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The influence of $CaS0_4.2H_20$ upon the hydration character of $3Ca0.A1_20_3$*

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Mr Feldman and Dr Ramachandran studied the hydration characteristics of mixtures of C_3A and gypsum in the form of pressed compacts of low porosity and from the results have drawn some far-reaching and interesting conclusions. In this contribution, an attempt is made to evaluate some of their conclusions in the light of the results they have presented.

A simple calculation will show that the volume ratios of C_3A/gypsum in their mixtures containing 2·5, 10 and 20% gypsum were 31, 7 and 3 respectively. The compacts contained 27% pores through which water could permeate to the reacting surfaces. Owing to this low porosity (considerably less than that of a normal paste), only a small fraction of the total mass will be exposed to water and, of this small mass exposed to reaction, the volume ratio of C_3A/gypsum will be the same as in the bulk phase. As every formula weight of C_3A requires three formula weights of gypsum for ettringite to form, it is easy to calculate the required relative rates of solution of C_3A and gypsum for each mixture. In view of this large difference in the required solution rates and the low mobilities of ions in narrow channels of water, it is not surprising that the authors found that "With the 2·5% [gypsum] addition, C_3AH_6 had formed in large quantities after only 6 min, even though gypsum still remained at this time" and that hexagonal hydro-aluminate had formed in all cases. Therefore the conclusion "that the hydration of a C_3A + gypsum mixture cannot be considered as equivalent to a system where C_3A is in a homogeneous solution, saturated with $(SO_4)^{2-}$ ions and where this homogeneous solution remains saturated until all the gypsum has been taken up" (page 191) is almost a truism.†

In their length-change measurements, the authors used compacts of C_3A + gypsum mixtures, which had been compacted at 48,000 lb/in^2. The porosity of the compacts is not reported, but it may be assumed that it is similar to that of the compacts used for investigating the hydration reaction. In these compacts, the framework is formed by the solids themselves, and water of hydration comes from outside. It is well known that the hydration products of this system have lower densities than the mean densities of the solid reactants, i.e. they have larger volumes than the solid reactants. Because of the low initial pore volume of the compact, which can only hold less than half the hydration products, continued formation of hydration products will set up an expansive force, irrespective of the mechanism of hydration. The rapid rate of expansion of pure C_3A compacts at 23°C corroborates this. According to an earlier paper(1) by the same authors, C_3AH_6 is the main product of hydration for 6 h at 23°C in this case and the mechanism of formation is probably 'through solution'. This expansion due to hydration will continue until the water transport to the reacting surfaces is hindered by the packing of the reaction products in the pores; then, of course, the rate of expansion will slow down. The rate of further expansion will depend upon how effective this packing is. Thus the expansion measurements have little bearing upon either the mechanism of hydration or the nature of retardation of C_3A hydration in cement pastes.

In their conclusions, Feldman and Ramachandran say that "the disruptive expansions that occur when the (high) sulpho-aluminate is formed suggest that it cannot form an impermeable layer". It is very doubtful whether the forces which cause expansion in a large block would necessarily cause disruption of a layer formed over a grain of C_3A but, if the reasoning is correct, it should apply to one of the new claims of the authors, that at higher temperature an impermeable growth of C_3AH_6 retards the hydration of C_3A (page 191 and reference 1). The formation of C_3AH_6 at higher temperature "has a high potential for expansion", as is evident from the high initial rate of expansion of C_3A paste at 52°C and the 21% expansion on autoclaving(1). A comparison of Figure 4 of reference 1 with Figure 7c of this paper will show that pure C_3A had a higher initial rate of expansion at 52°C than the C_3A + 10% gypsum mixture at any temperature. Thus, if sulpho-aluminate cannot form an impervious coating because of its disruptive expansion, how can C_3AH_6 form an impervious layer when it causes a higher expansion? This contradiction again shows how little relevance this type of expansion measurement has to the mechanism of reaction.

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* Pages 185 to 196 of *Magazine* No. 57. † See Note on page 196.

Reply by the authors

The total porosity of the unhydrated compact is 27% by volume, which is much lower than that of a normal paste. Nearly all of this pore volume is large, however, above 0·5 microns in diameter, and surface-area studies have shown that compaction of this type produces little or no reduction in available surface. Thus, when water is introduced to the compact, under vacuum, almost all of the surface of the solid should be rapidly wetted by the water. In Portland cement, the gypsum is dispersed through the solid (approximately 5% gypsum) and with the larger quantity of water added, it is almost certain that there will be some period during which C_3A is reacting in effect in the absence of sulphate ions. The 'slab' experiments of Seligmann and Greening(2) have shown the importance of the two extremes: (a) where C_3A is in a homogeneous solution saturated with sulphate ions and (b) where C_3A is hydrating for some period (the time taken for sulphate ions to travel from a slab $\frac{1}{4}$ in. away) in the absence of sulphate ions. This is an important point and no 'truism'; the hydration of normal cement paste appears to have been considered to occur according to (a) above, and it is doubtful whether this assumption is valid.

