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EFFECT OF RETARDING ADMIXTURES ON THE PORTLAND CEMENT HYDRATION

EFFECT DES ADJUVANTS RETARDANTS SUR L'HYDRATATION DES CIMENTS PORTLAND

SUMMARY: Type I and V Portland cements have been hydrated (water/cement ratio = 0.50) at 20°C with and without glucose, sodium gluconate and sodium lignosulfonate (0.3% by weight of cement).

Minislump tests have been carried out to determine the fluidifying effect of the admixtures on cement pastes. The cement hydration rate has been studied by thermal analysis (DTG).

Sodium gluconate, which appeared to be the most effective in fluidifying the cement pastes, retard both the ettringite production and the calcium silicates hydration. The retarding effect was much more remarkable on type V Portland cement with null C_3A content.

Sodium lignosulfonate did not significantly retard after ettringite production or calcium silicates hydration.

Glucose accelerated the ettringite production for type I and type V Portland cements, and this seems to be related with the reduction of fluidity caused by the addition of this admixture. On the other hand, glucose strongly retard the calcium silicates hydration particularly when type V Portland cement was used.

SUMÁRIO: Cimentos Portland Tipos I e V foram hidratados (relação de água/cimento = 0,50) a 20°C, com e sem glicose, gliconato de sódio e lignossulfonato de sódio (0,3% em peso do cimento).

Foram realizados testes de mini-trabalhabilidade para determinar o efeito fluidificante do aditivo sobre as pastas de cimento. Por análise térmica (DTG) se estudou a velocidade de hidratação do cimento.

O gliconato de sódio, que parece ser o mais eficiente em termos de fluidificação das pastas de cimento, retarda tanto a produção de etringita como a hidratação dos silicatos de cálcio. O efeito retardador foi muito mais marcante no cimento Portland tipo V com teor nulo de C_3A.

O lignossulfonato de sódio não retardou significativamente depois da produção de etringita ou da hidratação dos silicatos de cálcio.

A glicose acelerou a produção de etringita nos cimentos Portland tipos I e tipo V, e isto parece estar relacionado com a redução de fluidez causada pela adição deste aditivo. Por outro lado, a glicose retardou fortemente a hidratação dos silicatos de cálcio, em particular quando se usou o cimento Portland tipo V.

Introduction

In previous works (1-5) the influence of some water reducers/retarders on the hydration of pure components of Portland cement has been examined. In particular, the effect of glucose, gluconate and sodium lignosulfonate on the hydration of C_3A and C_4AF with and without lime and gypsum, and of the hydration of the C_3S-C_3A-gypsum and C_3S-C_4AF-gypsum systems was investigated.

In the present work the research program extends to the study of the hydration of Portland cement, choosing two samples of cement, having a significantly different content in C_3A and C_4AF.

Experimental

Two Portland cements were used: a white Portland cement type I and a ferric Portland cement type V substantially without C_4AF and C_3A respectively.

Table 1 Chemical analysis (%) of Portland cements used.

	WHITE CEMENT	FERRIC CEMENT
CaO	65.19	63.11
SiO_2	22.16	19.97
Al_2O_3	3.54	4.01
Fe_2O_3	0.29	5.71
Na_2O	0.66	0.24
K_2O	0.20	0.81
MgO	1.51	1.74
SO_3	2.75	2.97
Free CaO	0.77	0.77
C_3S	65.0	61.3
C_2S	13.5	9.9
C_3A	8.9	1.0
C_4AF	0.9	17.4

Glucose (G), gluconate (NG) and sodium lignosulfonate (LGS), are the same materials as those used in other works (1-5).

Hydration occurred at 20°C with a water/cement ratio (w/c) of 0.50 in the absence or in the presence of the admixtures (0.3% by weight of cement). The reaction was blocked at given times by grinding and vacuum drying some portions of paste in methyl alcohol.

To evaluate the influence of the admixtures on the hydration of silicates and aluminates, DTG analysis was carried out by the methods already described in a previous paper (1).

Minislump tests were also carried out, to determine the fluidity of cement pastes [7].

Results and Discussion

Figures 1 to 4 show the DTG curves for white cement.

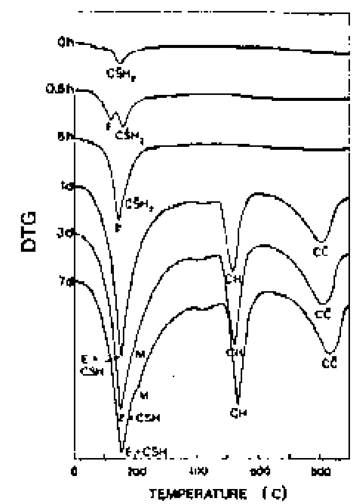

Fig.1 DTG curves of white cement hydrated up 7 days. E=ettringite; M=monosulfate.

