

## EFFECT OF TRIETHANOLAMINE ON THE TRICALCIUM SILICATE HYDRATION

## EFFET DE LA TRIETHANOLAMINE SUR L'HYDRATATION DU SILICATE TRICALCIQUE

SUMMARY: The effect of triethanolamine (TEA) on the  $C_3S$  hydration at  $20^\circ C$  with and without (or  $N_{0.25}C_2.75A$ ) and gypsum was studied.

Addition of TEA (0.1%) to a pure  $C_3S$  paste (water/solid ratio = 0.50) slightly retarded the early hydration process particularly during the first 6 hours. After 1 day no substantial change in  $C_3S$  hydration process was caused by TEA addition.

This retarding effect was almost completely eliminated when  $C_3S$  hydrated in the presence of  $C_3A$  (or  $N_{0.25}C_2.75A$ ) and gypsum. On the other hand, TEA accelerated the early ettringite production and its transformation into monosulfate particularly in the  $C_3S-N_{0.25}C_2.75A-C_3SH_2$  system. It would seem that the adsorption of TEA molecules on ettringite could remove the admixture from the aqueous phase and consequently decrease or eliminate the slight retarding effect on the  $C_3S$  hydration.

SUMÁRIO: Estudou-se o efeito da trietanolamina (TEA) sobre a hidratação do  $C_3S$  a  $20^\circ C$ , com e sem  $C_3A$  (ou  $N_{0.25}C_2.75A$ ) e gesso.

A adição de TEA (0,1%) a uma pasta de  $C_3S$  puro (relação de água/sólido = 0,50) retardou ligeiramente o processo inicial de hidratação, particularmente durante as primeiras 6 horas. Depois de 1 dia, a adição de TEA não causou mudança substancial no processo de hidratação do  $C_3S$ .

Este efeito retardador foi quase completamente eliminado quando o  $C_3S$  se hidratou em presença de  $C_3A$  (ou  $N_{0.25}C_2.75A$ ) e gesso. Por outro lado, a TEA acelerou a produção inicial de etringita e sua transformação em monossulfato, particularmente no sistema  $C_3S-N_{0.25}C_2.75A-C_3SH_2$ . Poderia parecer que a absorção de moléculas de TEA na etringita poderia remover aditivo da fase aquosa e, conseqüentemente, diminuir ou eliminar o ligeiro efeito retardador sobre a hidratação do  $C_3S$ .

### Introduction

Triethanolamine (TEA) is usually used as raw material in many concrete admixtures. Use of pure water reducing agents often prolongs setting time and extends induction period so that hydration of cement is significantly delayed. Addition of TEA achieves intent to limit retarding effect on these admixtures on cement hydration (1).

Triethanolamine alone has been found to act as a retarding on  $C_3S$  hydration (2) but an accelerator of ettringite formation (3).

In the present paper the effect of TEA on the hydration of  $C_3S-C_3A$  (or  $NC_3A$ ) system in the presence of gypsum has been studied.

### Experimental

#### a) Hydration

Tricalcium aluminate ( $C_3A$ ) and  $C_3A-N_3O$  solid solution ( $NC_3A$ ) were prepared according to a methodology employed in previous works (4) (5). Blaine specific surface area of  $C_3A$  and  $C_3A-N_3O$  solid solution were 3100 and 3050  $cm^2/g$  respectively.

Tricalcium silicate was also prepared from reagent grade  $CaCO_3$  and  $SiO_2$  according to the method described in a previous paper (6). The Blaine specific surface area of  $C_3S$  was about 1250  $cm^2/g$ .

Gypsum, calcium hydroxide, TEA reagent grade were also used.

Tricalcium silicate alone and mixes of  $C_3S$  (75%)- $C_3A$  (20%)- $CSH_2$  (5%) or of  $C_3S$  (75%)- $NC_3A$  (20%)- $CSH_2$  (5%) hydrated with water of a 2000 mg/l TEA aqueous solution. With water/solid ratio of 0.50, such as that used for the hydration, the TEA percentage by weight of solid was 0.11.

The hydration at 20°C was blocked after a certain period of time (from 0.5 hours to 7 days) by grinding the hydrated samples under methyl alcohol and then vacuum-drying them at about 2 mmHg.

Differential thermal analysis (DTA) and differential thermogravimetry (DTG) were

simultaneously carried out by a Netzsch thermoanalyzer to identify the hydration products. Only DTG curves are reported in the present paper. In some cases X-ray diffraction (XRD) analysis was also carried out to confirm the presence of certain phases.

#### b) Triethanolamine adsorption

One liter of TEA (2000 mg/l) aqueous solution was mixed with 25 g of ettringite prepared according to the method described by Mehra (7). After a certain period of time (from 0.5 hours to 1 day) the filtered aqueous solution was analyzed by UV method to determine the amount of TEA adsorbed on ettringite.

