

COMBINED EFFECT OF LIGNOSULFONATE AND CARBONATE
ON PURE PORTLAND CLINKER COMPOUNDS HYDRATION.
I. TETRACALCIUM ALUMINOFERRITE HYDRATION

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ABSTRACT

The combined effect of sodium lignosulfonate and sodium carbonate on the C_4AF hydration was examined by DTG and TG curves and by zeta potential measurements. In the presence of lignosulfonate-carbonate systems the C_4AF hydration is completely blocked. The higher the percentage of admixtures, the longer is this induction period. Moreover a strong change in the zeta potential is caused by the simultaneous addition of lignosulfonate and carbonate. Both the strong retarding action and the dispersing effect caused by the change in the zeta potential could explain the liquefying effect of the admixtures. After the induction period the C_4AF hydration is strongly accelerated by the lignosulfonate-carbonate system.

E' stata studiata l'azione congiunta di lignosolfonato e carbonato di sodio sull'idratazione del C_4AF mediante la DTG e TG e per mezzo di misure di potenziale zeta. In presenza del sistema lignosolfonato-carbonato l'idratazione del C_4AF è completamente bloccata. Maggiore è la percentuale degli additivi aggiunti, più lungo è il periodo di induzione. Inoltre i due additivi provocano una forte variazione di potenziale zeta. Sia la forte azione ritardante che l'effetto disperdente conseguente al cambio di potenziale zeta, potrebbero spiegare l'effetto fluidificante dei due additivi. Dopo il periodo di induzione l'idratazione del C_4AF è fortemente accelerata dal sistema lignosolfonato-carbonato.

Introduction

Brunauer and coworkers (1) studied the combined effect of water soluble lignosulfonates and carbonates on pastes from ground Portland clinker without gypsum. The combination of calcium lignosulfonates and potassium carbonate acted simultaneously as set regulator and liquefying agent. These cements were designated as "low porosity cements" because pastes could be prepared at low water/cement ratios.

Skalny et al. (2,3) reported some of the properties of concrete prepared by using "low porosity cements". Diamond and Gomez-Toledo (4,5) examined the influence of sodium bicarbonate and sodium lignosulfonate, produced from kraft-process pine lignin, on the consistency, setting, strength and microstructure of low porosity Portland clinker paste. Hanna (6,7) studied the effect of lignosulfonate and carbonate additions upon Portland clinker pastes and mortars. Odler and associates (8,9) studied the combined effect of the same sodium form of lignosulfonate and sodium carbonate on Portland clinker pastes. They examined the physical properties of the pastes (8) and in particular the effect of lignosulfonate-carbonate combination on the clinker hydration (9).

The main aim of our work was to study the influence of lignosulfonate-carbonate addition on the pure Portland compounds hydration, in order to elucidate the specific action of the admixture on the hydration of single products. In the present paper the results concerning the effect of lignosulfonate-carbonate combination on the tetracalcium aluminoferrite hydration are reported.

Materials and methods

Tetracalcium aluminoferrite (C₄AF) described in a previous paper (10) was used. It was blended with reagent grade calcium hydroxide (CH) in order to simulate the aqueous phase present in a Portland clinker paste. The C₄AF/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 C₄AF and CH as shown in Table 1. The percentages of NC and/or lgs were 0.625 % by weight of C₄AF. This value is of the same order of magnitude (0.5 - 1%) of the usual percentage used for Portland clinker. However, a quadruple dosage (2.5%) was also used as the usual percentage of admixture in Portland clinker paste is much higher if referred to ferrite phase only.

Table 1

Percentage composition of sodium carbonate (NC) and sulfonate (lgs) by weight of C₄AF

Mix	NC	LGS
A	-	-
B	0.625	-
C	-	0.625
D	-	2.500
E	0.625	0.625
F	2.500	2.500

Hydration at 20°C of pastes with H₂O/C₄AF of 0.4 was examined.

