

Hydration of C_3A in the presence of lignosulfonate-carbonate system or sulfonated naphthalene polymer

Hydratation du C_3A en présence de lignosulfonate et de carbonate ou de polymère de naphthalène sulfoné

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SUMMARY :

The combined addition of water soluble lignosulfonate and carbonates to Portland clinker without gypsum has been proposed to prepare flowable pastes with low water/cement ratios. On the other hand sulfonated naphthalene polymer (SNP) based admixtures are normally used as superplasticizers to obtain concretes with low w/c ratios.

In the present paper the influence of sodium lignosulfonate (LGS) and carbonate (NC) on the hydration of C_3A with lime and without gypsum was examined. The C_3A hydration rate is retarded by the simultaneous addition of LGS (0.6%) and NC (0.6%), and for some minutes the hydration is completely blocked. It may be speculated that this effect combined with the change in the zeta potential caused by LGS and NC could contribute to the flowability of clinker pastes. By C_3A hydration, hexagonal calcium aluminate hydrates are initially formed and then they are transformed into the cubic hydrate. The same products are obtained in the presence of LGS and NC.

The effect of SNP (0.6%) on the hydration of C_3A with lime and gypsum was also studied. No substantial change in the C_3A hydration rate is observed. The same products (ettringite and then monosulfate) are formed with and without SNP. Changes in zeta potential caused by SNP are recorded. It can be assumed that this is substantially responsible for the increase in flowability of cement pastes.

RESUME :

On a suggéré de préparer des pâtes très fluides avec un faible rapport eau/ciment en additionnant simultanément du lignosulfonate et du carbonate, solubles dans l'eau, au clinker portland sans gypse. Par ailleurs, des adjuvants à base de polymère de naphthalène sulfoné (PNS) sont déjà utilisés pour obtenir des bétons très fluides.

Dans cet article, on a examiné l'influence du lignosulfate de sodium (LGS) et du carbonate de sodium (NC) sur l'hydratation du C_3A avec de la chaux et sans gypse. La vitesse d'hydratation du C_3A est ralentie par l'addition simultanée de LGS (0,6%) et de NC (0,6%) et, pour quelques minutes, l'hydratation est complètement bloquée. On pourrait déduire que la combinaison de cet effet avec le changement du potentiel Zêta, causé par le LGS et le NC, pourrait contribuer à rendre fluide les pâtes de clinker. Lors de l'hydratation du C_3A se forment d'abord les aluminates de Ca hydratés hexagonaux qui sont ensuite transformés en hydrate cubique. Les mêmes produits se forment en présence de LGS et de NC.

L'effet du PNS (0,6%) sur l'hydratation du C_3A avec chaux et gypse a également été étudié. On ne note aucune modification significative dans la vitesse d'hydratation du C_3A . Les mêmes produits (ettringite et ensuite monosulfate) se forment avec et sans PNS. On a enregistré des modifications du potentiel Zêta dues au PNS. On peut considérer que ces modifications sont la principale cause de l'accroissement de la fluidité des pâtes de ciment.

INTRODUCTION

The so called superplasticizers are largely used, particularly in Europe and Japan, as additives that permit a concrete to have 20-30% of the mixing water removed without reduction in workability (1) or a strong increase in workability (for instance : from 20 to 220 mm in slump) without significant change in all the properties of the hardened concrete (2). They are substantially based on sulfonated-naphthalene-formaldehyde polymers (SNP) or sulfonated melamine-formaldehyde polymers (5). On the other hand, Brunauer and coworkers (4) studied the combined effect of water soluble lignosulfonates and carbonates on pastes from ground Portland clinker without gypsum. Therefore, superplasticizers based on SNP can be considered as liquefying agents for Portland cement pastes, whereas lignosulfonate-carbonate combinations act as both set regulator and liquefying agent for ground Portland clinker without gypsum. The purpose of the present work was to study the influence of SNP on the C₃A hydration in the presence of lime and gypsum, and the effect of lignosulfonate-carbonate combination on the C₃A hydration in the presence of lime without gypsum. The two systems correspond to the C₃A hydration in Portland cement and Portland clinker respectively.

EXPERIMENTAL Materials and methods

Tricalcium aluminate (free lime = 0.1% and Blaine fineness of about 3,500 cm²/g) was prepared according the method described in a previous paper(5). It was blended with reagent grade calcium hydroxide (CH) in order to simulate the aqueous phase present in Portland cement or Portland clinker pastes. The C₃A/CH weight ratio was 5:1 for all the mixes, whereas reagent grade gypsum (CS.H₂) was present (20% by weight of C₃A) only in mixes C and D as shown in Table I. Reagent grade sodium carbonate (NC), sodium lignosulfonate (LGS), said to be free of sugars or other carbohydrates, and SNP, produced as dry powder by MAC, were dry-mixed with the other ingredients. The percentages of NC, LGS and SNP were 0.6% by weight of C₃A. By taking into account the H₂O/C₃A ratio (0.5) the concentration of the additives in the liquid phase was 12 g/l.

