

COMBINED EFFECT OF LIGNOSULFONATE AND CARBONATE ON PURE PORTLAND CLINKER
COMPOUNDS HYDRATION. V. HYDRATION OF DICALCIUM SILICATE ALONE AND IN
THE PRESENCE OF TRICALCIUM ALUMINATE

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ABSTRACT

The effect of sodium carbonate and/or sodium lignosulfonate on the hydration of C_2S alone and in the presence of C_3A has been examined by DTG and TG curves and by zeta potential measurements. The combined addition of sodium carbonate and lignosulfonate retards the C_2S hydration to a lower extent than that observed for the C_3S hydration. The retarding effect on the C_2S hydration is significantly lower in the presence of 20% C_3A . On the other hand, the early C_3A hydration is completely blocked by admixtures simultaneously added. Addition of 0.9% sodium carbonate without lignosulfonate blocks the early hydration of both C_3A and C_2S . This effect was not found in the C_3S - C_3A system.

Introduction

In previous papers the effect of lignosulfonate and/or carbonate on the hydration of C_4AF (1) C_3A (2,3) and C_3S with and without C_3A (4) has been studied. In the present paper the influence of these admixtures on the hydration of β - C_2S with and without C_3A is examined.

Experimental

Materials and Methods

β -dicalcium silicate was synthesized from reagent grade $CaCO_3$ and silica by heating the mixture in the proper molar ratio at $1500^\circ C$ and using B_2O_3 (0.5%) as stabilizer for the β -form. The C_2S , with a free lime content lower than 0.4%, was ground to a Blaine fineness of about $3000 \text{ cm}^2/\text{g}$.

Tricalcium aluminate (C_3A) described in a previous paper (5) was used.

Reagent grade sodium carbonate (NC) and/or sodium lignosulfonate (lgs), said to be free of sugars or other carbohydrates, were dry-mixed with C₂S or C₂S and C₃A as shown in Table 1.

Paste Hydration

Hydration at 20° C of pastes with water/solid ratio of 0.5 was examined.

After a certain time (30 min - 28 days) the degree of hydration was evaluated by DTG and TG curves as it was described in a previous paper (4).

Zeta Potential Measurements on Suspensions

Zeta potential measurements were performed on suspensions using a Laser Zee Meter by Pen. Kem Inc. through electrophoretic measures in a fixed electric field, according to a methodology already described in a previous paper (4).

The suspensions were prepared by mixing 1 g of C₂S or C₂S-C₃A mixture and 100 ml of CH saturated water solution for 15 min. The concentrations of NC and lgs in the liquid phase have been changed from 0 to a maximum of 18 g/l. This value corresponds to the concentration of the admixture in the liquid phase of the paste experiment when 0.9% of admixture is used.

Results and Discussion

Influence of NC and lgs on C₂S Hydration

Figure 1 shows the DTG curves of the hydration products of C₂S with and without NC and/or lgs. When C₂S reacts with water without NC and lgs (Fig. 1A), C-S-H and CH are formed with a DTG peak at about 140° C and a sharper one at about 500° C respectively. A peak at about 750° C due to CaCO₃ is also observed.

The addition of NC (0.3%) to C₂S (Fig. 1B) does not cause any significant change.

In the presence of 0.3% of lgs (Fig. 1C) the C₂S hydration is completely blocked for at least 3 days. At 7 days the C₂S hydration starts, as small peaks

Table 1
Composition of Mixes

Mix	C ₂ S	C ₃ A	NC	lgs
A	100	—	—	—
B	100	—	0.300	—
C	100	—	—	0.300
D	100	—	0.300	0.300
A ₁	80	20	—	—
B ₁	80	20	0.300	—
C ₁	80	20	—	0.300
D ₁	80	20	0.300	0.300
A ₁ = A ₂	80	20	—	—
B ₂	80	20	0.900	—
C ₂	80	20	—	0.900
D ₂	80	20	0.900	0.900

