Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Perona, J. J. , Coroneos, A. C. , Kent, T. E. and Richardson, S. A.(1995) 'A Simple Model for Strontium Breakthrough on Zeolite Columns', Separation Science and Technology, 30: 7, 1259 — 1268
To link to this Article: DOI: 10.1080/01496399508010345
URL: http://dx.doi.org/10.1080/01496399508010345

SEPARATION SCIENCE AND TECHNOLOGY, 30(7-9), pp. 1259-1268, 1995

A SIMPLE MODEL FOR STRONTIUM BREAKTHROUGH ON ZEOLITE COLUMNS

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ABSTRACT

The Process Waste Treatment Plant (PWTP) at the Oak Ridge National Laboratory is designed to remove radioactive contaminants, principally ^{90}Sr, from process wastewater. Planned upgrades to the PWTP will use chabazite zeolite columns. Pilot-scale studies have shown that mass transfer zone lengths increase from 10 to about 30 cm as the superficial velocity increases from 5.5 to 22 cm/min. Calculations with a multicomponent equilibrium model showed that the distribution coefficient for strontium remains essentially constant over the process conditions, suggesting that a simple kinetic model (the Rosen long-bed solution) should adequately represent breakthrough behavior. Using a distribution coefficient of 4.87 L/g predicted by the equilibrium model, good agreement was found between

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experimental breakthrough curves and those calculated with the Rosen solution. This model allows prediction of bed depths and cycle times necessary to achieve the required decontamination factor at high zeolite utilization efficiencies over a wide range of flow conditions.

INTRODUCTION

The Process Waste Treatment Plant (PWTP) at the Oak Ridge National Laboratory (ORNL) is designed to remove radioactive contaminants, principally ^{90}Sr, from process wastewater collected from ORNL facilities. Previous laboratory and pilot-scale studies at the PWTP have shown that ion exchange on chabazite zeolite is a simple and effective way to remove radioactive contaminants from process wastewater while minimizing secondary waste generation (1). This process has been selected for both near-term and long-term upgrades to the PWTP. The near-term upgrade will install zeolite columns downstream of the current plant to remove ^{137}Cs from the PWTP effluent stream, which has a maximum flow capacity of 300 gal/min. Having undergone a water-softening process, this effluent water is relatively low in calcium and magnesium concentrations (around 10^{-5} to 10^{-6} eq/L) and relatively high in sodium (around 10^{-2} eq/L).

In an upcoming FY 1995 line-item project, the current PWTP will be replaced by a zeolite system designed to remove both ^{90}Sr and ^{137}Cs. The water to be treated will be higher in calcium and magnesium and lower in sodium compared to the current PWTP effluent. The anticipated composition of water to be treated follows (2):

- strontium: 750 Bq/L or 3.2×10^{-12} eq/L
- cesium: 110 Bq/L or 2.3×10^{-13} eq/L
- calcium: 75 mg/L or 3.75×10^{-3} eq/L
- magnesium: 12 mg/L or 1.0×10^{-3} eq/L
- sodium: 64 mg/L or 2.8×10^{-3} eq/L

The nonradioactive components are higher in concentration than the strontium and cesium by 9 or 10 orders of magnitude. The strontium concentration, much higher than that of cesium, will control the ion-exchange process.

Treatment studies over the last several years have shown chabazite to be the most economical ion-exchange material tested. Available in a natural form (TSM-300 from Steelhead Minerals) and a synthetic form (Ionsiv IE-95 from UOP (1)), chabazite is a zeolite with a structure built from linkages of the double six-ring secondary building unit (3). Chabazite exchange sites are occupied by sodium as received. Because calcium and magnesium exchange, as well as strontium and cesium, five components are involved. Equilibrium data on this system were published by Robinson, Arnold, and Byers (4). An equilibrium model developed by Perona (5) provides a means for predicting equilibrium loadings for any set of liquid compositions.

