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Discussion

A discussion of the paper “The alkali–silica reaction. The effect of monovalent and bivalent cations on the surface charge of opal” by F.A. Rodrigues, P.J.M. Monterio, and G. Sposito[☆]

S. Chatterji*

Carl Bernhardsvej 13B, St. 4, DK-1817 Frederiksberg C, Denmark

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This paper reports a type of information that is vitally necessary to understand the physicochemical processes of the alkali–silica reaction in and the accompanying expansion of cement based materials. I congratulate the authors for this information. However, I have some quarries. I hope the authors will have time to answer.

Fig. 1 shows that at pH 10, the surface charge density on opal powder is about 0.7 C/m^2 irrespective of the background electrolyte. However, between pH 7 and 10, the surface charge density depends on the background electrolyte. It is lowest with NaCl and highest with KCl, and LiCl gives the intermediate values. In all these cases, NaOH was used to raise the pH of the background electrolyte solutions. The authors suggested “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.” This explanation should also be applicable for LiCl. A question immediately arises whether surface charge vs. pH curves would have been super imposable if KOH and LiOH were used with KCl and LiCl background electrolytes instead of NaOH as has been used by the authors? Will the surface charge density at pH 10 then be different in each case?

Fig. 2 shows that for the bivalent cations the surface charge development is independent of the particular bivalent cation chloride used as the background electrolyte. In these experiments, NaOH was also used to raise the pH. At pH 10, the absolute charge density is about one-half of that with monovalent cations. One wonders if the use of NaOH has also affected these results.

This brings to my mind some zeta potential measurements I carried out in mid-1950s on silica powders. The zeta potentials were measured using $Ca(OH)_2$ and NaOH as the suspension media. The pH of the each solution was adjusted to 10 by dilution from a stronger solution. The zeta potential was about $+35$ mV in $Ca(OH)_2$ solution and about -35 mV in NaOH solution. This means that the numerical values of the zeta potentials were identical but opposite in sign. I rationalized the results on the assumptions that (i) only a limited number of sites are available for the cation attachment, (ii) these sites are widely separated from each other, (iii) only one cation, irrespective of its charge, attaches itself to one site, and (iv) Ca^{2+} ion forms specific or stronger attachment. Thus, each attached Ca^{2+} will have an unbalanced positive charge thus giving the positive zeta potential. However, Na^+ forms no such specific attachment and will have no unbalanced charge. This explains the negative zeta potential in the case of NaOH. I wonder if the half surface charge density shown in Fig. 2, compared to Fig. 1, could be due to a quarter of the all-available sites that are still being occupied by bivalent ions. If hydroxides of bivalent cations were used to raise the pH, then may be surface charge densities would have been similar to those in Fig. 1.

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* Tel.: +45-3321-0332; fax: +45-3321-0332.

E-mail address: Chatterji@get2net.dk (S. Chatterji).

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