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The alkali-silica reaction
The surface charge density of silica and its effect on expansive pressure

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Abstract

Electrical double-layer theory has been used successfully to explain the expansion caused by the alkali-silica reaction. The net proton surface charge density of the reactive aggregate is a critical parameter for this approach. However, little work has been done to measure the surface charge density of silica as a function of pH at background electrolyte concentrations that are relevant to the conditions existing in concrete pore solution. We therefore measured the net proton surface charge density of silica gel, opal, and quartz as a function of pH in 0.7 mol·L^{-1} electrolyte solution (NaCl and KCl). The effects of electrolyte concentration and pH on the electrical double-layer estimate of expansive pressure caused by the alkali-silica reaction are significant.

Keywords: Amorphous material; Durability; Electrochemical properties; Expansion; pH

The alkali-silica reaction is recognized as one of the most important degradation processes in concrete structures [1,2]. Although the mechanism of this degradation process is not fully understood, there is consensus on the major factors that influence it: the alkali content of cement, the mineralogy of the aggregates, the type and concentration of soluble salts (either added as admixtures or derived from cement hydration), and environmental conditions, especially temperature variation and cycles of wetting and drying [3,4]. Overall, the alkali-silica reaction comprises two basic steps [5,6]: 1) the dissolution of silica and 2) the formation of potentially expansive gel. Both steps are influenced by the four factors enumerated earlier, and both are believed to be determined by surface chemistry at the silica/pore solution interface [5–8].

Prezzi et al. [5,6] developed a predictive model of the alkali-silica reaction based on concepts in electrical double-layer theory. On this model, the swelling of reaction-product gels is attributed to double-layer repulsion effects. Qualitatively, this mechanism implies that, for a given ionic concentration in the pore solution, monovalent cations (e.g., Na^+) produce greater expansion of the gels than do bivalent cations (e.g., Ca^{2+}). Well-established correlation approaches that have been used to characterize expansive soil clays bearing adsorbed monovalent and bivalent cations [8] also can be applied to correlate increases of percent expansion to decreases in the fraction of total cation charge in the gel that is Ca^{2+} or Mg^{2+} [6,9,10]. Quantitatively, conventional diffuse double-layer equations [10] can be applied to calculate the expansive pressure in concrete affected by the alkali-silica reaction. An estimate of 2.2 to 10.3 MPa expansive pressure was calculated in this way by Prezzi et al. [5] based on published measurements of the surface charge density of "Ludox" silica gel reported by Bolt [11]. Unfortunately, a better estimate could not be given because of a lack of data on the surface charge density of silica at pH values and electrolyte concentrations relevant to those existing in concrete pore solutions. The objective of the present paper is to provide these data for both amorphous and crystalline silica materials suspended in NaCl or KCl solution at the realistic concentration of 0.7 mol · L^{-1} [7].

1. Materials and experimental methods

The following siliceous materials were used: silica gel with a BET specific surface area of 257 m^2 · g^{-1}; quartz with a BET specific surface area of 6.5 m^2 · g^{-1}; and opal, from Piaui, Brazil, with a BET specific surface area of 8.5 m^2 · g^{-1}. The opal was received as small rocks, then crushed and mixed using an automatic mill. These particles were washed several times with deionized water and dried at 120°C for at least 2 hours. All reagents were analytical grade.

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The surface charge density created by proton or hydroxide ion adsorption (σ_H) is proportional to the difference between the amount of substance of H^+ and OH^- ions adsorbed to a solid surface as given in Eq. (1) [12]:

$$\sigma_H = F(\Gamma_{H^+} - \Gamma_{OH^-}) \tag{1}$$

where F is the Faraday constant, and Γ_{H^+} and Γ_{OH^-} are the analytical surface excesses of H^+ and OH^-, respectively. The charge density σ_H can be expressed either per unit area or per unit mass, depending on the units of Γ [13].

