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Discussion

A reply to discussion of the paper, "The alkali–silica reaction the surface charge density of silica and its effect on expansive pressure"

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The authors wish to thank Dr. Chatterji for his interest in our paper. In his letter, he discusses many different topics; we shall attempt to address all his concerns. He states that our paper does not justify the assumption of applying double-layer models to the alkali–silica reaction (ASR). This is technically correct, since the justification for using these models has been described in detail in two previously published papers [1,2]. Prezzi et al. [1] presented a theoretical basis for using double-layer models to compute the stresses generated by the ASR, and in Ref. [2], an experimental program was designed and carried out to verify these predictions by studying the effect of a wide range of chemical admixtures on the expansion resulting from ASR. One of the critical parameters for determining the stress caused by the ASR is the surface charge density at ionic strengths relevant to the ones existing in concrete pore fluid. As discussed in our paper, there is a significant amount of data on the surface charge density of silica at low ionic strength, but few at concentrations relevant to concrete. Therefore, the purpose of our work was to provide documentation of the surface charge density of silica in such an environment. We selected the concentration of 0.7 mol l^{-1} NaCl to simulate the typical ionic strength reported for pore fluid. When we quoted Chatterji and Kawamura for this value as typical for pore solution, we were referring to the ionic strength and not that the pore solution has 0.7 mol l^{-1} NaCl. We regret any misunderstanding.

Our calculation of the repulsive pressure is for a mid-plane-to-particle-surface distance equal to $1/2k$, as stated in Prezzi et al. [1]. Thus, the interparticle separation is 4 Å at c_0=0.7 M, as indicated by Chatterji. The van der Waals interaction is attractive, thereby lowering somewhat the pressure estimate presented in Eq. (1).

Dr. Chatterji has misunderstood our proposal to apply double-layer models to the ASR. His discussion states that the expansion is caused by the overlap of double-layers between sand particles separated by less than 100 Å distance. Considering the granulometry of the aggregate and the typical spacing between aggregates in concrete, this requirement would be rarely met. More to the point, our goal was to model and predict the expansion of the *ASR gel*, which is formed by silica dissolution of the aggregates in the presence of the alkali pore solution existing in the matrix. Usually, it is difficult finding appropriate amounts of ASR gels in a structure with which to conduct experiments. Fortunately, we have been able to collect a respectable amount of ASR gel formed in the galleries of Furnas dam, a structure that after over 30 years of normal operation has shown expansion due to the ASR. This gel has been analyzed using X-ray microscopy [3], and currently, we are conducting surface charge density measurements under different conditions, as shown in Fig. 1. Comparing these results to the silica gel data reported in our paper, we find there is a remarkable agreement.

Dr. Chatterji refers to an experiment that he conducted in the late 1970s where reactive grains were stored in 0.50 M NaOH containing different amounts of NaCl. He reported

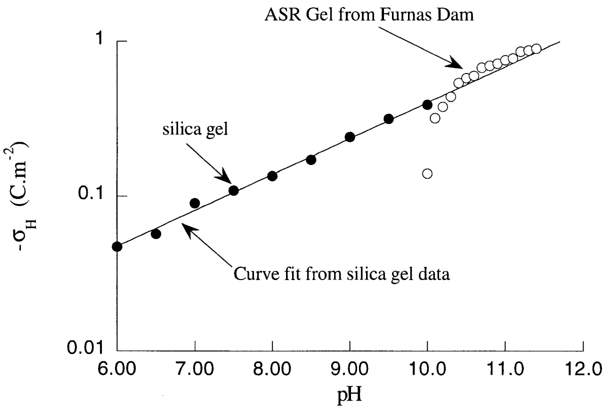

Fig. 1. The net proton surface charge density per unit area of silica gel and ASR gel as function of pH 0.7 mol L^{-1} NaCl background electrolyte solution.

