Measurement and Interpretation of Zeolite NaA Builder Performance[1]

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ABSTRACT: Ion exchange isotherms are commonly used to describe the distribution of ions between a solid and liquid phase under equilibrium conditions. In the detergent industry, the Ca–Na–zeolite A isotherm can be utilized to determine the builder performance of zeolite NaA under a specific set of experimental conditions. In this paper, we demonstrate how the Ca–Na–zeolite A isotherm is developed and utilized in measuring and interpreting the calcium exchange capacity score of zeolite NaA. Owing to the large number of testing parameters that affect the equilibrium distribution of calcium between the zeolite and solution phases, and hence the calcium exchange capacity score of the zeolite, a recommendation is made as to a standard set of test conditions that provide for both analytical precision and convenience. With this approach, builder performance differences between any two zeolites can then easily be measured and assessed. As an extension to the isotherm principles developed in this paper, the prediction of zeolite performance in real detergent systems is illustrated. Particular attention is given to the more efficient utilization of the ion exchange capacity of zeolite NaA by the recently developed concentrated detergent systems.

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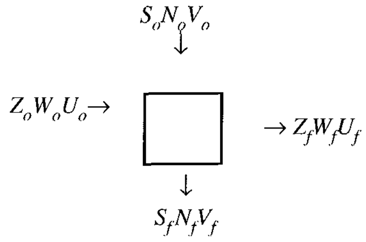
KEY WORDS: Builder performance, calcium exchange capacity, ion exchange, isotherm, zeolite.

Theory—ion exchange. Consider the exchange of the calcium ion into zeolite NaA at constant temperature and total normality. The chemical reaction is:

$$Ca^{2+} + NaA \Leftrightarrow 2Na^{+} + CaA \qquad [1]$$

such that, for every calcium ion exchanged into the zeolite, two sodium ions are displaced. That is, the ion exchange occurs on a constant equivalent basis and, hence, at constant total normality.

The flow diagram for a single stage ion exchange contact is:



where Z = equivalent fraction of Ca^{2+} ions in the zeolite, W = total ion exchange capacity of zeolite, equivalents per gram of anhydrous zeolite, U = grams of anhydrous zeolite, S = equivalent fraction of Ca^{2+} ions in solution, N = total normality and V = liters of solution. Subscripts o and f denote the initial and final states, respectively.

A material balance for calcium (in equivalents) about the ion exchange process results in the following equation:

$$Z_oW_oU_o + S_oN_oV_o = Z_fW_fU_f + S_fN_fV_f \qquad [1]$$

Although U and V vary throughout the ion exchange process, W and N vary in a reciprocal fashion so as to maintain the products WU and NV constant (1). These products, which represent the total equivalents of cations in the zeolite (WU) and total equivalents of cations in solution (NV), are constant throughout the ion exchange process because the exchange reaction proceeds on an equivalent basis. Therefore:

$$W_oU_o = W_fU_f = Q = \text{constant} \qquad [2a]$$
$$N_oV_o = N_fV_f = C = \text{constant} \qquad [2b]$$

Combining equations 1 and 2 yields:

$$Z_f - Z_o = -C(S_f - S_o)/Q \qquad [3]$$

Equation 3 is the equation of a straight line whose slope is $-C/Q$ and which passes through the points (S_o, Z_o) and (S_f, Z_f). Because (S_o, Z_o) and (S_f, Z_f) represent the concentrations of the streams entering and leaving the ion exchange step, respectively, the material balance equation is simply the equa-

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tion of a tie-line that connects the initial condition (S_o, Z_o) to the final (i.e., equilibrium) condition (S_f, Z_f). Note that (S_f, Z_f) is a point on the equilibrium isotherm. The slope of the tie-line is the dimensionless ratio of equivalents of total cations in solution (C) to the total exchangeable cations in the mass of zeolite (Q). This slope will remain constant throughout the ion exchange process because both C and Q remain constant.

The experimental data required to perform the above material balance, and hence establish the isotherm, are obtained by contacting a known quantity of zeolite with a calcium solution of known concentration and volume until equilibrium is reached. From the analysis of the solution phase, coupled with knowledge of the initial quantities and composition of the solution and zeolite phases, the final composition of the zeolite phase can be calculated. The weight of zeolite and volume of solution used are adjusted for each experiment so as to generate different tie-line slopes and, hence, locate different points on the isotherm.

