5
K ₂ O	11.47	0.65	1.06	0.81
BaO	15.5	16.9	16.6	15.9
CaO	1.23	1.41	1.32	1.30
TiO ₂	0.16	0.19	0.18	0.17
Fe ₂ O ₃	0.50	0.54	0.43	0.36
HgO	0.17	1.35	1.27	1.20
NaO	3.27	5.57	3.55	3.45
SiO ₂ /Al ₂ O ₃	2.66	2.65	2.62	2.63

Samples a, c treated with pond water

Samples b, d treated with sea water

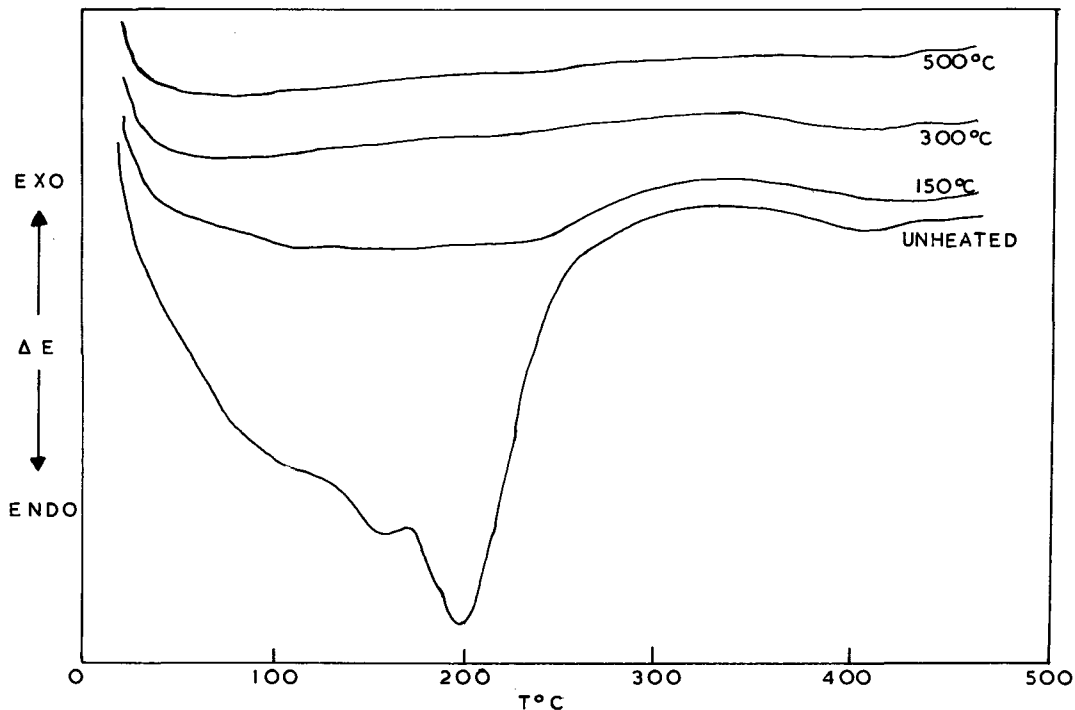


Fig. 7. DSC traces of Na Ba Cs A spheres (30% breakthrough) after various heat treatments.

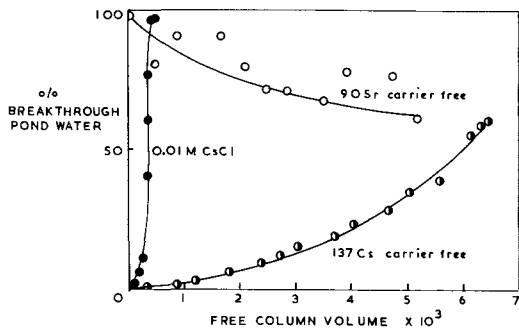


Fig. 8. Breakthrough curves for ^{137}Cs and $^{90}\text{Sr}/\text{Y}$ on NaA spheres.

little or no ion uptake as evidenced by the lack of increase in Na and Mg content with sea water treatment.