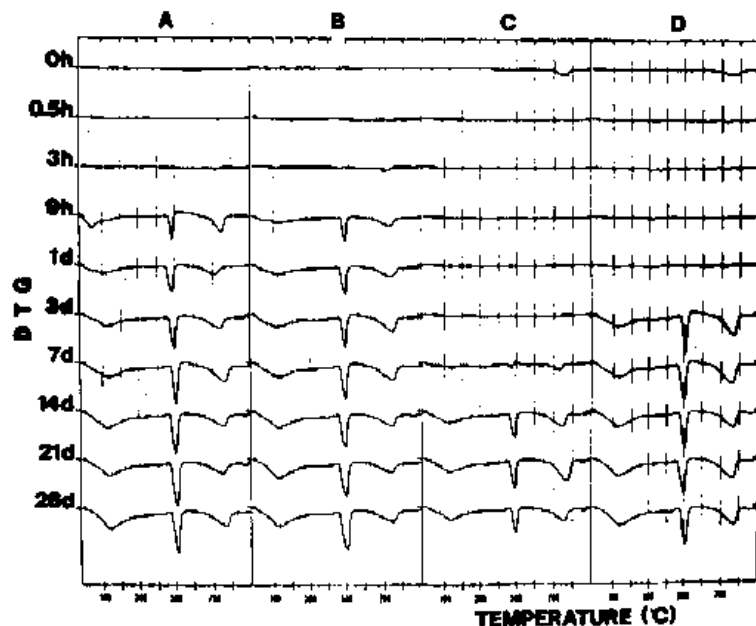


FIG. 1

DTG curves for C₂S pastes (See Table 1)

at about 140° C, 500° C and 750° C appear. Thus, it seems that lgs retards the C₂S hydration remarkably less than the C₃S hydration: in a previous paper it was found that 0.3% lgs completely blocked the C₃S hydration for at least 14 days. Similar results on the hydration of C₃S in the presence of lgs have been obtained by Young (6) and Ramachandran (7).

The combined addition of NC (0.3%) and lgs (0.3%) blocks the C₂S hydration for about 1 day (Fig. 1D). At 3 days C-S-H, CH and CaCO₃ peaks can be observed. Thus a combined addition of lgs and NC retards the C₂S hydration much less than lgs alone does (Fig. 1C and D). A similar effect was found also for the C₃S hydration (4). However, the combined addition of lgs and NC retard the C₂S hydration much less than that of the C₃S: 0.3% lgs and 0.3% NC simultaneously added completely block the hydration of C₃S for at least 7 days (4) and that of C₂S for about 1 day (Fig. 1D).

Figure 2 shows the percentage of CH including that transformed into CaCO₃ as a function of time for C₂S alone (control mix) and in the presence of 0.3% of additives. These data, based on TG curves, confirm that NC does not substantially change the C₂S hydration, whereas a combined addition of lgs and NC retards the C₂S hydration significantly less than lgs alone does.

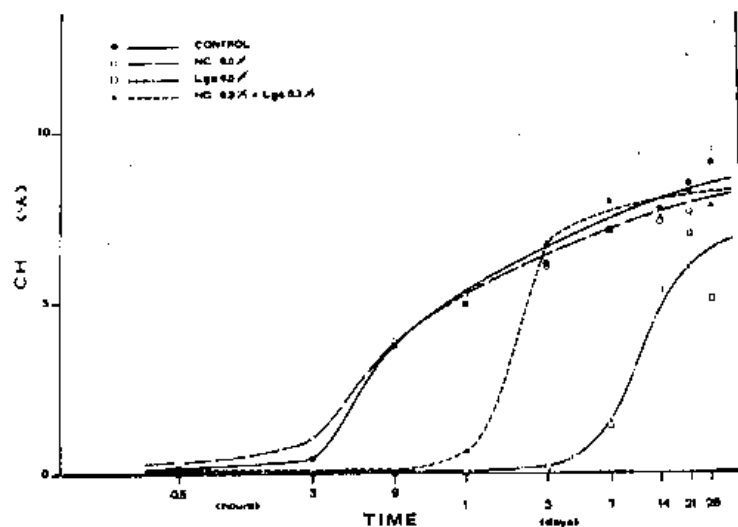


FIG. 2

Percentage of CH as a function of time for C₂S pastes.

In Fig. 3 the zeta potential as a function of NC and lgs concentration in the liquid phase is shown. The zeta potential value for C₂S without admixtures, even considering the relatively large scatter of the zeta potential of C₂S particles in the absence of admixtures, is about 0mV.

The addition of either NC or lgs lowers the zeta potential value. The latter seems to be a little more effective in the change of zeta potential, particularly at low concentrations.