Let's consider an example: Assume that 0.25 L of a 1000-ppm calcium solution (expressed as $CaCO_3$) and 0.5 g of NaA zeolite (anhydrous basis) are contacted at 21.1°C until equilibrium is reached, and the analysis of the filtrate shows that 410 ppm calcium (as $CaCO_3$) remain in the solution. Initially (i.e., prior to ion exchange), there are only calcium ions in the solution phase and sodium ions in the zeolite phase; thus S_o = 1.0 and Z_o = 0. After ion exchange, S_f = 0.41 because 41% of the total equivalents of cations in solution are now calcium. Because there are 7.04 milliequivalents of ion exchange capacity per gram of anhydrous zeolite NaA (1),

$$W_o = 7.04 \text{ milliequivalents of NaA/anhydrous gram} \quad [4]$$

$$Q = W_o U_o = \text{Milliequivalents of ion exchange capacity in 0.5 g of NaA} = 0.5 \text{ g} \times 7.04 \text{ meq/g} = 3.52 \text{ meq} \quad [5]$$

$$C = N_o V_o = \text{Total milliequivalents of cations in solution} = 20 \text{ meq/L} \times 0.25 \text{ L} = 5 \text{ meq} \quad [6]$$

And so,

$$\text{tie-line slope} = -C/Q = -5/3.52 = -1.43 \quad [7]$$

Therefore,

$$Z_f = -1.43(0.41 - 1.0) = 0.84 \quad [8]$$

That is, after equilibrium is achieved, 84% of the total equivalents of cations in the zeolite are now calcium. The point on the isotherm, established through this example, is (0.41, 0.84).

These concepts will be applied in this paper to the understanding of the measurement and interpretation of zeolite NaA builder performance. For the reader interested in the application of these concepts to multistage crossflow or countercurrent ion exchange processes, an earlier paper by one of us is recommended (1).

MATERIALS AND METHODS

Materials. The zeolite NaA used was a commercially available product (The PQ Corporation, Valley Forge, PA) synthesized by methods known in the art (2). The zeolite was characterized for phase purity by X-ray powder diffraction, ^{29}Si nuclear magnetic resonance (NMR) and atomic absorption spectroscopy. Table 1 summarizes the reagents and materials used in this investigation.

Calcium ion exchange measurements. The calcium exchange capacity of the zeolite NaA sample was determined as follows: A 1000-ppm calcium ion solution (expressed as $CaCO_3$) was prepared from calcium chloride dihydrate and buffered to pH 10 with 3 to 5 mL of a solution of NH_4Cl and NH_4OH. The ion exchange solution was buffered at pH 10 for this work to minimize competitive exchange with hydronium ions and to simulate a typical detergent pH condition. A predetermined amount of zeolite was reacted with a predetermined volume of calcium solution. The solution was maintained at 21.1°C and stirred continuously throughout the reaction. After 18 h of reaction time, a 15- to 20-mL aliquot was removed from the solution by drawing the suspension through a 0.45-micron filter into a syringe. The filtrates were then titrated for free calcium ions with 0.005M ethylenediaminetetraacetic acid (EDTA) and hydroxy naphthol blue as the indicator. All results are expressed as milligrams of $CaCO_3$ per gram of anhydrous zeolite NaA.

RESULTS AND DISCUSSION

Zeolite characterization. Figure 1, Table 2 and Table 3 show that the zeolite used in this work is relatively phase-pure. The X-ray powder diffraction pattern (Fig. 1) exhibits all the reflections characteristic of crystalline zeolite NaA, with no evidence of other crystalline species (3). The ^{29}Si and ^{27}Al NMR analyses (Table 2) exhibit chemical shifts consistent with the zeolite NaA structure (4). Specifically, the ^{29}Si signal at −89.41 ppm is indicative of Si(4Al) units, and the ^{27}Al signal at 58.61 ppm indicates tetrahedral framework Al linked to four Si atoms. Furthermore, the elemental composition of the zeolite, as determined by atomic absorption spectroscopy (Table 3), is consistent with the theoretical stoichiometry (i.e., $Na_2O{-}Al_2O_3{-}2SiO_2$) of zeolite NaA (5). Therefore, the available ion exchange capacity of the zeolite used in this study

