Pergamon

Cement and Concrete Research 31 (2001) 1549–1552

CEMENT AND
CONCRETE
RESEARCH

The alkali–silica reaction
The effect of monovalent and bivalent cations on the surface charge of opal

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Received 28 May 1998; accepted 19 June 2001

Abstract

The degree of expansion of alkali–silica reaction (ASR) gel is dependent on the valence and relative concentrations of cations present in the ASR gel. The electrical double-layer (EDL) model can predict which gel will be more expansive. If double-layer models are applied in a complex system, as in concrete, it is necessary to characterize the surface charge density of amorphous silica as a function of pH and electrolytes. The effects of Li^{+}, Na^{+}, K^{+}, Mg^{+2}, Ca^{+2}, and Ba^{+2} on the surface charge density of opal have been measured as a function of pH. The results indicate that bivalent ions produce much lower surface charge density than monovalent ions, resulting in less expansive gels. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: pH; Amorphous material; Alkali–aggregate reaction; Aggregate

1. Introduction

The degree of expansion of alkali–silica reaction (ASR) gel is dependent on the valence and relative concentrations of cations present in the ASR gel. Powers and Steinour [1,2] proposed a model to determine which ASR gels would be “safe” or “unsafe,” relative to the amount of calcium as compared to alkali adsorbed on the layer of a reactive aggregate; i.e., ASR gels that contain a high percentage of calcium are nonexpansive. When the diffusion of calcium toward the reaction site is hindered, expansive gels, with low calcium and high alkali content, are formed.

Little research has been conducted on the effect of cations other than calcium and alkali on gel expansion, nor have quantitative predictions on the amount of expansion caused by the gel formation have been made. Recently, the electric double-layer (EDL) theory has been used to model the expansion of ASR gel. One implication of particular interest is the effect of different cations on the expansive pressure generated by the reaction [3,4]. The EDL model predicts that the amount of expansion is determined by the valence of cations present in the ASR gel, with gel expansion decreasing as cation valence increases according to the sequence below:

$$\text{monovalent} > \text{divalent} > \text{trivalent}.$$

To calculate the expansion pressure predicted by EDL model, the surface charge density of the reaction products must be measured [3,4]. In addition, because the surface charge density is determined by the pH of the environment surrounding the solid, surface charge measurements for the prediction of ASR gel expansion should be obtained in conditions similar to those existing in concrete.

Surface charge density measurements can also furnish important information about the nature of interface interactions, such as between the reactive aggregate and the pore solution in concrete. For most oxides, the H^{+} and OH^{-} are called potential-determining ions. In this case, a general acid–base equilibrium can be written as:

$$-\underset{|}{\overset{|}{\mathrm{M}}}-\mathrm{O}^{-}\ \underset{\mathrm{OH}^{-}}{\overset{\mathrm{H}^{+}}{\Longleftrightarrow}}\ -\underset{|}{\overset{|}{\mathrm{M}}}-\mathrm{OH}\ \underset{\mathrm{OH}^{-}}{\overset{\mathrm{H}^{+}}{\Longleftrightarrow}}\ -\underset{|}{\overset{|}{\mathrm{M}}}-\mathrm{OH}_2^{+}$$

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PII: S0008-8846(01)00578-6

The net proton surface charge density, denoted by σ_H, is defined by:

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

where Γ_{H^+} and Γ_{OH^-} are the analytical surface excess of ions H^+ and OH^-, respectively, and F is the Faraday constant (96,485 C mol^{-1}). At a certain pH value, $\Gamma_{H^+} = \Gamma_{OH^-}$, therefore, $\sigma_H = 0$. This pH is defined as the point of zero charge, represented here as PZC.

When an oxide such as silica is in contact with an aqueous electrolyte solution, either physical and/or chemical adsorption can occur. In the case of physical adsorption, only electrostatic forces determine the adsorption. Ions that adsorb to a solid in this manner are called indifferent ions. For silica in an aqueous electrolyte solution, Li^+, Na^+, K^+, and Cs^+ behave as indifferent ions. In the case of chemical adsorption, ions with a certain nonelectrostatic affinity for the solid surface are called specifically adsorbed ions [5].

Specifically adsorbed ions cause changes in the pH versus surface charge density curve as compared to the state when only indifferent ions are adsorbed on the solid. In this case, the value for PZC must be modified in order to account this chemical interaction by introducing the Esin–Markov coefficient [6,7].

