

INFLUENCE OF LIGNOSULPHONATE, GLUCOSE AND
GLUCONATE ON THE C_3A HYDRATION

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ABSTRACT

The influence of desugarized sodium lignosulphonate, glucose and sodium gluconate on the C_3A hydration has been examined using DTG analysis. At relatively low concentration levels of admixtures in the aqueous phase (1 to 3 g/l), such as those practically used for concrete mixes, lignosulphonate and glucose retard only slightly the C_3A hydration. Sodium gluconate is significantly more efficient in retarding C_3A hydration than lignosulphonate and glucose.

Introduction

Lignosulphonate, gluconate and glucose are the main components used to manufacture water-reducing admixtures for concrete. They also affect setting times of cement mixes and are generally assumed to be set-retarders (1-8), although in some cases abnormal quick set has been experienced (9-12).

Commercial water reducers are aqueous solutions generally containing about 30% of active ingredients. Assuming for the concrete mix a water/cement ratio of 0.50 and an average dosage of commercial admixture of 0.3% by weight of cement, the concentration of the active ingredients in the mixing water is approximately 2 g/l. In works on the C_3A hydration much higher concentrations of pure water-reducing agents have been generally used (13-22). Moreover, comparative effects of the above three mentioned pure water reducers on the C_3A hydration were not extensively studied, particularly in the presence of gypsum.

The purpose of our work is to examine the influence of lignosulphonate, gluconate and glucose on the hydration of portland cement compounds. In the present paper the effect of these water-reducing agents, at concentration levels of 1 to 3 g/l in the aqueous phase, on the C_3A hydration is examined. In next

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papers the effect of these admixtures on the C₃A hydration in the presence of other compounds such as calcium hydroxide, gypsum and C₃S will be presented.

Experimental

Tricalcium aluminate was prepared in a laboratory furnace from reagent grade CaCO₃ and Al₂O₃. Then, C₃A with a free lime content of 0.1% was ground in a laboratory mill to a Blaine fineness of about 2800 cm²/g. It was dry-mixed (1:1 weight ratio) with pure finely ground ($\leq 40 \mu\text{m}$) quartz (S) used as inert material. In subsequent works quartz will be partly replaced by other compounds, such as Ca(OH)₂ and/or gypsum, without changing the percentage of C₃A. A certain amount (0.1 to 0.3% by weight of C₃A) of water-reducing agent was also added to the C₃A-S mix during the blending.

Industrial sodium lignosulphonate (NLS) said to be free of sugar or other carbohydrates and produced by MAC S.p.A., or reagent grade sodium gluconate (NG) and glucose (G) were used as water-reducing agents.

Hydration of pastes with and without admixtures was carried out at 20° C with a water/solid ratio of 0.50, so that the concentrations of the admixtures in the aqueous phase were 1 and 3 g/l. After a certain period of time (30 min to 7 days) the hydration was blocked by grinding the pastes with methyl alcohol. The filtered solids were kept over CaO + NaOH (1:1) for 1 day prior to thermal analysis. DTA, DTG and TG curves were simultaneously obtained. Only DTG curves are shown in the present paper. In some cases X-ray diffraction analysis has been carried out.

Results and Discussion

Figure 1 shows the DTG curves of hydrated C₃A without and with NLS. The specimens exhibit various peaks which can be assigned to the hydrated products as follows. The DTG peaks at about 200° C and 260-280° C are attributed to the dehydration of the hexagonal hydrates (C₂AH₆ and C₄AH₁₃). The peaks at about 300-350° C and 500-520° C correspond to a stepwise dehydration of the cubic hydrate C₃AH₆. A peak at about 100° C can be observed which is particularly evident in the presence of hexagonal hydrates. A peak at about 800° C is also present which is generally attributed to CaCO₃, formed by reaction between the CO₂ of air and the wet hydrated specimens. Possibly the CO₂ of air combines with hexagonal hydrates during the filtration. This seems to be confirmed by the fact that at longer ages, such as 7 days, when the cubic phase is predominant and the hexagonal phases are present in a negligible amount, the peak at about 800° C is substantially absent.

When C₃A hydrates without the addition of NLS, the hexagonal phases form at 30 min with traces of the cubic phase. At longer ages the hexagonal hydrates transform gradually into the cubic phase, so that the C₃AH₆ is the main phase existing at 7 days. The sequence of thermograms is substantially the same as that recorded by Ramachandran (15).