Table I - Composition (in grams) of mixes for paste hydration (H₂O/C₃A = 0.5)

Mix	H ₂ O	C ₃ A	CH	CS.H ₂	NC	LGS	SNP
A	5	10	2	-	-	-	-
B	5	10	2	-	0.06	0.06	-
C	5	10	2	2	-	-	-
D	5	10	2	2	-	-	0.06

Hydration at 20°C of these pastes was examined. After a certain time (5 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. Only DTG curves are shown in the present paper. XRD analysis was also carried out by a Philips apparatus and the intensity of the C₃A peak at 1.56 Å was determined.

Zeta potential measurements were performed using a Laser Zee Meter by Pen Kem Inc. which is based on electrophoretic technique (7) and gives the results directly in millivolt. The samples for zeta potential measurements were prepared by mixing for 5 min 100 g of lime saturated water solution with 10 g of C₃A, with or without 2 g of CS.H₂, 1.2 g of NC, LGS or SNP as shown in Table II. Therefore, the concentration of NC, LGS and SNP in the liquid phase (12 g/l) was the same as used for the paste samples. The liquid phase was separated by vacuum filtration. A small portion of the solid sample 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 by the microscope of the Laser Zee Meter.

Table II - Composition (in grams) of mixes for zeta potential measurements

Mix	CH saturated water solution	C ₃ A	CS.H ₂	NC	LGS	SNP	Zeta potential (mV)
A'	100	10	-	-	-	-	+ 37.4
B'	100	10	-	1.2	1.2	-	- 41.5
C'	100	10	2	-	-	-	- 8.5
D'	100	10	2	-	-	1.2	- 30.9

RESULTS AND DISCUSSION

C₃A - CH system

In Fig. 1 the XRD intensity peak of C₃A as a function of time is shown. When C₃A hydrates in the presence of lime without gypsum the reaction rate is very high. The addition of 0.6 % of LGS and NC to the C₃A-CH system retards the reaction between C₃A and water particularly during the initial period of hydration.

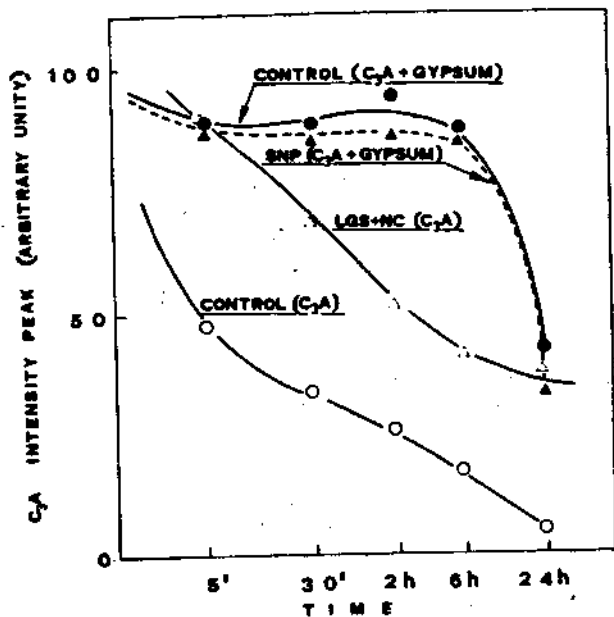


Fig. 1 - XRD intensity peak as a function of hydration time. All the mixes contain CH.

The DTG curves of Fig. 2 confirm this effect and show that the initial hydration of C₃A is substantially blocked by the addition of NC and LGS for 5 min. Similar results are obtained when NC and LGS (0.625%) are added to C₄AF-CH system as the C₄AF hydration is substantially blocked for about 30 min (8). By C₃A hydration (Fig. 2.A) hexagonal calcium aluminate hydrates (C₄AH₆ and C₂AH₈) are initially formed with DTG peaks at about 200 and 270°C. The peak at about 100°C, recorded in a previous paper (5), is not observed in the present work as the hydrated samples were dried for a longer time at 60°C before being analysed by DTG. Some cubic hydrate (C₃AH₆) with a DTG peak at about 320°C and a smaller one at about 500°C appears immediately. However, the transformation of the hexagonal calcium aluminate hydrates into the cubic hydrate occurs remarkably after 1 day only. The same products are observed when C₃A hydrates in the presence of NC and LGS (Fig. 2.B) although there

is a retardation during the initial period of hydration.

