Pergamon

Cement and Concrete Research, Vol. 27, No. 4, pp. 629–630, 1997
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0008-8846/97 $17.00 + .00

PII S0008-8846(97)00047-1

DISCUSSION OF THE PAPER TITLED DELAYED ETTRINGITE FORMATION IN A 4-YEAR-OLD CEMENT PASTE BY R. YANG, C.D. LAWRENCE AND J.H. SHARP

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(Received December 10, 1996)

In their interesting paper [1] the authors studied the texture of heat cured OPC pastes which exhibited expansion due to delayed ettringite formation. They tentatively attributed the expansion to the formation of "ettringite bands" (i.e. macrocracks filled with ettringite) which, together with empty cracks, were concentrated in a region close to the surface of the 40 × 40 × 160 mm large test specimens.

The question arises, how the cracks in the paste, both empty and filled with ettringite, were created. Did the formation of ettringite, found in a part of the cracks, produce these cracks, as assumed by the authors, or did ettringite just crystallize in cracks first formed by another mechanism? Several experimental observations and some deliberations may help to elucidate this problem.

As the paste specimens submitted to heat curing consisted of the same material both in the central and peripheral regions one would expect a uniform distribution of newly formed reaction products, including ettringite, within the specimen. And, in fact, the amount of ettringite found in both regions by x-ray diffraction was almost identical, i.e. 7.1 and 8 percent. Nevertheless, ettringite detectable microscopically was confined to a region close to the surface of the specimen, i.e. to a region in which empty cracks were also preferentially located. This suggests that a precipitation of this form of ettringite takes place only where sufficient space for crystal growth is available (i.e. within the cracks), whereas a microcrocrystalline form of this phase is formed within an intact, crack free cement paste. This conclusion is in line with our own earlier observations on the morphology of formed ettringite: while a microscopically detectable acicular form of ettringite is readily formed on surfaces of clinker submerged into a calcium sulfate solution, this form of ettringite is absent within dense cement pastes made from the same clinkers [2].

The question then arises, how do cracks within the heat cured paste form and why do they preferentially form in the surface region of the specimen? One possible explanation is that they form in response to mechanical stresses associated with thermal gradients within the specimen in the course of heat curing. Such a mechanism, however, seems to be rather unlikely, due to the limited size of the studied specimens and the absence of simultaneous water loss by evaporation, which takes place if heat curing is done in air. Also, the fact that cracks became apparent only months after heat curing suggests that this mechanism probably was not involved.

The possibility also exists that at least some of the cracks are formed during the course of drying, which had to precede the study of the specimen by SEM. This mechanism is probably the one responsible for the formation of cracks found in the reference specimens which did not undergo heat curing. It may also be responsible for the formation of the cracks in the heat cured specimens which were not filled with ettringite. However, the formation of cracks filled with ettringite, which had to exist in the material before the ettringite started to crystallize in them, cannot be explained by this mechanism.

In our opinion, the cracks found in the peripheral region of the heat cured hardened paste are mainly due to a delayed formation of microcrystalline ettringite, detectable by X-ray diffraction and DTA, but not by secondary electron imaging at magnifications used by the authors, within the hardened paste. The expansive forces generated by this reaction may well explain the observed overall expansion of the test specimen, as well as the formation of peripheral cracks due to tensile stresses which develop in this region under such conditions. This hypothesis seems to be supported by our own experiments conducted with significantly smaller specimens, less prone to crack formation (10 × 10 × 60 mm). Here, an expansion of heat cured specimens, associated with delayed formation of finely dispersed microcrystalline ettringite, was observed, even though neither visible cracks nor microscopically detectable regions of ettringite could be detected [3].

Admittedly, the oriented growth of microscopically detectable ettringite crystals in preexisting macrocracks (for which the designation "secondary ettringite" has been suggested) may also contribute to the expansion of the material and may have been responsible for the non-uniformity of the expansion and bending of some of the test specimens studied by the authors. However, we believe that his mechanism is of limited significance and may cause expansion only if enough cracks were previously created by another mechanism, to sufficiently weaken the cohesion of the material.

The "ettringite bands" described by the authors exhibit a similarity with ettringite filled gaps regularly seen at the macroaggregate-paste interface in heat cured concretes exhibiting delayed expansion. We believe, that such gaps are also first formed by an expansion of the paste due to delayed formation of microcrystalline ettringite and that the precipitation of microscopically detectable ettringite in the preexisting gaps is just a secondary phenomenon.

References

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