In the presence of NLS, only small differences can be observed. In particular the lignosulphonate used in the present work does not significantly retard the C₃A hydration nor stabilize the hexagonal phases, as other authors

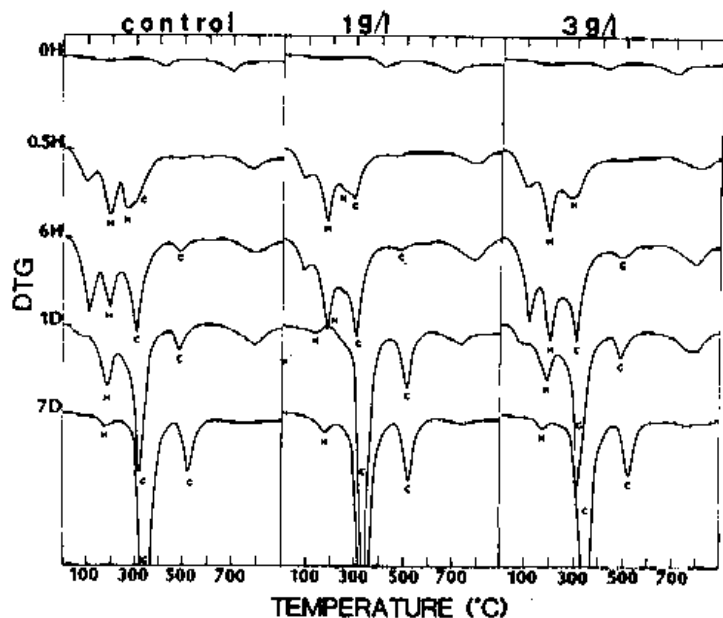


FIG. 1

Influence of NLS (1 to 3 g/l) on the C₃A hydration (H = hexagonal hydrates; C = cubic hydrate)

found (14-19). However, these authors used concentrations of lignosulphonate in the aqueous phase, such as 8 to 50 g/l, which are much higher than those used in the present paper (1 to 3 g/l) and in the practical applications.

Chatterji (13) studied the effect of a commercial calcium lignosulphonate (CLS) containing sugars and a purified sodium lignosulphonate (NLS) on the paste hydration of C₃A from 1 day to 3 months using XRD analysis. The C₃A used by Chatterji formed only traces of C₃AH₆ at 1 day in the absence of admixtures, whereas C₃AH₆ is the predominant phase at 1 day in the present work (Fig. 1). The concentration of the admixture dissolved in cooled (10° C) water was in the range of about 2 to 50 g/l for CLS and about 4 to 50 g/l for NLS. Chatterji found that at concentration level of about 50 g/l CLS completely blocks the C₃A hydration till to 1 day and the transformation of the hexagonal hydrates into the cubic phase till to 3 months. The effect of the admixture on the C₃A hydration was significantly less retarding when a 50 g/l NLS solution was used. At lower concentrations of CLS, such as 2 to 4 g/l, which could be compared to that of the present work, neither the C₃A hydration rate nor the transformation of the hexagonal hydrated into the cubic phase is affected by the presence of lignosulphonate during the first day of hydration. Where a 4 g/l NLS solution was used the C₃A hydration

appeared to be slightly accelerated at 1 day. These data substantially agree with the results of the present work. However, Chatterji found that a longer ages (14 days) both the hydration rate of C₃A and the conversion of the hexagonal hydrates into the cubic phase appear to be significantly retarded in the presence of relatively low concentration levels, such as 2 to 4 g/l, of CLS or NLS. These data are not confirmed by the results on the present paper, as no retarding effect is observed after 1 day of hydration (Fig. 1). The differences in materials (C₃A and lignosulphonate) temperature and experimental techniques (XRD and DTG) could possibly explain the differences.

A DTG peak at about 100° C is present both with and without admixtures (Fig. 1). So it is not confirmed that the thermal peak at about 100° C is present only in the presence of admixtures such as lignosulphonate (20) or gluconate (21). According to Milestone (20) and Sersale *et al.* (21), this peak is due to the formation of C₄AH₉ which would be stabilize by the presence of admixtures. The fact that the peak at 100° C is particularly evident in the presence of hexagonal phases, independently of the presence of admixture, seems to confirm the Ramachandran's hypothesis that this peak is due to the thermal desorption of water adsorbed on the hexagonal hydrates (5).

Figure 2 shows the influence of 1 to 3 g/l glucose on the C₃A hydration. The effect of G is very similar to that of NLS, the only difference being a slightly more retarded transformation of hexagonal phases into the cubic hydrate in the presence of G. For instance, at 1 day with 1 g/l of admixture or at 7 days with 3 g/l of admixture, the peak at about 200° C is evident in the presence of G (Fig. 2) and negligible with NLS (Fig. 1). Daugherty and Kowalewsky (22) found that glucose retards significantly C₃A hydration until 64 days, however these authors used a glucose concentration (16.7 g/l) much higher than that used in the present work.

