

COMBINED EFFECT OF LIGNOSULFONATE AND CARBONATE ON PURE  
PORTLAND CLINKER COMPOUNDS HYDRATION. IV. HYDRATION OF  
TRICALCIUM ALUMINATE-SODIUM OXIDE SOLID SOLUTION

Marco Pauri, Giorgio Ferrari\* and Mario Collepardi  
Department of Materials Science  
University of Ancona, Ancona, Italy

\* Research and Development Laboratories, MAC, Treviso, Italy

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ABSTRACT

The combined effect of lignosulfonate and sodium carbonate on the hydration of  $C_3A$  and  $C_3A-Na_2O$  solid solution was examined by DTG and TG curves, by XRD analysis and by zeta potential measurements. It is confirmed that the simultaneous addition of lignosulfonate and carbonate completely blocks the  $C_3A$  hydration with an induction period whose length is proportional to the percentage of admixtures. On the other hand, no induction period was observed in the hydration of  $C_3A-Na_2O$  solid solution in the presence of both lignosulfonate and carbonate. The effect of the admixtures on the zeta potential is substantially the same for  $C_3A$  and  $C_3A-Na_2O$  solid solution. The liquefying effect of NC and lgs combined addition seems to be more pronounced on  $C_3A$  than on  $C_3A-Na_2O$  solid solution.

Introduction

In previous papers the influence of lignosulfonate-carbonate addition on the hydration of  $C_4AF$  (1),  $C_3A$  (2),  $C_3S$  and  $C_3S+C_3A$  (3) was examined. In the present paper the combined addition of lignosulfonate and carbonate on the hydration of  $C_3A$  or  $C_3A-Na_2O$  solid solution is studied.

Experimental

Materials  
Tricalcium aluminate was synthesized from reagent grade  $CaCO_3$  and  $Al_2O_3$  by heating three times the mixture in the proper molar ratio at  $1350^\circ C$ . A tricalcium aluminate-sodium oxide solid solution was synthesized in a similar way by heating reagent

grade Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in the molar ratio of 1:8:3. After heating, the Na<sub>2</sub>O content was 5.71 % and the molar composition of the solid was about N<sub>0.25</sub>C<sub>2.75</sub>A. The free lime content of C<sub>3</sub>A and N<sub>0.25</sub>C<sub>2.75</sub>A was 0.1 and 0.2 % respectively. Both C<sub>3</sub>A and N<sub>0.25</sub>C<sub>2.75</sub>A were ground and sieved. Only the fractions with particles size smaller than 36 μm were used. The Blaine specific surface area was about 2600 and 2650 cm<sup>2</sup>/g for C<sub>3</sub>A and N<sub>0.25</sub>C<sub>2.75</sub>A respectively. The X-Ray diffraction analysis showed that N<sub>0.25</sub>C<sub>2.75</sub>A was a monoclinic crystal form on the basis of Regourd's results (4).

Reagent grade sodium carbonate (NC) and/or a sodium lignosulfonate (lgs), said to be free of sugars or other carbohydrate, were dry-mixed with C<sub>3</sub>A or N<sub>0.25</sub>C<sub>2.75</sub>A and CH as shown in Table 1.

TABLE 1  
Percentage Composition of Mixes

Mix	C <sub>3</sub> A	N <sub>0.25</sub> C <sub>2.75</sub> A	CH	NC	Lgs	S
A	50	-	10	-	-	40.00
B	50	-	10	1.250	-	38.75
C	50	-	10	-	1.250	38.75
D	50	-	10	0.625	0.625	38.75
E	50	-	10	1.250	1.250	37.50
A'	-	50	10	-	-	40.00
B'	-	50	10	-	-	38.75
C'	-	50	10	1.250	1.250	38.75
D'	-	50	10	0.625	0.625	38.75
E'	-	50	10	1.250	1.250	37.50

Pure finely ground (40-90 μm) quartz (S) was used as inert material so that the percentage of C<sub>3</sub>A or N<sub>0.25</sub>C<sub>2.75</sub>A in different mixes is not changed.

#### Methods

Hydration at 20°C of pastes with a water/solid ratio of 0.4 was examined. After a certain period of times DTG, TG and XRD were carried out on paste specimens according to the method described in a previous paper (2).