The data reported in Table II show that the zeta potential of C₃A in a lime saturated solution is positive (37.4 mV). This result agrees very well with the data of Tadros et al (9) who found a value of 34 mV for suspensions of 8 g of C₃A in 100 ml water. The high zeta potential would indicate that the C₃A suspension (Mix A' in Table II) is a well dispersed system. The deflocculation of Mix A' was actually confirmed by the difficulty in centrifugal sedimentation and vacuum filtration. On the other hand, the C₃A paste (Mix A in Table I) is a stiff system. It may be speculated that by going from Mix A' to Mix A the ionic strength is changed and the zeta potential decreases towards zero by favouring thus the flocculation. Alternatively, one could think that Mix A' and Mix A have approximately the same zeta potential, but the clusters formation in

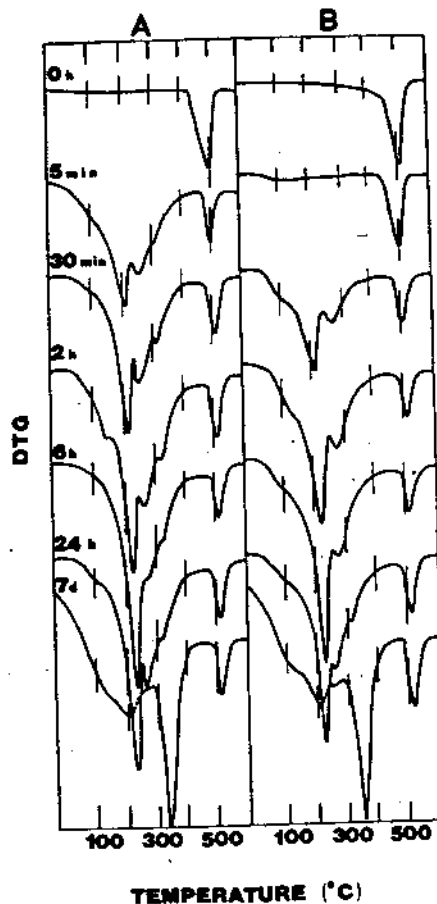


Fig. 2 - DTG curves for C₃A + CH pastes without (A) and with (B) NC and LGS.

the paste - due to hexagonal calcium aluminate hydrates - plays a prominent role in the stiffening of the system. On the other hand, the initial hydration products in Mix A' (Table II) and Mix A (Table I) are different, as the cubic hydrate is mainly formed in the C₃A suspension (Mix A') instead of the hexagonal hydrates in the C₃A paste (Fig. 2:A at 5 min). Traetterberg and Grattan-Bellew (10) and Colleparidi et al (11) have found that when, for some reason, the transformation of the hexagonal calcium aluminate hydrates into the cubic phase occurs during the initial period of hydration, the C₃A paste changes from a stiff system to a fluid one. In the present work it seems that a high water/solid ratio, such as that of Mix A', favours the transformation of the hexagonal hydrates into the cubic phase having a high positive zeta potential.

A sharp change of zeta potential to a negative value of -41.5 mV (Mix B' in Table II) is obtained in the presence of NC and LGS (12 g/l). Incidentally, in the presence of LGS (12 g/l) without NC a less remarkable change in zeta potential to about -20 mV is obtained. On the other hand the change in zeta potential caused by NC addition is still weaker. Similar results were obtained for the C₄AF-CH system (8).

C₃A - CH - C \bar{S} .H₂ system

The C₃A hydration is remarkably retarded by the addition of gypsum to the C₃A-CH system particularly during the first 6 hours (Fig. 1). During this period the amount of ettringite (with a DTG peak at about 130°C) increases, whereas the amount of C \bar{S} .H₂ (with a DTG peak at about 160°C) proportionally decreases (Fig. 3.C). Then ettringite is transformed into monosulfate (with DTG peaks at about 220 and 270°C) at 6 - 24 hours (Fig. 3.C) and C₃A hydration is remarkably accelerated (Fig. 1). Similar results were obtained by studying the influence of lime and gypsum on the C₃A hydration by an isothermal conduction calorimeter and DTG (5).

The addition of SNP to the C₃A-CH-C \bar{S} .H₂ system does not substantially change either the hydration rate (Fig. 1) or the hydration products (Fig. 3.D). Massazza et al (12) found that a SNP based superplasticizing admixture retarded the C₃A hydration. A different composition of the admixture used by Massazza et al could explain the apparent disagreement with the results of the present work.

