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EFFECT OF BASE CATION ON THE CESIUM KINETICS OF CLINOPTILOLITE

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ABSTRACT

The cesium loading kinetics of lithium, sodium, potassium, hydrogen, calcium, and barium-based clinoptilolite samples were determined by a "shallow bed" technique in the film and particle diffusion regions. Results showed cesium loading on lithium clinoptilolite to be the most rapid, and cesium loading on hydrogen clinoptilolite to be among the slowest reactions. Cesium loading on hydrogen-based clinoptilolite would be the faster if cation liquid diffusion velocities alone were rate-controlling. Both the hydrated replacement series and loading kinetics are influenced by cation-zeolitic water-anionic site interactions.

INTRODUCTION

Previous work (Ames, 1961) indicated that differences between the intensity of clinoptilolite cation replacement series and other zeolites was not due to differential particle diffusion rates. The term "intensity," as used here, refers to the degree of selectivity or relative preference shown by the zeolite between cesium and lithium in the alkali metal series, for example, or magnesium and barium in the alkaline earth metal replacement series. The conclusion was reached that interactions between cations and internal or zeolitic water caused the replacement series typical of open zeolites. The higher field strength incoming cations tend to attract the zeolitic water to a greater extent, and, therefore, to approach the anionic site less closely. The replacement series of clinoptilolite was particularly intense due to greater freedom of movement of its internal water.

Recent work on zeolite loading kinetics suggested that while differences in open zeolite loading kinetics do not cause cation selectivity differences. the cation selectivity differences do influence the loading kinetics (Ames, 1961). Consequently, a study of the effect of base cation on the cesium loading kinetics of clinoptilolite was initiated. The results and conclusions of this study are the subject of this paper. For a detailed analysis of the thermodynamic basis of cation selectivity as resulting from interactions between cation, water of hydration and anionic site, the reader is referred Eisenman (1962).

METHODS OF INVESTIGATION

The Hector, California, clinoptilolite (Ames, *et al.*, 1958), used in this study was crushed and screened. The resulting product consisted of 5 to 15 per cent unaltered glass, quartz, feldspar, calcite and montmorillonites, admixed with 85 to 95 per cent pure clinoptilolite. The 0.25 to 0.50

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mm size range was selected and washed with distilled water to remove fines. A ten per cent HCl wash of the clinoptilolite removed any calcite present and presumably destroyed possible admixed montmorillonites (Nutting, 1943). The acid-leached clinoptilolite was rinsed with several volumes of distilled water and air dried.

Fifty-gram portions of the air-dried clinoptilolite were placed in beakers at 40° C. with 400 ml, saturated solutions of LiCl, NaCl, KCl, $CaCl_2$ and $BaCl_2$, respectively. HCl was used as a 20 per cent solution. Six cycles were completed at half-hour intervals of discarding solution in contact with the clinoptilolite and adding fresh solution. On the seventh cycle, the clinoptilolite samples and salt or HCl solutions were in contact for eighteen hours. The variously-based clinoptilolite samples were then thoroughly washed with distilled water until chloride could not be detected in the wash water. Fifty milligrams of the above clinoptilolite samples were used in a previously described (Ames, 1961, 1962) shallow-bed technique for kinetic studies.

All clinoptilolite beds were fully loaded as indicated by a continuous recording of the total cesion-134 activity on the bed. Bed loads were determined by comparing the cesium activity in equal weights of influent and bed. The cesium concentration of the influent is known. From the bed activity influent activity ratio, bed loads can be determined. Background count was determined by using the same influent with Ottawa Sand, and subtracted from the original recording, yielding a curve that represented the cesium-134 loading of the zeolite. Cesium-134 was present as the chloride. Reagent grade chemicals in distilled water solutions were used throughout the study.

Results and Discussion

Figure 1 shows a portion of the curves for the fraction of cesium loaded vs. time for several clinoptilolite shallow beds. These curves are obtained as presented by continuous recording of the 50 mg bed during loading. Up to 90 minutes were required for complete loading. Experimental conditions are listed under Fig. 1.

Cesium loading rates can be determined under the experimental conditions of this study by application of Reichenberg's equation (11):

$$(d\phi/dt)_{\text{initial}} = \frac{3D^{Cs}[Cs]}{(r)(\Delta r)}$$

where

D^{Cs} = the cesium liquid diffusion coefficient at the experimental temperature in cm^2/sec,

r = the particle radius in cm,

Δr = the film diffusion thickness in cm,
[Cs] = the concentration of incoming cesium, and
$(d\phi/dt)_{\text{initial}}$ = the initial slope of the cesium loading curve in meq of cesium/ml of bed/second.