After a certain time (30 min + 7 days) the hydration was stopped by grinding the pastes with methyl alcohol. The filtered solids were dried at 60°C and analyzed by a Netzsch apparatus in which DTA, DTG and TG curves are obtained simultaneously (weight of samples = 200 mg; heating up rate = 10°C/min). 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, were calculated. In some cases x-ray diffraction analysis was also carried out.

Zeta potential measurements were performed using a Laser Zee Meter by Pen Kem Inc. which is based on electrophoretic technique (11) and gives the results directly in millivolt. Zeta potential is measured by determining the rate at which these particles move in a known electric field. The samples for zeta potential measurements were prepared by mixing for 15 min 1g of C₄AF, containing NC and/or lgs, with 100 ml of a saturated calcium hydroxide water solution. The percentages of NC and lgs were changed so that concentration from 0 to 15.6 g/l in the liquid phase were obtained. 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

A. DTG curves

Fig. 1 shows the DTG curves of all the samples hydrated for different times of hydration. When C₄AF reacts with water without NC and lignosulfonate (Fig. 1A) hexagonal hydrates, C₄(A,F)H₁₂ and C₂(A,F)H₆, are initially (0-6 hours) formed with a DTG peak at about 190°C and a smaller one at 270°C. In a previous paper (10) two small DTG peaks at about 100, and 270°C and a bigger one at 200°C were attributed to the hexagonal hydrates. However, in the present work the hydrated samples were dried for a longer time before being analysed by DTG. This might explain the reason why the small peak at 100°C is not present in the DTG curves of this work. After 9 hours of hydration the cubic hydrate C₃(A,F)H₆ appears with a DTG peak at 320°C and a smaller one at about 500°C. Between 3 and 7 days C₃(A,F)H₆ increases, whereas the amount of the hexagonal hydrates remains substantially constant.

The DTG peak at 500°C is due to Ca(OH)₂ and to the second thermal decomposition of the cubic phase [C₃(A,F)H₆ → C₃(A,F) + 1.5 H₂O]. Although there is an increase in the amount of C₃(A,F)H₆ particularly between 9 hours and 7 days, the DTG peak at 500°C decreases, thus indicating that the amount of free lime is reduced. This is partly due to the reaction of Ca(OH)₂ with CO₂ which produces some CaCO₃, whose DTG peak at about 800°C is not shown in Fig. 1. However, the increase of CaCO₃ is not proportional to the reduction of Ca(OH)₂, so that the combination of lime with hydrated products of C₄AF might be suggested.

The addition of NC to C₄AF (Fig. 1B) does not cause any significant change during the first 3 hours of hydration, whereas after 6 hours the 320°C/270°C peaks ratio is larger in the presence of NC. This indicates that NC favours the production of the cubic phase and hinders that of the hexagonal hydrates. However, at longer ages the total amount of the hydrated phase decreases because of the addition of NC, and this will be confirmed by the results shown in Fig. 2.

In all the anhydrous samples (0 hour) containing lignosulfonate (Fig. 1C and Fig. 1D) or NC and lignosulfonate (Fig. 1E and Fig. 1F) a "positive" DTG peak at about 570°C appears, corresponding to a surprising weight increase. This peak, which is accompanied by an exothermal peak on DTA curve not shown in the present paper, is larger in Fig. 1D and Fig. 1F (concerning mixes D and F with 2.5 % of lignosulfonate) than in Fig. 1C and Fig. 1E (concerning mixes C and E containing 0.625 % only of lignosulfonate). Therefore, the "positive" DTG peak at 570°C is

related to the amount of lignosulfonate. In supplementary tests $\text{Ca}(\text{OH})_2$ was removed from the anhydrous mixes C-D-E-F, and the "positive" DTG peak at 570°C was transformed into a "negative" DTG peak at 570°C corresponding to a weight loss, accompanied by a DTA exothermic peak. On the other hand, by carrying out the DTG and DTA experiments on the mixes C-D-E-F (all containing lignosulfonate) in the presence of nitrogen instead of air, a weight loss with a DTA endothermic peak

