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DISCUSSION

DISCUSSION OF THE PAPER "DELAYED ETTRINGITE FORMATION: THE EFFECT OF TEMPERATURE AND BASICITY ON THE INTERACTION OF SULPHATE AND C-S-H PHASE" BY L. DIVET AND R. RANDRIAMBOLOLONA[1]

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Drs. Divet and Randriambololona have shown that the adsorption capacity of SO_4^{2-} ions on C-S-H is high and dependent upon both the basicity of the concrete pore solution and the temperature to which the concrete structure is subjected, with higher pH and temperature favoring adsorption. The relationship between free and bound sulfates has been described by an adsorption isotherm of SO_4^{2-} ions on C-S-H being reversible (1). The physical adsorption of the sulfates onto the C-S-H samples, combined with the previously observed phenomenon (2) that the range of thermal stability of ettringite $C_3A{\cdot}3CaSO_4{\cdot}31–32H_2O$ is considerably reduced when high quantities of alkali and high temperatures are present, has been shown to cause a synergy that favors the advent of delayed ettringite formation (DEF) in cementitious systems (1). The authors' work (1) demonstrates the key importance of the sulfate ions interacting with the C-S-H during hydration of the Portland cement component in concrete or mortar.

Because gypsum and its derivatives (like the hemihydrate and insoluble anhydrite) in Portland cement allow the aluminate phase C_3A and the ferrite phase C_4AF to a lesser degree to react to form ettringite, thereby ensuring smooth set regulation by averting flash set (quick set), it is often forgotten that most of the sulfate actually ends up being associated with the C-S-H phase (3,4). Around 70–80% weight of the sulfate content ends up in the C-S-H phase in hardened cement pastes. Quantitative studies have demonstrated that only a minority amount of the aluminate phase reacts to form ettringite during early hydration (5) and that the prime cause of Portland cement setting is really due to formation of significant quantities of C-S-H as the hydration process ensues (6,7).

Consequently, there is a large quantity of sulfate around during early hydration and beyond that is not associated with the aluminate and ferrite phases in forming ettringite (AFt) and monosulfate-$C_4(A,F)H_{13}$ within the cementitious system. As indicated above, the authors have mentioned that some of this sulfate is adsorbed onto the C-S-H and that this adsorption is reversible (1). In addition, sulfate can enter into some degree of solid solution with the silicate encompassed within the C-S-H during the course of hydration. Such entry into solid

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solution is facilitated by these ions having tetrahedral configurations like the silicate ions and by the ability to form low chain polymers like dimers (4). Sulfate ions are therefore likely to be both adsorbed and absorbed by the C-S-H without very clear-cut borders arising between these two forms of sorption.

The causes of DEF in Portland cement hydration have been set out (8–15). The technique of scanning electron microscopy (16) is useful for demonstrating the nature and occurrence of the pseudohexagonal prisms of ettringite where DEF has taken place. Indeed, DEF also can arise in high alumina cement when the water-to-cement ratio employed is sufficiently high to permit ingress of sulfate ions under conditions of sulfate attack (17–19). Here, of course, there is insufficient sulfate present in the unhydrated cement to cause any primary ettringite formation during normal hydration. Nevertheless, when DEF does arise within high alumina cement, the morphology of the pseudohexagonal prisms of ettringite shows strong similarities with the morphology of those ettringite prisms produced by the occurrence of DEF in Portland cement based systems.

Overall, the studies undertaken and described by the authors (1) are a useful contribution towards our understanding more fully the basis for DEF. The type(s) of bonding that arises between the sulfate ions and the Portland cement surfaces, as well as the mechanism by which this bonding is established, are clearly complex and unlikely to be simple straightforward matters.

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