

Application of commercial zeolite-13X in the treatment of simulated and actual radioactive effluent containing caesium

P K Sinha*, K B Lal, P K Panicker, R V Amalraj & V Krishnasamy*
CWMF, NWM Group, BARC, Kalpakkam 603 102

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The removal of Cs^+ ions from aqueous solution and radioactive effluent, by ion-exchange with Na ions of indigenously available synthetic zeolite-13X, has been studied. The zeolite has been characterized with respect to chemical composition, stability to acid, XRD and IR spectral patterns. Batch studies on the kinetics of the Cs-Na exchange process indicate that at higher Cs concentrations in solution, such as 50 mM and 100 mM Cs, 'particle diffusion' is the controlling factor, as inferred from the observed linearity in the Bt-t plots. The linearity is absent in case of lower concentrations where the process may be controlled by 'film diffusion'. The K_d value are of the order of a few thousands to a few tens of ml/g, depending on the initial concentration of the Cs ions. Agitation affected the kinetics in such a way that the time required for attainment of equilibrium is reduced from about 48 h in an unstirred solution to 2 h in a thoroughly stirred solution. Equilibrium studies, carried out under isonormal solution conditions at two different total (Cs + Na) ionic concentrations, 0.025 N and 0.1 N, resulted into 'adsorption isotherms' showing replacement of 35% and 50% of the exchangeable Na^+ ions for the two cases, respectively. The column studies, conducted with a pure solution of ^{137}Cs in ordinary water and a 2g (= 3 ml) column of the zeolite, led to a removal of as high as 99.9% ^{137}Cs . When an actual radioactive waste solution, received from the Madras Atomic Power Station, Kalpakkam, and containing predominantly ^{137}Cs , is passed through a 1g (= 1.5 ml) bed of zeolite-13X, the per cent breakthrough is found to be less than 4% (96% removal) till the passage of 1000 bed volumes.

Among the numerous inorganic ion-exchangers, zeolites are considered to be very efficient and owing to their stability towards radiation and heat, their application to radioactive waste treatment has gained prominence. Chemically, they are aluminosilicates and are expected to be compatible with the cement or glass matrix, generally used for the fixation of the conditioned waste. Their rigid three-dimensional structure may also be considered for possible immobilization of the isotopes in the same matrix. These favourable factors have led to the large scale use of zeolites in various nuclear installations, including waste treatment plants¹⁻⁴.

Both natural and synthetic zeolites have been recommended for different applications in countries like USA, UK, Japan etc. Unfortunately, India does not have any rich, natural deposit of zeolites and only synthetic zeolites are commercially available. Some of them are supplied in powder form, unsuitable for column applications, while others are available as granules, prepared by using binders etc. A systematic study on the applicability of these indigenously

available zeolites as ion-exchangers to the treatment of radioactive liquid waste, was undertaken at the Centralised Waste Management Facility (CWMF), Kalpakkam. The present paper reports the results obtained in the studies on the removal of Caesium, using Zeolite 13X. The commercial sample of the zeolite was characterized and evaluated with respect to the kinetics and equilibrium of the uptake of Cs in batch tests. The nature of diffusion process, controlling the uptake of Cs, was investigated through these experiments. The column studies were also carried out with simulated and actual wastes to investigate its suitability for Cs removal.

Materials and Methods

The commercial sample of zeolite 13X, obtained in granular form containing binder (M/s Associated Cement Company, Thane, Bombay), was characterized with respect to chemical composition, stability to acid and its X-ray diffraction and infrared spectral patterns. The Si and Al contents were determined colorimetrically following the molybdate blue complex (wavelength 815 nm) and Alizarin Red-S complex (wavelength 475 nm) methods, respectively, in an alkaline solution of the zeolite,

*Department of Chemical Engineering, Anna University, Madras 600 025

prepared by fusing it with NaOH at 500°C and dissolving the fused mass in 1:1 HCl and water. The Na ion was determined by atomic absorption spectrophotometry in an acidic solution, prepared by dissolving the zeolite in a mixture of HF, H₂SO₄ and HNO₃. The loss on ignition (LOI), representing the moisture and volatile content, was estimated by heating the zeolite at 500°C for 2 h and calculating the weight loss.

