

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

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ABSTRACT

The effect of carbonate and/or lignosulfonate on the hydration of  $C_3S$  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 strongly retards  $C_3A$  hydration. However by mixing 20 %  $C_3A$  with  $C_3S$  the retarding effect is significantly lower. On the other hand the early  $C_3A$  hydration is completely blocked by sodium carbonate and lignosulfonate simultaneously added. It seems that the fluidifying effect of the combined addition of those admixtures could be ascribed to both the dispersing action and the completely blocking effect on the early  $C_3A$  hydration.

Mediante la DTG e TG ed attraverso misure di potenziale zeta è stata studiata l'effetto del carbonato e/o lignosolfonato sull'idratazione del  $C_3S$  da solo ed in presenza di  $C_3A$ . L'aggiunta combinata di carbonato di sodio e lignosolfonato ritarda fortemente l'idratazione del  $C_3S$ . Tutta via mescolando 20 % di  $C_3A$  con il  $C_3S$  l'effetto ritardante diminuisce sensibilmente. L'idratazione del  $C_3A$  risulta praticamente bloccata in presenza di carbonato e lignosolfonato. Sembra che l'effetto fluidificante degli additivi possa essere attribuito sia all'azione disperdente che all'arresto dell'idratazione iniziale del  $C_3A$ .

## INTRODUCTION

In previous papers the influence of lignosulfonate-carbonate addition on the C<sub>4</sub>AF (1) and the C<sub>3</sub>A (2) hydration was examined. In the present paper the combined effect of lignosulfonate and carbonate on the hydration of C<sub>3</sub>S alone or in the presence of C<sub>3</sub>A is studied.

## EXPERIMENTAL

### Materials and Methods

Tricalcium silicate (C<sub>3</sub>S) was synthesized from reagent grade CaCO<sub>3</sub> and silica by heating the mixture in the proper molar ratio at 1500°C. The C<sub>3</sub>S, with a free lime content of 0.4 % was ground to a Blaine fineness of about 3000 cm<sup>2</sup>/g.

Tricalcium aluminate (C<sub>3</sub>A) described in a previous paper (3) was used.

Reagent grade sodium carbonate (NC) and/or sodium lignosulfonate (lgs), said to be free of sugars or other carbohydrates, were dried-mixed with C<sub>3</sub>S or C<sub>3</sub>S and C<sub>3</sub>A as shown in Table 1.

### Paste Hydration

Hydration at 20°C of pastes with water/C<sub>3</sub>S or water/(C<sub>3</sub>S+C<sub>3</sub>A) ratio of 0.5 was examined.

After a certain time (30 min - 14 days) the hydration was stopped by grinding the pastes with methyl alcohol. The filtered solids were dried at 60°C for two hours and analyzed by a Netzsch apparatus in which DTA, DTG and TG curves are obtained simultaneously (weight of samples = 200 mg; heating rate = 10°C/min). Only DTG curves are shown in the present paper. From TG curves the percentage of CH by the weight of anhydrous sample were calculated. The weight

loss due to CaCO<sub>3</sub> at about 800°C was transformed into the equivalent CH weight and the total weight of CH is assumed to be proportional to the percentage of hydrated C<sub>3</sub>S.

TABLE 1  
Composition of Mixes

Mix	C <sub>3</sub> S	C <sub>3</sub> A	NC	lgs
A	100	-	-	-
B	100	-	0.300	-
C	100	-	-	0.300
D	100	-	0.300	0.300
A <sub>1</sub>	80	20	-	-
B <sub>1</sub>	80	20	0.300	-
C <sub>1</sub>	80	20	-	0.300
D <sub>1</sub>	80	20	0.300	0.300
A <sub>1</sub> = A <sub>2</sub>	80	20	-	-
B <sub>2</sub>	80	20	0.900	-
C <sub>2</sub>	80	20	-	0.900
D <sub>2</sub>	80	20	0.900	0.900

### Zeta Potential Measurements on Suspensions

Zeta potential measurements were performed using a Laser Zee Meter by Pen.Kem.Inc. as it was described in a previous paper (1).

