

THE CATION SIEVE PROPERTIES OF CLINOPTILOLITE*

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ABSTRACT

A zeolite was sought for use in columns that would selectively remove Cs from solutions containing large concentrations of competing cations. Clinoptilolite was found to be highly Cs-selective over wide pH, flow rate, and temperature ranges.

Factors affecting clinoptilolite cation selectivities included cation size, charge, electronic structure and, in the presence of Na, temperature.

The large Cs capacity, rapid approach to equilibrium, and high Cs selectivity of clinoptilolite are apparent from the data presented.

INTRODUCTION

A study was initiated in the fall of 1958 to examine the Cs selectivity of several natural and synthetic zeolites when utilized in cation exchange columns. A zeolite was sought that would selectively remove Cs from solutions containing large concentrations of competing cations. The zeolites tested included apophyllite, heulandite, brewsterite, stilbite, laumontite, chabazite, mesolite, gonnardite, thomsonite, datolite, and Linde Type A zeolites. Of these zeolites, clinoptilolite proved to be the most promising, and the cation exchange data pertaining to the kinetics of its Cs selectivity are presented herein.

The literature on clinoptilolite, including a chemical analysis, is given elsewhere (1). Mumpton has worked on clinoptilolite since (4), and Defeyes (3) reported two more occurrences of clinoptilolite associated with erionite. Clinoptilolite, as reported in the literature, appears to be a rather common weathering product of acidic tuffs throughout the western United States.

METHODS OF INVESTIGATION

Mine-run, Na-based clinoptilolite from the Hector, California leases of the Baroid Division of the National Lead Company, was utilized in this study. This clinoptilolite is contained in an altered tuff with about 15 per cent quartz, feldspar, and unaltered glass.

The influent solutions were passed through standard Pyrex glass columns containing clinoptilolite as shown in Fig. 1. Temperatures were maintained with blade heaters controlled by a thermostwitch. A Lapp "Microflo" pump was used to deliver standard flow rates through the columns. Influent and effluent solutions were collected and submitted to the Analytical Laboratory of the Hanford Laboratories Operation for radioanalysis.

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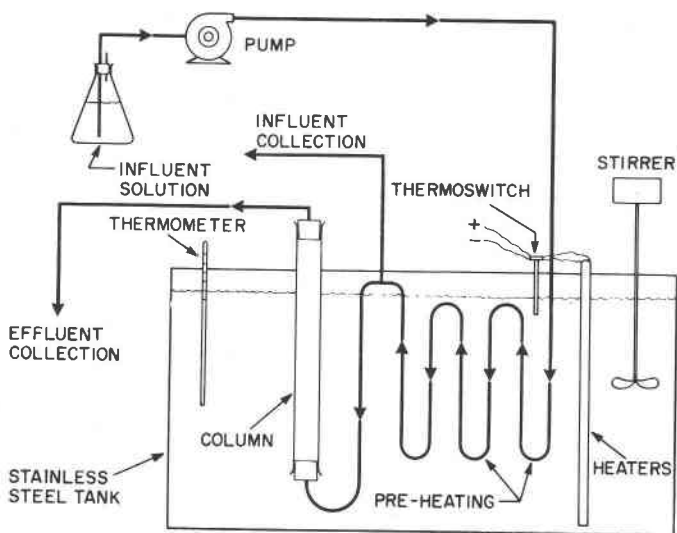


FIG. 1. Constant temperature apparatus.

The high-purity spikes used in this study were obtained from Oak Ridge. The chemicals used were of reagent grade in distilled water solutions.

Column throughput, when plotted *vs.* C/C_0 (C_0 =initial radioisotope concentration, C =final radioisotope concentration), resulted in the familiar S-shaped breakthrough curve (7) illustrated in Fig. 2. This S-shaped breakthrough curve may be "straightened out" to allow more accurate extrapolations (2). This is accomplished by plotting $\text{erf } C/C_0$ *vs.* linear column throughput in the case of the symmetrical S-shaped curve (normal distribution), or $\text{erf } C/C_0$ *vs.* \log column throughput in the case of the asymmetrical S-curve (skewed distribution) (2, 6).

The S-shaped breakthrough curve of Fig. 2, straightened in the above manner, is shown in Fig. 4 ($1N \text{ Al}^{+3}$). Note that data for only a portion of the curve are necessary to obtain the whole curve by a simple extrapolation.

