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CHARACTERIZATION OF A STRONTIUM-SELECTIVE ZEOLITE[1]

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Abstract

A group of several zeolites, including Type A, clinoptilolite, erionite, phillipsite, and alumina-silica gel, was examined for the ability to selectively remove small amounts of strontium from aqueous wastes containing high concentrations of sodium salts. The techniques used in choosing a strontium-selective zeolite were comparative equilibrium distributions between zeolites and strontium-85-traced solutions, and statistical treatment of column data using strontium-85 concentration as the dependent variable. Type A zeolite was the most selective of the group for strontium, but more than a simple reversible exchange reaction was responsible for this strontium selectivity.

Introduction

The problem of removing radiostrontium from relatively concentrated sodium solutions led to investigations of zeolites for the removal of specific radioisotopes from aqueous wastes. Inorganic cation exchange materials were preferred to organic exchangers for radionuclide removal and storage because of their higher radiation and thermal stabilities (Fullerton, 1961).

The problem was investigated by employing equilibrium, statistical, kinetic and column techniques and data to choose an appropriate zeolite. In order to provide better definition of criteria for zeolite strontium selectivity, a whole group of zeolites was studied, including many that were obviously not strontium-selective and ordinarily would be eliminated from consideration. The techniques used in the choice of a strontium-selective zeolite and the resulting data are the subject of this paper.

Methods of Investigation

The first experiments were designed to narrow the field under consideration to a relatively few zeolites capable of removing strontium in the presence of macro-amounts of sodium. Two complementary techniques were employed in the selection process.

The first technique consisted of obtaining equilibrium distribution coefficients with and without competing cations. The equilibrium distribution coefficient, or K_d, is defined by the following expression (Bensen, 1960):

$$K_d = \frac{(Sr_{zeolite})}{(Sr_{solution})}.$$

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where,

$Sr_{zeolite}$ = the amount of strontium on one gram of zeolite,
$Sr_{solution}$ = the amount of strontium remaining in one milliliter of solution.

The K_d contains two factors: one of capacity for a given cation, and another representing specificity for that cation. The specificity factor can be separated from the capacity factor by equilibration of the exchanger with two solutions, the first with the same cation as the tracing radionuclide, and the second with a different cation along with the same tracing radionuclide as used in the first solution. The specificity of a zeolite for strontium in the presence of sodium is determined with two equilibrations.

The first equilibration could be with a solution containing $0.01N$ $SrCl_2$ plus Sr^{85} (K_{d_1}), and the second with a solution containing $0.01N$ NaCl plus Sr^{85} (K_{d_2}). If K_{d_2}/K_{d_1} is greater than 1.0, the zeolite is strontium-selective. If the ratio is less than 1.0, the zeolite is sodium-selective, and if 1.0, non-selective. The K_d concept is invalid by itself with solutions as concentrated as those mentioned above (Samuelson, 1953), as K_d would not be a constant unless the sodium concentration on the zeolite remained essentially unchanged. However, the selectivity index derived from the two distribution coefficients yields a useful qualitative guide to choice of zeolites for subsequent study. Strontium capacities were determined from column or shallow bed data, rather than from the distribution coefficients.

The second technique used in the preliminary selection process was the statistical treatment of an effluent fraction from 10 g columns of exchangers. Figure 1 shows the design of the experiment. The effect of two levels each of column residence time, sodium concentration, calcium concentration and potassium concentration on strontium removal from a five-ml effluent sample between the first 100 and 105 ml through the column was ascertained. The dependent variable, C/C_0, was determined in a half replicate factorial design and treated statistically by use of Yates' method to obtain effect totals (Cochran and Cox, 1957). As used here, C_0 is the concentration of radioisotope in the influent solution and C–the concentration in the effluent solution. The resulting effect totals were evaluated for statistical significance at the 95 per cent confidence level.

