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Discussion

Reply to the discussion by G.M. Idorn of the paper "Mathematical model for kinetics of alkali-silica reaction in concrete"☆

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G.M. Idorn made a number of interesting comments. Many of them are helpful and we appreciate them deeply. Our response is as follows.

In his second paragraph, Idorn indicates that the observations made long ago by Vivian and Bredsdorff on powders of opal and flint should have been, regardless of the authors' study, sufficient to infer that the alkali-silica reaction of a very finely ground waste glass ought to be 'nonexpansive' and thus harmless. True, but only partly, and mainly for a different reason. Idorn's use of the term 'nonexpansive' explains why.

It might seem a plausible thought to an experimentalist, but such an inference is not logically consistent to a theoretician. In modeling, the same chemical reaction, the alkali-silica reaction must be considered to produce the same chemical substance, the silica gel, regardless of the particle size, and the same substance must have the same physical properties, including the same expansive properties. Under sufficient water supply, the potential relative ultimate expansion of small and large particles at the same temperature and pressure must be the same.

In view of the currently available limited experimental information, one might of course hypothesize that if the supply of water comes too late, the gel might have undergone some unknown chemical transformation that has deprived the gel of its swelling potential. However, the observations can be explained physically without such an artificial hypothesis.

The reason for the harmlessness of fine silica powders (including silica fume) need not be sought in any lack of

expansion. Rather (as pointed out by Bažant and described in his D.M. Roy Lecture at the Annual Convention of Ceramic Society in Indianapolis in April 2001), it can be logically found in (1) fracture mechanics, combined with (2) pressure-volume isotherm of swelling substances, and (3) scaling of diffusion of the silica gel.

• First, the fracture mechanics reason. Simply stated, the expansion of an inclusion of a very small diameter  $D$  produces a negligible stress intensity factor  $K_I$  on the cracks or flaws in the surrounding solid matrix near the surface of the particle. As made clear in the companion paper [1] (not yet published when Idorn wrote his discussion), the  $K_I$ -value engendered by the same relative volume increase of the inclusion is roughly proportional to  $\sqrt{D}$ . Thus, the  $K_I$  for  $D=0.1$  mm is 10 times smaller than it is for  $D=1$  cm (for the same pressure in the crack). If  $K_I=K_C$  (= fracture toughness of the matrix) for  $D=1$  cm, then  $K_I$  must be totally harmless for  $D=0.1$  mm, even if the relative volume expansion of the inclusion were the same.

• Second, the isotherm reason. The relative volume expansion for  $D=0.1$  mm should not in fact be the same. Rather, it should be less than it is for  $D=1$  cm. This follows by noting that the thermodynamic equilibrium of any swelling substance must be characterized by its pressure-volume isotherm. Unknown though this isotherm still is for the alkali-silica reaction, from analogy with other substances, it is logical to expect that, at a higher pressure the equilibrium water content, as well as the relative volume increase of the swelling gel, must be lower. Consequently, since fracture mechanics shows the smaller particles developing higher pressures (before any damage to concrete), the swelling of these particles must be smaller.

Third, the diffusion scaling reason. The cement mortar matrix surrounding an expanding silica particle always contains very fine pores. The expansion of silica

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gel would be harmless if the gel could be immediately injected into these pores. As assumed in the paper, the thickness  $\delta_c$  of the layer of the surrounding cement mortar whose pore volume can accommodate the silica gel expelled from the silica particle may be expected to be roughly constant. The volume of this layer is roughly proportional to  $D^2$  (assuming that  $\delta_c \ll D$ ), while the volume  $V_{\text{gel}}$  of the unswollen gel (called the basic gel) that can be produced from the particle after a complete reaction is proportional to  $D^3$ . Therefore, the ratio of the pore space available in layer  $\delta_c$  to the potential volume of swollen gel is proportional to  $1/D$ . By this rough estimate, for  $D=0.1$  mm, the relative space accessible for the swelling gel is 100 times larger than for it is  $D=1$  mm (this simple calculation is of course reasonable only if  $\delta_c$  is less than about  $D/5$  for the minimum  $D$ ). So, for smaller particles, there is much more opportunity for the gel produced to be expelled by diffusion into the surrounding matrix. Thus, it is, for example, possible that before the fracturing of the matrix takes place, virtually *none* of the swollen silica gel formed from the silica particle can be expelled into the pores when  $D=1$  cm, and virtually *all* of the gel can be expelled when  $D=0.1$  mm.