The Cs capacity in all cases was determined at $C/C_0=0.5$ as shown by the dashed line in Fig. 2, and this value was used for Cs capacity comparisons (7). This method for capacity determinations is not strictly valid with asymmetrical breakthrough curves, but a close approximation of capacity can be obtained.

The "column volumes" used herein represent the void spaces plus clinoptilolite volume occupied by 50 g. of clinoptilolite, and is 63 ml. in all cases. The dimensions of this volume are 1.9 cm. diameter by 22 cm.

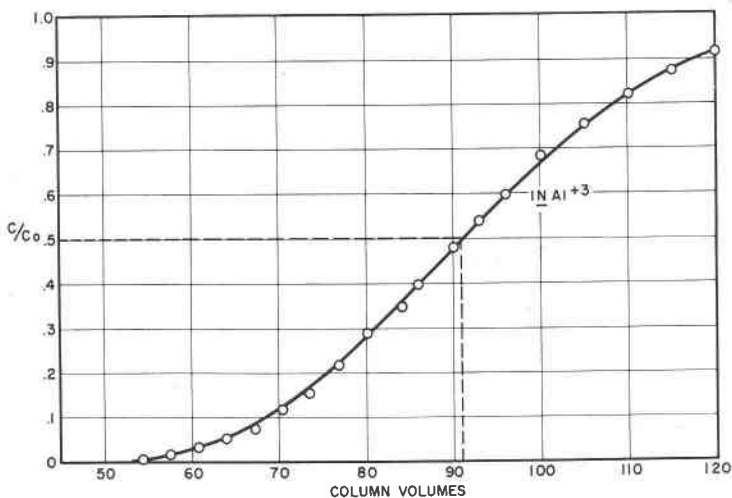


FIG. 2. Cesium Breakthrough Curve with Competing $1N\text{ Al}^{+3}$.

Influent solution— $1N\text{ Al}^{+3}$, $0.01N\text{ Cs}^+$, $1.74 \times 10^{-8}N\text{ Cs}^{137}$

Temperature 25° C .

Influent pH 1.2

Flow rate $294\text{ ml/cm}^2/\text{hr}$.

Column 50g, 0.25–1.0 mm, Na-based clinoptilolite.

long. Column volumes were measured as 63 ml. increments of effluent solution.

RESULTS

Table 1 shows a particle size distribution of the 0.25 to 1.0 mm. clinoptilolite used in this study. All size ranges in Table 1 were found to average

TABLE 1. PARTICLE SIZE DISTRIBUTION OF THE CLINOPTILOLITE USED IN THIS STUDY

Size range, mm.	Sample 1	Sample 2
	Weight per cent	Weight per cent
>1.000	1.3	1.2
0.840–1.000	15.5	13.8
0.590–0.840	27.0	25.2
0.420–0.590	23.4	22.5
0.297–0.430	19.7	21.0
0.250–0.297	9.3	11.3
0.210–0.250	2.8	3.5
<0.210	1.1	1.5

14 m.²/g. in surface area. The grains of clinoptilolite are set in a porous matrix that yields the same surface area for several gross grain sizes. Figure 3 shows the relationship between clinoptilolite grain size and Cs capacity. Above 1.0 mm. in size, Cs capacity diminishes rapidly. Below 1.0 mm., the Cs capacity is constant (at the $C/C_0=0.5$ point of measurement) with only the slope of the breakthrough curve changing.

Figure 4 gives data from which the variation of clinoptilolite Cs capacity with Cs concentration may be computed at $C/C_0=0.5$. A column of N^+ -based Dowex 50WX12 with the same 0.01N Cs^+ influent gave a Cs capacity of 233 meq./100 g at pH 7.0, compared to 133 meq./100 g for clinoptilolite. In a 1.0N Na^+ solution however, the Cs capacity of the Dowex is essentially zero, while the corresponding Cs capacity for clinoptilolite is 73 meq./100 g. Common experimental conditions are listed under each figure.

Figure 5 shows the clinoptilolite Cs capacity data for Cs competing with 1N solutions of Fe^{+3} and Al^{+3} .