TABLE 1
Experimental Materials

Reagent/material	Source
Zeolite NaA (Valfor® 100)	PQ Corporation (Valley Forge, PA)
Ammonium chloride (reagent-grade)	VWR (West Chester, PA)
Ammonium hydroxide (reagent-grade)	VWR
Calcium chloride dihydrate (reagent-grade)	VWR
Ethylenediaminetetraacetic acid	J.T. Baker (Phillipsburg, NJ)
Hydroxy naphthol blue	VWR

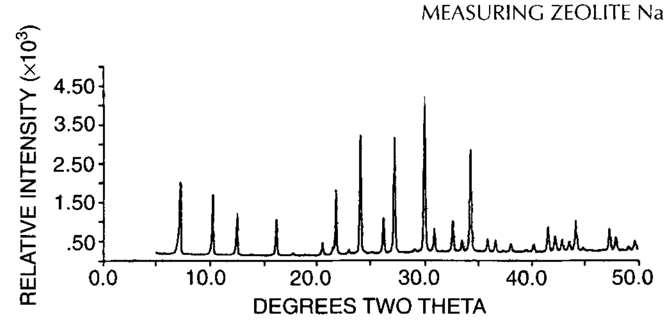

FIG. 1. X-ray powder diffraction pattern of zeolite NaA.

TABLE 2
Nuclear Magnetic Resonance Analysis

	Chemical shift (ppm)	
	^{27}Al	^{29}Si
Zeolite NaA	58.61	–89.41
Tetramethylsilane	—	0
$Al(H_2O)_6^{3+}$	0	_

(see Table 3) is identical to that of the theoretical zeolite NaA structure.

Ca–Na–zeolite isotherm. Figure 2 illustrates the Ca–Na–zeolite ion exchange isotherm at 21.1°C and a calcium ion concentration of 0.02N. By definition, the temperature and the solution normality of the ion exchange isotherm must be specified and held constant. At a higher temperature, the resulting isotherm would become more favorable for calcium ion exchange. At a higher solution ion concentration, the resulting isotherm becomes less favorable for calcium ion exchange due to an electroselective effect (6). Using data from Barri and Rees (6), this concentration–valency effect is demonstrated in Figure 3.

As previously defined, Z equals the fraction of cations in the zeolite that are calcium. When Z = 1, all the sodium ions in the zeolite have been replaced by calcium, and this condition represents the maximum possible calcium exchange capacity (CEC) of zeolite NaA. This theoretical limit is 352 mg $CaCO_3$/g anhydrous zeolite. In Figure 2 we have added a second y axis to the isotherm to indicate the equivalent calcium exchange capacity of the zeolite.

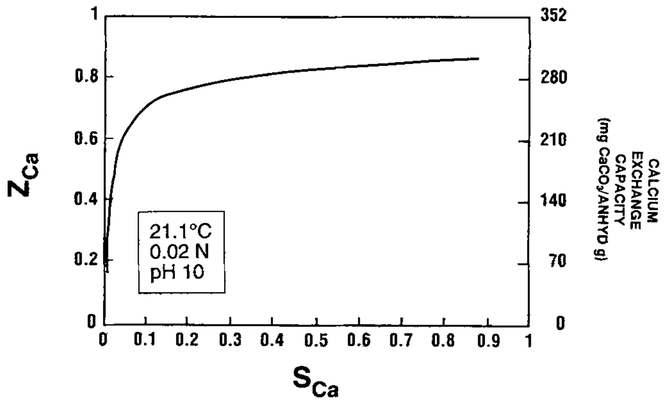

FIG. 2. Ca–Na–Zeolite A equilibrium isotherm at 21.1.°C and 0.02N showing calcium exchange capacity in units of mg $CaCO_3$/g anhydrous (ANHYD) zeolite.

