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Discussion

A discussion of the paper "The alkali–silica reaction. The surface charge density of silica and its effect on expansive pressure" by F.A. Rodrigues, P.J.M. Monteiro, G. Sposito

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In this very interesting paper, the authors have measured the surface charge density of powdered quartz and opal both suspended in NaCl and KCl solutions of different strengths and pH values. The measured values were used to calculated the repulsive pressure between two silica particles using electrical double-layer formalism. The authors simply identified the calculated repulsive pressure with the destructive pressure in alkali–silica reaction without justifying the assumption. It will be of interest to compare the predictions from the double-layer formalism with the known characteristics of alkali–silica reaction.

However, an ethical question has to be cleared first. The authors, on two instances, have credited Chatterji and Kawamura for the opinion that a 0.7 M concentration of NaCl or KCl is "typically found in concrete structures not exposed to deicing salt or sea water." In the quoted reference, no such opinion has been expressed [1]. In that paper, Chatterji and Kawamura exclusively dealt with 0.5 M NaOH solution as a typical pore solution without any chloride contamination. Only once was 0.7 M concentration mentioned in that paper, and even that was in connection with alkali hydroxide solution in a simulated pore liquid. As such, I must decline the credit kindly offered by Rodrigues et al. One wonders about fidelity to other references of the paper.

(i) The main discussion may start with the repulsive pressure Eq. (1) where Ψ_0 is the potential at a point midway between two charged particles, Ψ_D is a scaling parameter, R is the molar gas constant and T is the absolute temperature, and C_0 is the bulk electrolyte concentration. Eq. (1) seems to have been derived from a DLVO-type double-layer model

$$\Delta P = C_0RT[\exp(-\Psi_0/\Psi_D) + \exp(\Psi_0/\Psi_D) - 2] \qquad (1)$$

using a parallel plate approximation. Eq. (1) shows that, in a given electrolyte solution, the repulsive pressure is exclusively determined by Ψ_0. In a double-layer model, Ψ_0 depends on the inter-particle separation. If the inter-particle separation is 'infinite' compared to the "diffuse double-layer thickness," $1/\kappa$, then Ψ_0 is 0 and the pressure also becomes 0. For the repulsive pressure to be substantial, the inter-particle separation has to be of the same order of magnitude as $1/\kappa$; at least less than $10/\kappa$ [1]. One would like to know the inter-particle separations used to calculate the reported repulsive pressures. For a 1:1 electrolyte, $1/\kappa$ is 10 Å in a 0.1 M solution and less than 4 Å in a 0.7 M solution. This means that the inter-particle separations considered were less than 100 Å. At these separations, the van der Waal attraction between the large sand and gravel particles also becomes substantial. Eq. (1) does not seem to incorporate van der Waal attraction; in that case, the net repulsive pressure will be lower than those predicted by Eq. (1).

Experience with reactive Danish aggregates shows that a concrete structure suffers from alkali–silica distress if its sand fraction contains more than 2 vol.% reactive grains even though the gravels were non-expansive. It is highly improbable that in a concrete mix, reactive sand grains are separated by less than 100 Å distance. That means that the required inter-particle separations are cracks, etc., within individual reactive grains and a pressure development should cause fracturing of reactive grains. In late 1970s, the present author stored known reactive grains, including crushed pyrex glass, of definite size ranges in simulated cement pore solution of 0.5 M NaOH containing different concentration of NaCl. There were no fracturing of the reactive grains even after prolonged storage at 50°C. Incorporation of similar in Portland cement mortar bars followed by a storage in saturated NaCl solution at 50°C developed signs of alkali–silica distress in about 2 to 4 weeks. This lack of particle fracturing casts doubt on the

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identity between the double-layer repulsive pressure and destructive pressure of alkali–silica reaction.

One may examine the assumed identity of two pressures from another angle. In Fig. 5 of their paper, the authors showed that even powdered quartz has a surface charge density comparable to, if not slightly higher than, that of opal powder. In a normal concrete, it is more probable that quartz particles will satisfy the required inter-particle separations than 2–4 vol.% reactive grains of the sand fraction. If the assumed identity of the two pressures was valid, then one would expect that all concrete, irrespective of its reactive aggregate content, will suffer from alkali–silica damage when placed in a concentrated salt solution. This is definitely against all observations.

(ii) Pore solution of a Portland cement paste is not completely free of $Ca(OH)_2$. An electrical double-layer model suggests that divalent ions present in a pore solution preferentially accumulate in the double-layer solution and the repulsion pressure is drastically reduced; it may even lead to coagulation of the charged particles. The analyses of diffusion data (of various authors) show that in Portland cement pastes the diffused double-layer, around negatively charged cement hydration products, contains more Ca^{2+} ions than alkali ions [1–3]. Similar accumulation of Ca^{2+} ions is expected to occur in diffuse double-layers round negatively charged silica grains. Recent analyses of in situ alkali–silica gels in damaged concrete samples show high concentration of Ca in them, lending support to the accumulation of Ca^{2+} ion in the diffuse double-layer [4–6]. This is valid even for gels within partially reacted grains. Ca concentration in alkali–silica gel is of the order of 10–20% [6]. It is highly unlikely that such gel could form in the absence of a concentrated Ca^{2+} solution in its immediate vicinity. All of these mean that inter-particle repulsion pressure between charged silica particles is not operative in alkali–silica distress. Incidentally, one of the objectives of reference [1] was to explain this high Ca content of alkali–silica gel.

(iii) In 1979, Chatterji showed that the presence of free $Ca(OH)_2$ in a concrete structure is a pre-requisite of destructive alkali–silica reaction. It was also shown that in the absence of free $Ca(OH)_2$, in a consolidated structure containing reactive aggregates, no expansion occurs even in the presence of NaOH solutions [7]. Since then, other researchers have confirmed the above statements [8,9]. The role of free $Ca(OH)_2$ has even been acknowledged in a standard book on cement chemistry [10]. The above role of free $Ca(OH)_2$ is definitely against the prediction of the diffuse double-layer theory that the removal of free $Ca(OH)_2$ should increase the repulsive pressure and hence the destructiveness of alkali–silica reaction.

(iv) Remedies like high volume additions of ground granulated blast furnace slag, reactive flyash, ground pozzolans, or even ground reactive aggregate themselves all act through their ability to combine with free $Ca(OH)_2$ [11]. The case of adding ground granulated blast furnace slag is particularly interesting. Mortar bars made with blast furnace slag-Portland cement and reactive sand show no sign of alkali–silica reaction when tested by the saturated salt (NaCl) bath technique even after prolonged storage. However, an X-ray examination of the tested bars show the absence of free $Ca(OH)_2$ and the formation of substantial amount of monochloroaluminate hydrate with consequent release of substantial amount of NaOH within the bars [12]. The absence of any alkali–silica distress in these bars again speaks against the identity between the double-layer repulsion pressure and that in alkali–silica reaction.

In conclusion, it could be said that the assumed identity between the double-layer repulsion pressure and that in alkali–silica reaction is not in conformance with the reported characteristics of alkali–silica reaction. Analyses of the above type led to the postulation and testing of a different mechanism of alkali–silica reaction [5,13].

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