In order to study the stability of zeolite 13X in acidic medium, 1 g of the zeolite of grain size 0.25-0.30 mm was immersed in 50 ml nitric acid solutions of varying concentrations in the range 0.0001 *N* - 2.0 *N* for 24 h. The supernatant samples were subsequently analysed for residual acidity, Na⁺ and Al³⁺ contents, while the solid was weighed after washing with demineralised water and drying under IR lamp.

The XRD and IR spectral studies were carried out to confirm the structure and the type of zeolite by comparison with the patterns reported for zeolite X in literature.

In batch experiments, 0.5 g of the zeolite of grain size 0.25-0.30 mm, was contacted in a water bath maintained at ambient temperature 29 ± 1°C, with 100 ml of CsCl solutions of different concentration and spiked with 0.005 mCi/l of radioactive ¹³⁷Cs. The contact was made under thoroughly stirred as well as unstirred conditions. The samples of the supernatant, collected after preset time-intervals, were analysed for Cs by counting the gamma activity in a 2" × 2" NaI (TI) scintillation counter, connected with a multichannel analyser.

The isonormal solutions of CsCl + NaCl, containing varying amounts of Cs and Na but a constant total ionic concentration viz., 0.025 *N* in one case and 0.1 *N* in the other, were prepared. As mentioned in the above section, 100 ml of these solutions were contacted at ambient temperature with 0.5 g of the zeolite of grain size 0.25-0.30 mm, under thoroughly stirred conditions for 2 h, considered to be the adequate time for equilibrium. After the contact, the supernatants were analysed for both Cs and Na by atomic absorption spectrophotometry.

Through a packed bed containing 2 g of the zeolite (bed volume = 3 ml), was passed a pure solution of ¹³⁷CsCl in ordinary water (specific activity = 0.003 mCi/l) at a flow rate of 6 ml/min, using a peristaltic pump. The samples of the treated effluent were collected at fixed time-intervals and analysed for Cs content by counting.

Another experiment was carried out with an actual liquid waste, received from the Madras Atomic Power Station (MAPS), Kalpakkam, and containing predominantly ¹³⁷Cs in addition to other radio-

isotopes (initial specific activity = 0.001 mCi/l, as measured with a Geiger Muller counter). The waste was passed through a column of 1 g (bed volume 1.5 ml) of zeolite 13X, at a constant flow rate of 2 ml/min, using a peristaltic pump. The samples of the treated effluent were collected at definite time intervals and analysed for gross radioactivity using G.M. counter. The waste was also characterized with respect to relevant parameters, before and after treatment with the zeolite.

Results and Discussion

By chemical analysis of zeolite 13X, the weight percents of Si, Al and Na were determined as 14.2, 12.0 and 10.9% respectively. The corresponding oxides would be 30.4, 22.7 and 14.7%. The LOI content was found to be 16.4%. As the oxides and the LOI content add up to only 84.2%, the balance 15.8% was attributed to binder and other non-volatile impurities. From the Na content, the theoretical ion-exchange capacity was calculated to be ca 4.74 meq/g. The observed Si/Al ratio of ca 1.2 indicates¹ that the zeolite may not be stable at extremes of pH values. The experiments on stability of zeolite in nitric acid solutions indicated that it was stable upto acidity 0.01 *M* or below (pH 2 or above), as the loss in weight of zeolite was only about 1.5% (Table 1). At higher acidity, the zeolite disintegrated rapidly as indicated by the substantial loss in weight. The reports¹ also indicate that zeolite is not stable in highly alkaline solution having pH 12 and above. The XRD and IR spectra were found to be in close agreement with those reported in literature for zeolite-X.

From the data on the residual concentration of Cs in the solution at equilibrium, the per cent removal of

Table 1—Stability of zeolite 13X in nitric acid

Molarity of nitric acid (M)	H ⁺ consumed from soln. (mM)	Na ⁺ released into soln.	Al ³⁺ released into soln. (mM)	Wt. loss of zeolite (%)
2.22	340	82	5.10	65.41
1.09	210	81	3.10	63.65
0.49	202	77	2.80	48.30
0.091	59	41	0.80	15.82
0.045	37	29	1.10	9.22
0.010	8.9	9.1	0.30	1.45
0.005	4.6	4.7	0.34	1.54
0.001	0.6	1.7	0.29	0.65
0.0005	0.5	1.6	0.35	0.08
0.0001	0.1	1.6	0.17	0.64