When NC and lgs are simultaneously added, a minimum (-45mV) in the zeta potential curve is observed.

The concentration in the liquid phase of the admixtures corresponding to the minimum is about 4 g/l. Similar results have been obtained for the C₃S-water suspension (4).

Influence of NC and lgs on C₂S Hydration in the Presence of C₃A

Figures 4 and 5 show the DTG curves of C₂S-C₃A mixes hydrated for different periods of time and different dosages (0.3% and 0.9% respectively) of additives.

In the sample not containing admixtures (Fig. 4A₁ and 5A₂) four hydrated phases are observed: C-S-H (140° C), hexagonal hydroaluminates (190° C and 250° C), cubic hydrate (320° C) and CH (500° C). Within the first three hours of hydration only hexagonal hydroaluminates and traces of cubic hydrate can

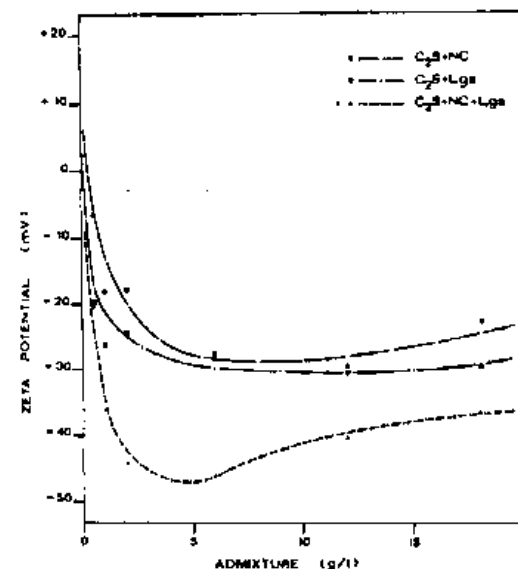


FIG. 3
Zeta potential of C₂S as a function of admixtures concentration in the liquid phase.

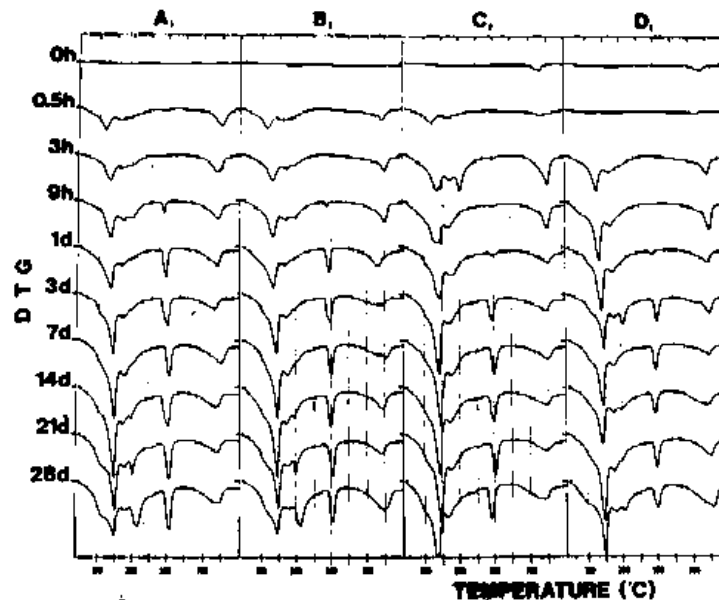


FIG. 4

DTG curves for C₂S-C₃A pastes with and without 0.3% of admixtures (See Table 1)

be detected. Calcium hydroxide is observed after 9 hours, whereas a shoulder at 140° C due to C-S-H can be detected at 3 days only. Calcium hydroxide is always accompanied by calcium carbonate with a DTG peak at about 800° C.

The addition of 0.3% NC slightly retards the C₃A hydration (Fig. 4B₁). At higher concentration of NC (0.9%) the C₃A hydration is stopped for at least 9 hours (Fig. 5B₂).