(ii) Fig. 9 summarizes the sea water leaches of ^{137}Cs -containing species. The effect of calcination is seen clearly and containment also reduces the leach rate. Pond water treatments (fig. 10) follow a similar pattern except that the leach from calcined

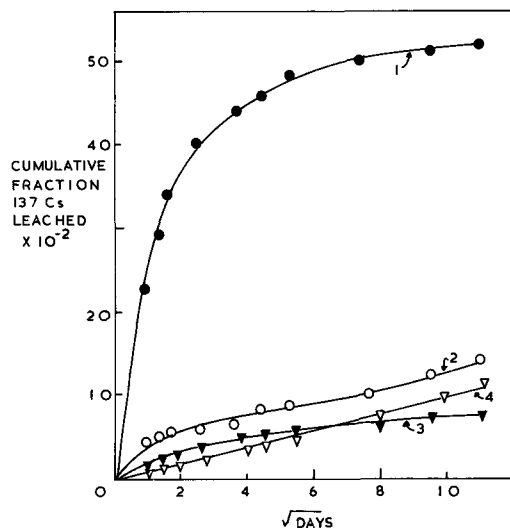


Fig. 9. Sea-water leach of Na Ba Cs* A spheres (75% breakthrough) and zeolite/cement composites (prepared using 0.01 M CsCl). (1) Uncalcined zeolite. (2) Calcined zeolite. (3) Calcined zeolite/cement. (4) Uncalcined zeolite/cement.

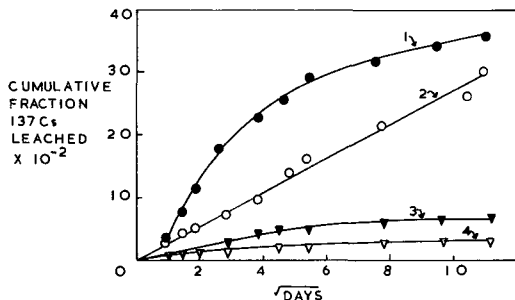


FIG. 10. Pond water leach of Na Ba Cs* A spheres (75% breakthrough) and zeolite/cement composites (prepared using 0.01 CsCl). (1) Uncalcined zeolite. (2) Calcined zeolite. (3) Calcined zeolite/cement. (4) Uncalcined zeolite/cement.

NaBaCs*A spheres is quite high. This may reflect the well-known solubility of zeolite A at high pH as reported by Guth *et al.* (1980) although the analyses and other evidence presented here do not show any large solubility effects, presumably the appearance of tracer ¹³⁷Cs is a good indication of a small solubility. Deionized water leaches (fig. 11) show that release of activity is proceeding beyond 3 months except in the calcined-contained sample which has reached a form of equilibrium. These results confirm recent criticisms by Roy (1981) of the 'absurdity' of leach data arising from deionized water treatment. Fig. 12 shows the similar effects observed on samples prepared under carrier free conditions.

Despite the poor breakthrough curve observed for ⁹⁰Sr uptake containment and leach tests were made on A containing ⁹⁰Sr. The results are summarized in fig. 13 and show a significantly lower leach rate than those for ¹³⁷Cs. The effect of

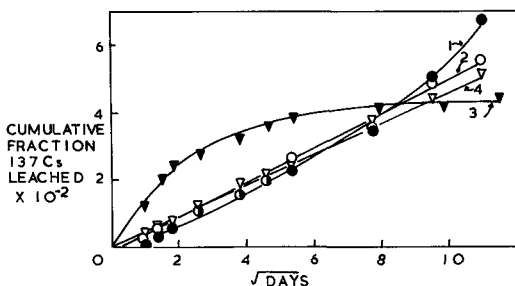


FIG. 11. Deionized water leach of Na Ba Cs* A spheres (75% breakthrough) and zeolite/cement composites (prepared using 0.01 CsCl). (1) Uncalcined zeolite. (2) Calcined zeolite. (3) Calcined zeolite/cement. (4) Uncalcined zeolite/cement.

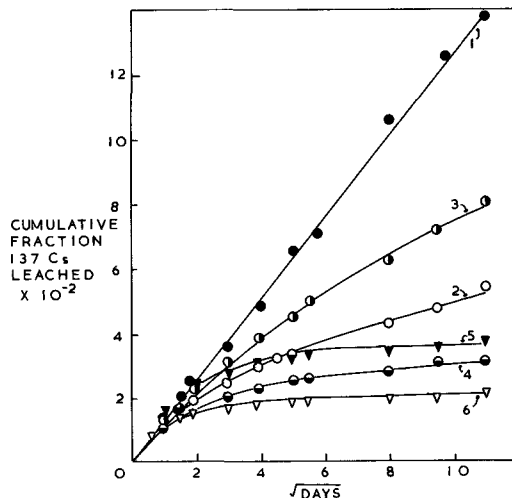


FIG. 12. Leaches of Na Ba Cs* A sphere (30% breakthrough) and zeolite/cement composites (prepared from 'carrier free' solution). (1) Uncalcined zeolite/cement sea water leach. (2) Calcined zeolite/cement sea water leach. (3) Uncalcined zeolite/cement deionized water leach. (4) Calcined zeolite/cement deionized water leach. (5) Uncalcined zeolite/cement pond water leach. (6) Calcined zeolite/cement pond water leach.

barium treatment with a calcination step is again evident.