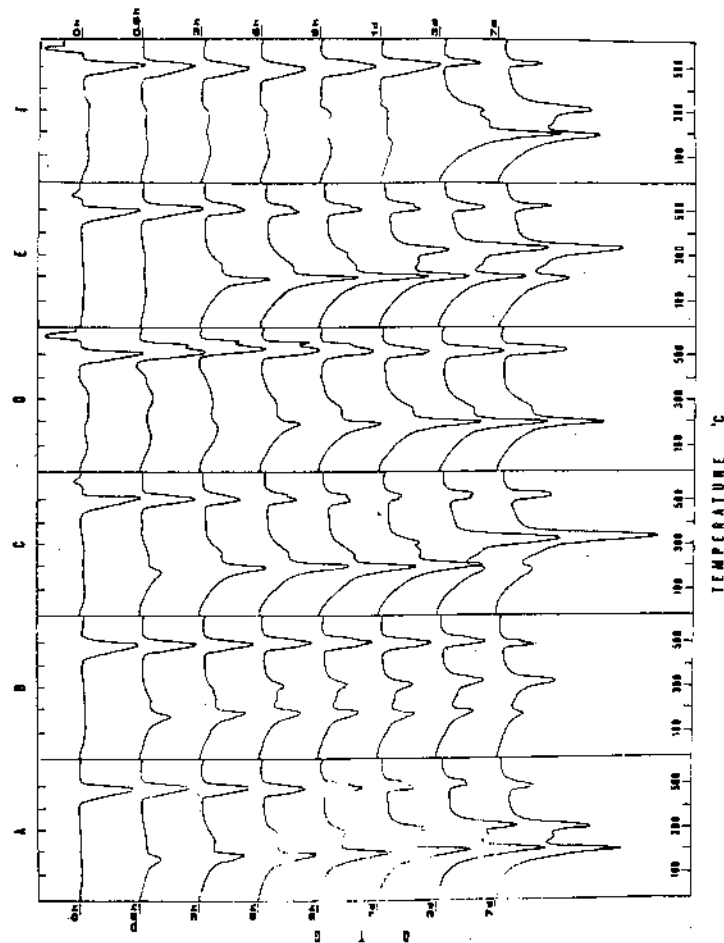


Fig. 1 - DTG curves for mixes A-8-C-D-E-F (Table I).

was recorded at a higher temperature. All these experiments suggest the following explanation for the "positive" DTG peaks at 570°C found in the anhydrous samples of Fig. 1C - 1F: in the presence of air at 570°C the carbon and hydrogen atoms of the lignosulfonate are transformed into CO_2 and H_2O liberating heat of combustion. Carbon dioxide reacts with the lime forming CaCO_3 thus increasing the weight of the samples.

When the anhydrous mixes C-D-E-F were analysed after treating them with methyl alcohol, as we normally did for the hydrated samples to stop the C_4AF hydration, the lignosulfonate was removed by washing the solid by methyl alcohol. This explains why the "positive" DTG peak at 570°C is not present in all the hydrated samples of Fig. 1C - 1F.

The influence of lignosulfonate on the C_4AF hydration is shown in Fig. 1C and Fig. 1D. No substantial change in the type of hydrated products is caused by 0.625 % of lignosulfonate (Fig. 1C) during the initial hydration (0-9 hours). At longer ages, particularly from 1 to 7 days, lignosulfonate causes a remarkable transformation of the hexagonal hydrates into the cubic phase. On the contrary, in the presence of a larger dosage of lignosulfonate (2.5 %) the formation of $\text{C}_3(\text{A,F})\text{H}_6$ is hindered even after 7 days, whereas only the hexagonal phases are produced (Fig. 1D). This could possibly be related to a more retarding effect of higher dosage of lignosulfonate.