Figure 3 indicates the action of 1 to 3 g/l NG on the hydration of C₃A. The peaks of the hydration products are negligible at 0.5 hr with 1 g/l and at 6 hr with 3 g/l NG. The DTG peak of the cubic hydrate is well evident only at 7 days in the presence of 3 g/l NG. Sodium gluconate appears to be much more retarding, for the C₃A hydration, than NLS or G do, thus confirming the results obtained by Milestone (20) who found that salts of sugar acids, including calcium gluconate, are significantly more efficient in retarding C₃A hydration than glucose. However, the results of the present work indicate that sodium gluconate does not retard the C₃A hydration as strongly as calcium gluconate does in Milestone work (20). This author found that using 1.67 g/l calcium gluconate aqueous solution (0.1% of admixture by weight of C₃A with a water/C₃A ratio of 0.60) the degree of hydration was negligible in comparison with that of the control mix; for instance, at 7 days it was approximately 10% and 80% with and without admixture. Possibly, the preliminary cooling treatment at 0° C, used by Milestone (20) before keeping the samples in a constant temperature room at 21° C, could partly explain the differences in the retarding effect.

The results of the present paper seem to be closer to the data of Sersale *et al.* (21) who found that, using 1.67 g/l NG, the degree of hydration of

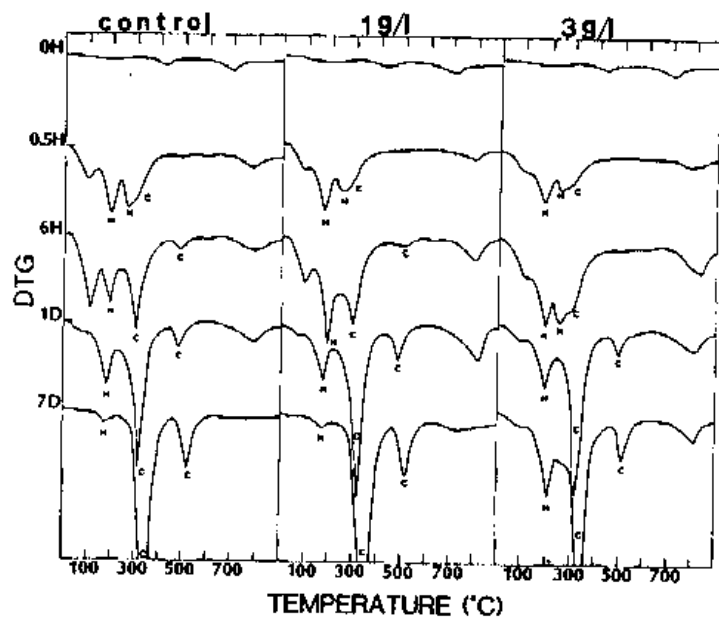


Fig. 2

Influence of G (1 to 3 g/l) on the C₃A hydration (H = hexagonal hydrates; C = cubic hydrate)

C₃A at 1 day is approximately the same as that of the control mix at 1 hr. This effect reasonably agrees with our results using 1 to 3 g/l NG (Fig. 3): at 1 day the retarding effect of 1 g/l NG is substantially finished, whereas with 3 g/l NG the degree of hydration at 1 day is lower than that of the control mix at 0.5 hr.

Conclusions

Desugared sodium lignosulphonate glucose and sodium gluconate, at concentration levels as those used in practice for concrete mixes (1 to 3 g per liter of mixing water) have been added to the C₃A - S - H₂O system.

Lignosulphonate does not cause any substantial changes in the C₃A hydration.

The influence of glucose on the C₃A hydration is very similar to that of sugar-free sodium lignosulphonate, except a slightly more retarding effect on the conversion of the hexagonal phases into the cubic hydrate.

Sodium gluconate is remarkably more efficient in retarding both C₃A hydration and conversion into the cubic phase than lignosulphonate and glucose.

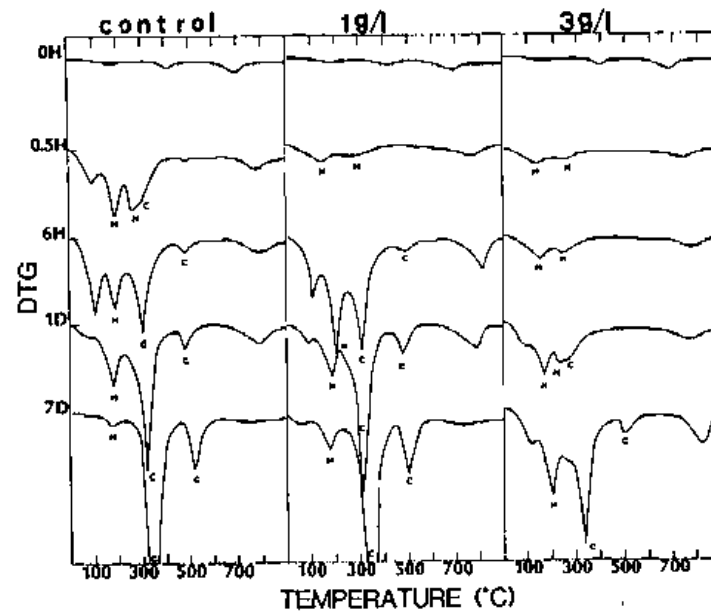


Fig. 3

Influence of NG (1 to 3 g/l) on the C₃A hydration (H = hexagonal hydrates; C = cubic hydrate)

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