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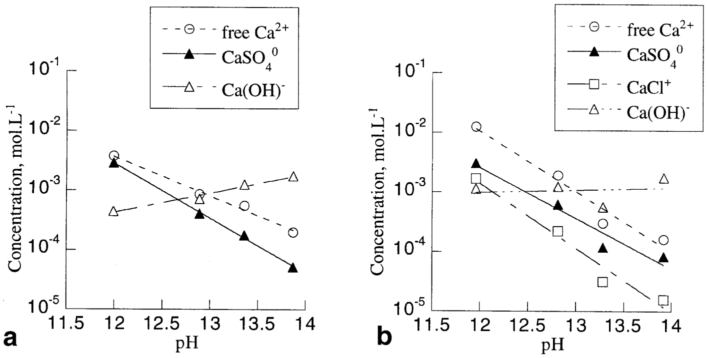

Fig. 2. Chemical speciation analysis of the pore solution (composition data from Page and Vennesland [4]). (a) cement paste—84 days. (b) cement paste with addition of 0.4% NaCl—35 days.

that, while the reactive grains did not show any fracture, the same reactive grains caused ASR distress when used in cement paste. Although we do not know the exact experimental arrangement, this is not surprising, since in aqueous solution at high pH, the reactive aggregate will dissolve, and the resulting gel will be able to expand freely, causing little or no damage to the aggregate. The condition changes drastically, however, when the aggregate is surrounded by a cement paste matrix, which does not allow the free expansion of the gel, thereby generating internal stresses.

Dr. Chatterji points out that powdered quartz has a surface charge density comparable to opal powder. Although it is true that both have approximately the same surface charge density, the dissolution rate of opal is much greater than that of quartz; therefore, the production of ASR gel is higher when compared with quartz. We do agree that bivalent ions can be important to the understanding of ASR. Indeed, we have submitted a paper in which the effect of bivalent ions on the surface charge density of opal is analyzed. As mentioned by Chatterji, the presence of bivalent ions can reduce the pressure and lead to coagulation of the charged particles. The pozzolanic reaction is a perfect example of this.

We disagree with the statement that the "pore solution of a Portland cement paste is not completely free of $Ca(OH)_2$." The presence of free $Ca(OH)_2$ in the pore solution is highly unlikely. For example, an analysis for the calcium chemical species in pore solutions extracted from cement paste by Page and Vennesland [4] is shown in Fig. 2. The speciation analysis was done with the SOILCHEM software [5], and the results clearly indicate the presence of free Ca^{2+}, $CaSO_4^0$, and $Ca(OH)^-$, but not free $Ca(OH)_2^0$. The addition of NaCl to the cement paste also produces $CaCl^+$ in addition to the previous chemical species.

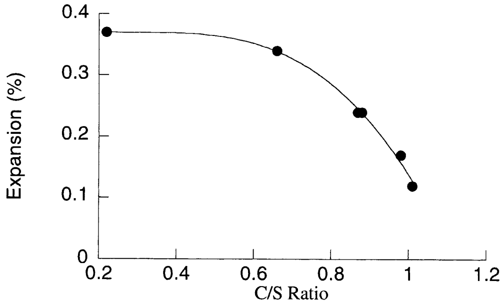

Fig. 3. Mortar-bar expansion as a function of the C/S ratio existing in ASR gel.

Our double-layer model as applied to the ASR gel indicates that gels containing higher amounts of bivalent ions should be less expansive. Since the pioneering work of Powers and Steinour [6], there are a number of experiments supporting this claim. Fig. 3 shows typical results generated by our research [1]. The authors are familiar with Chatterji's model, which requires the presence of free $Ca(OH)_2^0$ as a pre-requisite for a destructive ASR. Chatterji et al. (Ref. [5] in Chatterji's discussion) has proposed that "Ca^{2+}, Na^+, OH^-, and H_2O are pumped in reactive grains; at the same time Si^{4+} ions diffuse (leak) out." Expansion will develop depending on the rate of pumping and leakage; however, the mechanism of diffusion of the species existing in the cement paste pore fluid is more complex than that proposed by Chatterji. Molecular dynamics modeling should bring new insight to this important topic.

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