

COMBINED EFFECT OF LIGNOSULFONATE AND CARBONATE
ON PURE PORTLAND CLINKER COMPOUNDS HYDRATION

II. TRICALCIUM ALUMINATE HYDRATION

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ABSTRACT

The effect of the combined addition of sodium lignosulfonate and sodium carbonate on the C_3A hydration was studied. XRD analysis, zeta potential measurements, DTG and TG curves were carried out. The influence of the combined presence of lignosulfonate and carbonate on the C_3A hydration is very similar to that found for the C_4AF hydration examined in a previous paper. The liquefying effect of the admixtures could be ascribed to both a strong retarding action and a dispersing effect caused by the change in the zeta potential.

E' stato studiato l'effetto dell'aggiunta combinata di lignosolfonato e carbonato di sodio sull'idratazione del C_3A . Sono state eseguite analisi di XRD, misure di potenziale zeta e curve di DTG e TG. L'influenza dell'azione congiunta del lignosolfonato e del carbonato sull'idratazione del C_3A è molto simile a quella trovata per l'idratazione del C_4AF esaminata in un precedente lavoro. L'effetto fluidificante degli additivi potrebbe essere attribuito sia alla forte azione ritardante sia alla dispersione provocata dalla variazione di potenziale zeta.

INTRODUCTION

The combined effect of lignosulfonates and carbonates on pastes from ground Portland clinker without gypsum was studied by Brunauer and coworkers (1).

In order to elucidate the specific action of the admixtures on the hydration of pure Portland clinker compounds, the influence of the lignosulfonate-carbonate addition on the hydration of single products was studied. In a previous paper (2) the results concerning the effect of lignosulfonate-carbonate combination on the tetracalcium aluminoferrite hydration were reported. In the present paper the influence of lignosulfonate-carbonate addition on the tricalcium aluminate hydration is examined.

EXPERIMENTAL

Materials and methods

Tricalcium aluminate (C_3A) described in a previous paper (3) was used. It was blended with reagent grade calcium hydroxide (CH) in order to simulate the aqueous phase present in Portland clinker paste. The C_3A/CH weight ratio was 5:1 for all the mixes. Reagent grade sodium carbonate (NC) and/or a sodium lignosulfonate (lgs), said to be free of sugars or other carbohydrates, were dry-mixed with C_3A and CH as shown in Table 1. Pure finely ground (40-90 μm) quartz (S) was also used as inert material so that the percentage of C_3A in different mixes is not changed.

TABLE 1 Percentage Composition of Mixed

Mix	C_3A	CH	NC	lgs	S
A	50	10	-	-	40
B	50	10	0,625	-	39,375
C	50	10	-	0,625	39,375
D	50	10	0,625	0,625	38,750
E	50	10	1,250	1,250	37,500
F	50	10	2,500	2,500	35,000

Hydration at 20°C of pastes with a water/solid ratio of 0.4 was studied. After a certain time (5 min + 7 days) the hydration was blocked by grinding the pastes with methyl alcohol. The filtered solid were dried at 60°C for 5 hours and analyzed by a Netzsch apparatus in which DTA, DTG and TG curves are obtained simultaneously. Only DTG curves are shown in the present paper. From TG curves, the percentages of weight loss at 600°C, corrected for the initial CH present in the samples, have been calculated.

XRD analysis was also carried out by a Philips apparatus and the intensity of the C_3A peak at 1,56 Å was determined.

Zeta potential measurements were performed as it is described in a previous paper (2). The samples for zeta potential measurements were prepared by mixing for 5 minutes 1 g of C_3A , containing NC and/or lgs, with 100 ml of a saturated calcium hydroxide water solution. The amounts of NC and/or lgs were changed so that the concentrations of admixtures in the liquid phase from 0.25 g/l to 15.6 g/l were obtained. These values correspond to the concentrations of the admixtures in the liquid phase of the pastes (W/S = 0.4) with a percentage of admixtures of 0.01 and 0.625 % respectively by weight of C_3A .

