

INFLUENCE OF GLUCONATE, LIGNOSULFONATE OR GLUCOSE
ON THE C₃A HYDRATION IN THE PRESENCE OF GYPSUM WITH
OR WITHOUT LIME

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ABSTRACT

The influence of gluconate, lignosulfonate or glucose at 0.1-0.3% dosages on the C₃A hydration in the presence of gypsum with or without lime has been examined. In the presence of lime all the admixtures at 0.3% dosage stabilize ettringite and retard its conversion to monosulfate; only 0.3% glucose retards gypsum consumption and ettringite production. In the absence of lime stabilization of ettringite by admixtures at 0.3% addition appears to be much less effective; no admixture is able to retard the ettringite production or gypsum disappearance. At 0.1% addition, the influence of admixtures seems to be negligible except when glucose is used in the presence of lime; in this case, the conversion of ettringite into monosulfate is retarded.

Introduction

Gluconate, lignosulfonate and glucose are the most widely used raw materials in the production of water-reducing admixtures for concrete. They also retard the early hydration of portland cement. As C₃A* affects setting and early hydration of portland cement, many works have been devoted to the influence of water-reducing admixtures on C₃A hydration. Most work has been devoted to the influence of these admixtures (generally at relatively high dosages in comparison with those used in practice), on the hydration of pure C₃A without lime and/or gypsum (1-12). However, C₃A in a cement will react with an aqueous solution saturated with CH, produced by C₃S hydration, and

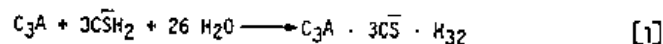
* A = Al₂O₃; C = CaO; S = SiO₂; \bar{S} = SO₃; H = H₂O; C = CO₂

CaSO₄ · 2H₂O. Therefore, it is very surprising that the effect of water-reducing admixtures on the C₃A-C \bar{S} H₂-CH-H₂O system has not been adequately studied. Only the effect of commercial lignosulfonate on this system has been examined (1, 13). Moreover, as these admixtures strongly retard the C₃S hydration (14), the aqueous solution in contact with C₃A in a cement could be saturated with gypsum but not with lime for a certain period of time. Thus, it should be useful to examine also the effect of these admixtures on the C₃A-C \bar{S} H₂-H₂O system. Again, very few papers (2, 15), only concerning lignosulfonate, have been devoted to this subject.

The purpose of the present work is to study the effect of gluconate, lignosulfonate or glucose on C₃A hydration in the C₃A-C \bar{S} H₂-H₂O system in the presence or absence of lime.

The hydration of C₃A in this system occurs in three successive stages (13).

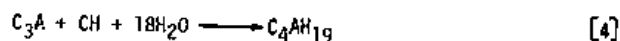
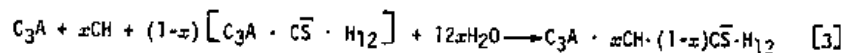
Stage I C₃A reacts with H₂O and C \bar{S} H₂ producing ettringite according to equation [1]



Stage II When C \bar{S} H₂ has been consumed, the transformation of ettringite into monosulfate occurs according to equation [2]



Stage III The remainder of the C₃A reacts with Ca(OH)₂ and monosulfate to form a solid solution, according to equation [3] and the rest combines with CH and H₂O forming C₄AH₁₉ according to equation [4]



Experimental

Tricalcium aluminate, quartz (S), sodium gluconate (NG), purified sodium lignosulfonate (NLS) and glucose (G) are the same as those used in a previous work (16). Calcium hydroxide and gypsum were dry-mixes with the above materials in the proportions shown in Table I.

Hydration of pastes with and without admixtures (0.1 and 0.3% by weight of C₃A) was carried out at 20° C with a water solid ratio of 0.50. At hydration times from 30 min to 7 days DTG analysis was carried out as it was described in a previous paper (16). In some cases XRD analysis has been carried out.