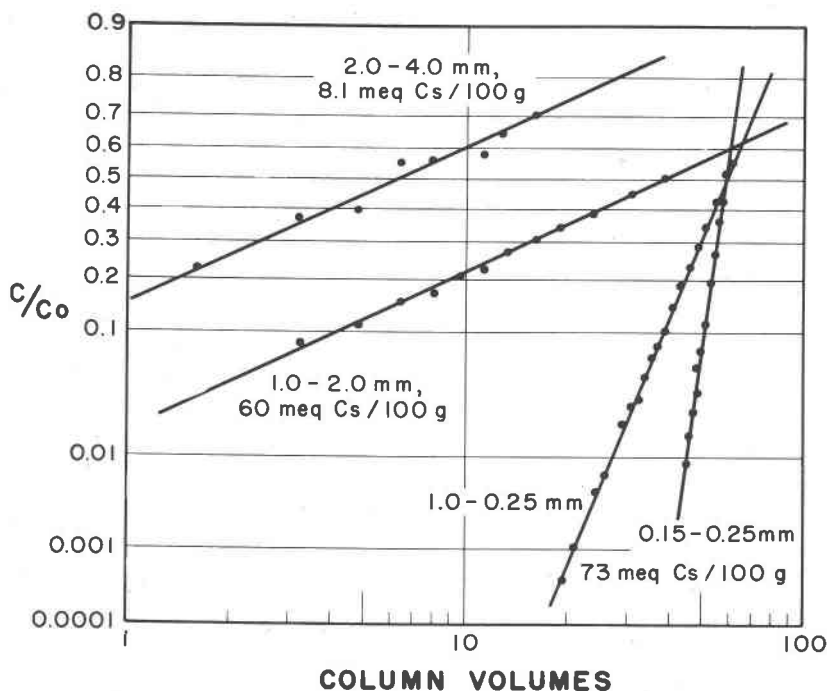


FIG. 3. Variation of Hector clinoptilolite Cs capacity with clinoptilolite grain size range.

Common influent solution—1N Na^+ , 0.01N Cs^+ , 1.74×10^{-8} N Cs^{137}
 Common temperature 25° C.
 Common flow rate 410 ml/cm²/hr
 Common columns 50g, Na-based clinoptilolite

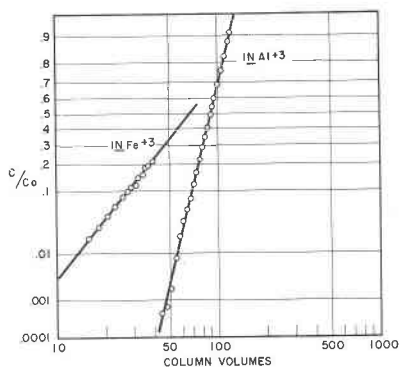
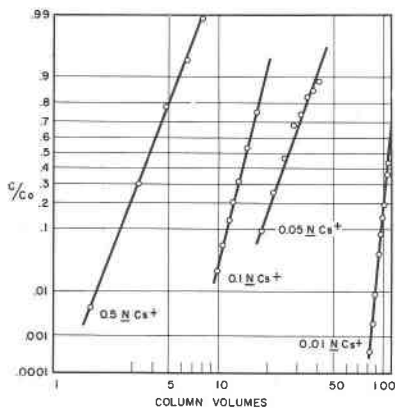


FIG. 4 (left). The Variation of Clinoptilolite Cs Capacity with Cs Concentration.

Common influent solution—Cs⁺ concentration as indicated, $1.74 \times 10^{-8} N$ Cs¹³⁷.
 Common temperature 25° C.
 Common influent pH 5.0
 Common flow rate 294 ml/cm²/hr.
 Common column 50g, 0.25–1.0 mm, Na-based clinoptilolite.

FIG. 5 (right). The effect of Al and Fe on the Cs capacity of clinoptilolite.

Common influent solution—1N Fe⁺³ and Al⁺³ as indicated, 0.01N Cs⁺,
 $1.74 \times 10^{-8} N$ Cs¹³⁷.
 Common temperature 25° C.
 Common influent pH 1.2
 Common flow rate 294 ml/cm²/hr.
 Common column 50g, 0.25–1.0 mm, Na-based clinoptilolite.

Figure 6 gives the same information for 1N solutions of the alkaline earth metals in the presence of the same concentration of Cs, and Fig. 7 for the alkali metals. Note that the experimental conditions for obtaining the data in Figs. 5, 6 and 7 are comparable except for competing cations.