Rodrigues et al. [8] reported the net proton surface charge density of silica gel, opal, and quartz as a function of pH in monovalent electrolyte solutions (NaCl and KCl). In the research presented below, the effect of monovalent (Na^+, K^+) and bivalent cations (Mg^{+2}, Ca^{+2}, and Ba^{+2}) on the net proton surface charge density of opal is determined. The final goal is to characterize fully the surface charge density of the gel formed during the ASR reaction. It is difficult to isolate this gel in a typical structure affected by ASR; however, enough material was collected to perform characterization tests that satisfy statistical precision requirements. Although the complete characterization of the expansion of ASR gel is still under way, the net proton surface charge density of ASR gel is presented here as compared with the net proton surface charge density of opal and silica gel.

2. Materials and methods

The opal studied in this investigation is from Don Pedro II in the State of Piaui, Brazil, with a BET surface area of 8.5 $m^2\ g^{-1}$. The opal was shipped as small rocks, and subsequently 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 h. All other reagents used were of analytical grade.

The surface charge density was determined by performing pairs of potentiometric titrations [9,10] under the same conditions. That is, the concentration of background electrolyte solution and the concentration of the base titrant added remained the same for both sets of titrations. The first titration was made in the presence of the solid and the second without it. Each titration started with the same pH value; the volume of base titrant added to attain a higher pH value was different in each titration because of the adsorption of OH^- on the opal surface. Under these conditions and including the addition of a strong base at a concentration much higher than that of H^+ or OH^- in the sample solution, Eq. (1), according to Sonnefeld et al. [9] and Sonnefeld [10], can be written as (Eq. (2)):

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

where σ_H is in units of coulombs per square meter, C_b is the concentration of strong base added, V_s is the 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} is the volume of base added to the system without the solid (blank). Titrations were performed under nitrogen atmosphere in the presence of NaCl, KCl, $BaCl_2$, $MgCl_2$, and $CaCl_2$ at a given concentration (0.1 mol l^{-1}; 1 g solid in 250 ml solution). The titrations began at pH 5.0 and were conducted until pH 10.0. In all cases, an NaOH solution was used to raise the pH. The results were obtained in triplicate.

The same experimental procedure was used to measure the surface charge density for the ASR gel obtained from Furnas Dam. In this case, however, titrations were performed in the presence of 0.7 mol l^{-1} NaCl concentration. The titrations began at pH 10.0 and were conducted until pH 12.0. For a discussion on gel chemistry and morphology, see Kurtis et al. [11].

3. Results and discussion

Figs. 1 and 2 show the surface charge densities of opal measured in presence of mono- and bivalent ions, respectively, as a function of pH. The surface charge density curve presented in Fig. 1 for NaCl and LiCl as background electrolyte shows that the surface charge density grows exponentially with pH. The surface charge density curve for KCl is different, in that the curve increases with pH, but not exponentially. One possible explanation is that an NaOH

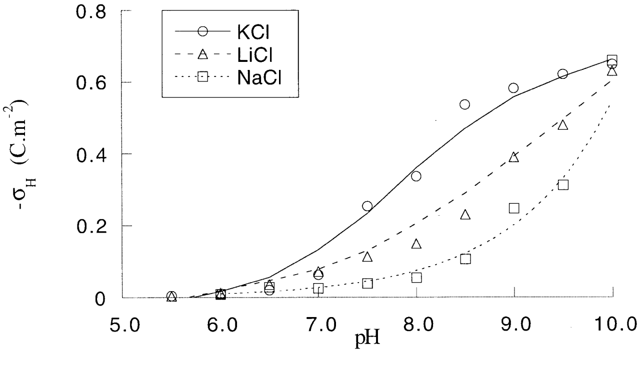

Fig. 1. The surface charge density of opal as function of pH and monovalent electrolyte solution.

solution was used to raise pH for samples in both background electrolytes. With KCl as the background electrolyte, the addition of a different cation (Na^+) may influence the surface charge measurement, since K^+ and Na^+ compete for the same sites on the opal surface. When the pH is equal to 10, the surface charge density measurements for both salts are quite similar.

The surface charge density measurements made when bivalent ions were used in the background electrolyte are presented in Fig. 2. In all cases, the surface charge density values are considerably lower (in absolute value) than when monovalent ions were used as background electrolytes. Israelachvili [12] showed that even small additions of bivalent cations have a pronounced effect on surface charge density. Furthermore, a reversal of surface charge density occurs when the pH equals 7. This effect is well established in the literature and can be predicted using Grahame's equation.