TABLE I
Proportions of Anhydrous Mixes

C ₃ A	CH	C \bar{S} H ₂	S	NG	NLS	G
50	-	10	40	-	-	-
50	10	10	30	-	-	-
50	-	10	39.95	0.05	-	-
50	10	10	29.95	0.05	-	-
50	-	10	38.85	0.15	-	-
50	10	10	28.85	0.15	-	-
50	-	10	39.95	-	0.05	-
50	10	10	29.95	-	0.05	-
50	-	10	38.85	-	0.15	-
50	10	10	28.85	-	0.15	-
50	-	10	39.95	-	-	0.05
50	10	10	29.95	-	-	0.05
50	-	10	38.85	-	-	0.15
50	10	10	28.85	-	-	0.15

Results and Discussion

Figure 1 shows the DTG curves of the hydration products for the C₃A-C \bar{S} H₂ system in the absence of admixtures, without and with CH. The specimens exhibit various peaks which can be attributed as follows. The DTG peak at about 150° C with a shoulder on the right side is assigned to a stepwise thermal decomposition of C \bar{S} H₂ into C \bar{S} H and C \bar{S} . The peak at about 120° C is attributed to the dehydration of ettringite (C₃A · C \bar{S} · H₃₂), whereas the peaks at about 200° C and 280° C are attributed to the thermal dehydration of the monosulfate. The peaks at about 500° C and 800° C are assigned to CH and CaCO₃ respectively. The disappearance of gypsum and the formation of ettringite (Stage I, e.g. [1]) and its conversion to monosulfate (Stage 2, e.g. [2]) are processes which occur more rapidly in the absence (Fig. 1A) than in the presence of CH (Fig. 1B). These data agree with XRD results showing that the C₃A disappearance in the presence of C \bar{S} H₂ was retarded by addition of CH. These results confirm the data obtained by Mehta (17) and the Forsen's results quoted by Taylor (18) indicating that CH addition retards the hydration of C₃A in the

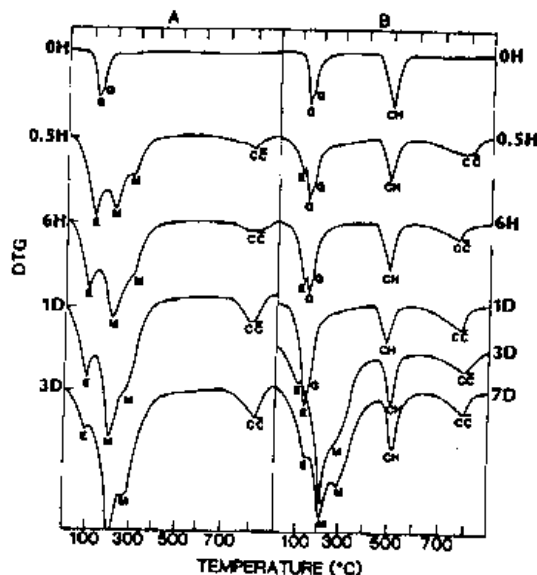


FIG. 1

DTG curves of the C_3A-CSH_2-H system without (A) and with (B) CH. G = Gypsum; E = Etringite; M = Monosulfate; CH - Calcium Hydroxide; cC = calcium carbonate.

presence of gypsum. According to Mehta, "colloidal" ettringite is produced in the presence of CH which would retard the C_3A hydration in a more efficient way (17).

In the system studied in the present work, CSH_2 disappears in less than 0.5 hr in the absence of CH, and in more than 1 day in the presence of CH. However, preliminary tests showed that using different batches of C_3A , gypsum combines with H and C_3A with different reactions rates, possibly because of differences in the reactivity of C_3A . This means that the results obtained in different laboratories using different batches of C_3A may be quite different, even if an equal composition of the mixes is used. Therefore, the effects of water-reducing admixtures on the C_3A-CSH_2 or C_3A-CSH_2-CH systems obtained by different authors should be compared in relationship with the specific reference mixes without admixtures used by different researchers. The peak at $800^\circ C$ is present also in the specimens without CH and it increases with the amount of monosulfate. It is confirmed that hexagonal aluminate hydrates are particularly reactive with CO_2 (16).

