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A DISCUSSION OF THE PAPER "ON THE DISTINCTION BETWEEN DELAYED AND SECONDARY ETTRINGITE FORMATION IN CONCRETE" BY Y. FU AND J.J. BEAUDOIN*

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The authors (1) have set out a clear and useful distinction between the terms delayed ettringite formation (DEF) and secondary ettringite formation (SEF). These terms are used interchangeably in the technical literature and are often confused (1,2). The distinction defined is of value in investigations of hardened concretes and mortars, particularly where problems of sulphate attack and other expansion phenomena actually arise. As the authors point out (1), DEF does not usually occur in concrete cured at normal temperature. This is an important point to bear in mind.

With the current high interest being shown in DEF, it needs to be emphasized that DEF (where expansion is slow) does not necessarily cause cracking per se. This cracking can also be dependent upon other factors, such as rate of expansion and competence of the immediate surroundings and the plasticity. Also, both DEF and SEF may coexist in the same concrete or mortar, depending upon the history of mixing, curing and placing into position in the given environment, as well as upon considerations of durability. Therefore care needs to be exercised when interpreting the precise causes of the later formation of ettringite in concretes or mortars. Importantly, the clear cut definitions for DEF and SEF only apply for ettringite formed later in Portland cement-based concretes and mortars. Primary ettringite formation (produced during the normal course of Portland cement hydration from the aluminate C_3A and the ferrite C_4AF phases) mostly arises early in the hydration when the mix is still relatively plastic and is thus not a cause per se of expansion to any significant extent. The subsequent change of ettringite (otherwise known as AFt phase) to the monosulphate (AFm phase) is normally incomplete and residual primary ettringite commonly exists in hardened concretes and mortars after many years.

Later formation of ettringite can also occur in calcium aluminate (high alumina) cements (CAC) that are cured and placed at unacceptably high water/cement (w/c) ratios in sulphate environments and where the effects of high temperatures are readily apparent. Ettringite is not a product of normal CAC hydration (3,4). Hence there is no "primary' ettringite being formed as with hydrating Portland cements. It is formed as a result of deterioration of CAC concrete or mortar in sulphated environments. After all, CACs only contain small sulphate levels, commonly around 0.05% SO_3 in the dark grey cements and often less in the white refractory cements. Therefore, there is neither a significant internal sulphate content nor any

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*Cem. Concr. Res. 26, 979–980 (1996)

residual calcium hydroxide (portlandite) available for encouraging any potentially expansive reaction with the SO_4^{2-} ions (5). Consequently, formation of ettringite within a hydrating or hydrated CAC can only be encouraged by the ingress of external SO_4^{2-} and other ions at unacceptably high w/c ratios, which can facilitate reaction with some of the calcium aluminate hydrates formed during hydration (CAH_{10}, C_2AH_8 and sometimes C_4AH_{13}) and subsequent conversion to C_3AH_6, in the presence of excess water. CAC normally gives very good sulphate resistance when the w/c ratio does not exceed 0.4. Even above 0.4, reasonable sulphate resistance may still arise at times up to *ca.* w/c 0.6, but is not recommended in practice for field use (6,7).

Scanning electron microscopic studies (8,9) on a dark grey Ciment Fondu mortar (sand: cement, 3:1), which had been cured at the unacceptably high w/c ratio of 0.6 under elevated temperature conditions and stored for one year in 5% sodium sulphate solution, showed evidence of DEF. This DEF bore a distinct resemblance to that encountered in Portland cement-based concretes and mortars. Clusters of long, well-defined pseudohexagonal prisms of ettringite had arisen, which were of a relatively large size in comparison with the rest of the cement matrix. This indicated that crystallization had taken place subsequent to pore formation and solidification. The ettringite crystals observed here had grown in the available space and had not per se caused the fine cracking found.

At even higher and therefore even more unacceptable w/c ratios, where the quality of the CAC concrete is obviously poor, the internal possibilities for transport within the hardened structures of ions such as Ca^{2+}, Al^{3+} and SO_4^{2-} in the aqueous medium are even greater than for the aforementioned situation. Such possibilities for transport are aided by the higher voids and permeability arising within the structures as a result of hydration and subsequent conversion. In these situations, the ettringite formed as a consequence of the sulphate attack is not as delayed in its appearance as that described above. As a result the sulphate attack being considered here is more severe and occurs much earlier than the DEF mentioned above. So, in CAC, DEF is in essence a relative phenomenon that arises when the permeability of the structure is still sufficiently low that ettringite can only slowly be formed by the ingress and transport of the necessary ions in the aqueous medium. Where the barriers to SO_4^{2-} ion ingress are much less and the internal transport of ions in water or moisture are much greater, such as those situations in which w/c ratios are in excess of *ca.* 0.6 and/or in more heavily sulphated environments, ettringite can be formed in appreciable quantities at much earlier ages, which would not be appropriate to describe as being delayed.

Our experiments (8,9) that had been undertaken at w/c 0.6 showed from EDAX analysis that the delayed ettringite formed $C_3(A,F).3CaSO_4.31\text{-}32H_2O$ contained surprisingly little iron, the Al/Fe ratio of the pseudohexagonal prisms examined being around 56-60. This could be contrasted with the original cement where the Al_2O_3/Fe_2O_3 ratio was 3.1, giving an Al/Fe ratio of 2.35. These results indicated that in the mortar we have studied, in which the internal transport of ions was relatively restrained, the ferrite phase provided much greater resistance against sulphate attack than the aluminate phases in the hydrated matrix (9).

In conclusion, the author's simple, neat classification of the distinction between DEF and SEF in Portland cement concrete and their critical appraisal of the Duggan accelerated test (10), which involves several thermal-drying/rewetting cycles followed by length-change measurements on concrete cores in water, have provided a significant contribution to our further understanding of both delayed and secondary ettringite formation. The situation for calcium aluminate cement is somewhat different on account of the lack of any primary ettringite during hydration coupled with the high resistance to sulphate attack under normal conditions of usage.

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