In the absence of admixtures (Fig. 1), the peak at about 150°C in the anhydrous specimen is attributed to the dehydration of gypsum. At 0.5 hour and at 6 hours the presence of a new peak at about 120°C is observed. This due to the thermal decomposition of ettringite which begins to form. At 1 day the peak is significantly higher also because at about the same temperature (130-140°C) C-S-H, produced by the hydration of silicates, decomposes. The formation of C-S-H is confirmed by the appearance of the CH peak at about 500°C and by that of $C\bar{C}$ at 800°C approximately. At 3 days, in addition to a higher degree of hydration of silicates, the conversion of ettringite into monosulfate starts, as shown by the shoulder in the thermogram at about 200°C.

Figure 2 shows the termograms of the same cement hydrated in the presence of lignosulfonate. This admixture has negligible effects on the kinetics of hydration of the various components: the peak of ettringite at 0.5 h is lower, while, at 1 day, a slight lowering of the C-S-H and CH peaks is observed.

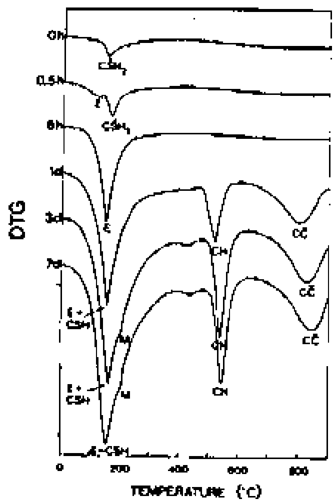

Fig.2 DTG curves of white cement hydrated in the presence of sodium lignosulfonate up to 7 days.

Figure 3 indicates the thermograms of the cement hydrated in the presence of gluconate. The retarding action of the admixture occurs quite clearly both on aluminates and on silicates. Only after 1 day of hydration an amount of ettringite comparable to that produced without admixture at 0.5 h is formed. Moreover, 7 days are required to obtain, in the presence of gluconate, the same CH as that obtained without admixture at 1 day.

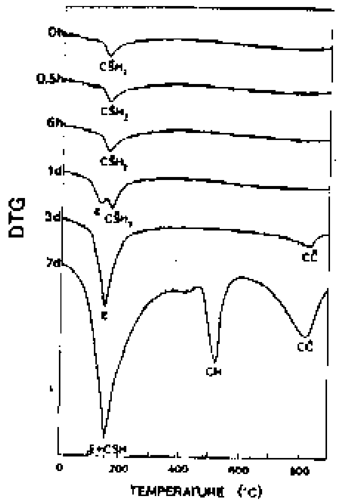

Fig.3 DTG curves of white cement hydrated in the presence of sodium gluconate up to 7 days.

Figure 4 indicates the accelerating effect of glucose on the ettringite production: after 6 hours only, the peak of gypsum is no longer evident and only the presence of ettringite is recorded. However, even at 7 days there is no tendency of ettringite to converse into monosulfate. Even this admixture, as well as gluconate, shows a strong retarding effect on the hydration of silicates. A significant increase of the peaks of C-S-H, CH and $C\bar{C}$ is observed only after 7 days.

Figures 5 to 8 show the thermograms of the hydration products of cement type V without C_3A. Fig. 5 concerns the DTG curves of the cement without admixtures. The effects of the three admixtures (Fig. 6-8) are comparable to the one found out in white

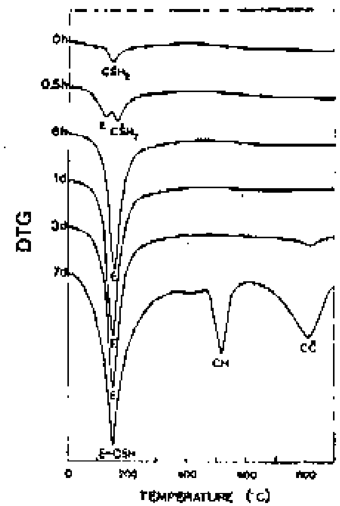

Fig.4 DTG curves of white cement hydrated in presence of glucose up to 7 days.

cement type I. The differences which can be noticed are certainly due to the kinetics of hydration of C_4AF that is slower than that of C_3A.

Lignosulfonate shows negligible effects on the hydration of both C_4AF and silicates (Fig. 6).

Gluconate (Fig. 7) is confirmed as the most efficient retarder: even at 14 days, in addition to the peak of ettringite, the peak of gypsum is present, while the hydration of silicates is still blocked.