For zeta potential measurements some suspensions were prepared by mixing 1 g of solid and 100 ml of CH saturated solution for 15 min. The composition of solid samples for the suspension experiments (water/solid = 100) was the same as that of Table 1 except for NC and lgs. The concentration of NC and lgs in the liquid phase of these suspensions have been changed from 0 to a maximum of 18 g/l. The 6 g/l or 18 g/l values in the suspension tests correspond to the concentration of the admixtures in the liquid phase of the paste experiments when 0.3 % or 0.9 % respectively have been used. The liquid phase was separated by vacuum filtration. A small portion of the solid samples was added to the filtered liquid phase and a suspension (10 mg/20 ml) was obtained with the same ionic strength of the original suspension and diluted enough to be observed to the microscope of the Laser Zee Meter.

## RESULTS AND DISCUSSION

### Influence of NC and lgs on C<sub>3</sub>S Hydration

Fig. 1 shows the DTG curves of the hydration of C<sub>3</sub>S with and without NC and/or lgs. When C<sub>3</sub>S 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 520°C respectively. A peak at about 800°C due to CaCO<sub>3</sub> is also observed.

The addition of NC (0.3 %) to C<sub>3</sub>S (Fig. 1B) does not cause any significant change, except a retarded C<sub>3</sub>S hydration.

In the presence of 0.3 % of lgs (Fig. 1C) the C<sub>3</sub>S hydration is completely blocked for at least 14 days. Similar results have been obtained by Young who found that in the presence of lgs (0.8 %) the C<sub>3</sub>S hydration is strongly retarded within 180 days (4). Ramachandran (5) found that by the addition of 0.8 % lgs the hydration of C<sub>3</sub>S is stopped almost indefinitely.

The combined addition of NC (0.3 %) and lgs (0.3 %) blocks the C<sub>3</sub>S hydration for at least 7 days (Fig. 1D). However, at 14 days C-S-H and CH peaks can be observed. So it seems that the C<sub>3</sub>S hydration is less retarded in the presence of NC and lgs than in the presence of lgs alone.

In experiments with higher dosages of lgs or NC and lgs, which are not here reported, DTG curves showed that the above mentioned retarding effects were much more pronounced.

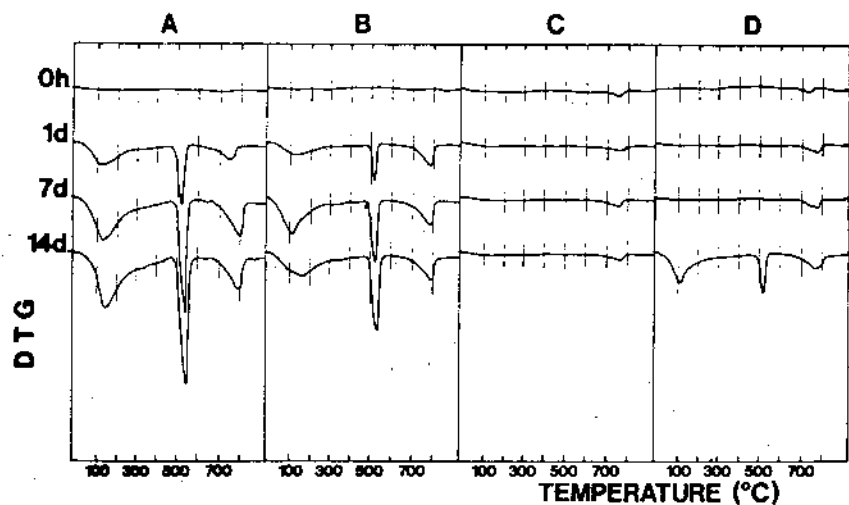


FIG. 1

DTG curves for  $C_3S$  pastes (See Table 1).

Fig. 2 shows the percentage of CH as a function of time for  $C_3S$  alone (control mix) and in the presence of 0.3% of additives.

When NC is added, no substantial change in the  $C_3S$  hydration rate is observed for times shorter than 8 hours. At longer ages the percentage of CH is remarkably lower in the presence of NC, thus indicating that NC retards the  $C_3S$  hydration.

In the presence of lignosulfonate the  $C_3S$  hydration does not occur even after 14 days, while the simultaneous addition of NC and lgs causes the blockage of  $C_3S$  hydration for 7 days only, thus confirming the DTG curves results.

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  $C_3S$  without admixtures is about 0 mV. However, the scatter of the zeta potential of  $C_3S$  particles in the absence of admixtures was relatively large. Similar results have been obtained by Daimon and Roy (6) for cement particles in de-ionized water in the absence of admixtures.

