SHORTER COMMUNICATIONS

UNIT CELL SIZE AND CESIUM LOADING ON TYPE A AND TYPE X ZEOLITES

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Barrer & Sammon (1955) and Barrer & Meier (1959) have reported a maximum in unit cell dimensions of chabazite and Type A zeolites which reflect a maximum in the sodium-calcium exchange data. The above-named authors suggested that distribution of cations with minimum free-energies exist for certain sodium plus calcium compositions in Type A and chabazite to explain the presence of reflective maxima. The present investigation was carried out to confirm the presence of the maxima and determine whether or not they also occurred in a sodium-cesium system with Type A or Type X.

Methods of investigation

Samples of Type A and Type X zeolites were contacted with solutions of sodium plus calcium or sodium plus cesium known to produce a given fraction of calcium or cesium on the zeolite. The basing method is discussed in detail elsewhere (Ames, 1964). The zeolite samples were then washed, dried in a constant humidity environment and powder photographs of the back-reflection region were obtained using Ni-filtered, Cu radiation. Measurements of the Cu$K\alpha_1$ and Cu$K\alpha_2$ reflections appearing in the back-reflection region were made and the $N(h^2 + k^2 + l^2)$ values determined for each $K\alpha_1$ and $K\alpha_2$ set. These data were used to compute a lattice constant extrapolated to 90° utilizing an IBM programme for the determination of precision lattice constants written by Goebel (1962). The resulting lattice constants varied approximately ±0.003 Å.

The κ_c values were derived from the respective isotherms, and are equal to the mass action quotients corrected for the activities of the cations in the equilibrium solution (Ames, 1964).

Results and discussions

The maximum in the Type A half-unit cell dimensions when plotted *vs.* the fraction of calcium on the zeolite at 70° C. resembles the curve given by Barrer & Meier (1959, p. 134) at 100° C. as shown in Fig. 1. The main difference is that the maximum of the curve shown in Fig. 1

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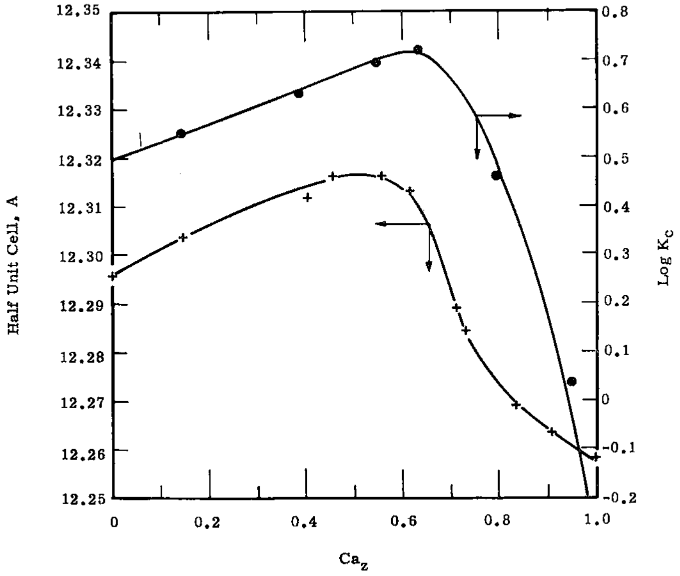

FIG. 1. Plot of log κ_c *vs.* Ca_z and half-unit cell dimensions *vs.* Ca_z for Type A zeolite in a sodium-calcium system at 70° C.

κ_c = a mass action quotient corrected for equilibrium solution activities.

Ca_z = an equivalent fraction of calcium on the zeolite.

does not attain the maximum log κ_c value shown in Barrer & Meier's curve. The reasons for the curve may be temperature or zeolite compositional differences (Ames, 1965) (the 25° C. curve showed no maximum of the above type) (Ames, 1964), or different data treatment methods. The point to be made is that the maxima do exist and are approximately reflective.

Barrer & Meier (1958, p. 1076, 1082) give values of 12.298 ± 0.003 Å for the sodium-Type A and 12.253 ± 0.003 Å for calcium-Type A, while the values found in this work were 12.296 ± 0.003 Å and 12.258 ± 0.003 Å for sodium and calcium-Type A, respectively. The agreement is good considering the probable differences in zeolite hydration states. The half-unit cell is used here because it is the dimension obtained in this instance rather than the unit cell (see Barrer & Meier, 1958, p. 1080).