Figure 2 shows the DTG curves of the hydration products of C_3A in the presence of 0.3% NG and gypsum without (Fig. 2A) and with (Fig. 2B) CH. As no significant effect has been found in the presence of 0.1% NG the results are not shown here.

In the absence of CH, it seems that 0.3% gluconate slightly accelerates the ettringite production (equation [1]) during the first 30 min (Fig. 1A and 2A) whereas the subsequent conversion of ettringite into monosulfate (equation [2]) is retarded.

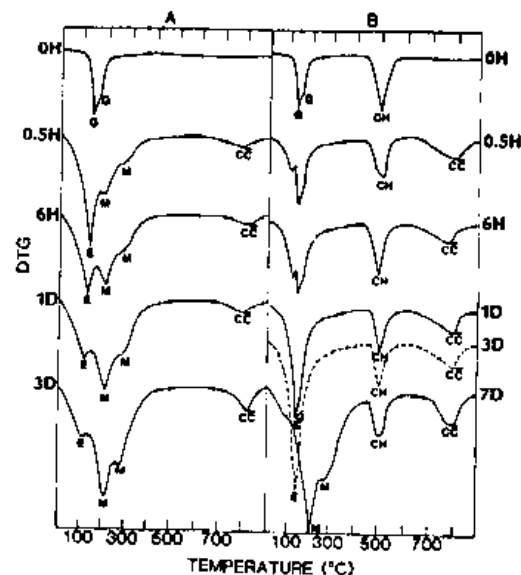


FIG. 2

DTG curves of the C_3A-CSH_2-H system in the presence of 0.3% sodium gluconate without (A) and with (B) CH.

In the presence of CH, the rates of ettringite production and gypsum disappearance between 0 and 24 hours are not substantially modified by 0.3% NG addition (Fig. 1B and 2B). The type of ettringite produced in the presence of CH, seems to protect the C_3A particles from hydration so efficiently that the NG effect becomes negligible. However, even in the presence of CH, ettringite appears to be stabilized by NG addition so that its conversion to monosulfate after 1 day is significantly retarded. This would indicate that after 1 day C_3A disappears more rapidly in the reference mix than in the mix with NG according to the reaction [2]. For instance, at 3 days ettringite appears still to be the only hydration product in the presence of NG (Fig. 2B), whereas in the reference mix without admixture monosulfate is the predominant phase (Fig. 1B).

The stabilization of ettringite by organic products has been ascribed to the penetration of organic molecules into the intercolumnar region of ettringite crystal structure (19).

Figure 3 shows the DTG curves hydrated in the presence of 0.3% NLS and gypsum without (Fig. 3A) and with (Fig. 3B) CH. No significant effect has been found using 0.1% NLS; therefore the DTG curves of the hydration products in the presence of 0.1% NLS are not shown here.

In the absence of CH, 0.3% NLS does not affect the ettringite production; conversion of ettringite into monosulfate (Fig. 1A and 3A) appears to be retarded only to a negligible extent. So it seems that NG retards the C_3A hydration in the presence of CSH_2 more remarkably than NLS does (Fig. 2A and 3A). Similar results have been obtained for the hydration of C_3A without gypsum (16). Masazza and Costa (15) and Chatterji (2) found that lignosulfonate acts as a