Ion exchange kinetics and some larger column experiments completed the second phase of the investigation. The kinetics of cation exchange have been reviewed elsewhere (Ames, 1961, 1962; Boyd *et al.*, 1947; Reichenberg, 1953). Briefly, there are two diffusion mechanisms known to control zeolite loading rates. The first is diffusion within the zeolite

Column Residence Time	Sodium Concentration	Calcium Concentration 0.0 N				0.2 N			
		Strontium Concentration 0.0 N		0.2 N		0.0 N		0.2 N	
		Potassium Concentration 0.0 N	0.2 N	0.0 N	0.2 N	0.0 N	0.2 N	0.0 N	0.2 N
1.21 min.	0.0N	X			X		X	X	
	1.0 N		X	X		X			X
6.04 min.	0.0 N		X	X		X			X
	1.0 N	X			X		X	X	

FIG. 1. Experimental design of the statistical experiments. Those experiments indicated by an "X" in the design were completed.

particle, generally occurring in a concentration region of greater than tenth normal incoming cation. Particle diffusion represents the upper limiting case in loading rate. The second mechanism is diffusion across a concentration film in the liquid immediately surrounding the zeolite particle, typical of lower concentrations of incoming cations. The "shallow bed" technique described earlier (Ames, 1961) was used to obtain both particle and film diffusion loading rates. From the particle diffusion loading rate data at two temperatures, an Arrhenius activation energy, E_a, (Daniels and Alberty, 1955) was computed for the exchange of strontium in solution for sodium on the zeolite. The practical utility of an activation energy will be demonstrated later in the case of the Type A zeolite.

The methods used in carrying out the column experiments were enumerated in an earlier paper (Ames, 1960). The experimental conditions pertinent to each group of column experiments given in the figures are listed under each. Column capacities were determined at the 50 per cent breakthrough point ($C/C_0=0.5$) as described in Samuelson (1953), and cannot be extrapolated to any other experimental conditions. The use of an error function scale for C/C_0 and a log scale for volumes of throughput result in a straight line for the breakthrough curve (Glueckauf, 1955).

The clinoptilolite used in this study, 85 to 90 per cent pure, was obtained from the National Lead Company's Hector, California, deposits.

The erionite and phillipsite, of the same purity, were from Nevada. Type A synthetic zeolite, pelledized with 20 per cent by weight attapulgite, was purchased from the Linde Company. The one-to-six, alumina-to-silica gel was purchased from the Permutit Division of Pfaudler-Permutit, Inc. The gel zeolites were equilibrated with 3.0*N* sodium solutions to insure that the exchangers were in fact sodium-based, and washed afterwards with distilled water.

Strontium-85 was obtained from Oak Ridge as the chloride. Distilled water and reagent grade chemicals were used throughout the study.

Experimental Results

Table 1 shows some of the equilibrium results. Type A zeolite would certainly be the most strontium-selective under the conditions listed in Table 1. Calcium was chosen as the competing cation to make the experimental conditions even more severe than with sodium as a competitor.

Table 2 gives the main effect totals for the independent variables listed. Only the underlined effect totals are statistically significant, as

Table 1. Equilibrium Experiments with Two Solutions at 25 °C. and One Hour Equilibration Time

Zeolite	K_{d_1} 0.02*N* $Sr^{2+}+Sr^{85}$	K_{d_2} 0.02*N* $Ca^{2+}+Sr^{85}$	K_{d_2}/K_{d_1}
Type A	225	1209	5.37
Clinoptilolite	102	130	1.27
Mordenite	38	39	1.03
Chabazite	28	27	—
Stilbite	8	7	—
Analcite	6	1	—
Sodalite	4	1	—

Table 2. A Summary of the Zeolite Statistical Data. Significant Effect Totals are Italicized

Main Effect Totals				Factors
Erionite	Clinoptilolite	Gel	Type A	
1.978	*−2.489*	*−3.173*	*−3.480*	Column residence time
−4.399	*−2.835*	*−2.890*	−1.283	Sodium concentration
1.552	*2.783*	0.214	0.598	Potassium concentration
1.896	0.898	1.674	1.226	Calcium concentration
±2.869	±2.091	±1.868	±1.490	95 per cent significance level

TABLE 3. STRONTIUM PARTICLE DIFFUSION DATA

Exchanger	Temperature, °C.	B, sec^{-1}	D^i, cm^2/sec	E_a, Kcal/mole
Type A	56	0.00888	3.11×10^{-7}	17.4
Type A	28	0.00075	2.62×10^{-8}	
Erionite	50	0.01166	4.13×10^{-7}	12.2
Erionite	28	0.00291	1.03×10^{-7}	
Gel	36	0.00583	2.07×10^{-7}	11.0
Gel	25	0.00300	1.06×10^{-7}	
Phillipsite	35	0.00917	3.25×10^{-7}	10.1
Phillipsite	26	0.00556	1.98×10^{-7}	
Clinoptilolite	54	0.00666	2.36×10^{-7}	9.8
Clinoptilolite	28	0.00181	6.41×10^{-8}	

