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REPLY TO THE DISCUSSION BY I. ODLER OF THE PAPER "DELAYED ETTRINGITE FORMATION IN 4-YEAR-OLD CEMENT PASTES"

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We should, firstly, thank Odler for his stimulating discussion of how the cracks in DEF expanded cement paste and concrete are formed. He accepts that our paper only offers tentative conclusions, and finds interesting similarities between our data and his results. We consciously did not comment too much on the mechanism of crack formation because we have further work on cement mortars [1] in progress to extend our studies of cement pastes.

We agree that there are currently two possible mechanisms to explain crack formation and associated expansion related to DEF [2-5]:

(i) Delayed formation of ettringite bands brings about development of cracks and causes the observed expansion.
(ii) Alternatively, cracks are formed by uniform paste expansion and subsequently ettringite crystallizes therein. The resulting ettringite bands give a small or no contribution to expansion. Many researchers have postulated that uniform crystallization of ettringite in cement paste (in C-S-H gel) is a cause of expansion.

In our experiments, we omitted any aggregate and tried to minimize conditions to bring about cracking of the paste, such as inadequate pre-curing, prior to heat treatment. The sample that was heat cured had many visible cracks in regions along one side surface of the prism. The surface with many visible cracks was vertical to the casting surface. Larger expansion was observed where visible cracking had occurred so that the prism was eventually bent. Backscattered electron imaging (not secondary electron imaging as was stated by Odler in his commentary) showed that many more ettringite bands appeared in this region of the prism than in the opposite surface. Few ettringite bands appeared in the central region of the prism.

Odler tries to interpret the current experimental phenomena in terms of an ill-defined volumetric expansion of the cement paste. He suggests that an expansive force was generated by delayed formation of microcrystalline ettringite, which was finely dispersed in the C-S-H gel so as to be only detectable by XRD or DTA but not by backscattered electron imaging. This expansive force brought about the development of cracks and resulted in the overall expansion of the paste. The subsequent infilling with crystalline secondary ettringite

to form bands is regarded as essentially non-expansive. On this basis, the ettringite bands are a consequence rather than a cause of the overall expansion.

The formation of microcrystalline ettringite within C-S-H gel, however, has been reported to occur at a relative early stage in the storage of the paste specimens after heat cure, without causing overall expansion [6]. Thus the formation of microcrystalline ettringite does not necessarily lead to expansion. Our experimental results also do not support Odler's hypothesis. When the results of x-ray microanalysis shown in Fig. 6(c) and in Fig. 6(e) in our paper are compared, it is seen that the S/Ca and Al/Ca ratios of the inner products and the outer products (C-S-H gel), in which microcrystalline ettringite possibly formed, were significantly higher in the central region of the prism than in the surface region, where visible cracks and ettringite bands concentrated and large expansion occurred. These observations imply that the process of DEF expansion corresponds to reducing the levels of sulphate sorbed by C-S-H gel and microcrystalline ettringite dispersed in C-S-H gel rather than increasing them. This observation has been confirmed during our further work on mortars [1]. Therefore, we suggest that formation of ettringite bands through reaction of sulphate and aluminate ions expelled from C-S-H gel is the reason for crack development and overall expansion.

We note, with interest, the experimental evidence [7] provided by Odler which seems to give some support to the uniform paste expansion hypothesis. 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. Nevertheless this statement is at variance with the record set out, since both cracked and bent specimens are mentioned by Odler and Chen [7]. No micrograph nor even a sentence about the microstructure of the heat cured cement pastes is presented. We have observed the microstructure of many heat cured mortars and two heat cured cement pastes, which have shown different extents of expansion associated with DEF, by backscattered electron imaging. Ettringite bands have appeared in all of them.

The evidence in our paper is that two sets of disturbances are present in the cement paste microstructure in the heat-cured material, viz. a network of nearly empty microcracks, averaging about 2-5 μm width, and a set of ettringite bands, of the order of 10-20 μm wide, running for considerable distances through apparently sound paste matrix. Thus, our evidence is not for ettringite bands forming in pre-existing microcracks or gaps, as suggested by Odler, but rather for ettringite bands being generated spontaneously in sound cement paste. The generation of ettringite bands probably leads to expansion and possibly also to microcracking.

It should be noted that for cement mortars and concretes, the character of the expansion can be related to the type of aggregate present. For example, limestone aggregate results in a much delayed expansion compared with that shown by quartz aggregate [3]; thus the type of aggregate paste interface has a major influence on the subsequent expansion behaviour. A mechanism that regards the aggregate particles as inert inclusions, taking no part in the chemical or microcrystalline processes involved in DEF, is clearly incomplete.

Odler's final paragraph discusses the behaviour of mortars, and much of the discussion in his 'comment' has been developed for the case of mortar expansion. His mechanism of mortar expansion is similar to that of Johanson et al. [2]. In our study on DEF of portland cement mortars [1], we report evidence to show that formation of ettringite bands can create, extend and widen the cracks, and hence cause the overall expansion of the heat cured mortars.

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