The experimental determination of σ_H was carried out by performing pairs of potentiometric titrations [11–16] under the same conditions (e.g., concentration of background electrolyte solution and of the base titrant added). The first titration is made in the presence of the solid and the second without it. For the same starting pH value in both cases, the volume of base titrant added to attain a certain pH value is different in each titration because of the adsorption of OH^- on the silica surface. Under these conditions and for the addition of a strong base at a concentration much higher than that of H^+ or OH^- in the sample solution, Eq. (1) can be written as Eq. (2), following Sonnefeld et al. [14,15]:

$$\sigma_H = FC_b(V_s - V_{ws})/a_s c_s \tag{2}$$

where σ_H is in units of coulombs per square meter, C_b = concentration of strong base added, V_s = volume of base added to the suspension containing a solid with specific surface area a_s at a concentration of c_s, and V_{ws} = volume of base added to the system without the solid (blank). Titrations were performed under nitrogen atmosphere in the presence of NaCl or KCl at a given concentration (0.1 or 0.7 mol · L^{-1}; 1 g solid in 250-mL solution). The titrations began at pH 5.5 and were conducted until pH 10 to avoid silica dissolution. All results were obtained in triplicate.

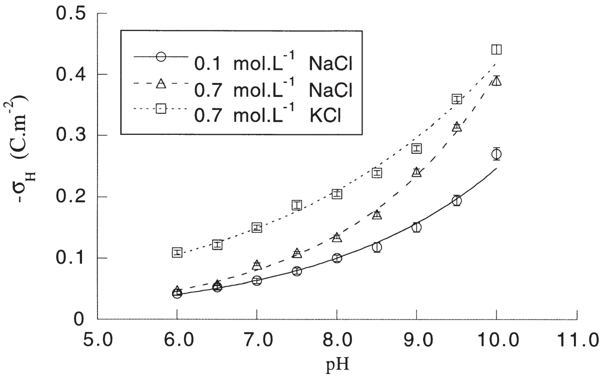

Fig. 2. Net proton surface charge density per unit area of silica gel as function of pH and the type or concentration of background electrolyte solution.

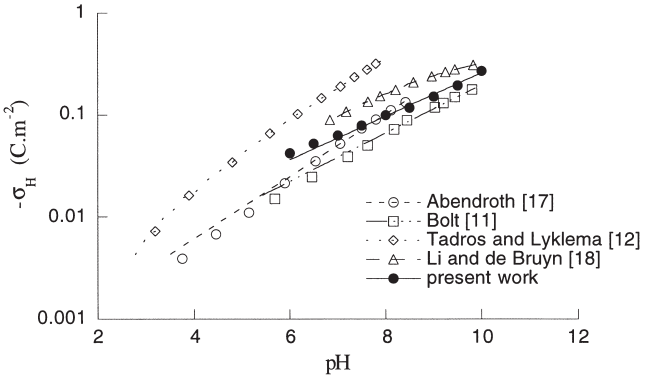

Fig. 1. Semilog plot of the net proton surface charge density per unit area of silica gel suspended in 0.1 mol · L^{-1} NaCl solution as a function of pH.

2. Results and discussion

Measured values of σ_H for silica gel suspended in 0.1 mol · L^{-1} NaCl solution as obtained in the present study are compared in Fig. 1, with results for colloidal silica or silica gel taken from the literature [11,12,17,18]. Small discrepancies among the various data sets can be attributed to different kinds of silica used, titration method, and surface pretreatment [16,19,20]. In all cases, however, the order of agreement is reasonable. The pH value at which $\sigma_H = 0$ is termed the point of zero net proton charge (p.z.n.p.c.) [13]. Values of p.z.n.p.c. reported for silica suspended in 0.1 mol · L^{-1} NaCl are near 3.5–3.9 [12,21], which is consistent with the data shown in Fig. 1. Sverjensky and Sahai [22] recently applied a comprehensive electrostatic model of solid surface acid–base reactions to the classic titration data of Bolt [11] to infer p.z.n.p.c. = 3.5 from model equilibrium constants for surface proton and hydroxide ion adsorption.

The effect of salt concentration on the acceleration of the alkali-silica reaction is well known [23,24]. To correlate this effect with the surface charge density of silica gel, titrations were performed in 0.7 mol · L^{-1} NaCl and KCl solutions to determine σ_H as a function of pH. These electrolyte conditions are similar to those typically found in concrete structures not exposed to deicing salts or sea water [7]. The results are shown in Fig. 2. As the salt concentration is increased, σ_H becomes more negative (NaCl system). This effect can be explained by greater replacement of surface H^+ by Na^+ at higher NaCl concentrations (mass action law).