The addition of either NC or lgs lowers zeta potential value. However, the latter is much more effective in the change of zeta

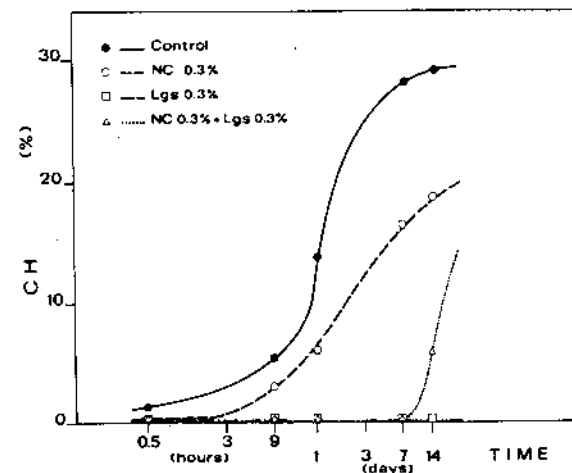


FIG. 2

Percentage of CH as a function of time for  $C_3S$  pastes.

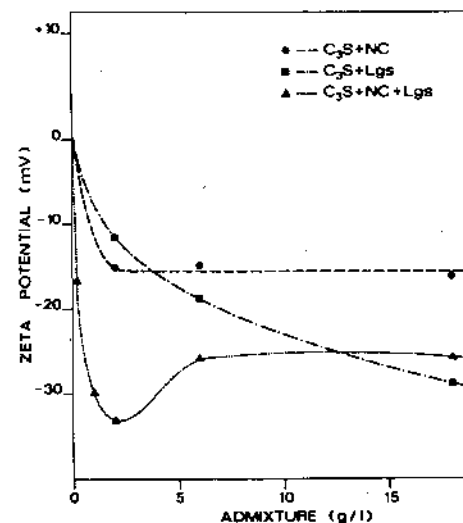


FIG. 3

Zeta potential of  $C_3S$  as a function of admixtures concentration in the liquid phase.

potential. For instance, with a concentration in the liquid phase of 18 g/l (corresponding to 0.9 % in the paste experiment) the zeta potential was about -17 mV or -29 mV when NC or lgs respectively were used.

When NC and lgs were simultaneously added, a minimum (-33 mV) in the zeta potential curve was observed. The concentration in the liquid phase of the admixtures corresponding to the minimum was about 2 g/l.

#### Influence of NC and lgs on C<sub>3</sub>S hydration in the presence of C<sub>3</sub>A

Fig. 4 and Fig. 5 show the DTG curves of C<sub>3</sub>S-C<sub>3</sub>A mixes hydrated for different periods of time.

In the sample not containing admixtures (Fig. 4A<sub>1</sub>) three hydrated phases are observed : C-S-H (140°C), hexagonal hydroaluminat (200°C and 270°C) and CH (520°C). After 0.5 hours of hydration only the DTG peak of hexagonal hydroaluminat at about 200°C can be detected. Calcium hydroxide is observed after 9

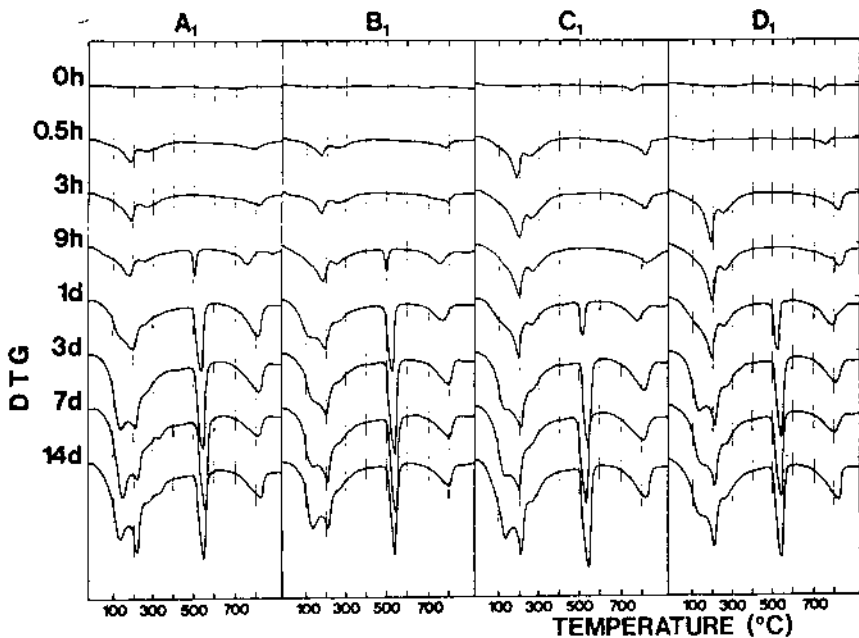


FIG. 4

DTG curves for C<sub>3</sub>S-C<sub>3</sub>A pastes with 0.3 % of admixtures (See Table 1).