1 g 13X contacted with 50 ml nitric acid for 24 h

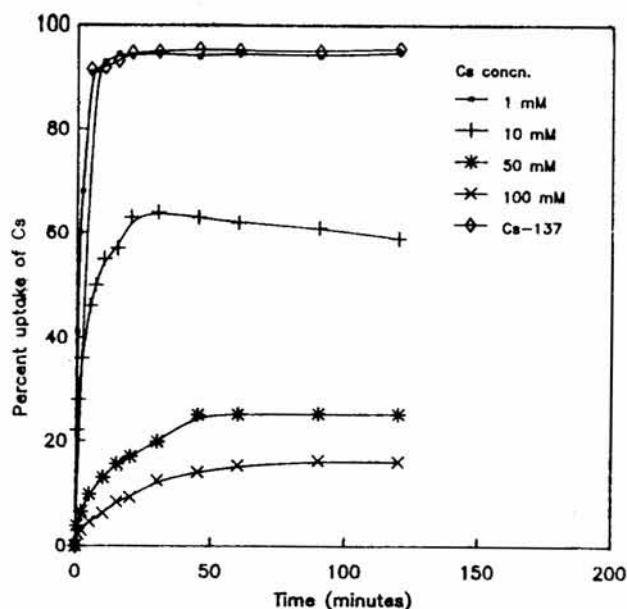


Fig. 1—Per cent removal of Cs with time at different concentrations by treatment with zeolite 13X - batch experiment under stirred conditions

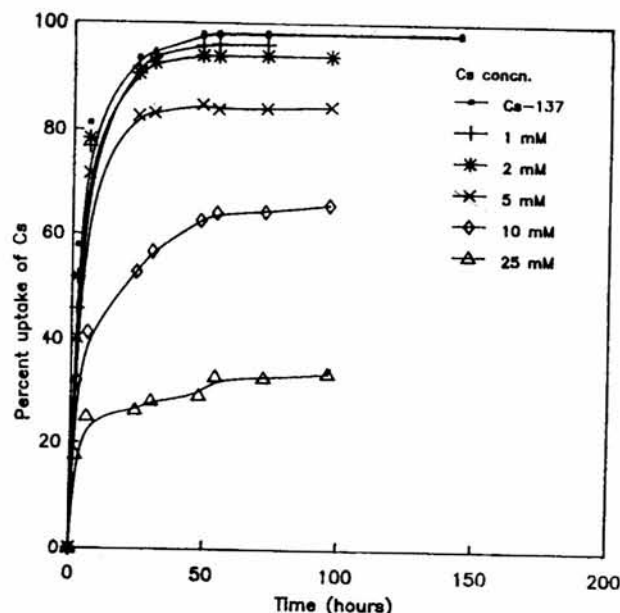


Fig. 2—Per cent removal of Cs with time at different concentrations by treatment with zeolite 13X - batch experiment under unstirred conditions

Cs was calculated at different concentrations of Cs, using the following equation

$$\text{Per cent removal} = 100 (C_{S_0} - C_{S_t}) / C_{S_t}$$

where C_{S_0} and C_{S_t} are the concentrations of Cs, initially and after time t .

The obtained data on per cent removal were plotted against time. Figures 1 and 2 present the graphs for contact under stirred and unstirred conditions, respectively. It may be seen from the figures that due to stirring, the time required for attaining equilibrium, as indicated by the position of the plateau, was reduced from 48 h to 2 h. Also the extent of removal decreased with increasing concentration of Cs in the solutions

From the values of per cent removal at equilibrium, the distribution coefficient (K_d) values were calculated using the following equation for contact under both stirred and unstirred conditions.

$$K_d (\text{ml/g}) = (C_{S_0} - C_{S_e}) \cdot V \cdot 1000 / C_{S_e} \cdot W$$

where, C_{S_0} and C_{S_e} are the initial and equilibrium concentrations of Cs, V is the volume of solution in litres and W is the weight of the zeolite in grams.

The K_d values were found to be dependent on the initial caesium concentration, for both stirred and unstirred contacts (Table 2).