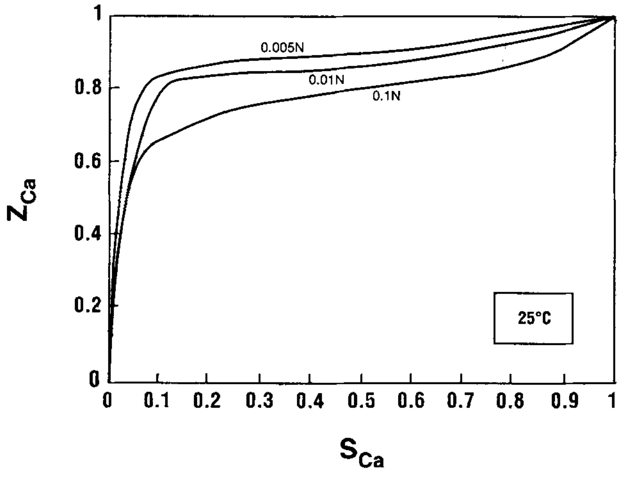

FIG. 3. Ca–Na–Zeolite A equilibrium isotherms at 25°C and 0.005N, 0.01N, and 0.1N.

TABLE 3
Elemental Analysis

	Anhydrous weight percent			Ion-exchange capacity (mmols per anhydrous gram)
	Na_2O	Al_2O_3	SiO_2	
Zeolite NaA	21.81	35.90	42.29	7.04
Theoretical NaA structure (Na_2O–Al_2O_3–$2SiO_2$)	21.83	35.92	42.25	7.04

Measuring zeolite NaA builder performance. Now that the isotherm has been established, it is evident that there are many options available for the selection of test conditions to evaluate the quality of a zeolite NaA product. Conditions can be selected to match any point on the isotherm (tie-line) to evaluate the calcium exchange performance of a zeolite NaA material of unknown quality against the isotherm developed for a highly crystalline zeolite NaA. In the laboratory, it is important to select conditions that are both practical and analytically precise. In Figure 4, we have divided the isotherm into three separate regions to discuss the relative merits of selecting a particular location on the isotherm in which to conduct the calcium exchange test. The test conditions required for each region have been addressed below:

Region A: Because the slope of the isotherm in this region is steep, the effect of any experimental error associated with sample weight, solution volume and solution concentration will be magnified. That is, a slight deviation in the tie-line slope will translate into a large difference in the observed calcium exchange capacity test score.

Region C: Because the slope of any tie-line in this region is steep, the test conditions would require either: (i) a small quantity of zeolite sample for testing, which would magnify any experimental weighing error; or, (ii) large volumes of testing reagents (EDTA and calcium carbonate solution),

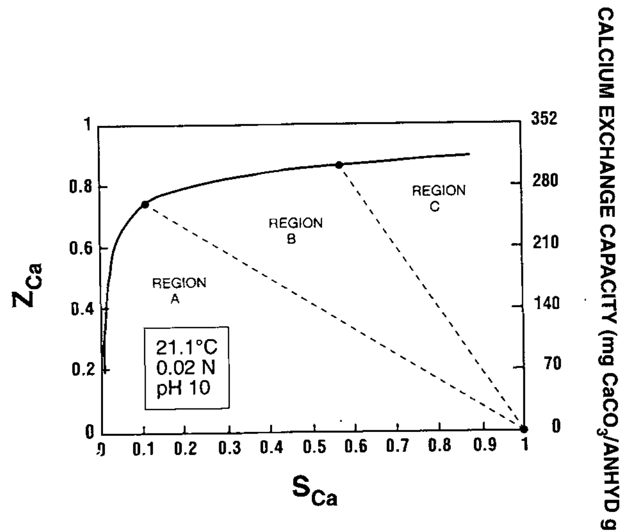

FIG. 4. Ca–Na–Zeolite A equilibrium isotherm at 21.1.°C and 0.02N showing three potential regions in which to conduct calcium exchange test. ANHYD, anhydrous.

which would be expensive and inconvenient to handle; or (iii) highly concentrated reagents, which would lead to a high relative error due to standard error of measurement or addition. In addition, due to the relatively flat isotherm in Region C, we have found that the test conditions do not clearly discriminate between good- and poor-quality zeolite materials.