The log κ_c *vs.* cesium on the zeolite and unit cell dimensions *vs.* cesium on the zeolite are shown for Type X in Fig. 2. The two curves do not show maxima in a sodium-calcium system, but the curves are reflective in that they fall and rise together. The sodium-cesium curves for Type A are not reflective as seen in Fig. 3. The curve of log κ_c *vs.* cesium on the Type A falls rapidly while the curve of half-unit cell *vs.* cesium on the

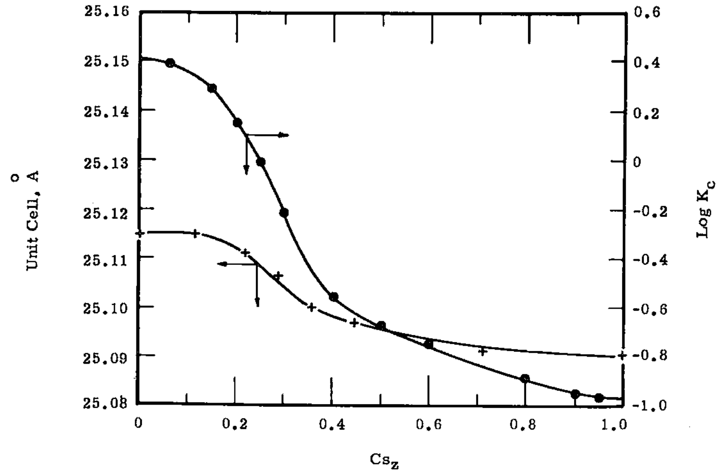

FIG. 2. A plot of log κ_c *vs.* Cs_z and unit cell dimensions *vs*; Cs_z for Type X zeolite in a sodium-cesium system at 25° C.
κ_c = a mass action quotient corrected for equilibrium solution activities.
Cs_z = an equivalent fraction of cesium on the zeolite.

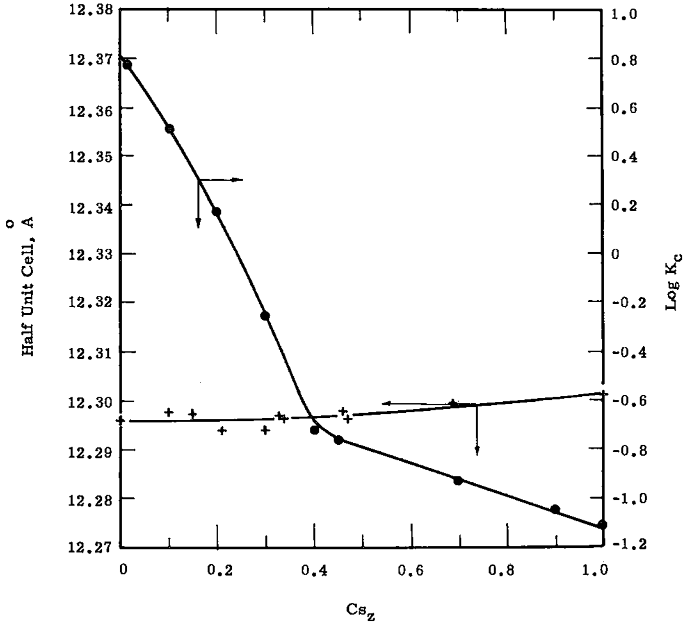

FIG. 3. A plot of log κ_c *vs.* Cs_z and half-unit cell dimensions *vs.* Cs_z for Type A zeolite in a sodium-cesium system at 25° C.
κ_c = a mass action quotient corrected for equilibrium solution activities.
Cs_z = an equivalent fraction of cesium on the zeolite.

Type A actually rises. If the relatively large magnitude changes in the curves shown in Fig. 1 are caused by differences in cation plus water volume within Type A, at least an equally large effect of cation plus water volume change should be found in a cesium-sodium system. Barrer & Meier (1958, p. 1082) consider the ion-exchanged forms of Type A but do not give data for the intermediate ion-exchanged forms with the exception of the sodium-calcium system compositions. Therefore the shape of the curve of half-unit cell *vs.* the intermediate sodium-cesium compositions was unknown. That there are slight differences in unit cell dimensions due to changes in the volume of cations plus water is probable from the data shown in Fig. 3. The magnitude of the unit cell dimension changes in Fig. 3 are relatively small compared to the unit cell changes shown in Fig. 1 for the sodium-calcium system. It is concluded, therefore, that the cation plus water changes of Type A are relatively small and cannot account for the relatively large unit cell size changes of Type A in a sodium-calcium system. Barrer & Meier's suggestion of a minimum free-energy for certain sodium-calcium compositions is still pertinent. On the other hand, the data for Type X shown in Fig. 2 suggest that changes in water plus cation volume probably can give rise to curves of the reflective sort for other zeolites.

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