These kinds of mechanisms operate not only in the aggregate–silica reaction but in all the expansive reactions. If the expansion produces a fluid, as in the case of silica gel, all the three aforementioned arguments (mechanisms) contribute to the enormous beneficial effect of greatly reducing the particle size. If the particle during the expansion remains a solid, the diffusion reason disappears, which means that the effect of particle size is less pronounced and a greater reduction of particle size is necessary to make the expansion harmless. Nevertheless, a sufficient particle size reduction must exist to make any given expansion harmless.

When the silica gel fills the very fine pores in the hardened Portland cement paste and mortar in the vicinity of the silica particle matrix, one must expect the matrix to be strengthened. Indeed, when the pores get filled, the microstructure becomes more homogeneous, and so the stress concentrations in the microstructure caused by applied load become smaller. This is likely to be the proper physical explanation of the pozzolanic action, applicable to the strengthening of concrete caused by adding silica fume and other very fine siliceous powders. Silica particles that are too large cannot strengthen concrete because their expansion causes fracturing before the reaction product can fill the fine pores. When they are small enough, filling of the fine pores occurs before fracturing can take place.

Regarding Idorn's first set of bulleted comments, directed at the main objectives, the following response is pertinent.

- As stated in the paper, the numerical calculations were confined to the case of the waste glass aggregate,

in which case the question of presaturation does not arise. However, the general model covers this case: it suffices to set the self-desiccation term  $h_s(t_c)$  from Eq. (24) to zero. The model will then automatically yield pore humidity of 100%, unless a front of drying arrives from the surface.

- We agree with the comment that the pore liquid is a saturated  $\text{Ca}(\text{OH})_2$  solution, but this fact does not detract from the validity of the model and is in fact mentioned in the paper.

- Similarly, although we were aware that calcium ions can diffuse into the alkali–silica gel after it has formed, we did not model this process, for the sake of simplicity. To model it, one would need to add to the model a diffusion equation for these ions, while their reaction at the front could probably be considered instantaneous compared to the diffusion times.

- Idorn's point that "in closed systems, . . . the creation of alkali–silica gel causes shrinkage, not swelling," is puzzling. We have noticed such comments in the literature, however, the situation has never been described clearly enough to allow setting up a mathematical model. The alkali–silica gel can, of course, shrink if it is exposed to dry environment, but it is hard to see how it could shrink to a smaller volume than that of the silica from which it has previously formed. These observations in the literature probably stem from overlooking other shrinkage-causing processes, which might have prevailed in some field situations. To resolve the question, one would need a well-documented, detailed investigation under precisely defined conditions.

- We of course agree that the kinetics of ASR follows Arrhenius' law. In mathematical modeling, however, one should consider the temporal scaling. The assumption that a tiny element of silica at the diffusion front within the silica particle reacts almost immediately should be understood in relative terms. It means that the duration of the reaction of each tiny element is small compared to the time needed for the diffusion of ions to the reaction front. This assumption is certainly realistic, which means that the reaction can be modeled as instantaneous. Even if the temperature was considered to vary, the temperature dependence of the Arrhenius law would not matter because, under the aforementioned assumption, the overall temperature effect would be controlled by the temperature dependence of the diffusion coefficients (or permeability) and possibly the hydration reactions, but not by the time taken by the chemical reaction per se.

In his second set of bulleted points, Idorn remarks on the reaction occurring along localized paths through a piece of mineral aggregate. Such an alternative form of the reaction was discussed in the paper. But it was also stated that the analysis would focus on the case of waste glass, which has a nearly homogeneous composition. The mathematical model could, of course, be adapted to take

into account inhomogeneity of the reactive particles, as typically found in mineral aggregates. The paper included some comments on such an adaptation (for example, it was pointed out that when silica veins are present in the mineral aggregate pieces, the diffusion is not spherically converging but geometrically linear). Although the adaptation would be easy, it was not carried out because of space limitations and the focus of the funded project.

In conclusion, we would like to thank Idorn for a very stimulating discussion.

### References

- [1] Z.P. Bažant, G. Zi, C. Meyer, Fracture mechanics of ASR in concretes with waste glass particles of different sizes, *J. Eng. Mech., Div. Am. Soc. Civ. Eng.* 126 (3) (2000) 226–232.