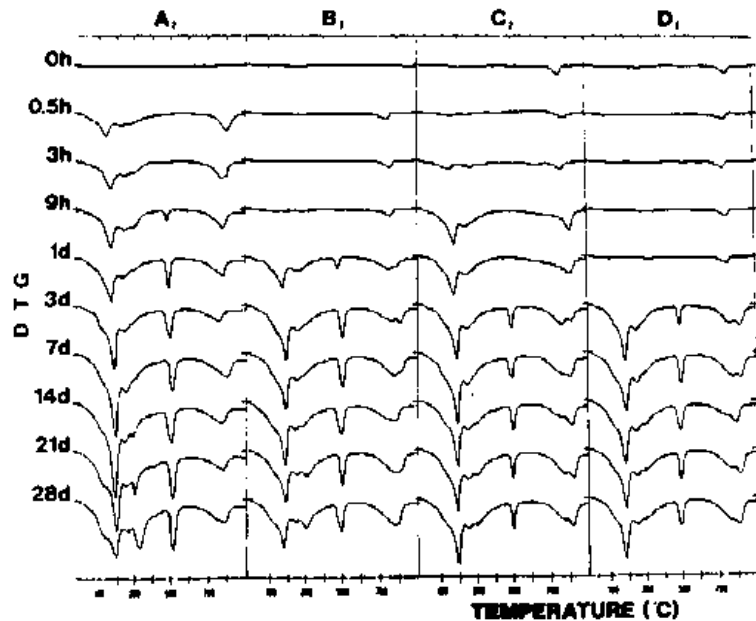


FIG. 5

DTG curves for C₂S-C₃A pastes with and without 0.9% of admixtures (See Table 1)

A high dosage of NC does not block the early C₃A hydration either in the C₃S-C₃A system (4) or in the C₃A-CH system (2). So, it seems that the initial blocking effect of 0.9% NC on the C₃A hydration in the C₂S-C₃A system (Fig. 5B₂) is related to the absence of a CH saturated solution during the first hours, as also the early C₂S hydration is stopped (Fig. 5B₂). In order to confirm this hypothesis, mixes E, F and G (Table 2) were hydrated at 20° C with a water/solid ratio of 0.50 in the presence of 0.9% NC. The DTG curves shown in Fig. 6 confirm the above hypothesis as the formation of hexagonal hydrates is blocked by 0.9% NC for about 9 hours only when C₃A hydrates without CH (Fig. 6E). Addition of lime to either C₃A (Fig. 6F) or C₂S-C₃A system

(Fig. 6G) removes the initial blocking effect caused by 0.9% NC. It seems that, in the absence of lime, high dosages of NC could cause precipitation of calcium carboaluminate and carbonate in form of a thin coating on the surface of C₃A and C₂S respectively, so blocking their early hydration. In the presence of CH, precipitation of CaCO₃ for the most part would occur in the CH saturated water phase without blocking the early C₃A hydration.

The influence of 0.3% and 0.9% lgs on the hydration of C₂S-C₃A system is shown in Fig. 4C₁ and 5C₂ respectively. Addition of 0.3% lgs blocks the C₂S hydration within the first day, whereas hexagonal hydroaluminates can be detected within 30 minutes. In the presence of a higher dosage (0.9%), lgs does not seem to cause a significant stronger retarding effect on C₂S hydration, whereas the C₃A hydration appears to be retarded particularly within the first 3 hours.

Figures 4D₁ and 5D₂ show the DTG curves for the C₂S-C₃A system in the pre-

Table 2

Composition of Mixes E, F and G

Mix	C ₃ A	CH	C ₂ S	NC	S
E	20	-	-	0.9	80
F	20	4	-	0.9	76
G	20	4	76	0.9	76

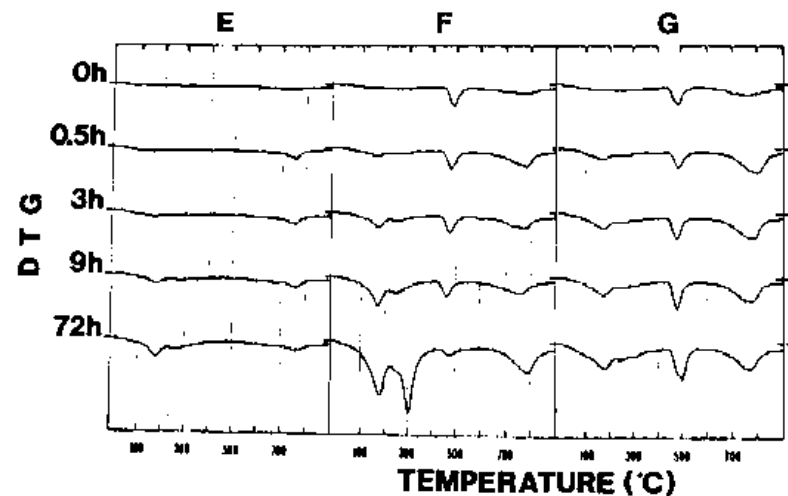


FIG. 6

DTG curves for C₃A pastes with 0.9% NC without CH (E), with CH (F) and in the presence of C₂S and CH (G) (See Table 2)