In the presence of lignosulfonate, particularly with 2.5 % of admixture, a DTG peak (accompanied by a DTA endothermic effect) at about 550°C is observed at intermediate ages. It is particularly evident at 6 hours and then it disappears at longer ages (Fig. 1D). X-ray diffraction analysis does not show any significant information that could be related with this DTG peak. It is very difficult to find an explanation for this, and an intermediate product possibly including lignosulfonate can only be hypothesized.

In the presence of 0.625 % of NC and lignosulfonate (Fig. 1E) the C_4AF hydration is completely blocked for 0.5 hour. Then the hexagonal hydrates are formed at 6-9 hours and finally they are transformed into the cubic phase at 1-7 days. Also in this case a DTG peak at about 550°C is observed at intermediate ages (3 hours - 1 day). The hydration products obtained in the presence of NC and lignosulfonate (Fig. 1E) are substantially the same as in the presence of lignosulfonate alone (Fig. 1C). The only difference between the two systems is that the C_4AF hydration is completely blocked for 0.5 hour, whereas lignosulfonate alone as well as NC alone do not block the reaction completely. This indicates that NC and lignosulfonate initially retard the C_4AF hydration more strongly than lignosulfonate alone.

In the presence of a higher dosage (2.5 %) of NC and lignosulfonate (Fig. 1F) the C_4AF hydration is completely blocked for 1 day. So also in this case NC and lignosulfonate retard the C_4AF hydration more strongly than lignosulfonate alone (Fig. 1D). However, at 3 days the hexagonal phase is abundantly formed and then begins to transform into the cubic phase at 3-7 days. In this case the DTG peak at about 530°C was not found.

B. TG curves

Fig. 2 shows weight loss as a function of time for the control mix without admixture, and for the sample containing 0.625 % of NC. No substantial change in the C_4AF hydration rate is observed for times shorter than 6 hours. At longer ages weight loss is remarkably lower in the presence of NC, thus indicating that NC retards the C_4AF hydration.

Fig. 3 shows the influence of lignosulfonate on the C_4AF hydration rate. At lower dosage (0.625 %) lignosulfonate is a slight accelerator, whereas a higher dosage (2.5%) of additive retards the C_4AF hydration particularly after 1 day.

Fig. 4 shows the effect of the combined addition of NC and lignosulfonate on the weight loss of C_4AF hydrated samples. At lower dosage (0.625 %) NC and lignosulfonate substantially block the C_4AF hydration for only 0.5 hour and then they accelerate the hydration rate, so that after 3 hours weight loss is higher in the presence of the two additives. At higher dosage the induction period is prolonged, and with 2.5 % of the additives, the C_4AF hydration is substantially blocked for about 1 day. However, after the induction period the C_4AF hydration is strongly accelerated by the additives and at 7 days weight loss is slightly higher in the presence of 2.5 % of NC and lignosulfonate than in the control mix.

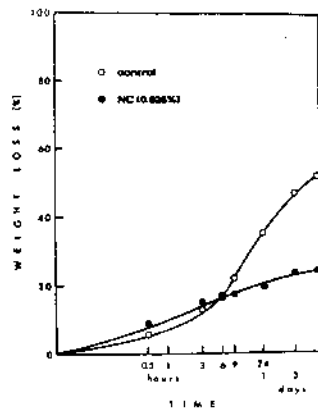


Fig. 2

Weight loss as a function of time.

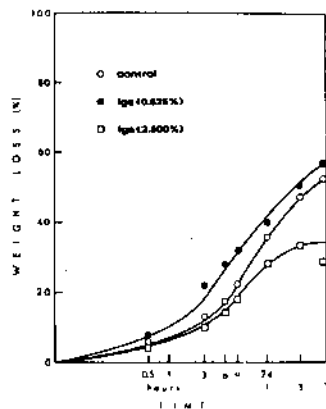


Fig. 3

Weight loss as a function of time.