From the ratio of fractions of caesium removed at any time t (Q_t) and at equilibrium (Q_e), the fractional attainment of equilibrium, F , at time t was determined. The kinetic equation governing particle controlled diffusion process is given as⁵

Table 2— K_d values for Cs on zeolite 13X, effect of concentration and stirring (batch test)

Conc. of Cs mM	K_d values (ml/g) (stirred)	K_d values (ml/g) (unstirred)
(¹³⁷ Cs+) 0	4244	5860
(do) 1	3436	5690
(do) 2	—	3440
(do) 5	—	1070
(do) 10	326	370
(do) 25	—	100
(do) 50	66.7	—
(do) 100	38.1	—

0.5 g zeolite + 100 ml spiked Cs-chloride soln.

$F = Q_t / Q_e = 1 - (6/\pi^2) \sum (1/n^2) \exp(-n^2 Bt)$
where, $B = \pi^2 D_z / r^2$, D_z = effective diffusion coefficient of ions through the zeolite beads, r = radius of the beads, t = time and n = constant; the summation is for $n = 1$ to ∞ .

The corresponding value of Bt for each F was obtained from literature⁶ and then Bt - t plots drawn, as shown in Figs 3 and 4 for contact under stirred and unstirred conditions, respectively. It may be seen that the Bt - t plots for lower concentrations for stirred contact (Fig. 3) and all concentrations for unstirred contact (Fig. 4) do not show any linearity. This indicates that particle diffusion cannot be the controlling phenomenon under these conditions. However, for higher concentration of Cs (0.05 N and

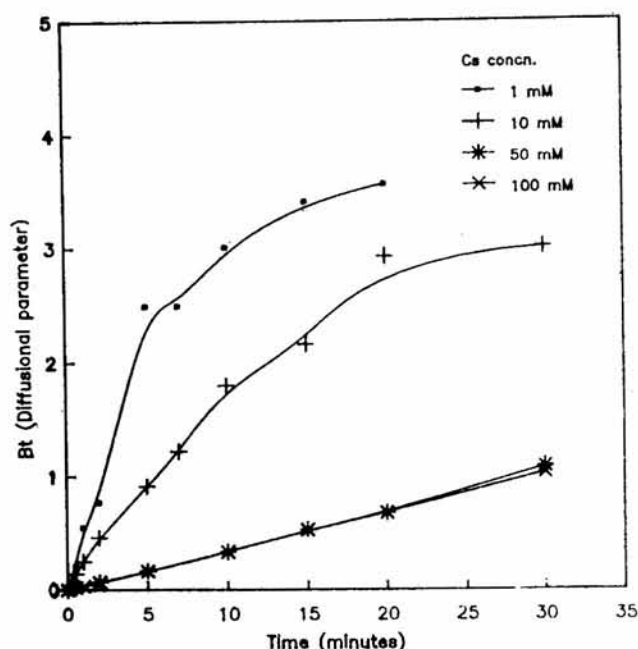


Fig. 3—Bt-t plots showing the nature of diffusion process controlling the uptake of Cs ions by zeolite 13X under stirred conditions

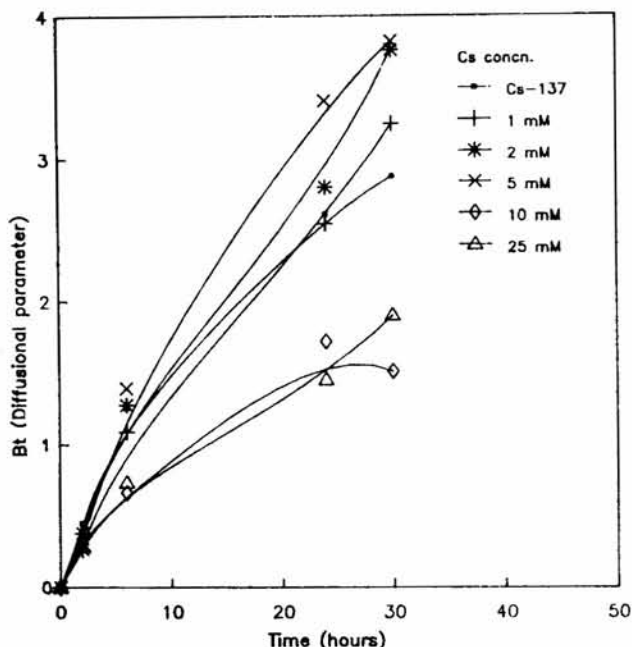


Fig. 4—Bt-t plots showing the nature of diffusion process controlling the uptake of Cs ions by zeolite 13X under unstirred conditions