sence of both NC and lgs in percentages of 0.3% and 0.9% respectively. The combined addition of NC and lgs completely stops both C_2S and C_3A hydration for a certain period of time. The C_3A hydration is blocked for 0.5 hours with 0.3% NC and lgs (Fig. 4D₁) and at least for 1 day with 0.9% of admixtures (Fig. 5D₂). Moreover, the combined addition of admixtures retards the C_2S hydration (Figs. 7 and 8) to a higher extent than lgs alone does. At a given dosage of admixtures (0.3%), lgs or lgs and NC are much less effective in retarding the hydration of C_2S in the presence of C_3A (Fig. 7) than in the absence of C_3A (Fig. 2). Similar results were obtained in the C_3S - C_3A system. Hydrating C_3A strongly adsorbs lignosulfonate and may act as a sink for the admixtures (5,7), so that the lgs concentration in the aqueous phase decreases and the C_2S hydration is not retarded in the presence of C_3A to the same extent as in the absence of C_3A . The combined addition of NC and lgs retards the C_2S hydration in the presence of C_3A to a greater extent than lgs alone does (Figs. 7 and 8) and this effect is different from that observed for the hydration of C_2S in the absence of C_3A (Fig. 2). Similar results were obtained examining the effect of lgs and NC on the hydration of C_3S or C_3S - C_3A mixture (4). As the combined addition of lgs and NC blocks the C_3A hydration for a longer time than that observed with lgs alone (Figs. 4C₁-D₁ and 5C₂-D₂), the concentration of lgs in the aqueous phase during the first hours is expected to be much higher when both NC and lgs are used. This hypothesis seems to be confirmed by the results obtained by Jawed et al. (8). This effect results in a stronger retarding action of lgs and NC on the C_2S hydration than lgs alone (Figs. 7 and 8).

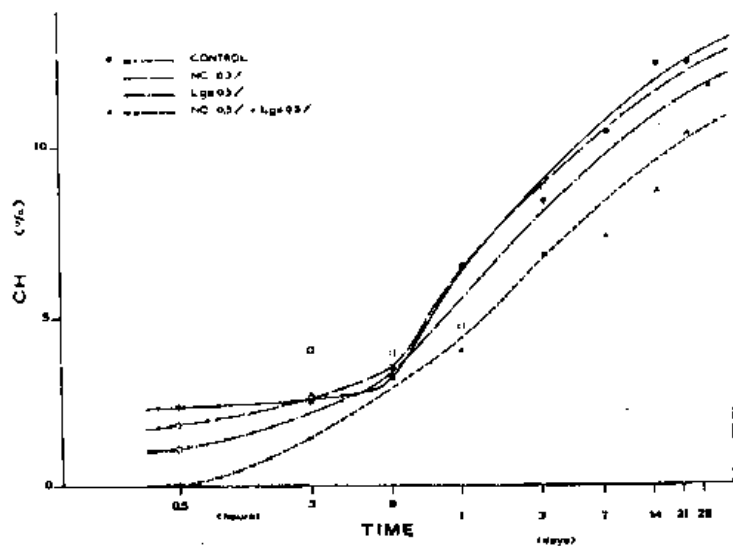


FIG. 7

Percentage of CH as a function of time for C_2S - C_3A pastes with 0.3% of admixtures