Figure 8 shows the Cs breakthrough data at 25° C. and 60° C. for 0.5N Na⁺, 1N Na⁺, and 3N Na⁺ solutions, and 25° C. for 6N Na⁺ solutions, all containing the same concentration of Cs. Note that the only appreciable temperature effect is with 0.5N Na⁺ and 1N Na⁺ solutions.

Table 2 shows the effects on clinoptilolite Cs capacity of flow rate, influent pH, and temperature with a given Cs concentration.

Note that with the exception of temperature, the effects of these experimental variations over the range studied was slight. Clinoptilolite proved to be considerably more acid-resistant than the other zeolites, as previously reported by Mumpton (4).

Figure 9 shows the effect on clinoptilolite Cs capacity of a 1N Na⁺ solu-

tion and varying Cs concentrations. These data are comparable to those of Fig. 4 without $1N$ Na^+ .

Figure 10 is the data for clinoptilolite Sr capacity from a $0.01N$ Sr^{+2} solution. This Sr capacity was one-third that of the Cs capacity obtained under comparable conditions, or 45 meq./100 g., a consequence of the marked Cs selectivity of clinoptilolite. The Sr capacity of pelletized Linde Type 4A synthetic zeolite under comparable experimental conditions was 24 meq./100 g.

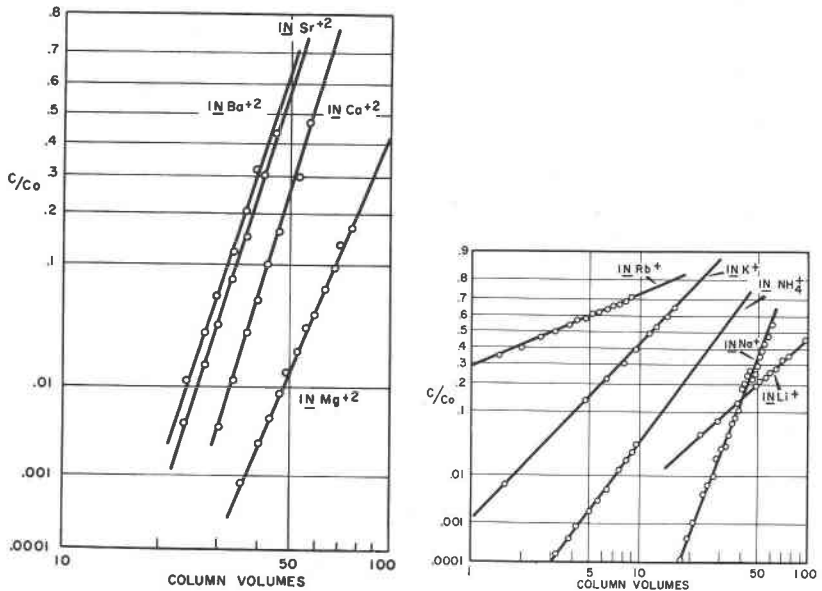


FIG. 6 (left). The effect of the alkaline earth metals on the Cs capacity of clinoptilolite

Common influent solution— $1N$ Ba^{+2} , Sr^{+2} , Ca^{+2} , and Mg^{+2} as indicated,
 $0.01N$ Cs^+ , $1.74 \times 10^{-8}N$ Cs^{137} .

Common temperature $25^\circ C.$

Common influent pH 3.0

Common flow rate 294 ml/cm²/hr.

Common column 50 g, 0.25–1.0 mm, Na-based clinoptilolite

FIG. 7 (right). The effect of the alkali metals on the Cs capacity of clinoptilolite.

Common influent solution— $1N$ Rb^+ , K^+ , Na^+ , and Li^+ as indicated,
 $0.01N$ Cs^+ , $1.74 \times 10^{-8}N$ Cs^{137} .