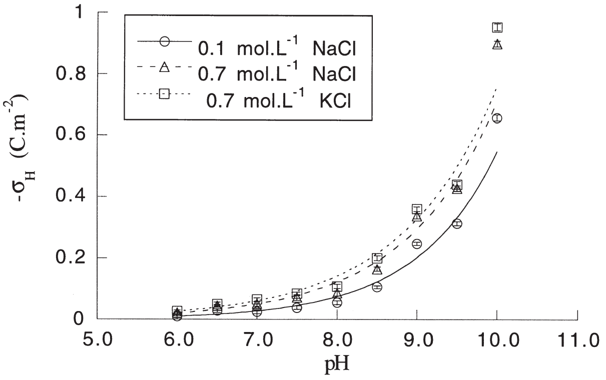

Fig. 3. Net proton surface charge density per unit area of opal as function of pH and the type or concentration of background electrolyte solution.

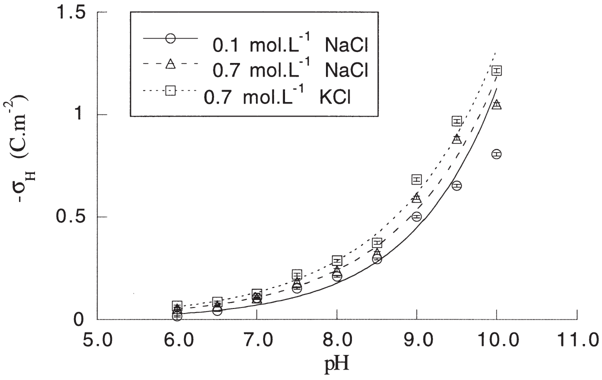

Fig. 4. Net proton surface charge density per unit area of quartz as function of pH and the type or concentration of background electrolyte solution.

The results also show that K^+ has a greater effect on σ_H than Na^+ for silica gel (i.e., greater H^+ displaced by K^+ than by Na^+). This is in agreement with previous titration studies at lower electrolyte concentrations [12,14] and with Na^+–K^+ exchange data for silica gel [25].

The surface charge density of quartz and opal, shown in Figs. 3 and 4, follows the same trends as described for silica gel. Silica gel has a significantly more negative surface charge per unit mass than opal and quartz. This is shown more directly in Fig. 5, which also demonstrates that σ_H is an exponential function of pH. Table 1 gives the values of the least-square fits for the data.

Prezzi et al. [5] calculated the values of the pressure ΔP exerted by an expansive gel in concrete using the double-layer theory equation as given in Eq. (3) [13]:

$$\Delta P = C_0RT[\exp(-\psi_0/\psi_D) + \exp(\psi_0/\psi_D) - 2] \qquad (3)$$

where C_0 is the bulk electrolyte concentration, R is the molar gas constant, T is the absolute temperature, and ψ_0 is the surface potential at a point mid-way between two charged particles, found as the solution of the transcendental equation given in Eq. (4) [5,13]:

$$y_0^{1/2} = 2\tan^{-1}(-\beta\sigma_H/2Fky_0^{1/2}). \qquad (4)$$

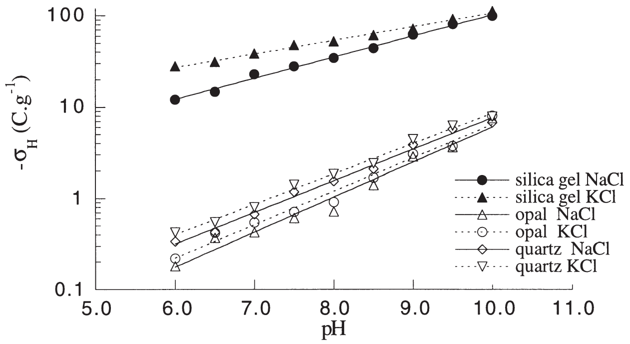

Fig. 5. Semilog plot of the net proton surface charge density per unit mass of silica gel, opal, or quartz as a function of pH and type of background electrolyte (0.7 mol · L^{-1} concentration).