At any time in the loading process, a column can be divided into three zones: a saturated zone, a mass transfer zone (MTZ), and an unused zone. The solid loading in the MTZ is near saturation in the direction of the water inlet end of the column and near zero toward the outlet end. The MTZ moves down the column during loading, and breakthrough occurs when it reaches the end of the column. Ideally, the MTZ will occupy a relatively short fraction of the column length, so that nearly all of the column is saturated at the time of breakthrough, when the column must be taken off stream and changed out with fresh zeolite. Experiments gave strontium MTZ lengths ranging from 10 to 30 cm. Because process columns are planned to be at least 10 ft long, zeolite utilization will be greater than 90% of saturation if similar MTZ lengths can be achieved in full-scale columns. The objective of this modeling effort was to provide a quick, easily used method for estimating MTZ lengths in full-scale columns accounting for different feedwater compositions and velocities.

EXPERIMENTS

Pilot-scale data were collected in 3-in.-diameter beds holding 2.5 L of zeolite. The columns were loaded with TSM-300 natural chabazite (-20 + 50 mesh) with an average particle radius of 0.0285 cm. Two beds were used in series for some runs, giving bed volumes of 5 L. Corresponding bed depths were 55 or 110 cm. Experimental data were analyzed for the runs shown in Table 1.

Experimental MTZ lengths were calculated for the first run as illustrated below. The breakthrough curve for this run is shown in Figure 1. The calculation assumes a

TABLE 1. EXPERIMENTAL RUNS

Flow Rate (L/min)	Breakthrough (Bed Volumes)	Bed Volumes (L)	MTZ Length (cm)
0.25	3000	2.5	10.8
0.50	3750	5.0	18.3
0.50	3500	2.5	13
1.0	3300	2.5	33
1.0	3500	5.0	22

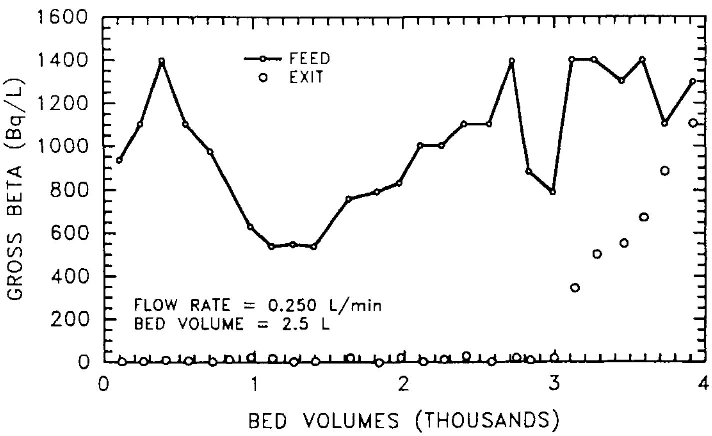

FIGURE 1. Strontium breakthrough for TSM-300.

constant feed concentration, while the actual feed concentration is seen to vary significantly. The average feed concentration of ^{90}Sr was about 1000 Bq/L.

- At 5% breakthrough (50 Bq/L), 3010 bed volumes had been processed.
- At 70% breakthrough (700 Bq/L), 3750 bed volumes had been processed.
- Bed length = 55 cm.
- Length of MTZ = 55 × (3750 − 3010)/3750 = 10.8 cm.

MTZ lengths were calculated at 70% (rather than a more customary number, such as 90%) because data were not available at the higher values for some runs.

The MTZ would be expected to exhibit square-root spreading because the distribution coefficient for strontium is constant (discussed in the "Theory" section). The two runs at 0.50 L/min show this effect, where the bed length which is twice as long has an MTZ greater by a factor of $\sqrt{2}$. The effect for the runs at 1.0 L/min was reversed, indicating that data scatter is significant. Some of the variation in MTZ lengths at the same flowrates in Table 1 is probably cause by feed composition fluctuations.