Interpretation of leach curves

The interpretation of curves such as those in fig. 9 often has been based upon its elucidation as a fast process followed by a slow process. This approach can be misleading and any attempt to apply this reasoning to the results in fig. 11 will clearly demonstrate this. One problem seems to arise from the calculation of 'diffusion' rates from cement composites, using the dimensions of the composite to feed into a suitable equation (Matsuzuru and Ito, 1978). We would argue that this is inappropriate if the rate controlling step is from the zeolite particle.

The diffusion of species from zeolites has been studied widely (e.g. Dyer and Townsend, 1973) and their kinetics interpreted on the basis of the application of the Carman-Haul equation describing the movement of a species from a sphere of known volume into a limited, well-stirred, volume.

With this premise in mind certain of the results herein were analysed by a computer program written for solutions to the Carman-Haul equation and they are presented in fig. 14.

The results show that, in one of the cases examined, the diffusion coefficients are little affected by the presence of cement as expected if the

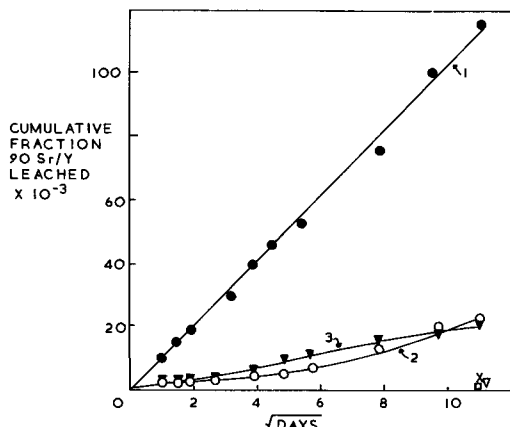


FIG. 13. Leaches of Na Ba Sr* A (75% breakthrough) zeolite/cement composites (prepared from 'carrier free' solution). (1) Uncalcined sea water leach. (2) Calcined sea water leach. (3) Calcined deionized water leach. X uncalcined de-ionized water leach; ∇ uncalcined pond water leach; \square calcined pond water leach.

rate determining step was release from the zeolite alone. In the other case a discrepancy is noted which can be explained as arising from a cement/zeolite interaction which does not, necessarily, mean that the premise is incorrect. Further work in this area is in progress.

Conclusion

The treatment of zeolite A containing both ^{137}Cs and ^{90}Sr by a barium solution followed by a calcination at 300°C successfully reduces the

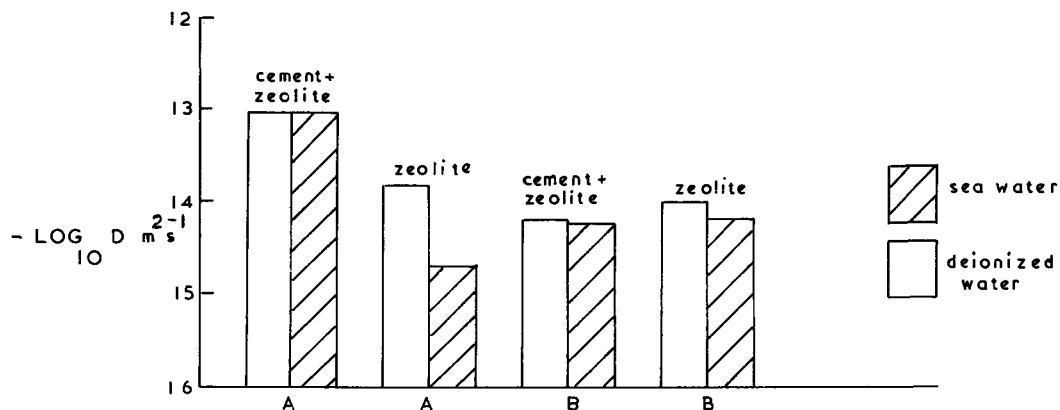


FIG. 14. Diffusion coefficients calculated by Carman-Haul equation for (A) calcined Na Ba Cs* A and (B) calcined natural zeolite loaded with ^{90}Sr .

leach rate of the isotopes from both the zeolite and equivalent zeolite/cement composites.

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