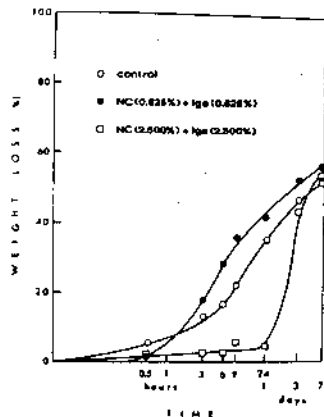


Fig. 4

Weight loss as a function of time.

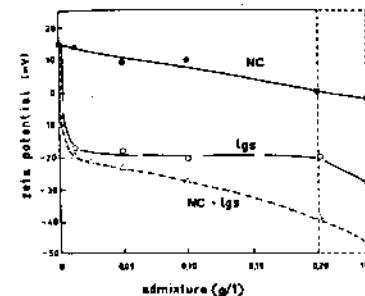


Fig. 5

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

C. Zeta Potential

In Fig. 5 the zeta potential as a function of NC and lgs concentration in the liquid phase is shown. The average value of zeta potential for C_4AF without admixtures is positive (about 15 mV).

The addition of NC causes a slight decrease in zeta potential which is about zero with a concentration in the liquid phase of 0.2 g/l.

A sharp decrease of zeta potential to a negative value of -15 mV is obtained with a lignosulfonate concentration of about 0.01 g/l. A further reduction (about -30 mV) is observed by increasing the concentration to 15.6 g/l. This corresponds to the concentration of the liquid phase in the paste with a water/ C_4AF ratio of 0.4 and a percentage of admixture of 0.625 % by weight of C_4AF .

When NC and lgs are simultaneously added to C_4AF , the zeta potential is reduced to -20 mV with a concentration of 0.01 g/l. Further stronger reductions in zeta potential are observed in the presence of NC and lignosulfonate and a value of about -45 mV is recorded for a liquid phase containing 15.6 g of NC and lignosulfonate per liter of water, corresponding to a dosage of about 0.625 % used for the paste. So, the combined addition of NC and lignosulfonate (200 mg/l) reduces the zeta potential more efficiently than either NC or lignosulfonate alone. Higher negative values in zeta potential could be expected with higher concentration of NC and lgs as those usually found for pastes with a w/c ratio of 0.3 and 0.5 - 1% of admixture by weight of clinker. On the other hand, a zeta potential of -45 mV at a concentration of NC and lgs of 15.6 g/l only, is of the same order of magnitude of the values found for flowable cement pastes containing superplasticizers admixtures (12,13). So it seems that the liquefying effect of NC and lgs is related to a dispersing effect of solid particles caused by a strong reduction in zeta potential. Odler and coworkers (9) arrived at the same conclusion by determining the clinker particle size distribution in suspensions.

Conclusions

The type of hydrated products is not substantially changed by the simultaneous presence of the two admixtures, as the initial hexagonal hydrates are initially formed and then are transformed into the cubic hydrate. The conversion occurs at longer time in the presence of the lignosulfonate-carbonate combination as a consequence of the retardation of C_4AF hydration.

In the presence of sodium carbonate and lignosulfonate the C_4AF hydration is completely blocked for a certain period of time. The higher the percentage of admixtures, the longer is this induction period.

The formation of large clusters of hexagonal calcium hydrates sticking together could cause lower workability in a C_4AF paste. When such aggregation is prevented, as the C_4AF is completely blocked, more flowable pastes could be obtained. A similar mechanism was proposed by Odler et al (9), following an hypothesis of Locher and coworkers (14) to explain the liquefying effect of the carbonate-lignosulfonate systems on clinker paste.

On the other hand, sodium carbonate and lignosulfonate strongly change the zeta potential, thus dispersing the C_4AF particles and causing their mutual repulsion.

The liquefying effect of the lignosulfonate-carbonate combination could be ascribed to both the dispersing action and the completely blocking effect on the early C_4AF hydration.

After the induction period the C_4AF hydration is strongly accelerated by the lignosulfonate-carbonate combination and at 7 days the percentage of hydrated C_4AF is slightly higher in the presence of the two admixtures.

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