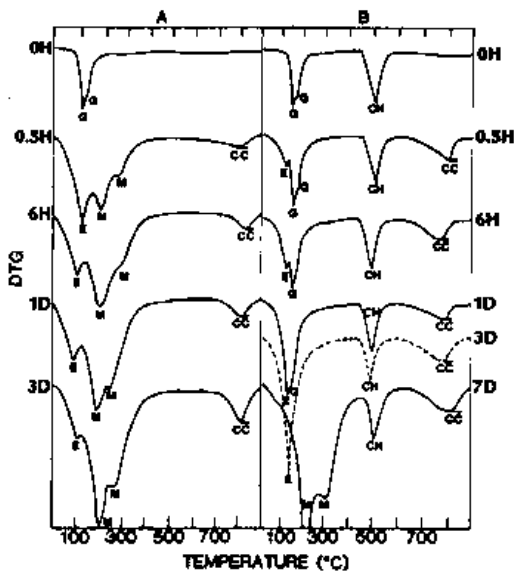


FIG. 3

DTG curves of the C_3A - CSH_2 -H system in the presence of 0.3% sodium lignosulfonate without (A) and with (B) CH.

retarder for the hydration of C_3A in the presence of CSH_2 and in the absence of CH. However, they worked in quite different experimental conditions. Mas-sazza and Costa (15) worked with the same CSH_2/C_3A and H/C_3A ratios as those used in the present work. Moreover, the kinetics of the reactions (ettringite production and its conversion into monosulfate) in their reference mix without lignosulfonate is very similar to that of the present work. However, they used a much higher dosage (1% by weight of C_3A) of sodium purified lignosulfo-nate and this can explain why they found a significant retarding effect for lignosulfonate. Chatterji (2) worked with the same CSH_2/C_3A ratio as that of our work and a lower H/C_3A (= 0.6) ratio than that of the present work. He found that lignosulfonate significantly retards gypsum consumption, ettringite production and its conversion into monosulfate even with relatively low admixture dosages similar to those used in the present work. However, his C_3A - CSH_2 system without admixture appears to be remarkably less reactive than that of the present work as, for instance, gypsum is still present at 1 day. Moreover, Chatterji used unrefined calcium lignosulfonate containing reducing sugars and organic acids which could be responsible for the retarding effect at low lignosulfonate dosage (0.2 - 0.4%).

In the presence of both CH and CSH_2 , 0.3% NLS affects the C_3A hydration (Fig. 3B) to the same extent as NG does (Fig. 2B): the rate of ettringite pro-duction during the first day is not substantially modified, whereas the trans-formation of ettringite into monosulfate after 1 day is significantly retard-ed. Similar results have been obtained by Seligmann and Greening (13) and Young (1) although they used higher dosages of commercial lignosulfo-nate.

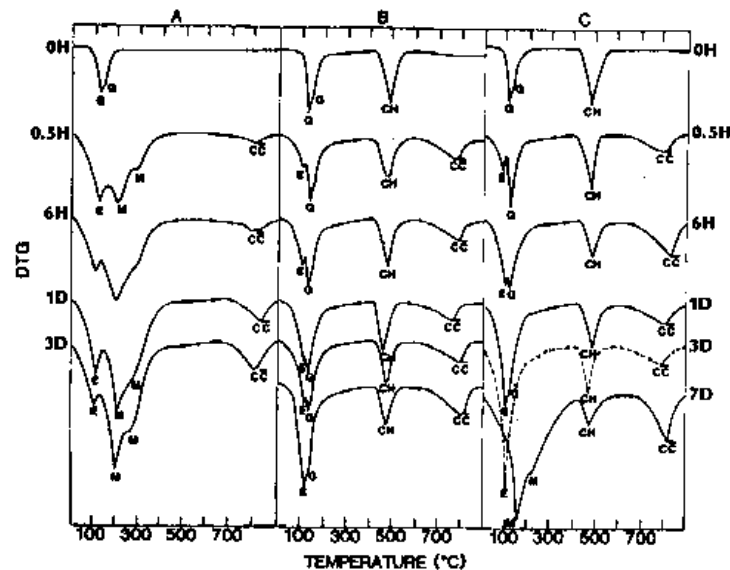


FIG. 4

DTG curves of the C_3A - CSH_2 -H system in the presence of glucose without and with CH. (A = without CH and with 0.3% G; B = with CH and 0.3% G; C = with CH and 0.1% G).