Common temperature $25^\circ C.$, or as indicated

Common influent pH 3.0

Common flow rate 294 ml/cm²/hr

Common column 50g, 0.25–1.0 mm, Na-based clinoptilolite

TABLE 2. EFFECT ON CLINOPTILOLITE Cs CAPACITY OF FLOW RATE, INFLUENT pH, AND TEMPERATURE VARIATIONS. ALL INFLUENT SOLUTIONS CONTAINED 0.01 *N* Cs⁺, 1.74 × 10⁻⁸ *N* Cs¹³⁷, 1*N* Na⁺

Columns = 50 g., 0.25–1.0 mm., Na-based clinoptilolite			
Influent pH	Temperature ° C.	Flow rate ml./cm. ² /hr.	Cs capacity meq/100 g. to C/C ₀ = 0.5
1.2	25	294	75.0
1.3	60	294	52.6
1.3	60	850	53.8
1.0	25	850	71.2
7.0	25	294	72.0
7.4	60	850	53.0
11.2	25	294	71.8
10.9	60	294	53.2
11.5	60	850	50.6

DISCUSSION

Figure 11 summarizes the clinoptilolite Cs capacity data from Figs. 5, 6 and 7. Two, and probably three, replacement series are evident, consisting of the cations of the alkali metals, the alkaline earth metals, and trivalent Al and Fe. With a given series, the more closely a cation approaches Cs in size, the more selective clinoptilolite becomes for that cation. The order of magnitude of Cs selectivity is shown by the fact that the concentration of competing cations in Figure 11 is 100 times greater than that of the Cs.

It is evident, from the development of three replacement series, that size alone is not the only deciding factor. Cation charge is also important. The intermediate position of NH₄⁺ between the alkali metal and alkaline earth metal series indicated that the electronic structure of elemental cations or the bond type of compound cations also had an effect on its place in a replacement series. Temperature had an appreciable effect only with Na⁺, and the use of a competing cation as the chloride, nitrate and sulfate made no appreciable difference in its effect on Cs capacity.

The placement of a given cation in a series, then, is determined by the complex relationships between cation size, cation charge, electronic structure and sometimes temperature.

Table 3 brings out the relationship between Cs capacity, Na concentration, and temperature. Note that the depression of Cs capacity was the same with 0.5*N* Na⁺ and 1.0*N* Na⁺ from 25° C. to 60° C., while with 3.0*N* Na⁺ the depression of Cs capacity is negligible at 60° C.

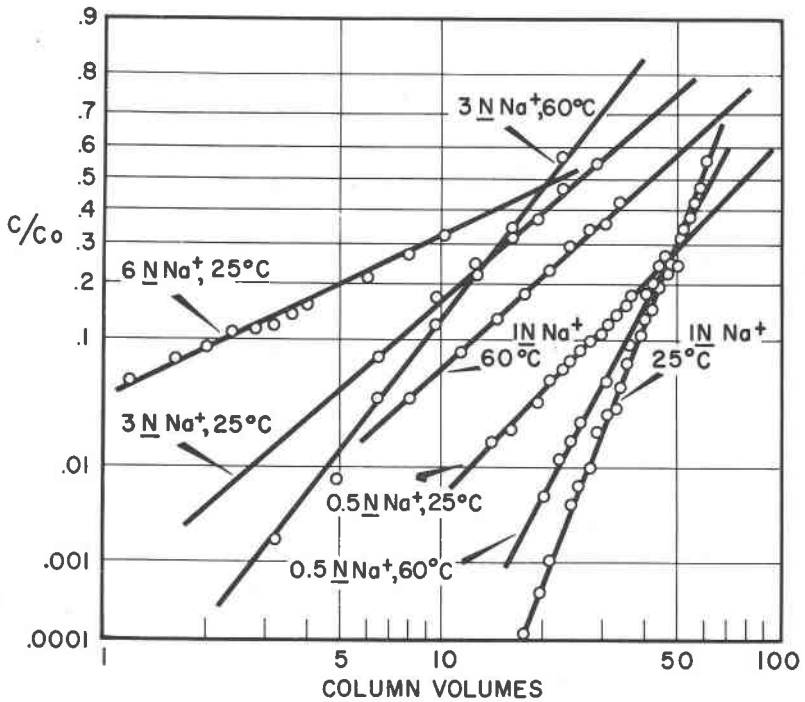


Fig. 8. The effect of temperature and Na concentration on the Cs capacity of clinoptilolite.

