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A Discussion of the Paper "EFFECT OF SULPHATES ON THE SETTING TIME OF CEMENT AND STRENGTH OF CONCRETE"

by S. Kumar and C.V.S. Kameswara Rao*

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In their paper, Drs Kumar and Kameswara Rao have described some very interesting experiments in which the effects of different sulphates in solution upon the setting times of ordinary Portland cements and the 28 day compressive strengths of Portland cement concrete have been investigated(1). They found that the type of sulphate and the ionic concentrations present in the aqueous phase have a significant effect upon the setting times of cement and also upon the relative reduction in the compressive strength of concrete at different ages.

The authors(1) rightly attribute the greater destructive effect of magnesium sulphate to its decomposition of the calcium silicate hydrate. However, such decomposition can involve not only the production of gypsum, magnesium hydroxide (brucite) and silica gel as reported(1), but also (normally at longer ages) some formation of a non-bonding magnesium silicate hydrate M_2SH_x as an ultimate deterioration product(2,3).

Sulphate-resisting cements, by their particular compositions, give greater protection against sulphate attack than ordinary Portland cements do. However, such cements are not totally sulphate resistant under extreme conditions of sulphate attack or where the permeability of the hardened cement/concrete is insufficiently low to prevent significant ingress and transportation of SO_4^{2-} and other ions through the hardened cement, mortar or concrete.

A case in point is calcium aluminate (high alumina) cement, which gives very good sulphate resistance over a wide range of conditions(4,5). Even here, at high water/cement ratios, particularly above the recommended maximum value of 0.4 for minimising high early transient strength loss through conversion (transformation) of the initially formed metastable hexagonal hydrates CAH_{10}, C_2AH_8 - and sometimes C_4AH_{13} as well - into the denser stable cubic hydrogarnet C_3AH_6(6-8), ingress of SO_4^{2-} ions and their transport within the structure can increasingly take place. This causes the cement to become more susceptible to the deleterious effects of sulphate ingress as a consequence of the greater porosity and permeability normally present after conversion.

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For example, recent results from an electron microscopic examination of Ciment Fondu mortar (sand:cement 3:1) cured under elevated temperature conditions at the unacceptably high water/cement ratio of 0.6 and stored for one year in 5% sodium sulphate solution has shown evidence of delayed ettringite formation (see Figure 1). This is akin to that encountered with Portland cements(9-11), in that clusters of pseudohexagonal prisms have formed after several months in available spaces. The porosity and permeability of the calcium aluminate cement have been high, as would be expected with a water/cement ratio of 0.6. The appearance of clusters of long, well defined pseudohexagonal prisms of ettringite $(C_3A,F).3CaSO_4.31\text{-}32H_2O$ and their relatively large size compared with the rest of the cement matrix suggests that these clusters have crystallised subsequent to pore formation and solidification. The high water/cement ratio would have led to high voids through hydration and conversion, which would have aided internal transport of ions like SO_4^{2-}, Ca^{2+} and Al^{3+} in the aqueous medium.

Figure 1: Clusters of ettringite formed in a void after one year's hydration (2400x mag.)

In conclusion, the authors' work (1) has shown that the setting times of ordinary Portland cement increase monotonically with SO_4^{2-} concentration up to around 3000 ppm SO_4^{2-}, after which there is a drop in the percentage increase in the initial setting time, with the different cations influencing the degree of attack, and the compressive strengths being adversely affected to different degrees by the respective cations. These results indicate the importance of a number of factors. Such factors include the ionic solubilities promoting internal transport of ions through the hardened Portland cement structure coupled to the relative rates of diffusion of the sulphate solutions into the concrete and to the precise hydration products formed, which are all influenced by the permeabilities of the hardened concrete structures. Thus this paper(1) is a useful contribution towards our greater appreciation of the numerous practicalities of attack upon Portland cement concrete in sulphate environments.

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A Reply to the Discussion by J. Bensted and J. Munn of the Paper "EFFECT OF SULFATES ON THE SETTING TIME OF CEMENT AND STRENGTH OF CONCRETE"*

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The authors are thankful to Bensted and Munn for their interest in the paper and their comments. The authors agree that the formation of non-bonding magnesium silicate hydrate M_2SH_x can also occur and influence the basic chemistry of the phenomenon. Further work in this area will add to our understanding of the influence of sulfate environments on the behaviour of portland cement concretes.

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