RESULTS AND DISCUSSION

In Fig. 1 DTG curves of the mixes hydrated at different times are shown. When C_3A reacts with water without NC and lignosulfonate (Fig. 1 A) hexagonal hydrates (C_4AH_x and C_4AH_8) are formed with a DTG peak at about 220°C and a smaller one at about 270°C. The other very small peak at about 120°C found in a previous work (3) is not present in the DTG curves of the present paper. This might be ascribed to the drying treatment at 60°C before analysing the hydrated samples of the present work. Only traces of the cubic phase (C_3AH_6) with the main DTG peak at 320°C are observed from 0.5 hours to 1 day.

In the presence of NC substantially the same products are formed, the only difference being a slightly greater amount of the cubic phase at 1 day (Fig. 1 B).

When C_3A reacts with water in the presence of lignosulfonate only hexagonal hydrates are formed till to 1 day (Fig. 1 C).

A DTG "positive" peak corresponding to an increase of weight is observed at about 570°C on the anhydrous samples containing lgs or lgs and NC (Fig. 1 C-F). This peak increases by increasing the amount of lignosulfonate and disappears in the hydrated samples. These phenomena have been explained in an other paper (2) where similar results have been obtained.

In the presence of lgs and NC (0.625 %) the C_3A hydration is blocked for about 5 min (Fig. 1 D). At later ages substantially the same products of hydration have been formed as in C_3A hydration without admixtures.

By increasing the percentage of lgs and NC the C_3A hydration is blocked for a longer period of time: about 2 hours with 1.25 % (Fig. 1 G), and about 6 hours with 2.5 % (Fig. 1 F). A larger amount of C_3AH_6 is produced at 1-7 days in the presence of 1.25 % of lgs and NC (Fig. 1 E). However, when the percentage is increased to 2.5 % the C_3A hydration is so retarded that the transformation of hexagonal hydrates into C_3AH_6 seems to be postponed after 7 days.

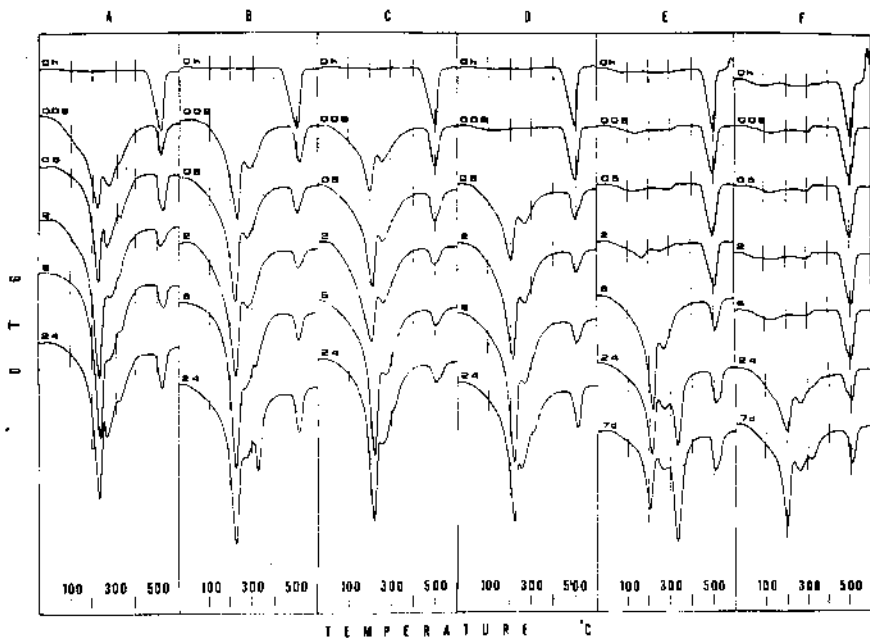


FIG. 1

DTG curves for mixes A-B-C-D-E-F (Table 1).