Although no quantitative measurement has been carried out, during the mixing of the pastes it was observed that the liquefying effect due to the combined addition of NC and lgs was more pronounced with C<sub>3</sub>A (mixes D and E) than with C<sub>3</sub>A-Na<sub>2</sub>O solid solution (mixes D' and E').

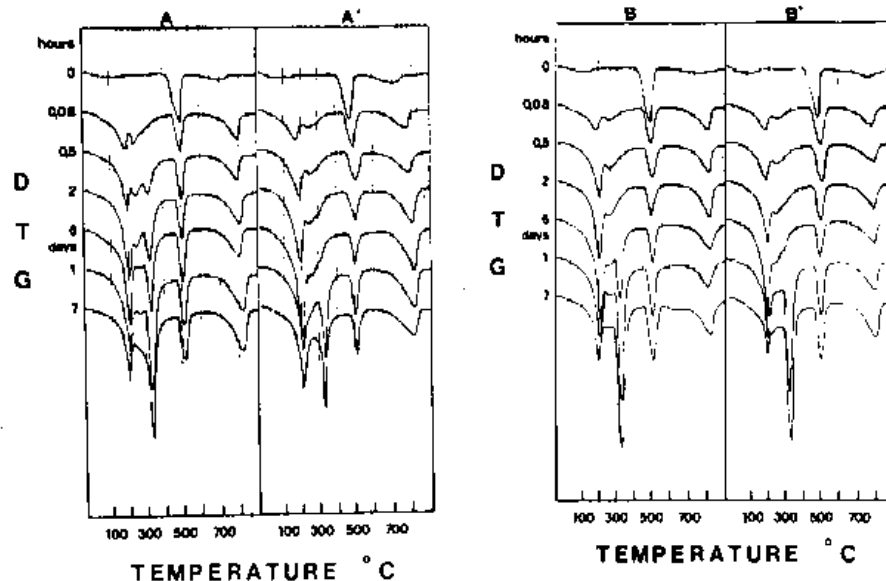


FIG. 1

DTG curves for C<sub>3</sub>A (mix A) and N<sub>0.25</sub>C<sub>2.75</sub>A (mix A') without NC and lgs.

FIG. 2

DTG curves for C<sub>3</sub>A (mix B) and N<sub>0.25</sub>C<sub>2.75</sub>A (mix B') in the presence of NC (1.25 %).

Zeta potential measurements were performed as it is described in previous papers (1,2). The samples for these measurements were prepared by mixing for 5 minutes 1 g of C<sub>3</sub>A or N<sub>0.25</sub>C<sub>2.75</sub>A containing NC and/or lgs, with 100 ml of a saturated CH water solution.

#### Results and discussion

##### 1. DTG curves

In Fig. 1 DTG curves for C<sub>3</sub>A (mix A) and N<sub>0.25</sub>C<sub>2.75</sub>A (mix A') without NC and lgs are shown. In both the specimens hexagonal hydrates (C<sub>4</sub>AH<sub>x</sub> and C<sub>2</sub>AH<sub>8</sub>) are immediately formed with a DTG peak at about 200°C and a smaller one at about 250°C. After a certain period of time (0.5 hour for mix A and 1 day for mix A') the cubic phase (C<sub>3</sub>AH<sub>6</sub>), with the main DTG peak at about 320°C is observed.

In the presence of NC (1.25 %) substantially the same products are formed (Fig. 2). However, it seems that the formation of C<sub>3</sub>AH<sub>6</sub> is retarded at earlier times and favoured at longer ages, particularly after 1 day.

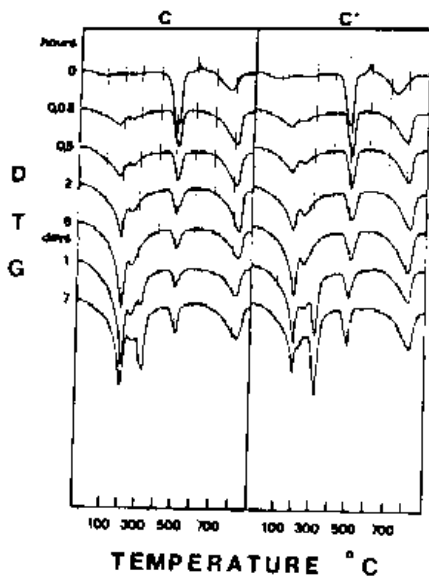


FIG. 3

DTG curves for  $C_3A$  (mix C) and  $N_{0.25}C_{2.75}A$  (mix C') in the presence of lgs (1.25%).