THEORY

A detailed study of mass-transfer kinetics of the five components in chabazite zeolite was reported by Robinson (6). She determined that micropore diffusivities, the most significant mass-transfer resistance, were on the order of 10^{-10} cm^2/s for the five components. Effective macropore diffusivities, which included surface diffusion, were on the order of 10^{-4} cm^2/s. An "effective" micropore diffusivity of 1.5×10^{-8} cm^2/s was reported for strontium. A rigorous column breakthrough model must include parallel molecular and surface diffusion occurring in series with micropore diffusion in the zeolite crystal. Using such a complex model for process design purposes is cumbersome. Because the MTZ is known to be short, a simple model that successfully accounts for equilibria and flow rate variations may be adequate for process design purposes.

A simple model for consideration is the long-bed solution of Rosen (7). The term "long bed" denotes the physical situation where the MTZ has formed and traveled at least several times its own length down the bed. For breakthrough calculations, this is the situation of interest. The model represents the diffusion within the sorbent pellet by a single effective diffusivity, which becomes insignificant in the long-bed approximation. Mass-transfer resistance at the pellet surface is accounted for.

Rosen solved the partial differential equations for unsteady state column adsorption for the case of a linear isotherm. A study of the equilibria of the present five-component system showed that the distribution coefficients for strontium and cesium were constant even when their concentrations were increased by several orders of magnitude, so long as the calcium and sodium concentrations were constant (5).

The Rosen solution for long beds is

$$\frac{C_A}{C_{Ao}} = \frac{1}{2}\left(1 + erf\left(\frac{(3Y/2X) - 1}{2\sqrt{\nu/X}}\right)\right); \tag{1}$$

where

$$X = \frac{3 D_A K_D \rho_S (1 - \epsilon) Z}{\epsilon U_z R^2} \quad \textit{(bed length parameter)}, \tag{2}$$

$$\nu = \frac{D_A K_D \rho_S}{R k_f} \quad \textit{(film resistance parameter)}, \tag{3}$$

and

$$Y = \frac{2 D_A}{R^2} (t - Z/U_z) \quad \textit{(contact-time parameter)}. \tag{4}$$

Equation 1 is a good approximation if X is greater than 40, which is the mathematical definition of the long-bed condition.

The distribution coefficient for strontium at the anticipated calcium, magnesium, and sodium concentrations was reported as follows (5):

$K_D = (15.6 \times 10^{-9}$ meq/gm$)/(3.2 \times 10^{-12}$ eq/L $\times$ 1000 meq/eq$) = 4.87$ L/gm

Equations 1-4 were used to construct breakthrough curves at the conditions of five experimental runs.

RESULTS AND CONCLUSIONS

Model-predicted breakthrough curves were calculated by setting the bed length (Z) equal to 55 or 110 cm, depending on the bed volume, and finding C_A/C_{Ao} as a function of time (t). The run time can be related to the number of bed volumes processed using the feed rate and the bed volume. For the first run, for example, 3000 bed volumes is equivalent to 500 h of run time. The parameter ratios that occur

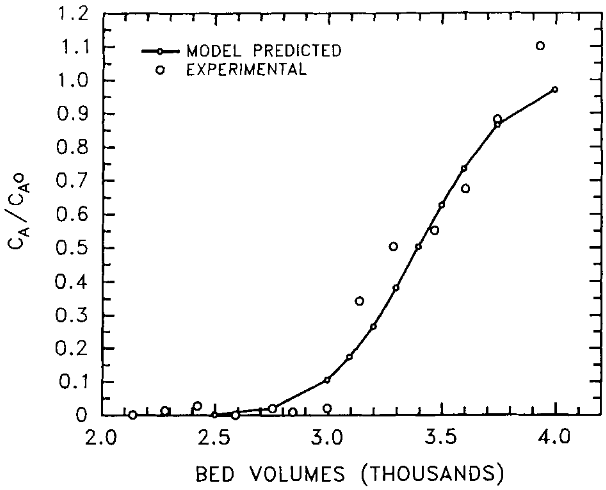

FIGURE 2. Model-predicted breakthrough curve flowrate 0.25 L/min.

in the Rosen long-bed solution can be simplified as follows:

$$\frac{Y}{X} = \frac{2\, \epsilon\, U_z \left(t - \frac{z}{U_z} \right)}{3\, K_D\, \rho_s\, (1 - \epsilon)\, z}, \tag{5}$$

and

$$\frac{\nu}{X} = \frac{\epsilon\, U_z\, R}{3\, k_f\, (1 - \epsilon)\, z}. \tag{6}$$

The strontium diffusivity in the pellet (D_A) drops out of the ratios.

