Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 933–934

CEMENT AND CONCRETE RESEARCH

Discussion

A reply to the discussion by S. Chatterji of the paper "The alkali–silica reaction: the effect of monovalent and bivalent cations on the surface charge of opal"☆

F.A. Rodrigues[1], P.J.M. Monteiro*, G. Sposito

Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA

Received 21 November 2002

The authors wish to thank Dr. Chatterji for his insightful comments on our paper. His first query deals with the procedures used to obtain Fig. 1 and gives us the opportunity to elaborate further the methodology and the significance of the data. It should be pointed out that the results shown in Fig. 1 are conditional curves, i.e., they are system-dependent. Having said that, a 250-ml solution with a 0.1-mol/l of background electrolyte concentration is a small amount having little effect. For example, Huang and Fuerstenau [1] assumed that quartz has 5 hydroxyl groups/nm^{-2}, therefore, the number of available sites for a similar value for opal is about 10^{19} OH/m^2. Even in the unrealistic case of 100% salt adsorption, the number of occupied sites is only 25 mmol/g or the equivalent to 3.125 mmol/m^2. Because the solid–solution ratio can also influence the result, the experimental program described kept this ratio constant at 1:250. The presence of CO_2 can also affect the results, particularly at intermediate pH. Therefore, we kept an inert atmosphere through continuous purge of dry N_2.

Fig. 1 provides an insight to the attractive interaction between the electrolytes and the support surface (opal). Monovalent ions appear to have no specific interaction with opal, which means that the adsorption mechanism is based mainly on electrostatic interaction. Results presented in this paper are corroborated by other researchers [2–5]. Based on this assumption, the effect of the hydroxide used to raise the pH should not interfere with surface charge and these values should always be the same. Note that some kind of "preferential" interaction may occur. For example, in 1965 Tien [6] discussed the preferential selectivity of alkali monovalent ions on the basis of Hofmeister series and/or crystal radii. In this study, the affinity between silica and the cations are described by Cs > Rb>K>Na>Li, which is the Hofmeister series. Another important point raised by Dr. Chatterji is that the surface charge densities are about the same at pH = 10 and independent of the background electrolytes, although at lower pH levels the difference is more pronounced. We believe that this behavior is due to the compression of the electrical double layer; at higher pH, the electric double layer is compressed, causing a decrease in the Debye screening length [7].

In the case of bivalent cations, the question of specific interaction arises. Milonjić [8] studied the sorption of alkaline cations on silica surface and compared the effect of sulphate and chloride anions on the overall adsorption behavior. Interestingly, the amount of adsorbed cations is little influenced by the anion. Also, Huang and Fuerstenau [1] studied the adsorption of lead and cadmium onto quartz and talc. Despite some natural differences related to chemical aspects, they found no specific interaction between these divalent cations and quartz surface. These examples show that there is no direct relation between divalent cations and specific interactions. Although Dr. Chatterji makes a clear and rational assumption, we believe that our experimental results are not enough to corroborate his viewpoint.

References

[1] P. Huang, D.W. Fuerstenau, The effect of the adsorption of lead and cadmium ions on the interfacial behavior of quartz and talc, Colloids Surf. A Physicochem. Eng. Asp. 177 (2001) 147–156.

[2] G.H. Bolt, Determination of the charge density of silica sols, J. Phys. Chem. 61 (9) (1957) 1166–1169.

[3] J. Sonnefeld, A. Gobel, W. Vogelsberger, Surface charge density on spherical silica particles in aqueous alkali chloride solutions: 1. Experimental, Colloid Polym. Sci. 273 (10) (1995) 926–932.

[4] T.F. Tadros, J. Lyklema, Adsorption of potential determining ions at silica–aqueous electrolyte interface and role of some cations, J. Electroanal. Chem. 17 (267) (1968) 3–4.

☆ Cem. Concr. Res. 31 (11) (2001) 1549–1552.

* Corresponding author. Tel.: +1-501-643-8251; fax: +1-510-643-8928.

E-mail address: monteiro@ce.berkeley.edu (P.J.M. Monteiro).

[1] Present address: Universidade de Mogi das Cruzes, SP, Brazil, CEP: 08780-911.

doi:10.1016/S0008-8846(02)01070-0

[5] F.A. Rodrigues, P.J.M. Monteiro, G. Sposito, The alkali–silica reaction—the surface charge density of silica and its effect on expansive pressure, Cem. Concr. Res. 29 (4) (1999) 527–530.

[6] H.T. Tien, Interaction of alkali metal cations with silica gel, J. Phys. Chem. 69 (1) (1965) 350–352.

[7] G.V. Franks, S.B. Johnson, P.J. Scales, D.V. Boger, T.W. Healy, Ion-specific strength of attractive particle networks, Langmuir 15 (1999) 4411–4420.

[8] S.K. Milonjić, A relation between the amounts of sorbed alkali cations and the stability of colloidal silica, Colloids Surf. 63 (1992) 113–119.