hours, whereas a shoulder at 140°C due to C-S-H can be detected at 1 day only. Calcium hydroxide is always accompanied by calcium carbonate with a DTG peak at about 800°C. A very small peak at about 320°C due to C<sub>3</sub>AH<sub>6</sub> is observed at 7-14 days.

The addition of NC at low concentration (0.3 %) to the C<sub>3</sub>S-C<sub>3</sub>A system does not cause any significant change (Fig. 4B<sub>1</sub>), while at higher concentration (0.9 %) it seems that the total amount of the hydrated phase decreases (Fig. 5B<sub>1</sub>), especially at longer ages.

In the anhydrous samples (0 hour) containing lgs (Fig. 4C<sub>1</sub> and Fig. 5C<sub>1</sub>) or NC and lgs (Fig. 4D<sub>1</sub> and Fig. 5D<sub>1</sub>) a DTG peak at about 720°C appears. This peak, in the presence of 0.9 % of lgs or NC and lgs (Fig. 5D<sub>1</sub>) is preceded by a slight "positive" DTG peak at about 700°C, corresponding to an exothermal peak on DTA curves, not shown in the present paper. The phenomenon is attributed to the reaction between the carbon dioxide caused by the lgs thermal decomposition and the lime present in the starting mixture, thus forming CaCO<sub>3</sub> and increasing the weight of the sample. The same

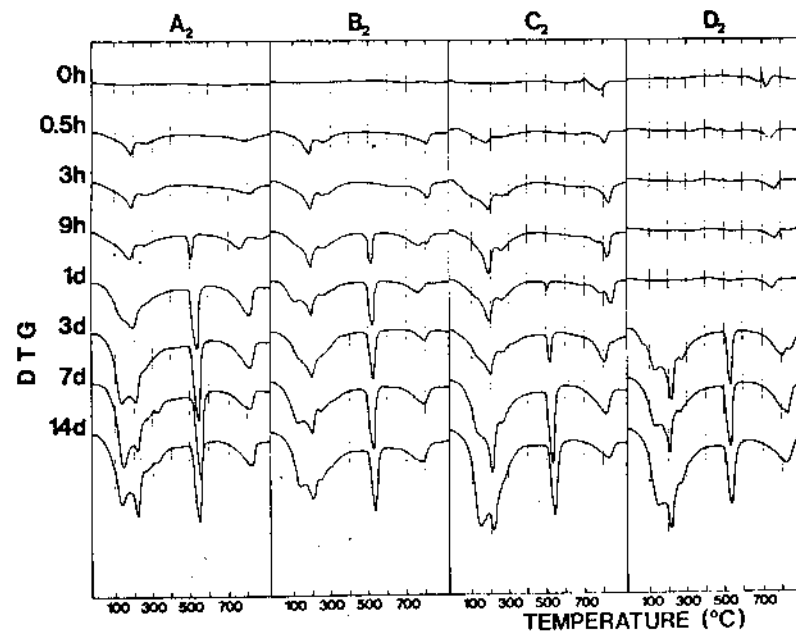


FIG. 5

DTG curves for C<sub>3</sub>S-C<sub>3</sub>A pastes with 0.9 % of admixtures (See Table 1).

effect was found in previous works (1,2) for the system  $C_4AF$ -CH-quartz and  $C_3A$ -CH-quartz in the presence of lgs or NC and lgs. In these systems, the "positive" DTG peak was found at about  $570^\circ C$ , and the difference in the temperatures ( $700^\circ C$  and  $570^\circ C$ ) is probably due to the presence of quartz. Indeed with additional DTA-DTG-TG tests on the system  $C_4AF$ -CH with lgs or NC and lgs, mixed in the same proportions used in the previous work (1) but excluding quartz, the "positive" DTG peak is shifted to the same temperature of about  $700^\circ C$  as found in the present work. Moreover, the "positive" DTG peak disappears in all the hydrated samples containing lgs or NC and lgs (Fig. 4C, -4D, -5C, -5D<sub>2</sub>) as they have been treated with methyl alcohol to stop hydration, thus causing the removal of lgs (1).