Common influent solution—Na concentration as indicated,	$0.01N$ Cs^+ , $1.74 \times 10^{-6}N$ Cs^{137}
Temperature	as indicated
Common influent pH	3.0
Common flow rate	294 ml/cm ² /hr
Common column	50g, 0.25–1.0 mm, Na-based clinoptilolite

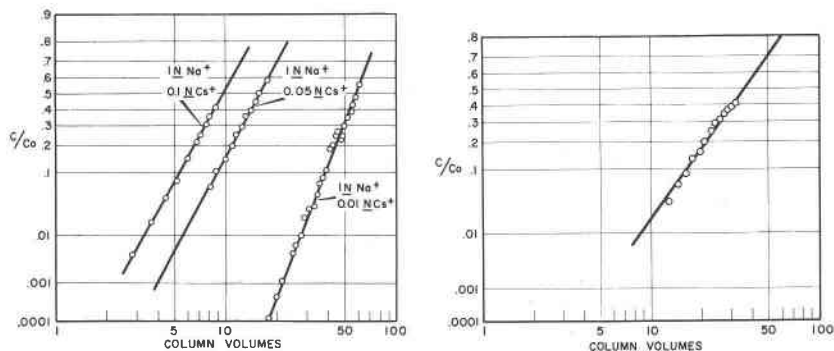


FIG. 9 (left). The effect on clinoptilolite Cs capacity of varying Cs concentration in the presence of 1N Na⁺.

Common influent solution—Na and Cs as indicated, 0.01N Cs⁺,
 $1.74 \times 10^{-8} N$ Cs¹³⁷.
 Common temperature 25° C
 Common influent pH 3.0
 Common flow rate 294 ml/cm²/hr
 Common column 50g, 0.25–1.0 mm, Na-based clinoptilolite

FIG. 10 (right). Clinoptilolite Sr breakthrough curve.

Influent solution—0.01N Sr⁺², $9 \times 10^{-9} N$ Sr⁹⁰
 Temperature 25° C.
 Influent pH 5.0
 Flow rate 294 ml/cm²/hr
 Column 50g, 0.25–1.0 mm, Na-based clinoptilolite.

TABLE 3. THE EFFECT OF TEMPERATURE ON CLINOPTILOLITE Cs CAPACITY IN THE PRESENCE OF Na. THESE DATA ARE FROM FIGURE 7

All solutions contained 0.01N Cs⁺, $1.74 \times 10^{-8} N$ Cs¹³⁷, Na concentrations as indicated, pH=3.0, flow rate 294 ml./cm²./hr., 50 g., 0.25–1.0 mm., Na-based clinoptilolite

Na ⁺ , N	Temperature, ° C.	Cs capacity, meq./100 g. to C/C ₀ =0.5
0.5	25	101
0.5	60	78
1.0	25	73
1.0	60	55
3.0	25	35
3.0	60	34
6.0	25	29

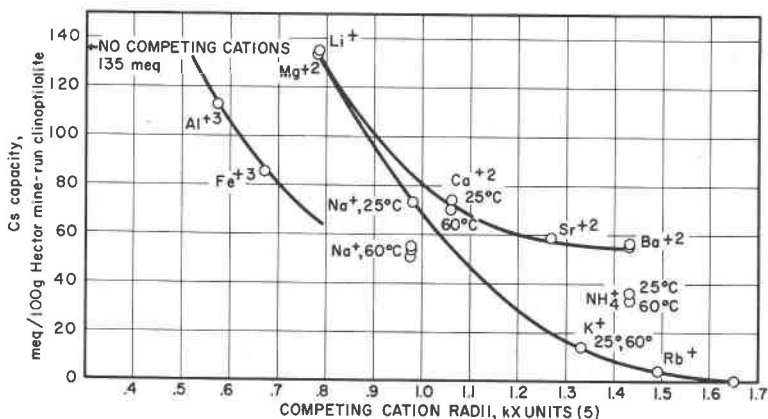


FIG. 11. The effect of competing cations on the Cs capacity of clinoptilolite. The point for Cs⁺ at 0 Cs capacity is theoretically correct because Cs cannot compete with itself.