A plot of meq of cesium/ml of clinoptilolite vs. time gives the results in Fig. 2. The relative positions of all cesium loading curves, except for lithium-based clinoptilolite, have changed. Note that two groups result and two initial loading rates are obtained rather than a single loading rate. One group includes the alkali metal cation-based clinoptilolites and the other the alkaline earth metal cation-based clinoptilolite samples.

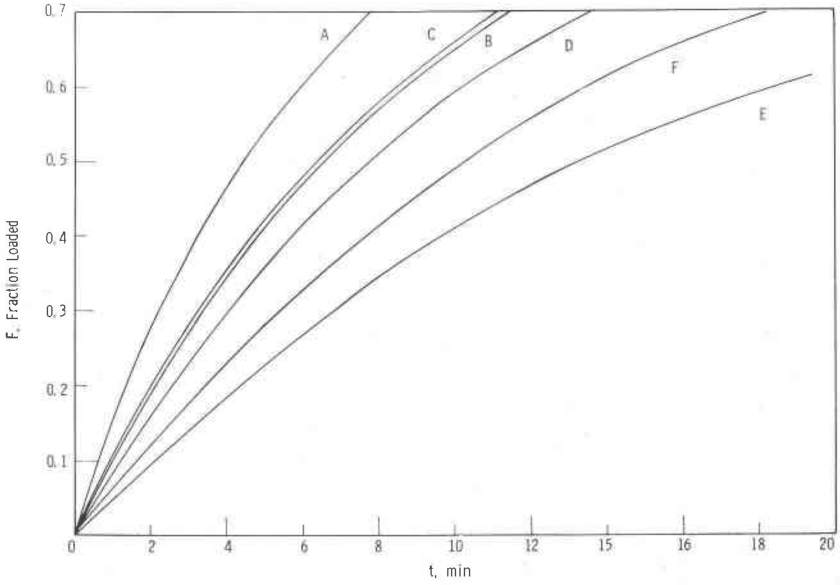

FIG. 1. Fraction of clinoptilolite loading vs. time in the film diffusion region of cesium concentration.

Influent solution—$1.0 \times 10^{-3} N$ CsCl plus $1.0 \times 10^{-8} N$ Cs^{134}
Influent pH —6.0
Temperature —41° C.
Flow rate —15.4 1/cm²/hr
Shallow beds —50 mg, 0.25 to 0.50 mm clinoptilolite

Curve designation	*Cation on clinoptilolite*
A	Li^+
B	Na^+
C	K^+
D	H^+
E	Ca^{2+}
F	Ba^{2+}

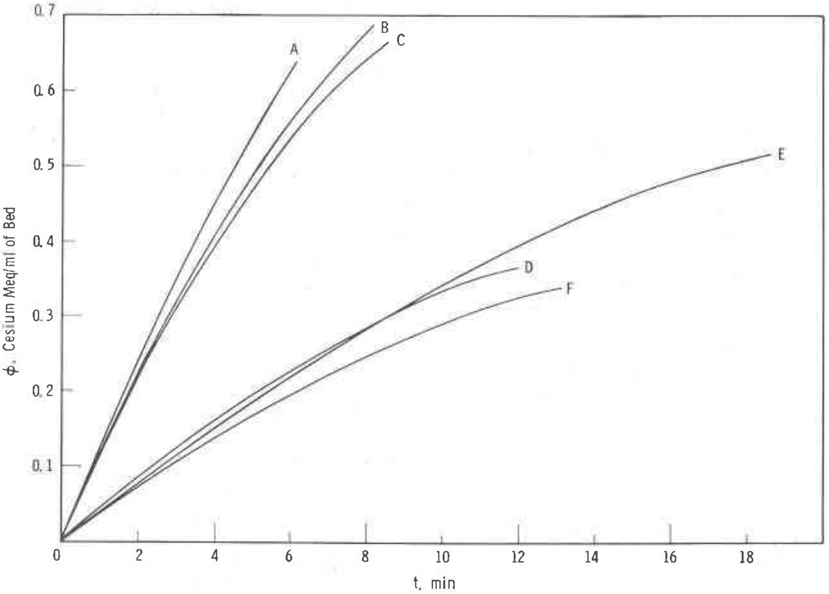

FIG. 2. Curves of meq of cesium/ml of clinoptilolite bed *vs.* time, derived from the data of Fig. 1.