In Fig. 3 the DTG curves for  $C_3A$  (mix C) and  $N_{0.25}C_{2.75}A$  (mix C') in the presence of lgs (0.25%) are shown. Before 1 day only hexagonal hydrates are formed in both the mixes. At 1 and 7 days  $C_3AH_6$  appears, however its amount seems to be lower because of the lgs addition.

The "positive" DTG peak at about  $580^\circ C$  in the anhydrous mixes of Fig. 3, as well as in those of Fig. 4 and 5, is due to the presence of lgs (1-3).

The NC-lgs combined addition (0.625%) completely blocks the  $C_3A$  hydration (Fig. 4) for at least 0.5 hour (mix D), whereas the hydration of  $N_{0.25}C_{2.75}A$  (mix D') does not appear to be retarded in comparison with that in the presence of lgs only (mix C' in Fig. 3). Hexagonal hydrates DTG peaks appear only at 2 hours for mix D and at 5 minutes for mix D' (Fig. 4). In the presence of NC and lgs, the cubic phase is observed only after 1 day for both  $C_3A$  and  $N_{0.25}C_{2.75}A$ , as it has been found in the presence of lgs only (Fig. 3).

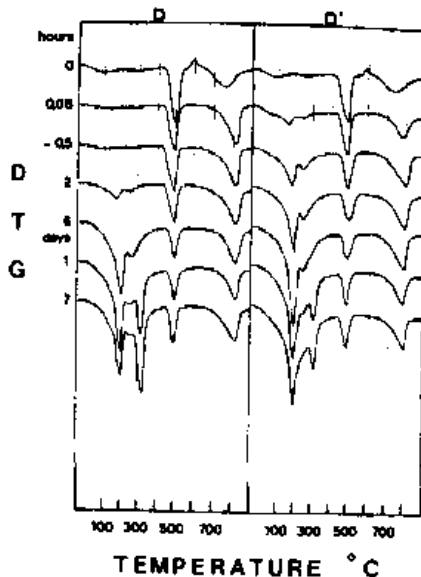


FIG. 4

DTG curves for  $C_3A$  (mix D) and  $N_{0.25}C_{2.75}A$  (mix D') in the presence of NC (0.625%) and lgs (0.625%).

By increasing the amount of NC and lgs to 1.25% (Fig. 5) the induction period for the  $C_3A$  hydration (mix E) is prolonged and the hexagonal hydrates DTG peaks are observed only at 5 hours, whereas  $C_3AH_6$  is detected only at 7 days. The hydration of  $N_{0.25}C_{2.75}A$  is not even blocked by the combined addition of 1.25% of NC and lgs (mix E').

By comparing the  $C_3A$  hydration of this paper with that of a previous paper (2) the  $C_3A$  sample of the present work appears to be a little less reactive and more retarded by the addition of NC and lgs, perhaps because of its lower specific surface area. However, the influence of NC and lgs on the  $C_3A$  hydration seems to be substantially the same. In particular it is confirmed that the higher is the percentage of NC and lgs simultaneously added to  $C_3A$ , the longer the induction period of the  $C_3A$  hydration. On the other hand, the induction period is not observed in the  $N_{0.25}C_{2.75}A$  hydration.

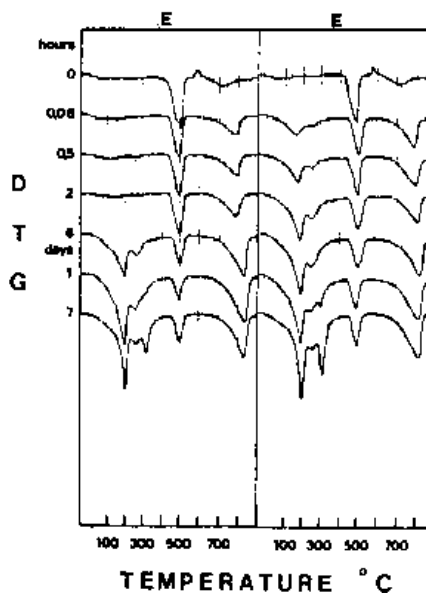


FIG. 5

DTG curves for  $C_3A$  (mix E) and  $N_{0.25}C_{2.75}A$  (mix E') in the presence of NC (1.25%) and lgs (1.25%).