The final structure of an agglomeration of particles of a solid which may undergo a reaction with water depends upon many factors. The morphology of the product and the place that it is deposited must be considered as part of the over-all reaction mechanism; reaction conditions may affect all of the above. The state of the structure and the length change reflect the morphology of the product and its place of deposition; length change may be large or small, a large length change not necessarily leading to a weak and soft body. When the expansion leads to a weak and soft structure, it is considered here to be disruptive.

Compaction of the solid reactant tends to emphasize some of the properties of the reaction by bringing particles in contact and, although it may alter the relative periods at the different stages of the reaction, it must be kept in mind that a body of low porosity is also the final product of paste hydration.

The fact that 'hydration' reactions involve an increase in the volume of solid product over solid reactants does not account for the type of length change and structuring during reaction. At the beginning of hydration, expansion of the compact is caused by the thrust of the product at or close to the points of contact of the grains of the reactants. In some cases, this expansion is slight, and a fairly dense impermeable product is built around each grain and into the pore spaces. The sample structure then would consist of a dense impermeable product and should be and is of good strength and low porosity; the hydrate product is probably continuous but the unhydrated material is embedded in it, and the reaction is terminated or almost so by the lack of space or water. Examples of this type of reaction with the solid in compact form are C_3S and β-C_2S, both with linear expansions of 0·10 to 0·15%* and Portland cement with 0·3%(3).

The hydration of $CaSO_4.\frac{1}{2}H_2O$ compacts is(4) accompanied by somewhat larger linear expansions from 1 to 4%, depending upon the hydration conditions, but also produces a strong, fairly dense, body; the expansion in this case is certainly not disruptive. Slurries of the above may produce 0·5% linear expansions and it is interesting that the strength-porosity relationship for the compacts and slurries appeared to be at different regions of the same curve*. CaO hydrates with a disruptive expansion in the presence of water vapour(5); there is a weakening of the structure during hydration, little or no reduction in reaction rate, and a complete disintegration of the body, leaving only a powder. Under these conditions, one cannot visualize a dense impermeable product having formed around the CaO particles because this would have led to the unhydrated material being joined and surrounded by the dense product, thereby forming a strong body, and the reaction rate would have been drastically reduced.

The reaction of CO_2 with compacts of $Ca(OH)_2$* in the presence of water vapour is an example of another type of structuring. Although the reaction produces an increase in solid volume, densification of the body is accompanied by shrinkage of up to 0·3% linear measurement.

The above examples show something of the complex nature and relationship of length change to structuring and reaction mechanism.

The expansion behaviour observed for the C_3A with 10 and 20% gypsum mixtures, at 23°C, was disruptive; the specimen was, in fact, a mush. It is inconceivable, in the light of the above discussion, that this can be the result of a special dense and impermeable product of high sulpho-aluminate. The retardation of C_3A hydration by gypsum was considered to be due to sorption of sulphate ions on C_3A surfaces when the surface reaction is rate-controlling, and the effect of the electric field intensity of sulphate ions upon the movement of water through small pores when diffusion is the rate-controlling factor.

The expansion of C_3A at 52°C(1) was not disruptive; a firm strong product was the result of the hydration, and the expansion was not large—0·7% after 4 days. The high initial rate of expansion was due to the rapid initial rate of hydration (approximately 17% hydrated, most of this taking place in less than one hour). The hydration of C_3A at 23°C is somewhat disruptive, although not to the extent of C_3A + 10% and + 20% gypsum mixtures; expansion was sometimes 9% in 25 h

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* Unpublished information.

with 52% hydration and at other times disintegration occurred. The product, however, was generally a weak one. The autoclave treatment is considered irrelevant to this discussion because of the vast change in conditions.

The results from the C_3A hydration are not a contradiction and, in fact, generally support the arguments

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Note added in proof by Dr Jeffery

The existence of an $(SO_4)^{2-}$ ion concentration gradient in Portland cement paste (where SO_4/Al_2O_3 is much higher than 2·5%) from 4 min onwards has been demonstrated previously. (See CHATTERJI, S. and JEFFERY, J. W. The effect of various heat treatments of the clinker on the early hydration of cement pastes. *Magazine of Concrete Research.* Vol. 16, No. 46. March 1964. pp. 3–10.)

Corrigendum to the original paper

Figure 7

The information in the caption and the key should be transposed. The four parts of the Figure are for three different mixtures as follows: (a) C_3A + 2.5% gypsum (b) and (c) C_3A + 10% gypsum (d) C_3A + 20% gypsum. The symbols on the Figure denote different temperatures as follows:

○ 2°C
□ 12°C
◊ 23°C
△ 52°C