Curve designation	*Cation on clinoptilolite*
A	Li^+
B	Na^+
C	K^+
D	H^+
E	Ca^{2+}
F	Ba^{2+}

Hydrogen apparently behaves like a divalent cation as far as exchange on clinoptilolite is concerned. The above hydrogen behavior was substantiated by earlier column results. Clinoptilolite strontium capacity was substantially reduced when influents of less than pH 4 were used. The alkali metal cation capacities, on the other hand, were little affected by increasing hydrogen ion concentration down to pH 1. Hydrogen ions do not effectively compete with the alkali metal cations for clinoptilolite exchange sites (Ames, 1960; Ames and Mercer, 1961). Alkali metal cations gave a $(d\phi/dt)_{\text{initial}}$ value of 0.00208 meq/ml of clinoptilolite/second, and alkaline earth metal cations and hydrogen, 0.00064 meq/ml/sec.

The cesium $(d\phi/dt)_{\text{initial}}$ value for the alkali metal cations of 0.00208 meq/ml/sec obtained in the present study should be comparable to a $(d\phi/dt)_{\text{initial}}$ value of 0.00116 meq/ml/sec for a sodium-based clinoptilolite from a previous study (Ames, 1962). Given the same chemical system for both studies, the two different $(d\phi/dt)_{\text{initial}}$ values are a result of differences in temperature and flow rate. The temperature increase is from 25 C. in the previous study to 41 C. in this study, and the flow rate increase from 12.8 to 15.4 l/hr/cm.^{2} Beginning with the lower $(d\phi/dt)_{\text{initial}}$ value of 0.00116 meq/ml/sec, the change in the associated cesium liquid diffusion coefficients is approximately a two per cent increase/degree of temperature rise (Glasstone, 1946). The flow rate effect is linear (Ames, 1962), and amounts to about a 17 per cent increase. Assuming the two effects to be additive, the computed $(d\phi/dt)_{\text{initial}}$ value is 0.00186 meq/ml/sec compared to the experimentally determined value of 0.00192 meq/ml/sec, a satisfactory agreement.

The separation of alkali metal-based clinoptilolite from alkaline earth metal-based clinoptilolites to yield two $(d\phi/dt)_{\text{initial}}$ values illustrates the effect of cation bonding and position within the clinoptilolite. Univalent and divalent cation positions are apparently not thermodynamically equivalent, an assumption borne out by the substantial differences in Arrhenius activation energies reported previously for cesium and strontium exchanges on sodium-based clinoptilolite (Ames, 1962 and in press).

The kinetics of the lithium- and barium-based clinoptilolites were determined in the particle diffusion region of cesium concentration. The results are presented in Table 1. Loading rate differences also are present at high cesium concentrations.

TABLE 1. PARTICLE DIFFUSION DATA

Cation on clinoptilolite	Cesium capacity meq/g	B^i sec^{-1}	D^i, cm^2/sec
Li^+	1.7	0.0350	1.25×10^{-6}
Ba^{2+}	1.7	0.0122	4.33×10^{-7}

Influent solution—0.2N CsCl plus $1.0\times10^{-7}N$ Cs^{134}
Influent pH —6.0
Temperature —42 C
Flow rate —15.4 l/cm^2/hr
Shallow beds —500 mg. 0.25 to 0.50 mm clinoptilolite
B —a specific loading rate
D^i —an apparent coefficient of diffusion

As shown previously (Ames, 1961), the cation exchange kinetics of clinoptilolite do not influence the intensity of its replacement series. Rather, it is the type and intensity of the clinoptilolite replacement series that influences exchange kinetics. Clinoptilolite is characterized by an intense hydrated cation replacement series up to approximately 325 C., where a substantial portion of the internal or zeolitic water has been lost. The cesium loading rates of the alkali metal cation-based series, or the alkaline earth metal cation-based series shown in Fig. 1 seemed to contradict the assumption that a hydrated replacement series prevailed. Lithium cations, as indicated by the liquid diffusion coefficients in Table 2, should migrate the slowest and hydrogen ions the fastest. From Fig. 1, the apparent opposite condition of faster lithium cation migration is true.

TABLE 2. LIQUID DIFFUSION COEFFICIENTS COMPUTED FROM IONIC MOBILITY AND OTHER DATA GIVEN IN DANIELS AND ALBERTY, 1955

Cation	D^1, cm^2/sec at 25° C. and infinite dilution
H^+	1.38×10^{-5}
Cs^+	1.03×10^{-5}
K^+	0.98×10^{-5}
Ba^{2+}	0.81×10^{-5}
Ca^{2+}	0.76×10^{-5}
Na^+	0.63×10^{-5}
Li^+	0.45×10^{-5}

An explanation can be found by assuming a stronger interaction between the lithium cation and internal water, resulting in a greater distance between anionic site and cation than with the relatively nonhydrated, low field strength cesium cation. Lithium, being least tightly bound to its anionic site, is the cation most easily and speedily replaced by cesium.

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