Glucose (Fig. 8) accelerates the production of ettringite and strongly retards the hydration of silicates: a moderate peak of CH is present only at 14 days.

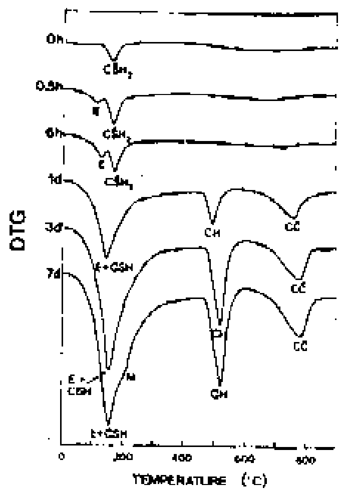

Fig.5 DTG curves of ferric cement hydrated up to 7 days.

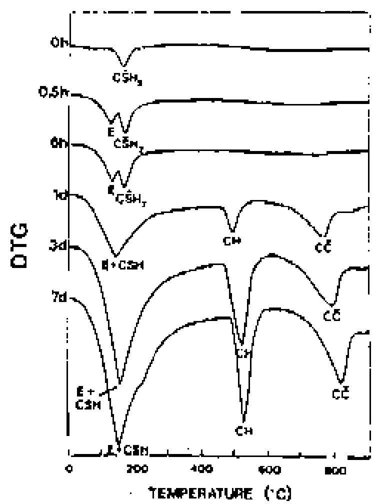

Fig.6 DTG curves of ferric cement hydrated in presence of sodium lignosulfonate up to 7 days.

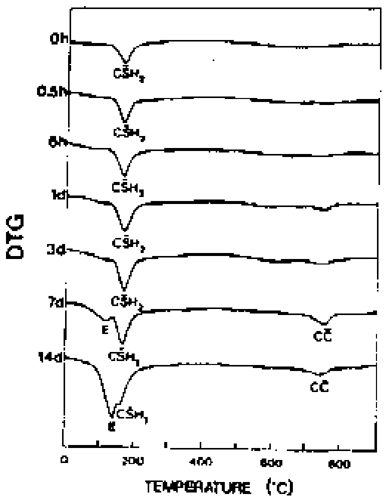

Fig. 7 DTG curves of ferric cement hydrated in presence of sodium gluconate up to 7 days.

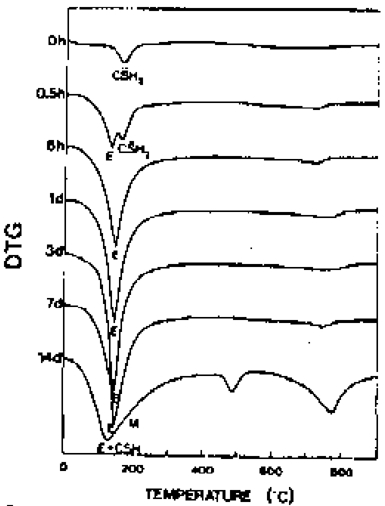

Fig. 8 DTG curves of ferric cement hydrated in presence of glucose up to 7 days.

Figure 9 shows the minislump of the pastes manufactured with the two cements in the presence and in the absence of admixtures. Among the admixtures tested, gluconate is markedly the most plasticizing one; in cement type V, the effect is more noticeable and extends for a longer period of time, this being in accordance with the higher retardation in the production of ettringite. Also lignosulfonate plasticizes the paste manufactured with the low C_3A cement more than it does with the white cement rich in C_3A. Conversely, glucose reduces the fluidity of the cement pastes and this behaviour has to be correlated with the accelerating effect on the initial production of ettringite.

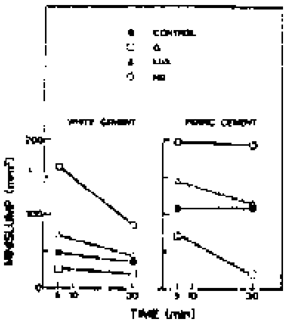

Fig.9 Minislump of cement pastes with and without admixtures (G = glucose; LGS = lignosulfonate; NG = gluconate).

Conclusion

The effects of three chemical products used as raw materials for admixtures in concrete were tested on two cements, one without C_4AF, the other without C_3A.

Gluconate, which proves to be the most effective plasticizer of cement pastes, retards both the production of ettringite and the hydration of silicates; the effects are more marked on cement without C_3A and rich in C_4AF.

Lignosulfonate does not retard the hydration of cement significantly, even if it shows an initial fluidifying effect.

Glucose has no fluidifying effect; this has to be correlated with the accelerating effect on the production of ettringite. Glucose retards the hydration of C_3S only.

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