Figure 4 shows the hydration products of C_3A in the presence of G and gypsum without (Fig. 4A) and with (Fig. 4B and C) CH.

In the absence of CH, 0.3% G does not change significantly the ettringite production; the transformation of ettringite into monosulfate appears to be retarded to a negligible extent (Fig. 1A and 4A). Similar results have been obtained using 0.1% G.

In the presence of CH, 0.3% G remarkably retards the ettringite production and gypsum disappearance (Fig. 4B). Consequently, the transformation of ettringite into monosulfate is delayed. For instance, at 3 days monosulfate is the predominant hydration product phase in the C_3A - CSH_2 -CH-H system without admixture (Fig. 1B), whereas ettringite and gypsum are still present in the presence of 0.3% G (Fig. 4B). In the presence of a lower dosage (0.1%) of glucose, ettringite only is present at 3 days (Fig. 4C). At 7 days, monosulfate is not yet present when a high dosage (0.3%) of glucose is used (Fig. 4B), whereas it becomes the predominant phase in the presence of a lower amount (0.1%) of glucose (Fig. 4C).

Conclusions

At 0.1% addition, the effect of gluconate and lignosulfonate on the C_3A hydration in the presence of gypsum appears to be negligible, whether lime is present or not. At 0.1% dosage, glucose retards the conversion of ettringite into monosulfate only in the presence of lime.

At 0.3% addition, in the absence of lime all the admixtures retard the conversion of ettringite into monosulfate to a small extent; no retardation in the ettringite production or gypsum consumption is caused by all the admixtures.

At 0.3% addition, in the presence of lime all the admixtures stabilize ettringite and retard its conversion; only 0.3% glucose retards ettringite production and gypsum disappearance.

References

1. J.F. Young, Magazine of Concrete Research 14, 137-42 (1962).
2. S. Chatterji, Indian Concrete Journal 41, 151-60 (1967).
3. E.D. Clach and E.G. Swenson, Cement and Concrete Research 1, 143-58 (1971).
4. V.S. Ramachandran and R.F. Feldman, Matériaux et Constructions 5, 67-76 (1972).
5. N.B. Milestone, Cement and Concrete Research 6, 89-102 (1976).
6. N.B. Milestone, Cement and Concrete Research 7, 45-54 (1977).
7. V.S. Ramachandran, Zement-Kalk-Gips 31, 206-10 (1978).
8. M. Collepari, M. Corradi, G. Baldini and M. Pauri, VII International Symposium on Cement Chemistry, Vol. IV, 524-28 (1980).
9. V.S. Ramachandran, VII International Symposium on Cement Chemistry, Vol. IV, 535-40 (1980).
10. M. Pauri, G. Baldini and M. Collepari, Cement and Concrete Research 12, 271-77 (1982).
11. M. Pauri, G. Ferrari and M. Collepari, Cement and Concrete Research 13, 61-68 (1983).
12. V. Lorprayoon and D.R. Rossington, Cement and Concrete Research 11, 267-277 (1981).
13. P. Seligmann and N.R. Greening, Highway Research Record, Highway Research Board No. 62, 80-105 (1964).
14. N.B. Milestone, Journal of American Ceramic Society 62, 321-24 (1979).
15. F. Massazza and U. Costa, VII International Symposium on Cement Chemistry, Vol. IV, 529-34 (1980).
16. S. Monosi, G. Moriconi, M. Pauri and M. Collepari, Cement and Concrete Research 13, 568-574 (1983).
17. P.K. Mehta, Journal of American Ceramic Society 56, 315-19 (1973).
18. H.F.W. Taylor, The Chemistry of Cement, Vol. 1, 37-18, Academic Press, Inc. New York (1964).
19. J.F. Young, Transportation Research Record, No. 564, 1-9 (1976).