Fig. 2-4 show weight loss as a function of time for the control mix without admixtures and for the samples containing NC and/or lgs. Sodium carbonate (Fig. 2) and lignosulfonate (Fig. 3) separately added seem to retard the C_3A hydration. These results substantially confirm those obtained for C_4AF (2) except a slight accelerating effect for NC during the first 2-3 hours of C_4AF hydration. When NC and lgs are simultaneously added to C_3A a more remarkable retarding effect is recorded. An induction period from 5 min to about 6 hours is observed by increasing the percentage of NC and lgs from 0.625 % to 2.5 % (Fig. 4).

The combined addition of NC and lgs causes an initial retardation of C_4AF . However the percentage of hydrated C_4AF is not substantially changed by the simultaneous presence of NC and lgs (from 0.625 to 2.5 %) for hydration time of 7 days (2). It seems that the combined addition of NC and lgs retards more remarkably the hydration of C_3A than that of C_4AF , since the percentage of hydrated C_3A is lower in the presence of admixtures even after 7 days (Fig. 4).

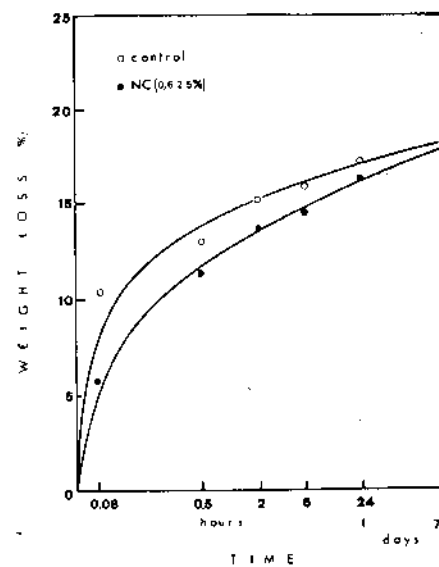


FIG. 2

Weight loss as a function of time.

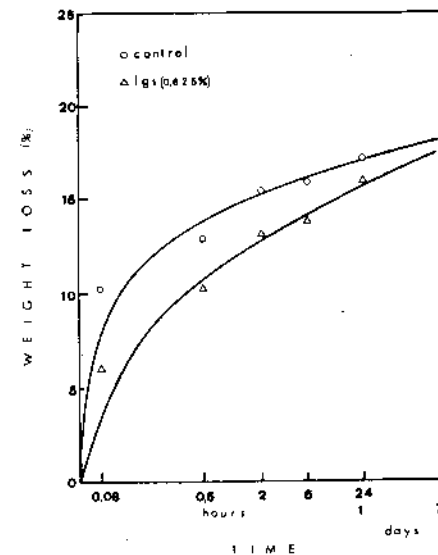


FIG. 3

Weight loss as a function of time.

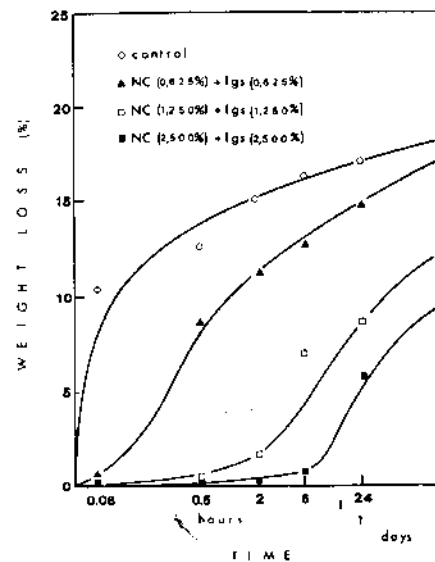


FIG. 4

Weight loss as a function of time.