Common influent solutions—	1 Normal competing cations as indicated, 0.01N Cs ⁺ , 1.74×10 ⁻⁸ N Cs ¹³⁷
Common temperatures	25° C. unless otherwise indicated
Common influent pH	3.0 in all cases except 1.2 for Al ⁺³ and Fe ⁺³
Common flow rate	294 ml/cm ² /hr
Common column	50g, 0.25–1.0 mm, Na-based clinoptilolite

The reason for this temperature effect is unknown. However, the size of Na+H₂O simulates that of Cs. It is possible that some geometrical arrangement between the Na and water is required within the clinoptilolite crystal structure to effectively simulate Cs. This arrangement may be facilitated by increasing temperatures if the solution is less than 3N Na⁺. Consequently, the arrangement is facilitated to the same degree with the same rise in temperature.

The negligible effect of increasing flow rate over the range studied showed that equilibrium between cations in solution and clinoptilolite was reached very rapidly.

Adsorption of any cation by a cation exchanger is a function of the concentration of that cation in the system (7). This mass action relationship is linear when plotted as in Fig. 12. One may obtain the slope of these "curves," which is 0.142 in the case of "no Na⁺" and 0.222 in the case of "1N Na⁺". Assuming no changes in the slopes of these curves at 10⁻⁹ N Cs⁺, the Cs capacity with no Na⁺ is 11 meq./100 g. clinoptilolite and with 1N Na⁺, 2 meq./100 g. clinoptilolite. Hence, even at tracer concentrations of Cs¹³⁷, the Cs capacity of clinoptilolite remains high. One hundred grams of clinoptilolite with an influent Cs concentration of 10⁻⁹ N and 1N Na⁺ will require a throughput of 2×10⁻³/1×10⁻⁹

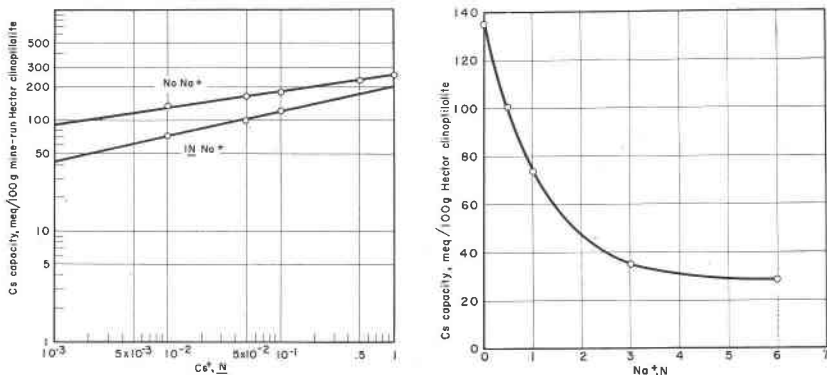


FIG. 12 (left) Fig. 12. A log plot of clinoptilolite Cs capacity vs. Cs concentration in the absence and presence of 1N Na⁺.

Common influent solution—Na concentration as indicated, 0.01N Cs⁺,
 1.74 × 10⁻⁸N Cs¹³⁷
 Common temperature 25° C.
 Common influent pH 3.0
 Common flow rate 294 ml/cm²/hr
 Common column 50g, 0.25–1.0 mm, Na-based clinoptilolite

FIG. 13 (right). The effect of Na concentration on clinoptilolite Cs capacity.

Common influent solution—Na concentration as indicated, 0.01N Cs⁺,
 1.74 × 10⁻⁸N Cs¹³⁷
 Common influent pH 3.0
 Common temperature 25° C.
 Common flow rate 294 ml/cm²/hr
 Common column 50g, 0.25–1.0 mm, Na-based clinoptilolite

= 2 × 10⁶ liters to C/C₀ = 0.5 at 25° C. This large volume of throughput is required to reach C/C₀ = 0.5 even though the Na/Cs ratio is 10⁹.

Figure 13 summarizes the data concerning the effect of Na concentration on clinoptilolite Cs capacity. Approximately nine equivalents of Na⁺ are soluble in distilled water at 25° C. as nitrate. The effect on Cs capacity of increasing Na concentration to greater than 3N is small. This decreasing effect is due chiefly to the decreasing Na⁺ activity of the increasing NaNO₃ concentrations.

Clinoptilolite, on the basis of its cation exchange properties, can be considered a separate zeolite species. The cation exchange properties of heulandite and clinoptilolite are quite dissimilar.

The unusual cation sieve properties of clinoptilolite emphasize the fact that the zeolites have many specialized uses, and have perhaps been

neglected as exchange materials since the advent of the high-capacity, organic exchangers.

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