Discussion on an article published in the

Magazine of Concrete Research

Vol. 14, No. 42 : November 1962

Hydration of tricalcium aluminate with lignosulphonate additives*

by J. F. Young, M.Sc.

Contribution by S. Chatterji, M.Sc., D.Phil.
and J. W. Jeffery, B.A., Ph.D., F.Inst.P.
(University of London: Birkbeck College)

Mr Young has assigned all endothermic peaks below 400°C to mixtures of C_4AH_{13} and C_2AH_8 (p. 139). But Kalousek⁽¹⁾ has shown that C_4AH_x has no peak at about 300°C and there appears to be no published evidence of a peak at this temperature for C_2AH_x . However, C_3AH_6 has an endothermic peak at about 300°C.^(1,2) Mr Young's thermograms (Figure 3, 7 day sample) also show that the peak at about 300°C is due to C_3AH_6 .

If we assume that the 300°C peak is due to C_3AH_6 the following points need clarification. On comparing Figures 3 and 4 we find that a certain amount of C_3AH_6 had formed by 7 days in the paste containing lignosulphonate, but Table 1 does not show any C_3AH_6 formation. A similar anomaly is also present for the C_3A -gypsum-lime paste (Figure 5, 3 day sample) and C_3A -gypsum-lime-lignosulphonate paste (Figure 6, 7 day sample).

Table 1 shows that in the C_3A -gypsum-lime paste, "low sulphaaluminate" had started to form by 3 h and C_2AH_8 had appeared by 3 days. The appearance of C_2AH_8 presumably means that all lime had been consumed by this time to form C_4AH_{13} . But in the case of the C_3A -gypsum-lime-lignosulphonate paste, "high sulphaaluminate" was the only compound found at 1 day and no C_2AH_8 had appeared by 7 days, i.e. insufficient C_3A had hydrated to consume all the lime. It seems, therefore, that the presence of lignosulphonate depresses the reactivity of C_3A by some unknown means.

Mr Young is of the opinion that "The lignosulphonate has, therefore, in some way, stabilized C_4AH_{13} and C_2AH_8 with respect to C_3AH_6 " (p. 140). From

the above discussion it seems more probable that lignosulphonate depressed the reactivity of C_3A , so that smaller amounts of the hexagonal phases and therefore of C_3AH_6 had formed, and that the C_3AH_6 phase was missed in X-ray diffractometry. If this is so, it reinforces our opinion that the X-ray diffractometer is an inefficient instrument for general identification work, which can be done much more effectively by means of a Guinier camera.

REFERENCES

1. KALOUSEK, G. L., DAVIS, C. W. JR. and SCHWERTZ, W. E. An investigation of hydrating cements and related hydrous solids by differential thermal analysis. *Journal of the American Concrete Institute*. Vol. 45. June 1949. p. 693.
2. MAJUNDAR, A. J. and ROY, R. The system $CaO-Al_2O_3-H_2O$. *Journal of the American Ceramic Society*. Vol. 39. 1956. pp. 434-442.

Reply by the author

In order to make useful interpretations of DTA data, thermograms were run of the calcium hydro-aluminates occurring during hydration. These were synthesized by published methods and shown to be free of other hydrates by X-ray diffractometry. The major endotherms are shown in Table I.

It was found that the endotherms of C_3AH_6 and of high sulphaaluminate were quite reproducible but that a significant variation occurred in the thermograms of the three hexagonal-plate phases when several runs were made on the same, or different, preparations. The peak temperatures varied within a range of up to 40°C and there were also differences in the peak intensities, which, in extreme cases, produced a change-over in relative intensities. When the 300°C peak was affected, its intensity was usually reduced. It would appear that the hexagonal-plate crystals have dehydration characteristics which are very sensitive to such

*Pages 137 to 142 of *Magazine* No. 42.

TABLE I: Major endotherms of calcium hydroaluminates.*

C_3AH_6	350 (vs) 550 (s)
C_4AH_{13}	120 (s) 205 (vs) 305 (m)
C_2AH_8	120 (s) 200 (m) 295 (ms)
Low sulphoaluminate	180 (m) 210 (s) 240 (s) 300 (m)
High sulphoaluminate	160 (vs)

*Mean peaking temperatures in °C

vs = very strong; s = strong; m = medium

factors as dilution with α -alumina, packing, and crystal size and orientation. When these hydrates were run together in various mixtures, similar changes in peak temperatures were again observed but intensity changes were generally more marked. In particular, the 300°C endotherm was often much weaker and sometimes completely absent. It must be concluded that the dehydration of any one hydrate is particularly affected by the presence of others of similar crystal structure.

The above observations give a possible explanation for the absence in earlier work of a peak at 300°C for C_4AH_x . They also provide a reasonable basis, in this

work, for assigning the endotherm at 300°C to mixtures of the hexagonal-plate phases rather than to C_3AH_6 , as the latter is not backed up by X-ray diffraction results. It seems unlikely that C_3AH_6 will have missed detection in X-ray diffractometry. Its presence was detected without difficulty in pastes of pure C_3A at an early stage of hydration when the endotherm at 320°C (Figure 3, 6 min sample) was still quite weak. Therefore one would expect that if other peaks at about 300°C, of comparable intensity, are really due to C_3AH_6 , then it would have been detected in the X-ray patterns. The crystal structure of C_3AH_6 gives rise to many strong sharp lines very favourable for detection in the presence of the weaker and more diffuse pattern of the hexagonal-plate phases. In view of the variations that can occur in DTA data, as shown above, and the consequent uncertainties, it is preferable to make an assignment of peaks which is supported by complementary data from X-ray diffractometry, whose limitations are better understood.

It is no doubt true that the lignosulphate depresses the reactivity of C_3A in view of its set-retarding properties, and this can certainly explain the absence of C_2AH_8 in C_3A -gypsum-lime-lignosulphonate pastes. But, at the same time, observations (p. 140 of *Magazine* No. 42) do suggest that lignosulphonate definitely inhibits the change from C_2AH_8 and C_4AH_{13} to C_3AH_6 under normal conditions.