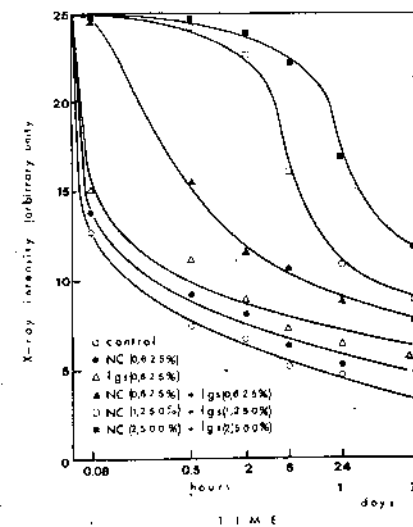


FIG. 5

XRD intensity peak of C_3A as a function of time.

The results concerning TG curves (Fig. 2-4) are confirmed by X-ray analysis (Fig. 5). Sodium carbonate and lignosulfonate separately added (0.625 %) slightly retard C_3A hydration, whereas the combined addition of NC and lgs (0.625 %) retards more remarkably the C_3A hydration. It is confirmed that the induction period increases by increasing the percentage of the admixtures.

In Fig. 6 the zeta potential as a function of NC and lgs in the liquid phase is shown. The zeta potential of C_3A in saturated CH water solution is about 40 mV. This result agrees with the data of Tadros et al. (4) who found a value of 34 mV for suspension of 8 g of C_3A in 100 ml of water. The addition of NC or lgs decreases the zeta potential. However the combined addition of NC or lgs reduces the zeta potential more efficiently than either NC or lgs alone. By using 15.6 g of admixture per liter of liquid phase the zeta potential is about -7 mV for NC, -15 mV for lgs and -40 mV for NC and lgs. Similar effects were found for C_4AF except that NC addition caused smaller changes in zeta potential.

CONCLUSIONS

The influence of the combined addition of NC and lgs on the C_3A hydration is very similar to that described in a previous paper for C_4AF (2).

In the presence of NC and lgs the C_3A hydration is completely blocked for a certain period of time which is proportional to the percentage of admixtures. The retarding effect caused by the simultaneous presence of admixtures is more remarkable for the C_3A hydration than for that of C_4AF .

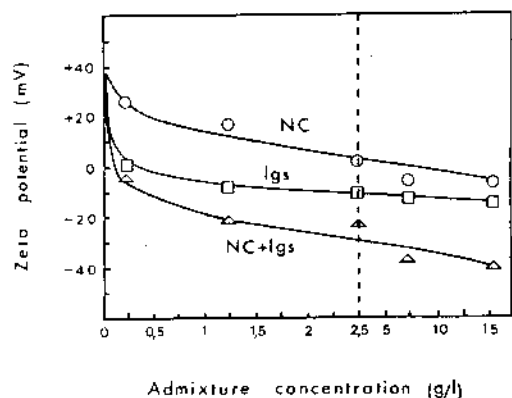


FIG. 6

Zeta potential as a function of admixture concentration in the liquid phase.

Both sodium carbonate and lignosulfonate change the zeta potential thus dispersing the C_3A grains and causing their mutual repulsion. However when NC and lgs are simultaneously added to C_3A , the change in the zeta potential is more evident than in the presence of either NC or lignosulfonate alone.

It is confirmed that the liquefying effect of the carbonate-lignosulfonate combined addition could be related with both the dispersing action and the completely blocking effect on the early hydration (2).

REFERENCES

1. S. Brunauer et al., *Cem. Conc. Res.* 2, 313; 2, 331; 2, 463; 2, 577; 2, 731 (1972); 3, 129; 3, 279 (1973).
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3. M. Collepardi, M. Corradi, G. Baldini and M. Pauri, *Cem. Conc. Res.*, 8, 571 (1978).
4. M.E. Tadros, W.Y. Jackson and J. Skalny, *Colloid and Interface Science*, 4, 211 (1976).

We take the opportunity to point out and apologize for an error in reference (2) pg. 460 in Fig. 2-4 "weight loss %" should read "Weight loss (arbitrary units)".