The mass-transfer coefficient at the pellet surface (k_f) was investigated by Robinson (6). From her results, a value of 0.006 cm/s was selected at the lowest flow rate of 0.25 L/min. The Reynolds number based on pellet diameter is 1.3. The preponderance of the literature indicates that the mass-transfer coefficient depends on the Reynolds number (and the velocity) to the 1/3 power (8–10); this factor was used for the higher flow rates. Figure 2 compares the resulting breakthrough curve

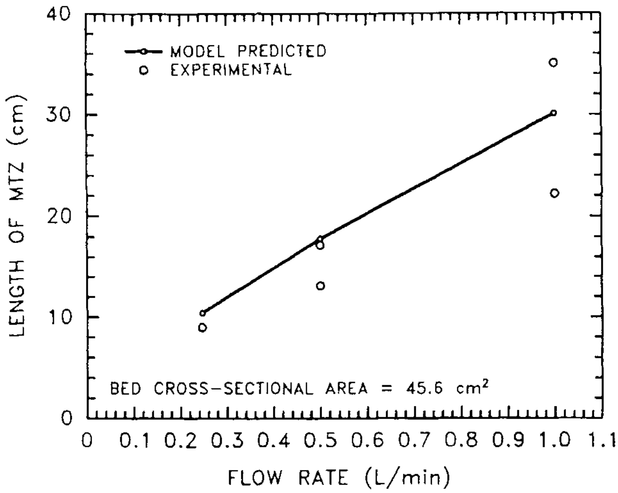

FIGURE 3. Height of mass transfer zone for strontium on TSM-300 zeolite.

for the first run in Table 1 to the experimental curve. The agreement is good, considering the scatter in the experimental points.

The "long-bed" condition for the validity of Eq. (1) requires that X be larger than 40. Substituting into the equation all known values of the variables yields

$$X = 7.5 \times 10^9 D_A .$$

The long-bed criteria will be met if D_A is larger than 5×10^{-9}. Robinson (6) reported an effective micropore diffusivity of 1.5×10^{-8} cm^2/s for strontium, which indicates that long-bed conditions were met.

Lengths of MTZs were obtained by setting the time at 400 h, a value large enough for the MTZ to be well established. Values of the bed location Z were calculated for C_A/C_{A_0} values of 0.05 and 0.70. The length of the MTZ is the difference in the Z values. Figure 3 shows the results. Agreement appears to be within the accuracy of the experimental results. The model can be used for scale-up designs accounting for bed velocity effects. The distribution coefficient can be varied for other feed water compositions, and column breakthrough can be predicted.

NOTATION

C_A = concentration of strontium in liquid (Bq/L or meq/L)

C_{Ao} = concentration of strontium in feed stream (Bq/L or meq/L)

D_A = diffusivity of strontium in pellet (cm^2/s)

k_f = mass-transfer coefficient at pellet surface (cm/s)

K_D = equilibrium-distribution coefficient (4.87 L/g)

R = pellet radius (0.0285 cm)

t = time (s)

U_z = interstitial liquid velocity (cm/s)

X = bed-length parameter (dimensionless); see Eq. 2

Y = contact-time parameter (dimensionless); see Eq. 4

Z = bed length (cm)

Greek:

ϵ = void fraction in bed (0.4 dimensionless)

ν = film-resistance parameter (dimensionless)

ρ_s = solid density (1150 g/L)

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