The influence of 0.3 % and 0.9 % lgs on the hydration of the  $C_3S$ - $C_3A$  system is shown in Fig. 4C, and Fig. 5C, respectively. By the addition of 0.3 % lgs the  $C_3S$  hydration is stopped within the first 9 hours, while no substantial change appears in the products of  $C_3A$  hydration whose rate seems to be slightly accelerated. At longer ages the C-S-H and CH peaks may be observed and at 14 days the amount of the hydrated products becomes comparable to the one present at the same hydration time in the system without additives.

In the presence of a higher dosage (0.9 %), lgs remarkably retards the  $C_3S$  hydration till to 1 day. At 3 days the same degree of hydration of  $C_3S$  seems to be reached (Fig. 5C<sub>2</sub>) as the one obtained after 1 day with a dosage of 0.3 % of lgs (Fig. 4C<sub>1</sub>).

The  $C_3A$  hydration is not substantially changed by the addition of 0.9 % lgs except a slight retardation during the initial 30 min. The results concerning the influence of lgs addition on the hydration of  $C_3S$  alone (Fig. 1C) or in the presence of  $C_3A$  (Fig. 4C, -5C,) confirm the data obtained by Young (4) and Ramachandran (5) : in the presence of  $C_3A$  the lgs addition causes a remarkably lower retarding effect on the  $C_3S$  hydration. It seems that  $C_3A$  and/or its hydration products adsorb lgs by decreasing its concentration in the liquid phase so that the  $C_3S$  hydration is affected by the admixture to a significant lower extent.

The Fig. 4D, and 5D, show the DTG curves for the  $C_3S$ - $C_3A$  system in the presence of both NC and lgs in percentages of 0.3 % and 0.9 % respectively.

The combined addition of NC and lgs completely stops both  $C_3S$  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. 4D<sub>1</sub>) and at least for 1 day with 0.9 % of admixtures (Fig. 5D<sub>2</sub>). This effect is specific for the combined addition of NC and lgs, since no substantial retardation in the  $C_3A$  hydration has been observed when NC (Fig. 4B<sub>1</sub> and 5B<sub>2</sub>) or lgs (Fig. 4C<sub>1</sub> or 5C<sub>2</sub>) were separately added.

Moreover, the combined addition of NC and lgs retard the  $C_3S$  hydration (Fig. 6 and 7) to a higher extent than lgs alone does particularly with a dosage of 0.9 % (Fig. 7).

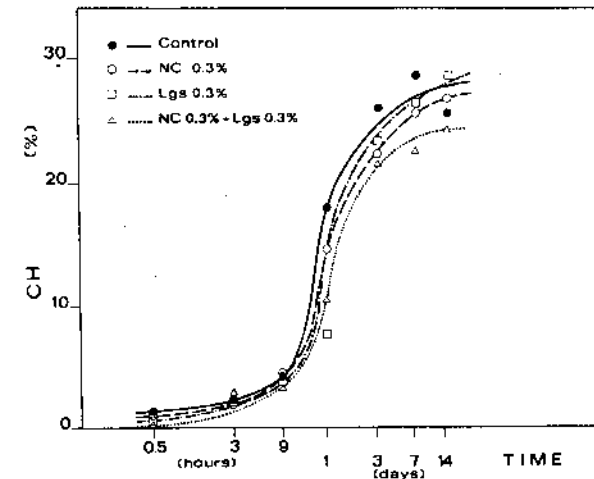


FIG. 6

Percentage of CH as a function of time for  $C_3S$ - $C_3A$  pastes with 0.3 % of admixtures.