Influent solution—$0.3N$ Sr^{2+} plus $1.0\times10^{-7}N$ Sr^{85}
Influent pH —6.0
Temperature —as indicated
Flow rate —12.8 $1/hr/cm^2$
Shallow beds —100 mg, 0.25 to 0.50 mm, sodium based exchangers
B —loading rate, sec^{-1}
D^i —apparent particle diffusion coefficient, cm^2/sec.

shown by the values for 95 per cent confidence limits. Note that Type A is the only exchanger whose initial removal of strontium is not significantly affected by the presence of accompanying one normal sodium.

Table 3 presents the strontium particle diffusion data for the sodium-based cation exchangers used in this study. Activation energies for the exchange of sodium on the zeolite with strontium are considerably higher than those of cesium for sodium (Ames, 1962). The high activation energy shown by Type A zeolite borders on that expected for the formation of a chemical compound, rather than a simple cation exchange reaction.

Table 4 shows the effect of competing sodium on strontium loading rates in the film diffusion region. The strontium loading rate of Type A is least affected by the presence of competing sodium.

Figure 2 gives the breakthrough curve for several zeolites, as a plot of C/C_0 on an error function, or normal distribution scale, vs. column volumes on a log scale. Note that both curves for each exchange material pass through the same 50 per cent breakthrough point.

Figure 3, showing the effect of competing sodium on the strontium capacity of columns under the same experimental conditions, confirms the

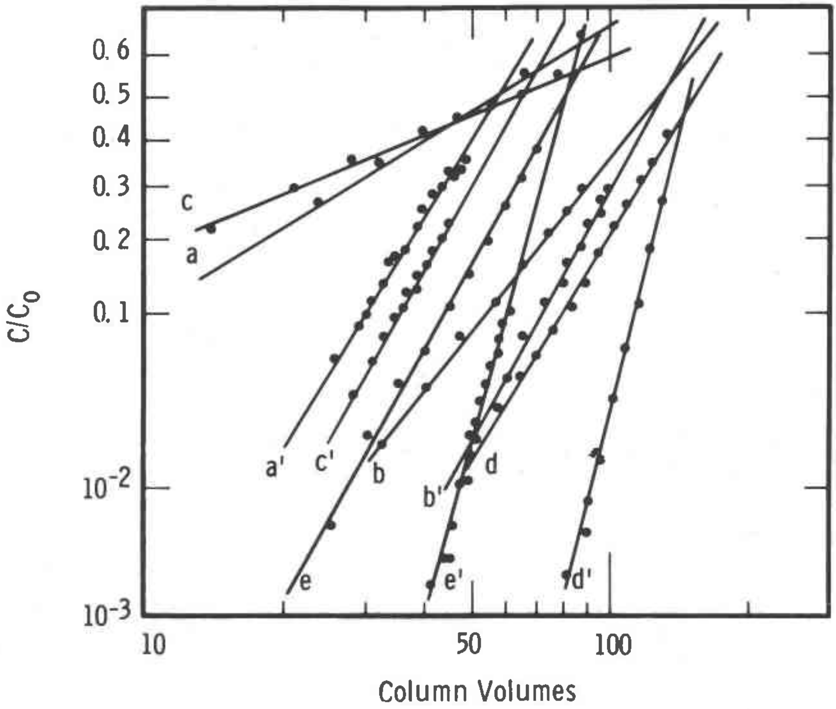

FIG. 2. The effect of column residence time on the slope of strontium breakthrough curves. C/C_0 is the fraction of the original radioisotope concentration in the effluent solution.

Influent solution—$0.008N$ Sr, $1.0\times10^{-8}N$ Sr^{85} and $0.1N$ $Mg(C_2H_3O_2)_2$
Influent pH —7.0
Temperature —25° C.
Column —1.0 to 0.25 mm, sodium-based exchangers; cross-sectional area, 2.84 cm^2; weight 50 g.
Column residence time—as indicated.