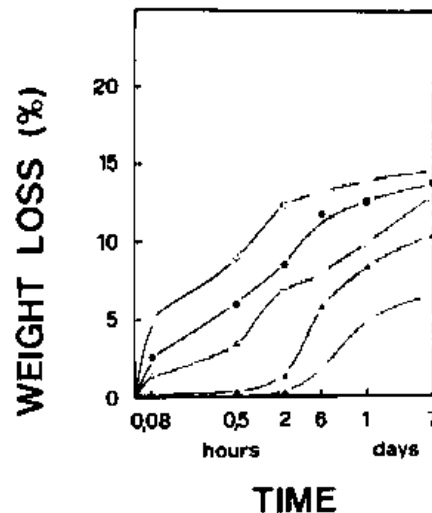


FIG. 6

Weight loss as a function of time for  $C_3A$ .

- control mix
- with NC at 1.25%
- △ with lgs at 1.25%
- ▲ with NC and lgs both at 0.625%
- with NC and lgs both at 1.25%

## 2. Weight Loss Curves

From TG curves, the percentages of weight loss at 600°C, corrected for the initial CH present in the samples, have been calculated. So this weight loss, due to C<sub>4</sub>AH<sub>x</sub>, C<sub>2</sub>AH<sub>8</sub> and C<sub>3</sub>AH<sub>5</sub> is assumed to be proportional to the percentage of hydrated C<sub>3</sub>A.

Fig. 6 shows the weight loss as a function of time for C<sub>3</sub>A without admixtures and for the samples containing NC and/or lgs. Sodium carbonate and lignosulfonate separately added retard the C<sub>3</sub>A hydration. However, when NC and lgs are simultaneously added the retarding effect is much more pronounced particularly at earlier ages, and an induction period, whose length is proportional to the percentage of NC lgs, is observed. Incidentally, it was observed that the paste containing both NC and lgs was much more workable than that without admixtures or with only one admixture.

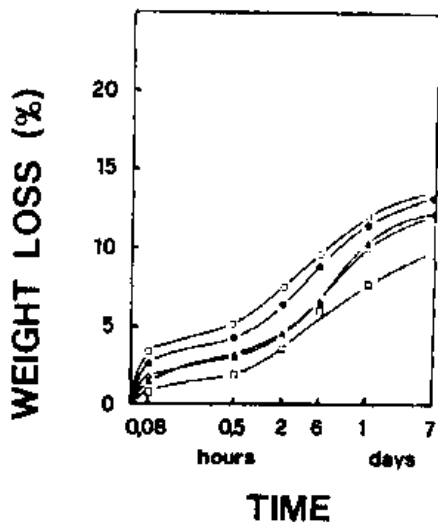


FIG. 7

Weight loss as a function of time for N<sub>0.25</sub>C<sub>2.75</sub>A.

- control mix
- with NC at 1.25 %
- △ with lgs at 1.25 %
- ▲ with NC and lgs both at 0.625 %
- with NC and lgs both at 1.25 %

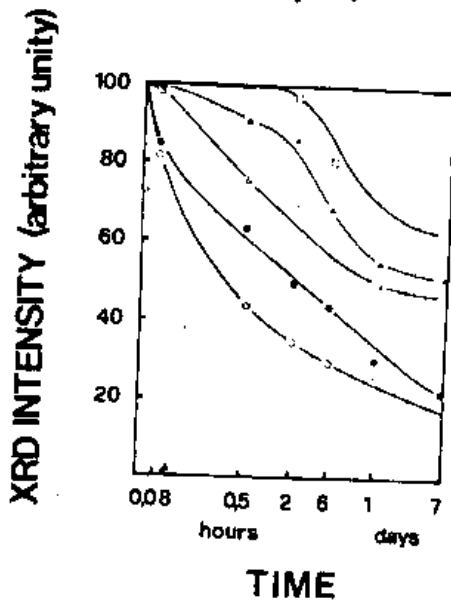


FIG. 8

XRD intensity of C<sub>3</sub>A (1.555 Å) as a function of time.