Region B: This area represents the best compromise between regions A and C. The testing conditions discriminate between good- and poor-quality zeolite, the reagents are inexpensive, and the solution volumes are convenient to maintain. In addition, the analytical precision is good, with a standard deviation of about 3 mg $CaCO_3$ per gram of anhydrous zeolite.

Recommended test conditions. The test conditions we recommend in Region B are 0.5 g anhydrous zeolite contacted with 250 mL of a 1000-ppm calcium solution (as $CaCO_3$) for 15 min, with the resulting filtrate being titrated with 0.005M EDTA. These conditions result in a tie-line slope of −1.43 with $S_o = 1$ and $Z_o = 0$. It has been determined that, at these conditions, 15 min is sufficient time to reach equilibrium. For a highly crystalline zeolite NaA, the equilibrium condition will be $(S_f, Z_f) = (0.41, 0.84)$, such that the calcium exchange capacity is approximately 296 mg $CaCO_3$ per anhydrous gram of zeolite.

Zeolite performance in detergent systems. To this point, we have considered the ion-exchange performance of zeolite NaA for the simple system of a pure calcium solution. This treatment is necessary to isolate the true builder properties of the zeolite and is useful when comparing the quality of two or more zeolite products. In real detergent systems, predicting the ion-exchange performance of the zeolite follows the same general principles outlined above. However, the large number of possible competing chemical reactions makes the analysis somewhat complex. It is possible, however, to evaluate the relative differences in calcium ion exchange performance of zeolite NaA between two formulations.

Consider two zeolite-based detergent formulations, a traditional one-cup and a related concentrated powder (Table 4). Assume the traditional one-cup dosage to be 1 g/L and the concentrate dosage to be 0.62 g/L, so as to provide for an equivalent zeolite usage basis. Also assume that the wash solution is 25°C and contains 100 ppm calcium (expressed as $CaCO_3$). The analysis of zeolite builder performance can be made, provided the following considerations are addressed: (i) The sequestration, chelation and precipitation of calcium ions by the Na_2CO_3, surfactants and sodium silicate present may lower the calcium ion concentration. However, because the concentrations of these ingredients would be the same in the wash liquor for both formulations, as provided for by different detergent dosages, their contribution to calcium depletion would be similar. Thus, for the purposes of establishing relative differences in zeolite performance in the two detergent systems, the effects of these ingredients on calcium activity reduction will be discounted. The calculation that follows could well incorporate these effects, provided adequate data are available. In a future publication, consideration will be given to the effect of Na_2CO_3 on zeolite builder performance. (ii) The magnesium ion concentration in solution may compete with calcium for ion exchange into the zeolite. However, at a temperature of 25°C, the ion exchange of magnesium into zeolite is far less favored than that for calcium (6). Furthermore, the presence of sodium silicate in the formula-

TABLE 4
Typical Zeolite-Based Detergent Formulations[a]

	Traditional one-cup		Concentrated formulation	
Component	Wt%	Wt (100-g basis)	Wt%	Wt (62-g basis)
Zeolite NaA (80% active)	30	30	48.4	30
Alcohol Ethoxylate				
(C_{12}–C_{15}, 7 EO groups)	4	4	6.5	4
Na-LAS (100% active)	10	10	16.1	10
Na_2CO_3	15	15	24.2	15
Na-Silicate (SiO_2/Na_2O = 2.4)	2	2	3.2	2
CMC	1	1	1.6	1
Na_2SO_4	38	38	0	0
	100%	100 g	100%	62 g

[a]EO, ethylene oxide; Na–LAS, sodium linear alkyl sulfonate; CMC, carboxy methyl cellulose.

tions will dramatically reduce the magnesium ion activity (7,8), so that the competition with calcium for ion exchange is negligible.