Curve designation	*Exchanger*	*Col. residence time, min.*	*Strontium capacity, meq/100 g*	*Surface area, m^2/g*
a	clinoptilolite	1.01	58.4	15–20
a′	clinoptilolite	5.05	58.4	
b	Gel	1.05	128.0	120–150
b′	Gel	5.25	128.0	
c	Type A	1.18	72.7	10–15
c′	Type A	5.90	72.7	
d	Phillipsite	2.02	187.2	400–450
d′	Phillipsite	10.10	187.2	
e	Erionite	1.68	128.0	350–400
e′	Erionite	8.40	128.0	

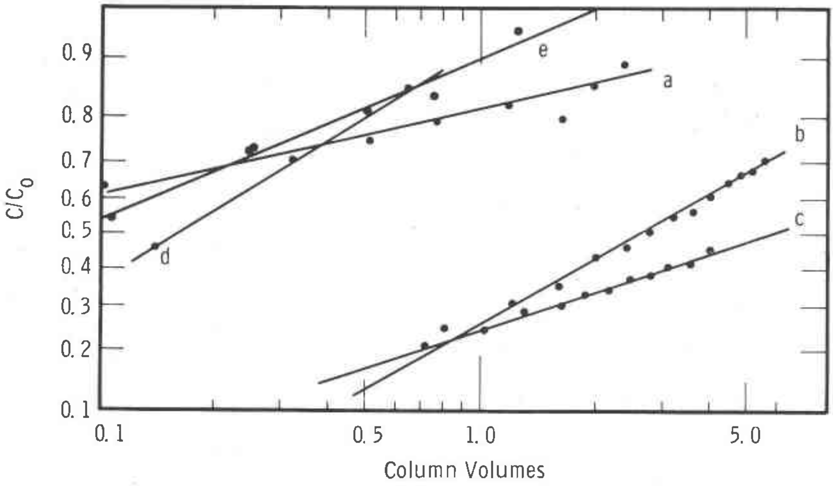

FIG. 3. The effect of competing sodium on the strontium capacity of several zeolites. The breakthrough curves of Fig. 3 and 4 are directly comparable to their shorter residence-time counterparts in Fig. 2. C/C$_0$ is the fraction of the original radioisotope concentration in the effluent solution.

Influent solution—1.0N Na$^+$, 0.008N Sr^{2+}, 1.0×10^{-8}N Sr^{85} and 0.1N Mg (C$_2$H$_3$O$_2$)$_2$.
Influent pH —7.0
Temperature —25° C.
Column —1.0 to 0.25 mm, sodium-based exchangers; cross-sectional area, 2.84 cm^2; weight, 50 g.
Column residence time—same as lesser values given in Fig. 2.

Curve designation	*Zeolite*	*Strontium capacity, meq/100 g*
a	clinoptilolite	0.03
b	Gel	4.17
c	Type A	12.50
d	Phillipsite	0.19
e	Erionite	0.14

above results indicating superior strontium selectivity for Type A relative to the other zeolites tested.

Figure 4 mainly shows the acid resistivity of the various zeolites. Most zeolites are not stable in pH 3.0-buffered solutions, and hence have little or no cation exchange capacity under these conditions. Clinoptilolite, stable under these conditions, becomes the superior strontium remover by default.

DISCUSSION

In order to permit selection of the best zeolite for the specific removal of a cation under given conditions, equilibrium, statistical and kinetic

TABLE 4. EFFECT OF COMPETING SODIUM ON STRONTIUM LOADING RATE

Exchanger	$1.0\times10^{-3}N$ Sr^{2+} R, sec^{-1}	$1.0\times10^{-3}N$ Na^+ R, sec^{-1}	Temperature, °C.
Type A	0.00145	0.00041	43
Erionite	0.00220	0.00028	44
Phillipsite	0.00180	0.00027	44
Gel	0.00110	0.00022	42
Clinoptilolite	0.00106	0.00014	41

Influent solution—$0.001N$ Na^+ or Sr^{2+} as indicated, plus $1.0\times10^{-8}N$ Sr^{85}
Influent pH —6.0
Temperature —as indicated
Flow rate —12.8 1/hr/cm²
Shallow beds —100 mg, 0.25 to 0.50 mm, sodium-based exchangers