0.1 *N* Cs) and contact under stirred condition (Fig. 3), the Bt-t plots were found to be linear, passing through the origin indicating that under these conditions, the process was controlled by diffusion of ions through the particles⁶. The linear slope of the straight line gives $B (= 0.0337 \text{ min}^{-1})$, which was used for calculating $D_z (= 1.08 \times 10^{-8} \text{ cm}^2/\text{s})$. This value of D falls in between organic and some inorganic exchangers^{5,8}. For dilute solutions and unstirred contact, the process may be governed by film diffusion.

Using the data obtained on Cs and Na concentration in the liquid, the equivalent ionic fractions of Cs in the liquid phase, S_{Cs} , and in the solid phase, Z_{Cs} , were calculated as the ratio of ionic equivalent of Cs in a given phase (solid or liquid) to the total ionic equivalent of Cs + Na in that phase. The Z_{Cs} values were then plotted against S_{Cs} values to get the adsorption isotherms at ambient temperature, for thoroughly stirred solutions at two different total ionic concentrations of Cs + Na, 0.025 *N* and 0.1 *N*, as presented in Fig. 5.

The maximum values of Z_{Cs} are ca 0.35 for 0.025 *N* and ca 0.50 for 0.1 *N* total concentrations, indicating exchange of 35 and 50% respectively, of the available Na ions in the zeolite at the two normalities. The latter value of 50% is found to be smaller than the 62-65% reported by Sherry⁷ for the same 0.1 *N* Cs + Na solution and zeolite X, which may be attributed to

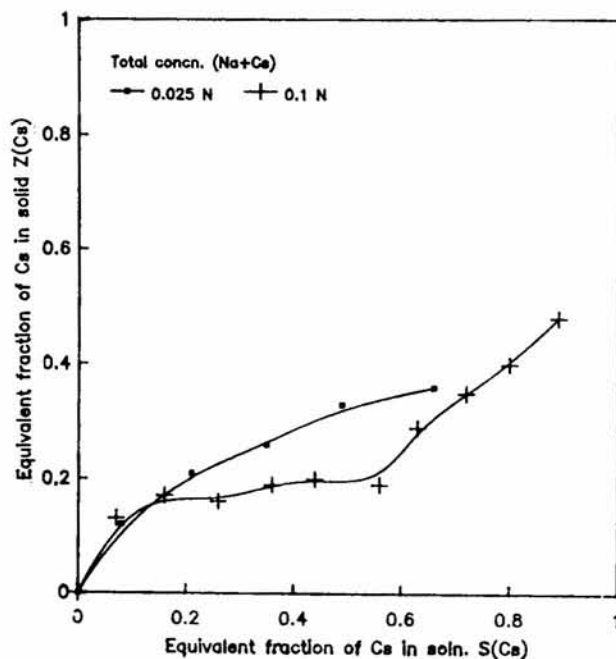


Fig. 5—Adsorption isotherms for the uptake of Cs by zeolite 13X for two isonormal solutions of total concentrations (Cs + Na) as 0.025 *N* and 0.1 *N*

the impurities (binder etc.) present in our commercial sample.

Figure 6 gives the per cent breakthrough for Cs when a pure solution of ¹³⁷Cs in ordinary water was passed through a 3 ml bed of zeolite-13X, as well as when an actual waste from a power reactor (MAPS)