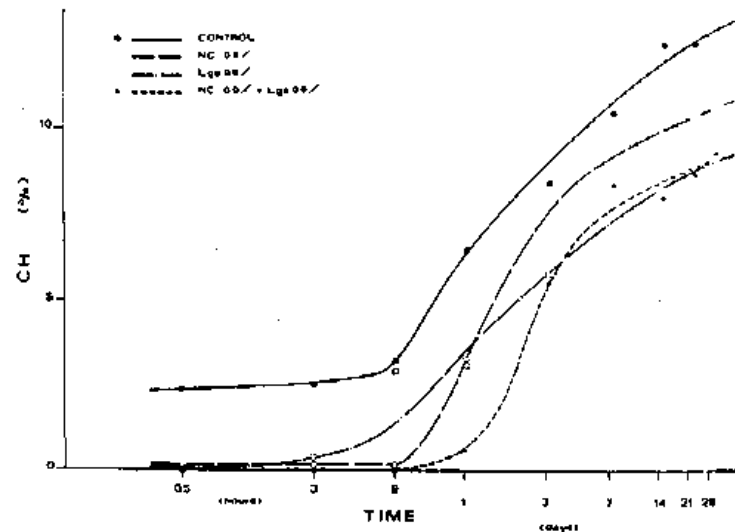


FIG. 8

Percentage of CH as a function of time for C_2S - C_3A pastes with 0.9% of admixtures

In Fig. 9 the influence of the admixtures on the zeta potential for the C_2S - C_3A system is shown. The effect is very similar to that discussed for the addition of NC and/or lgs to C_2S alone (Fig. 3). In particular it seems that also in the C_2S - C_3A system, as well as in the C_3S - C_3A one (4), there is a minimum in the zeta potential - concentration curve when NC and lgs are simultaneously added. Since no minimum has been observed for C_3A alone (2) it would seem that this minimum could be ascribed to the effect of NC and lgs on calcium silicates.

Conclusions

1. At a given dosage (0.3%), lgs alone retards the C_2S hydration in the absence of C_3A much more effectively than in the presence of C_3A (Figs. 2 and 7). This could be explained by the strong adsorption of lignosulfonate on hydrating C_3A , so that the lgs concentration is remarkably lower in the presence of C_3A .
2. Relatively high dosages of NC alone (0.9%) blocks the early hydration of both C_3A and C_2S (Fig. 5B₂). This specific effect disappears in the presence of lime (Fig. 6) or when C_3S substitutes for C_2S (4).
3. The combined addition of lgs and NC blocks the early C_3A hydration. The higher the dosage of the admixtures, the longer the induction period (Figs. 4D₁ and 5D₂). The combined addition of NC and lgs retards the C_2S hydration much more effectively in the absence than in the presence of C_3A (Figs. 2 and

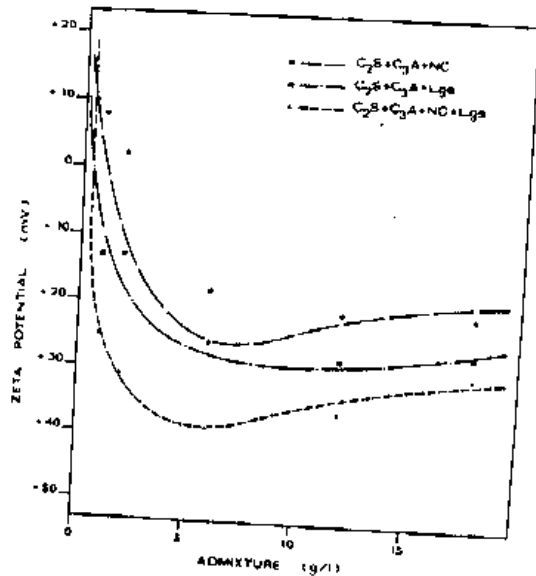


FIG. 9
Zeta potential of C_2S-C_3A as a function of admixtures concentration in the liquid phase.

- 7). The higher the dosage of lgs and NC simultaneously added, the longer is the induction period of the C_2S hydration in the presence of C_3A . Similar results were obtained in the C_3S-C_3A system (4).
4. In the absence of C_3A the combined addition of NC and lgs retards the C_2S hydration less effectively than lgs alone does (Fig. 2). The opposite is true in the presence of C_3A (Figs. 7 and 8). Similar results were obtained in the C_3S-C_3A system (4).
5. The effects caused by the combined addition of NC and lgs on the zeta potential of C_2S or C_2S-C_3A system are similar to the ones in the C_3S or C_3S-C_3A system, with the appearance of a minimum in the zeta potential - concentration curve.
6. The dispersion action and the completely blocking effect on the early C_3A hydration also in this case seem to be the determinant factors for the fluidifying effect caused by the combined addition of NC and lgs to a clinker Portland cement.

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