Table 1
Least-square fit of the equation, $\text{Log}|\sigma_H| = a\,\text{pH} + b$, to the data shown in Fig. 5 (0.7 mol · L^{-1} concentration) and to the data for silica suspended in 0.1 mol · L^{-1} NaCl solution

Material	Type and concentration of electrolyte solution	a	b	R^2
Silica gel	0.1 mol · L^{-1} NaCl	0.196 ± 0.005	−0.16 ± 0.04	0.995
	0.7 mol · L^{-1} KCl	0.149 ± 0.005	0.53 ± 0.04	0.992
	0.7 mol · L^{-1} NaCl	0.232 ± 0.007	−0.30 ± 0.05	0.994
Opal	0.1 mol · L^{-1} NaCl	0.43 ± 0.03	−3.7 ± 0.2	0.966
	0.7 mol · L^{-1} KCl	0.37 ± 0.02	−2.8 ± 0.2	0.980
	0.7 mol · L^{-1} NaCl	0.38 ± 0.02	−3.1 ± 0.2	0.973
Quartz	0.1 mol · L^{-1} NaCl	0.40 ± 0.04	−3.2 ± 0.3	0.944
	0.7 mol · L^{-1} KCl	0.33 ± 0.01	−2.4 ± 0.1	0.993
	0.7 mol · L^{-1} NaCl	0.34 ± 0.01	−2.6 ± 0.1	0.992

In Eq. (4), $\beta = 1.084 \times 10^{16}$ m · mol^{-1} at 25°C is a double-layer model parameter depending on T and the dielectric constant of water as given in Eq. (5) [13],

$$k = (\beta C_0)^{1/2} \qquad (5)$$

is a parameter whose inverse gives the "diffuse double-layer thickness" [13], and, as given in Eq. (6):

$$y_0 = \exp(-\psi_0/\psi_D) \qquad (6)$$

where the potential scaling factor $\psi_D = RT/F = 25.69$ m · V at 25°C [13]. Prezzi et al. [5] discuss the numerical solution of Eq. (3) and the calculation of ΔP given a value for σ_H expressed per unit area. Fig. 6 shows values of ΔP computed for opal suspensions using the data on σ_H given in Fig. 3. The highly significant effect of electrolyte concentration and the insignificant effect of the type of monovalent cation (Na^+ vs. K^+) are apparent.

3. Conclusions

The net proton charge density of silica gel, opal, and quartz was measured at an electrolyte concentration (0.7 mol · L^{-1} NaCl or KCl) relevant to that existing in concrete pore solution. The results indicate that σ_H is an exponential

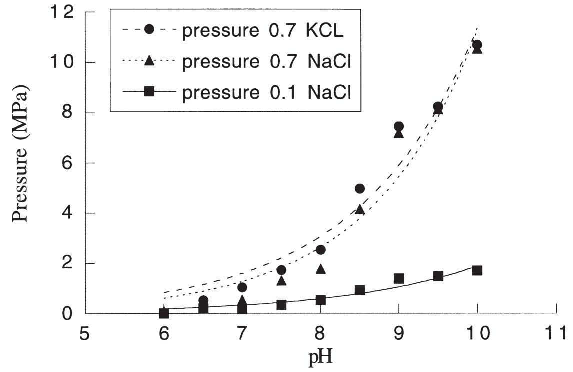

Fig. 6. Expansive pressure computed with Eq. (3) and the data from Fig. 3 for opal (a_s = 8.5 m^2·g^{-1}).

function of pH and that silica gel has a greater surface charge per unit mass than opal and quartz. The results also show that K^+ has a greater ability than Na^+ to create negative charge on the surfaces of the siliceous materials studied.

The expansive pressure in concrete caused by the alkali-silica reaction was calculated using standard diffuse double-layer equations and measured values of the net proton surface charge density. The expansion pressures for opal were found to be very influenced by pH and electrolyte concentration, but little by the type of monovalent cation (Na^+ or K^+).

Acknowledgments

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