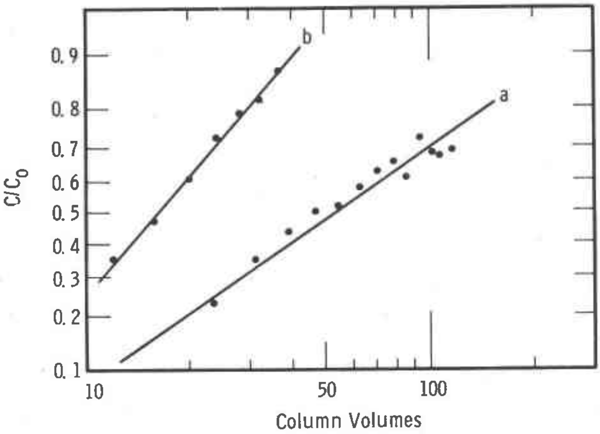

FIG. 4. The effect of competing H^+ on the strontium capacity of gell and clinoptilolite. Type A, phillipsite and erionite are not stable at pH 3.0. C/C_0 is the fraction of the original radioisotope concentration in the effluent solution.

Influent solution—$0.008\ N$ Sr^{2+}, $1.0\times10^{-8}N$ Sr^{85}, and $0.1N$ CH_3COOH.

Influent pH —3.0
Temperature —25° C.
Column —1.00 to 0.25 mm, sodium-based exchangers; cross-sectional area, 2.84 cm²; weight, 50 g.
Column residence time—same as lesser values given in Fig. 2.

Curve designation	*Zeolite*	*Strontium capacity, meq/100 g*
a	clinoptilolite	55.3
b	Gel	16.0

data were obtained, and the results checked with some actual column experiments. As shown in Table 1, the selective zeolites become apparent when subjected to environments with and without competition for the tracing cation. Statistical methods may be effectively utilized to study further certain of the zeolites with the desired cation exchange properties.

There is a need to study the exchange kinetics of the zeolites exhibiting favorable equilibrium results. There are many highly specific adsorbents with prohibitively slow loading rates, resulting in very low apparent column capacities. Where equilibration time is lengthy and the strontium concentration low, materials such as muscovite might appear to be satisfactory cation exchangers from consideration of equilibrium data alone. There is no relationship between strontium selectivity of a zeolite and the rate at which a zeolite removes strontium. Vermiculite, for example, gives very high equilibrium distribution coefficients in a sodium-cesium system, but very poor loading rates in the particle diffusion region. To study either distribution coefficients or loading kinetics alone, is to complete only half of a meaningful study.

The high activation energy shown by Type A in Table 3 probably results from formation of higher-energy, chemical bonds, as well as those bonds typical of cation exchange. However, the *x*-ray diffraction pattern of a strontium-based Type A does not show the presence of another chemical compound. As reported previously be Breck, *et al.* (1956), only barium of the alkaline earth metals causes the complete destruction of the Type A lattice. To check the possibility of a partially irreversible strontium exchange for sodium, a 500 mg bed of sodium-based, 0.25 to 0.50 mm Type A was fully loaded with $0.2N$ $SrCl_2$ plus Sr^{85}, as shown by a recording of the Sr^{85} activity. The same Type A bed was then unloaded with $0.2N$ NaCl solution, until equilibrium was established between bed and solution. At this equilibrium, failure to elute about 35 per cent of the strontium from the bed indicates that more than simple cation exchange has occurred. A duplication of the above experiment with Type A containing no attapulgite bonding agent eliminated the possibility that the attapulgite was responsible for fixing the strontium.

Since the advent of commercially available organic exchange resins, inorganic cation exchange zeolites have been little utilized, mainly because the principal use for exchangers has been in water softening processes.

As the technology develops, however, new uses are found for which the zeolite family is especially well suited. One of these new uses is in the atomic energy industry for the removal and storage of specific radioisotopes from radioactive wastes. Most organic resins are poorly suited as radioisotope extraction and storage media because of their poor radiation and thermal stabilities, and inability to selectively remove radioisotopes from macro-concentrations of non-radioactive salts.

The instability of most zeolites in acid environments considerably limits their application. No acid-resistant, natural zeolites are known with the exception of the two high-silica species, mordenite (Kenough and Sand, 1961) and clinoptilolite (Ames, 1960). In the author's opinion, if zeolites are to have any future in acidic cation exchange applications, they must have at least the cation selectivity and pH stability range of mordenite and clinoptilolite in order to compete successfully with the organic exchange resins.

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