With the formulations outlined in Table 4, it can now be established that at a dosage of 1 g/L, the traditional one-cup formulation will contribute approximately 200 ppm sodium to the wash liquor, and the total normality, *N*, will be approximately 0.01N and $S_0 \cong 0.19$. Similarly, for the concentrated powder, a dosage of 0.62 g/L will contribute approximately 75 ppm sodium to the wash liquor, so that $N \cong 0.005$N and $S_o \cong 0.38$. We have taken the Na–LAS, Na_2CO_3, Na–silicate and Na_2SO_4 to contain 6.6, 43.4, 22.3 and 32.4% by weight Na, respectively. In each case, the zeolite usage level will be 0.24 g/L, assuming the zeolite is 80% active (i.e., 20% hydrate). This results in approximately 1.69 milliequivalents of available ion-exchange capacity per liter, which, in turn, yields tie-line slopes of 6.3 and 3.1 for the traditional one-cup and concentrated powder, respectively.

A graphical representation of this information can be seen in Figure 5 where the 0.005N and 0.01N isotherms from Barri and Rees (6) were used. From Figure 5, it is evident that the concentrated detergent system results in a more favorable condition for calcium ion exchange (i.e., $Z_f \cong 0.83$) than that for the traditional one-cup powder system (i.e., $Z_f \cong 0.69$). This difference is significant. The zeolite NaA in the traditional one-cup system will exchange about 243 mg $CaCO_3$ per anhydrous gram whereas in the concentrated system, the same zeolite will exchange about 292 mg $CaCO_3$ per anhydrous gram, a 20% increase in ion-exchange capacity.

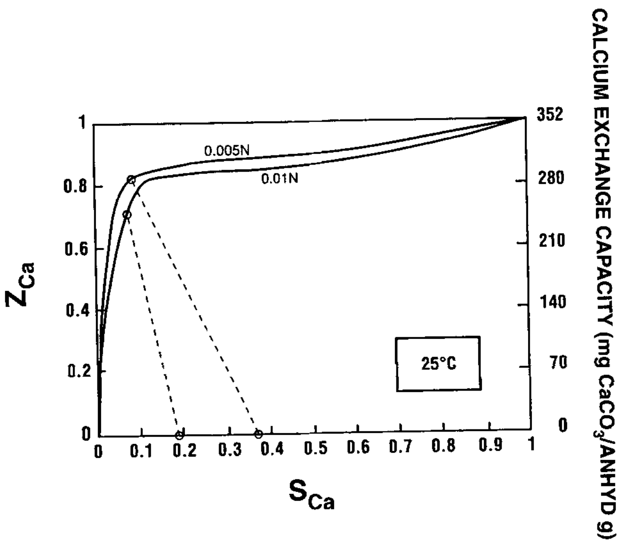

FIG. 5. Ca–Na–Zeolite A equilibrium isotherms at 25°C and 0.005N and 0.01N showing tie-lines for a traditional one-cup and a concentrated detergent powder. ANHYD, anhydrous.

Note that the fundamental difference between the two formulations is the presence or absence of Na_2SO_4. With traditional powders, the presence of Na_2SO_4 raises the sodium ion content and total normality of the wash solution. Both of these factors (i.e., sodium ions, higher normality) result in a suppression of the zeolite ion-exchange reaction outlined in Equation 1. The sodium ions suppress calcium ion-exchange as expected from Le Chatelier's principle, whereas the higher normality condition gives rise to a concentration–valency effect (6), which results in a less favorable ion-exchange isotherm. Given these two effects, concentrated detergent systems provide for a more efficient utilization of the zeolite's ion-exchange capacity.

Based on the work reported in this paper, the following conclusions can be made: (i) The Ca–Na–zeolite A isotherm should be used to measure and interpret the calcium ion-exchange capacity of zeolite NaA. (ii) To compare the calcium exchange performance of two or more different zeolite NaA products, the test method and conditions must be identical for each sample tested, or when zeolite NaA calcium exchange performance is reported in the literature, it is important to know what portion of the ion-exchange isotherm is being utilized to evaluate the reported performance quality against the corresponding isotherm generated from a highly crystalline, well-washed zeolite NaA material. (iii) A specific calcium exchange capacity test method has been recommended that yields analytical precision, yet discriminates between calcium exchange performance at practical solution concentrations and volumes. (iv) Zeolite NaA performance is enhanced in concentrated detergent formulations because of the lower total salt normality and lower background level of Na^+ ions.

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