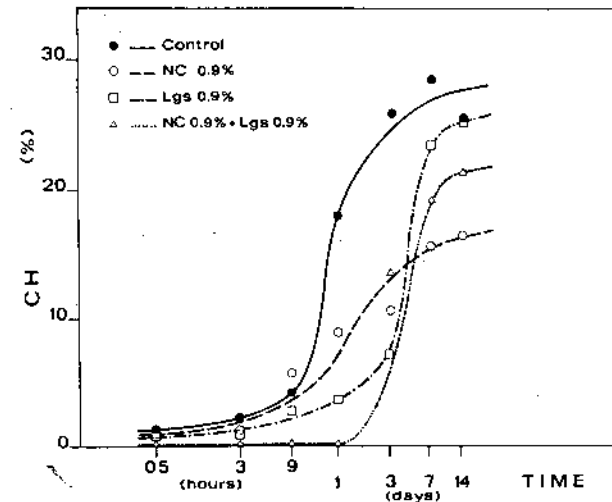


FIG. 7

Percentage of CH as a function of time for  $C_3S$ - $C_3A$  pastes with 0.9 % of admixtures.

In Fig. 8 the influence of the admixtures on the zeta potential for the  $C_3S$ - $C_3A$  is shown. The effect is very similar to that discussed for the addition of NC and/or lgs to  $C_3S$  alone (Fig. 3). In particular it seems that also in the  $C_3S$ - $C_3A$  system there is a minimum in the zeta potential-concentration curve when NC and lgs are simultaneously added. Also in this case the lowest zeta potential value (-33 mV) occurs at a concentration of NC and lgs of about 2 g/l. Since no minimum has been observed for  $C_3A$  alone (2) in the presence of NC and lgs (2) it would seem that this minimum could be ascribed to the effect of NC and lgs on  $C_3S$  particles.

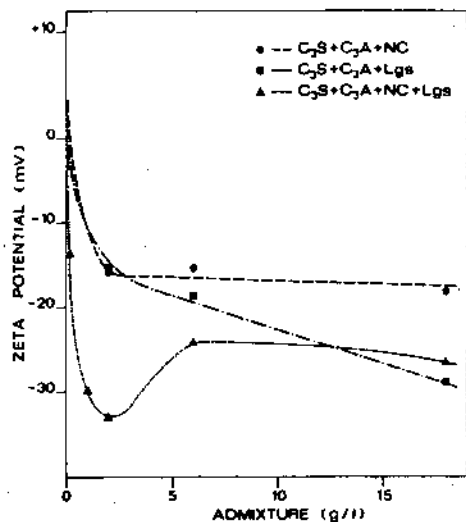


FIG. 8

Zeta potential of  $C_3S$ - $C_3A$  as a function of admixtures concentration in the liquid phase.

#### CONCLUSIONS

1. In the presence of 0.3 % lgs the  $C_3S$  hydration is stopped for at least 14 days (Fig. 2), whereas by mixing 20 %  $C_3A$  with  $C_3S$  the hydration of  $C_3S$  is only slightly retarded (Fig. 6). These results confirm those obtained by Young (4) and Ramachandran (5). It seems that  $C_3A$  and/or its hydration products adsorb lgs by decreasing its concentration in the liquid phase so that the  $C_3A$  hydration is retarded by the admixture to a lower extent.

2. In a similar way the combined addition of NC and lgs (0.3 %) strongly retards the  $C_3S$  hydration (Fig. 2), whereas a much lower retarding effect is caused by the admixtures (0.3 %) when 20 %  $C_3A$  is mixed with  $C_3S$  (Fig. 6).
3. The combined addition of NC and lgs completely blocks the  $C_3A$  hydration for a certain period of time in the  $C_3S$ - $C_3A$  system. Similar results have been obtained for  $C_4AF$  or  $C_3AF$  alone (1,2). The higher the percentage of NC and lgs the longer is the period of induction for  $C_3A$  hydration (Fig. 4D, and 5D). This effect is specific for the combined addition of NC and lgs, whereas lgs alone does not retard in a significant way the  $C_3A$  hydration (Fig. 4C, and 5C).
4. Sodium carbonate and lignosulfonate separately added reduce the zeta potential of  $C_3S$  (Fig. 3) or  $C_3S$ - $C_3A$  system (Fig. 8). However the combined addition of NC and lgs causes a larger reduction in the zeta potential for both  $C_3S$  and  $C_3S$ - $C_3A$  system. This could result in a better dispersion of  $C_3S$  and  $C_3A$  particles due to their mutual repulsion. Moreover a minimum in the zeta potential-concentration curve is found when NC and lgs are simultaneously added.
5. It would seem that the well known fluidifying effect of NC and lgs simultaneously added to a clinker Portland cement could be ascribed to both the dispersing action and the completely blocking effect on the early  $C_3A$  hydration.

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