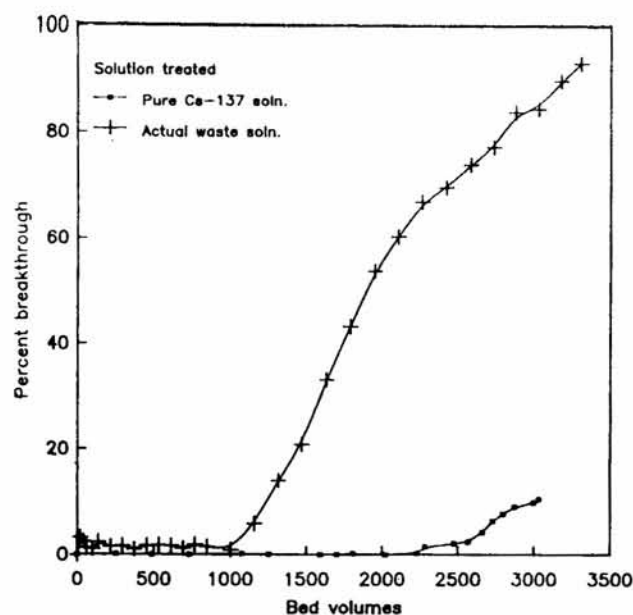


Fig. 6—Per cent breakthrough curve for the uptake of Cs by zeolite 13X column from a simulated and an actual waste solution

was treated by a 1.5 ml bed of zeolite 13X. It may be seen from the figure that in the first case, till the passage of 2000 bed volumes of the solution at a flow rate of 6 ml/min, the treated effluent contained very low activity and the per cent removal was of the order of 99.9%. The removal declined to 98% and 96% respectively, at the passage of 2500 and 3000 bed volumes of the solution. In the second case, however, the per cent removal was only 96-97% till the passage of about 1000 bed volumes, even at a small flow rate of 2 ml/min. This is attributed to the presence of other dissolved cationic impurities in the waste. Table 3 gives the relevant characteristics of the waste before and after treatment of 1000 bed volumes of the waste, by zeolite 13X.

These studies indicate that zeolite 13X can be used for the treatment of radioactive liquid waste containing Cs isotopes. The per cent removal of Cs and K_d values depend on the concentration of Cs ions in solution. Stirring reduces the time to reach equilibrium from 48 h to 2 h. At high concentration viz., 0.05 and 0.1 N Cs, and contact under stirred condition, the uptake is governed by particle controlled diffusion; for dilute solutions and inadequate stirring, the mechanism may be con-

Table 3—Characteristics of waste containing Cs, before and after treatment with zeolite 13X bed

Parameter	Before	After breakthrough (passage of 1000 bed volumes)
pH	8.10	8.21
Dissolved solids (ppm)	141.1	154.2
Suspended solids (ppm)	6.5	1.8
Gross beta-gamma (mCi/l)	1.13* [-3]	2.07* [-5]
Gross alpha (mCi/l)	7.56* [-7]	Not detectable
Tritium (mCi/l)	4.52* [-1]	4.53* [-1]
Cs-137 (mCi/l)	2.11* [-3]	1.88* [-5]
Cs-134 (mCi/l)	2.64* [-4]	5.72* [-6]
Co-60 (mCi/l)	2.60* [-5]	8.29* [-6]

Liquid waste received from MAPS, Kalpakkam.

trolled by film diffusion. The equilibrium studies indicate that upto 50% of the available Na ions undergoes exchange with Cs at a total ionic concentration of 0.1 N in the solution. The commercial granular sample is found to be suitable for column applications with solutions of moderate pH values and dissolved solid content.

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References

- 1 Dyer A, *An introduction to zeolite molecular sieves* (John Wiley, Bath Press Ltd., Bath, Avon, UK) 1988.
- 2 Bray L A & Fullam H T, *Molecular sieves-I*, edited by R F Gould, *Second International Conference on Zeolites*, Worcester, (1971), pp 450-455, *A C S Symposium Series*, 101.
- 3 Komarneni Sridhar & Roy Rustom, *J nucl chem Waste Management*, 2 (1981) 259.
- 4 Mimura Hitoshi & Kanno Takuji, *J Nucl Sci Tech*, 22 (1985) 284; Mimura Hitoshi, Shibata Masahiro & Akiba Kenichi, *J Nucl Sci Tech*, 27 (1990) 167.
- 5 Boyd G E, Adamson A W & Myers L S Jr, *J Am chem Soc*, 69 (1947) 2836.
- 6 Reichenberg D, *J Am chem Soc*, 75 (1953) 589.
- 7 Sherry H S, *Molecular sieves-I*, edited by R F Gould, *Second International Conference on Zeolites*, Worcester, (1971), pp 350-379, *A C S Symposium Series*, 101.
- 8 El-Naggar I M & El-Absy M A, *J Radioanal Nucl Chem*, 157 (1992) 313.