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Discussion

Reply to the discussion by S. Chatterji of the paper "Delayed ettringite formation in heat-cured Portland cement mortars"☆

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We are grateful to Dr. Chatterji for his kind comments about our paper [1]. He asks two very perceptive questions that we are attempting to address in our continuing research into the vexed questions of delayed ettringite formation and its consequences.

Chatterji's first query relates to the sequence of formation of ettringite and monosulfate in the mortars cured at ambient temperatures. He notes correctly that the ettringite content decreased and then increased slowly. Two comments have to be made before we attempt to answer his specific question about the source of the sulfate ions for this late formation of ettringite. The first is that he has quoted the times at which this phenomenon was observed incorrectly. The amount of ettringite determined after various times is shown in Fig. 2 of Ref. [1] plotted against the *square root* of time, so that the amount of ettringite formed in the control mortar cured at room temperature increased to reach an apparent maximum of 5% after 7 days, decreased to 4% after 28 days, then gradually increased to 7% after 360 days. These data correlate rather better with the qualitative data relating to the formation of monosulfate that Chatterji correctly estimated from Fig. 3 of Ref. [1]. The second comment relates to the errors associated with the data shown in Fig. 2. Quantitative X-ray diffraction (QXRD) is a difficult technique, especially when applied to a phase such as ettringite. It is inevitable that there is an experimental error associated with each individual determination. Although we are confident about the general trends indicated by the data shown in Fig. 2, we would be cautious about the detailed interpretation of changes between each individual pair of experimental points.

Two of the authors have extended the reported study [1] to include QXRD studies on three further mortars based on different Portland cements, and full reports on them have been written [2,3]. In Ref. [3], we report on the almost immediate formation of ettringite in these mortars when cured at room temperature, followed by the expected conversion of ettringite to monosulfate, leading to a maximum in the amount of monosulfate and a corresponding minimum in the amount of ettringite. Subsequent conversion of monosulfate to ettringite was distinctly observed in two of the three mortars studied. It is not yet apparent what the driving force is that results in such late formation of ettringite. No evidence for even a slow release of sulfate ions from the anhydrous clinker was observed by XRD or SEM. In heat-cured samples stored at ambient temperatures, there is now overwhelming evidence in favour of the gradual release of sulfate ions, that had been sorbed during the heat cure, from C–S–H gel, and these ions provide the potential for the formation of delayed ettringite in such systems. It is possible that a slow release of sulfate ions from C–S–H gel occurs even in some cementitious materials cured at ambient temperature, hence providing the driving force for the observed late formation of ettringite. C–S–H gel formed at ambient temperature is capable of sorbing a certain amount of sulfate [4]. The X-ray microanalysis data reported in Fig. 11 of Ref. [1] indicate that the sulfate content of the C–S–H gel (the inner and outer products) gradually decreased on ageing. The sulfate released from the C–S–H gel may react with monosulfate to form ettringite, and also with the interstitial clinker phases (C3A and ferrite) to form monosulfate. In fact, our results for the degree of hydration of the cements studied [2] showed that the interstitial phases were mostly hydrated after 90 days, and subsequent hydration of the remaining anhydrous interstitial phases was very slow. Hence, it is concluded that the sulfate released from the C–S–H gel is most likely to react with monosulfate, resulting in late ettringite formation as reported.

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Chatterji's second question relates pertinently to the most fundamental problem concerning DEF. Why is it that sometimes formation of ettringite is associated with expansion, whereas on other occasions no such expansion is observed? To provide a complete answer may require much further research, but we do have some embryonic ideas and would be interested to hear the views of other scientists in the field.

Although sulfate expansion of cementitious materials is frequently attributed to formation of ettringite, a simple correlation between the quantity of ettringite formed and the magnitude of the resulting expansion is not apparent. In many situations ettringite formation does not even result in expansion [5], although an increase in the extent of expansion with increasing amount of ettringite formed as determined by QXRD has been reported in many expansive cement systems [6–9]. This complexity suggests that sometimes ettringite formation can contribute to expansion, but on other occasions it does not. We believe that the location and distribution of the ettringite that is formed are important criteria for the distinction between expansive and non-expansive ettringite. For the mortars cured at room temperature, the SEM and X-ray microanalysis results [1] indicated that the ettringite was finely intermixed with the C–S–H gel and widely distributed in the outer products. The additional ettringite formed beyond 28 days hydration remained widely dispersed in the mortar. In such circumstances, a large amount of ettringite has to be formed to generate an observable expansion, because the expansive force is also dispersed. Portland cement mortars cured at room temperature cannot produce a sufficiently large force to bring about expansion.

In the case of heat-cured mortar, however, the initial heat treatment alters the distribution of the ettringite that is formed. The delayed ettringite is not well intermixed with the C–S–H gel, nor is it dispersed in the outer products; instead it is concentrated in the observed ettringite bands. The SEM micrographs shown [1] indicated the formation of bands in the heat-cured mortars, whereas there were very few concentrated areas of ettringite apparent in the room temperature-cured mortars. The random X-ray microanalysis results shown in Fig. 12 (b) and (c) indicated that only a small proportion of the analyses in the outer products of the heat-cured mortars contained high levels of sulfate, indicating that the ettringite was locally concentrated rather than widely dispersed. Although the amount formed is not large and is not more than that present in room temperature-cured mortar, this concentrated formation of ettringite in the dense microstructure of the mortar may result in sufficient expansive force to generate observable expansion.

References

[1] R. Yang, C.D. Lawrence, C.J. Lynsdale, J.H. Sharp, Delayed ettringite formation in heat-cured Portland cement mortars, Cem Concr Res 29 (1) (1999) 17–25.

[2] R. Yang, J.H. Sharp, Hydration characteristics of Portland cement after heat curing: Part I. Degree of hydration of the anhydrous cement phases, J Am Ceram Soc, submitted for publication.

[3] R. Yang, J.H. Sharp, Hydration characteristics of Portland cement after heat curing: Part II. Evolution of crystalline aluminate-bearing hydrates, J Am Ceram Soc, submitted for publication.

[4] I. Odler, Investigations between gypsum and the C–S–H gel formed in C3S, 7th International Congress on the Chemistry of Cement, Paris Vol. IV, (1980) 496–503.

[5] H.F.W. Taylor, Sulfate reaction in concrete — microstructural and chemical aspects, in: E.M. Gartner, H. Uchikawa (Eds.), Cement Technology, Ceramic Transactions Vol. 40, American Ceramic Society, Westerville, OH, 1994, pp. 61–78.

[6] I. Odler, M. Gasser, Reply to comment by S. Chatterji on the paper Mechanism of sulfate expansion in hydrated Portland cement by I. Odler, M. Gasser, J Am Ceram Soc 7 (11) (1988) 1015–20, J Am Ceram Soc 74 (1) (1988) 251.

[7] Y. Wang, M. Su, R. Yang, B. Liu, A quantitative study of paste microstructures and hydration characteristics of sulfoaluminate cement, 9th International Congress on the Chemistry of Cement, New Delhi, India Vol. 4, National Council for Cement and Building Materials, New Delhi, India (1992) 454.

[8] I. Odler, Y. Chen, Effect of cement composition on the expansion of heat-cured pastes, Cem Concr Res 25 (4) (1995) 853–862.

[9] M.C. Lewis, K.L. Scrivener, S. Kelham, Heat curing and delayed ettringite formation, Mater Res Soc Symp Proc 370 (1990) 67–76.