The zeta potential of the C₃A-CH-C \bar{S} .H₂ system (Table II) changes from -8.5 mV to -30.9 mV by addition of SNP (12 g/l). So, the effect of SNP on the zeta potential of the C₃A-CH-C \bar{S} .H₂ system seems to be less remarkable than that of LGS + NC on the zeta potential of the C₃A-CH system. On the other hand, the influence of SNP on the zeta potential seems to be more remarkable in Portland cement paste

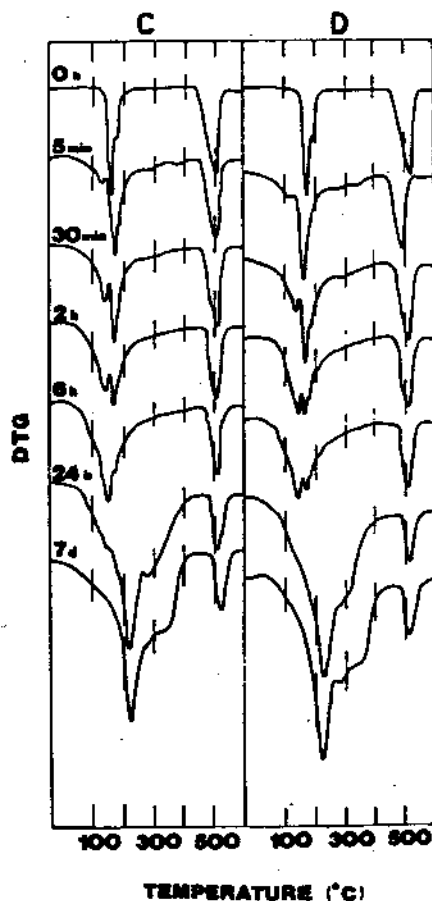


Fig. 3 - DTG curves for C₃A + CH + C \bar{S} .H₂ pastes without (C) and with (D) SNP.

than in the C₃A-CH-C \bar{S} .H₂-H₂O system. When the concentration of SNP in the liquid phase is 7.5 g/l, the zeta potential of Portland cement is about -50 mV (6), so that a still more negative value could be expected with a higher concentration of SNP (12 g/l) as that of the present work.

CONCLUSIONS

By paste hydration of C₃A in the presence of lime, hexagonal calcium aluminate hydrates (C₄AH_x and C₂AH₈) are initially formed and then they are transformed into the cubic hydrate (C₃AH₆) after 1 day. The same products are obtained when LGS and NC (both 0.6% by weight of C₃A) are added to the C₃A-CH system. However, the C₃A hydration is retarded by addition of LGS and NC and in particular the reaction is completely blocked for some minutes. The zeta potential - determined on a C₃A suspension - is remarkably changed from a positive value (37.4 mV) to a negative one (-41.5). Similar effects on the hydration rate and

zeta potential were caused by NC and LGS in the C₃A-CH system (8). It may be speculated that both the change in zeta potential and the retardation of the initial hydration of C₃A and C₄AF could substantially contribute to the flowability of Portland clinker pastes containing NC and LGS. The high negative value of zeta potential on all the Portland clinker compounds - possibly including C₃S and C₂S - due to the addition of NC and LGS, could cause the mutual repulsion of clinker particles and then their dispersion (13). On the other hand, the formation of large clusters of hexagonal calcium aluminate hydrates sticking together could cause lower workability in a Portland clinker paste without gypsum (14, 15). When this aggregation is prevented, as the C₃A and C₄AF hydrations are completely blocked, more flowable clinker pastes could be obtained. Therefore, the liquefying effect of NC and LGS in Portland clinker pastes without gypsum could be partly ascribed to both the dispersing action caused by a negative zeta potential and the retardation in C₃A and C₄AF hydrations.

In the presence of lime and gypsum ettringite is initially (0-6 hours) formed causing retardation in C₃A hydration (5). When ettringite is transformed into monosulfate (6-24 hours) the C₃A hydration rate is accelerated. No substantial change either in the C₃A hydration rate, type of products or transformations are caused by the addition of SNP (0.6% by weight of C₃A). Therefore, it can be assumed that - as far as the C₃A-CH-CS₂H₂ system is concerned - the increase in flowability of Portland cement pastes, caused by SNP addition, is mainly due to a change in zeta potential resulting in a mutual repulsion of cement particles and then in their dispersion.

ACKNOWLEDGMENTS

The authors are grateful to Miss S. Malgherini for the drawing and to Misses D. Larese for typing the manuscript.

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