- control mix
- with NC at 1.25 %
- △ with lgs at 1.25 %
- ▲ with NC and lgs both at 0.625 %
- with NC and lgs both at 1.25 %

The retarding effect of NC and/or lgs on the hydration of N<sub>0.25</sub>C<sub>2.75</sub>A is much less pronounced (Fig. 7). In particular, no induction period is caused by the simultaneous addition of NC and lgs to the C<sub>3</sub>A-Na<sub>2</sub>O solid solution, although the hydration of N<sub>0.25</sub>C<sub>2.75</sub>A without admixtures (Fig. 7) is remarkably slower than that of pure C<sub>3</sub>A (Fig. 6). The paste of N<sub>0.25</sub>C<sub>2.75</sub>A with lgs and NC did not appear to be more flowable than the plain mix or the paste with only one admixture.

## 3. XRD Curves

The XRD intensity of the peak at 1.555 Å and at 1.565-1.551 Å as a function of time is shown for C<sub>3</sub>A (Fig. 8) and N<sub>0.25</sub>C<sub>2.75</sub>A (Fig. 9) respectively. The XRD curves substantially confirm the result concerning weight loss curves (Fig. 6 and 7). In particular, the hydration of C<sub>3</sub>A-Na<sub>2</sub>O solid solution (Fig. 9) seems to be slower than that of pure C<sub>3</sub>A (Fig. 8), thus confirming the result obtained by other researchers (5-8).

However NC and/or lgs retard much less the hydration of N<sub>0.25</sub>C<sub>2.75</sub>A than that of C<sub>3</sub>A. The induction period caused by the simultaneous addition of NC and lgs to C<sub>3</sub>A disappears in the N<sub>0.25</sub>C<sub>2.75</sub>A hydration.

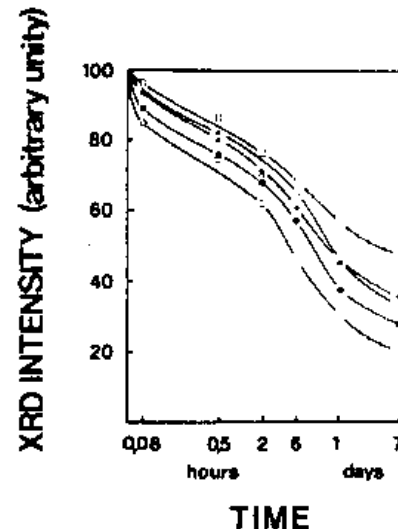
## 4. Zeta Potential Measurements

In Fig. 10 the zeta potential as a function of NC and lgs in the liquid phase is shown for N<sub>0.25</sub>C<sub>2.75</sub>A. The combined addition of NC and lgs reduces the zeta potential more efficiently than either NC or lgs alone. Similar results have been obtained for C<sub>3</sub>A (2).

FIG. 9

XRD intensity of N<sub>0.25</sub>C<sub>2.75</sub>A (1.565 - 1.551 Å) as a function of time.

- control mix
- with NC at 1.25 %
- △ with lgs at 1.25 %
- ▲ with NC and lgs both at 0.625 %
- with NC and lgs both at 1.25 %



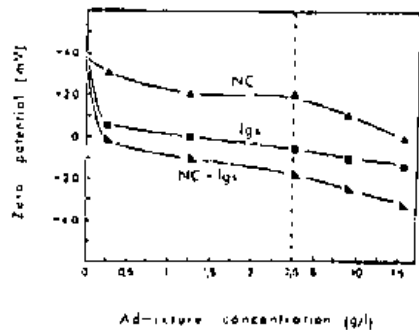


FIG. 10

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

### 5. Conclusions

It is confirmed (2) that in the presence of both NC and Igs the  $C_3A$  hydration is completely blocked for a certain period of time. The induction period is proportional to the percentage of admixtures (Fig. 6 and 8). Similar results have been found in the  $C_4AF$  hydration (1). On the other hand, the combined addition of NC and Igs does not completely block the hydration of  $C_3A-Na_2O$  solid solution (Fig. 7 and 9), although the hydration of  $N_0.25C_2.75A$  without admixtures appears to be much slower than that of pure  $C_3A$ .

The influence of NC and/or Igs on the zeta potential of  $C_3A$  or  $N_0.25C_2.75A$  seems to be substantially the same.

During the mixing of the pastes it was observed that the liquefying effect of NC-Igs combined addition was much more pronounced on  $C_3A$  than on  $N_0.25C_2.75A$ . Therefore, it would seem that the blocking effect plays a more important role than the dispersing action due to the change in zeta potential.

### References

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