The same behavior can be attributed to the specific adsorption of these bivalent ions on the opal surface. All of the bivalent ions included in this investigation display a specific adsorption on the opal surface. Lyklema [13] proposed the following expression (Eq. (3)) to discriminate between the physical and chemical adsorption processes at the interface:

$$u(x) = zF\psi(x) + g_{\mathrm{esp}}(x) \tag{3}$$

where $u(x)$ is the total energy involved in adsorption, $zF(x)$ is the portion due to electrostatic energy, and $g_{\mathrm{esp}}(x)$ is the chemical component of the adsorption. Note that $g_{\mathrm{esp}}(x)$ does not distinguish the nature of interaction. The chemical component of the adsorption may result from chemical bonding, hydrogen bridging, van der Waals attraction, hydrophobic bonding, or solvent-mediated affinities. The variation of surface charge density or, more specifically, the point of charge reversal, is directly associated with the chemical interaction. Assuming that all experiments were conducted under identical conditions, it may be presumed that the bivalent cations studied in this investigation appear to have approximately the same value for chemical interaction $g_{\mathrm{esp}}(x)$; however, any hypotheses regarding this chemical interaction are restricted to the experimental conditions described here and cannot be directly extended to other systems.

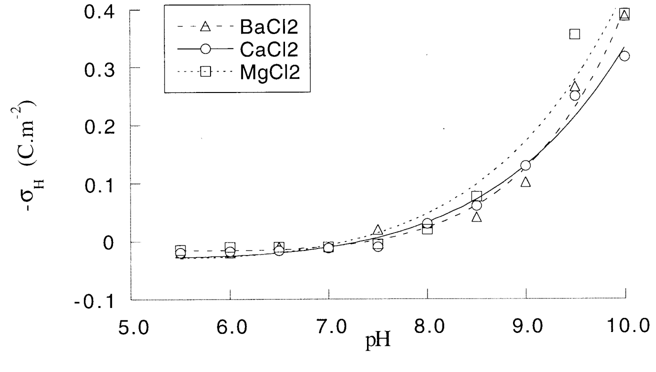

Fig. 2. Surface charge density of opal as function of pH and the type of bivalent electrolyte solution.

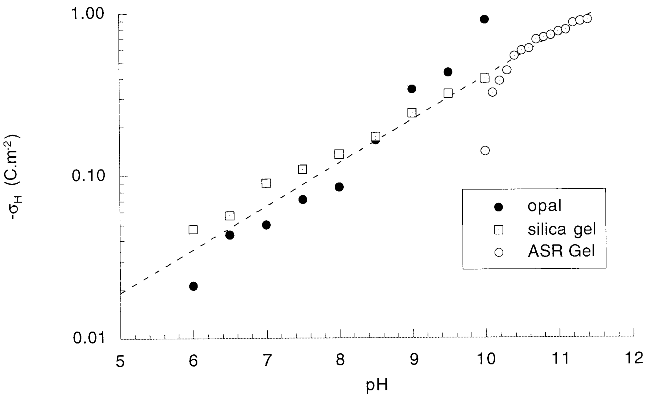

Fig. 3. The net proton surface charge density per unit area of opal, silica gel, and ASR gel as function of pH (0.7 mol l^{-1} NaCl background electrolyte solution).

Fig. 3 compares the net proton surface charge density per unit area of opal, silica gel, and ASR gel as function of pH. The results for silica gel and opal were obtained from Rodrigues et al. [8] and measured in 0.7 mol l^{-1} NaCl background electrolyte solution. A single equation was adequate to fit the net proton surface charge density opal, silica gel, and ASR gel as function of pH. This is very interesting, because the ASR gel is a silicate containing up to 20% K_2O.

4. Conclusions

The plots of opal surface charge density versus pH show that the monovalent cations studied (K^+ and Na^+) are indifferent ions, whereas the bivalent cations (Ca^{+2}, Mg^{+2}, and Ba^{+2}) are specifically adsorbed ions. These differences in adsorption behavior result in lower surface charge density measurements for opal in the presence of bivalent ions as compared to measurements obtained in the presence of monovalent ions. All results are in concordance with predictions obtained using the EDL model.

Acknowledgments

Flavio Rodrigues wishes to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support. Paulo Monteiro wishes to acknowledge the financial support given by the NSF and the Federal Highway Administration (Award CMS-9812757).

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