### Results

From DTG curves the area corresponding to the peak of  $Ca(OH)_2$  produced by  $C_3S$  hydration was determined by taking into account also the  $Ca(OH)_2$  transformed into  $CaCO_3$ . The amount of  $Ca(OH)_2$  in arbitrary units is shown as a function of time in Fig. 1. The two curves are representative of the  $C_3S$  hydration kinetics with and without TEA. The addition of TEA blocks the  $Ca(OH)_2$  production at 0.5 hours and retards the  $C_3S$  hydration until 6 hours, whereas no substantial change is recorded after 1 day of hydration.

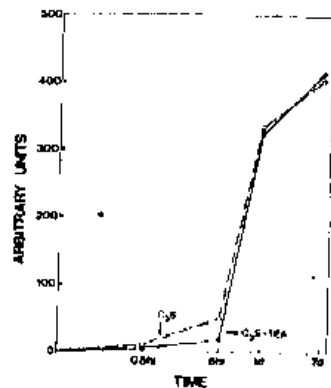


Fig. 1 Amount of  $Ca(OH)_2$  produced by  $C_3S$  hydration as a function of time for the  $C_3S$  and  $C_3S+TEA$  systems.

The DTG curves for the  $C_3S-C_3A-CSH_2$  system with and without TEA at different hydration times are shown in Fig. 2. In the presence of TEA the ettringite production appears to be accelerated confirming the results obtained by Ramachandran (3). For example at 6 hours the DTG gypsum peak is present only in the absence of TEA. The XRD analysis confirmed that in the presence of TEA gypsum was absent after 6 hours of hydration.

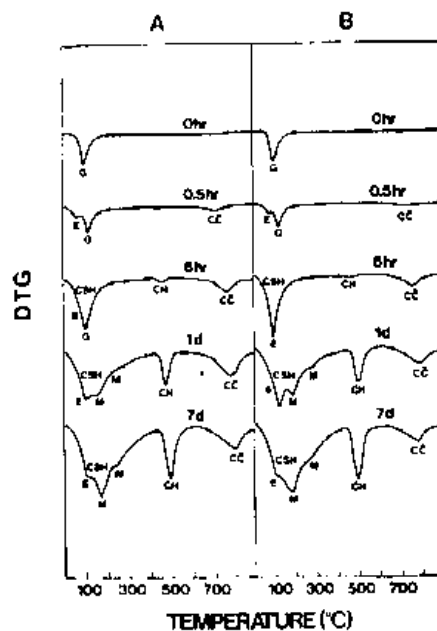


Fig. 2 DTG curves mixes of  $C_3S-C_3A-CSH_2$  (A) and  $C_3S-C_3A-CSH_2+TEA$  (B) hydrated from 0.5 hours to 7 days. The top curve refers to the anhydrous mix. G = gypsum; E = ettringite; M = monosulfate; CH = calcium hydroxide; CC = calcium carbonate; CSH = calcium silicate hydrate.

In Fig. 3 the effect of TEA on the  $Ca(OH)_2$  production for the  $C_3S-C_3A-CSH_2$  system is shown. The TEA addition retards the  $C_3S$  hydration less than it does when  $C_3S$  hydrates alone (Fig. 1).

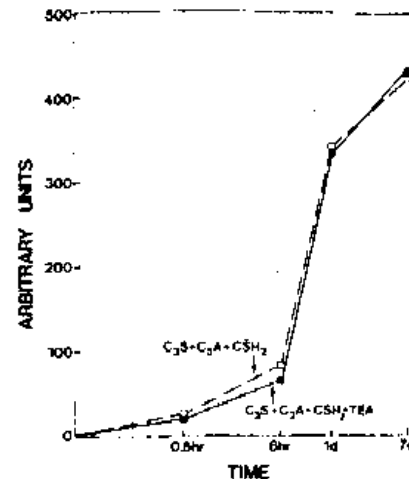


Fig. 3 Amount of  $Ca(OH)_2$  produced by  $C_3S$  hydration as a function of time for the  $C_3S-C_3A-CSH_2$  and  $C_3S-C_3A-CSH_2+TEA$  systems.

In Fig. 4 the DTG curves for  $C_3S-NC_3A-CSH_2$  mixes hydrated with and without 0.1% TEA are shown. During the first 6 hours ettringite production and its transformation into monosulfate appears to be accelerated by TEA addition. At subsequent times the effect of TEA on  $C_3A$  hydration seems to be negligible. The  $Ca(OH)_2$  production for the  $C_3S-NC_3A-CSH_2$  system with and without TEA is shown in Fig. 5. The  $C_3S$  hydration rate is slightly retarded in the presence of TEA, however the retarding effect, particularly during the first 6 hours, is much smaller than that found for the hydration of  $C_3S$  alone (Fig. 1).

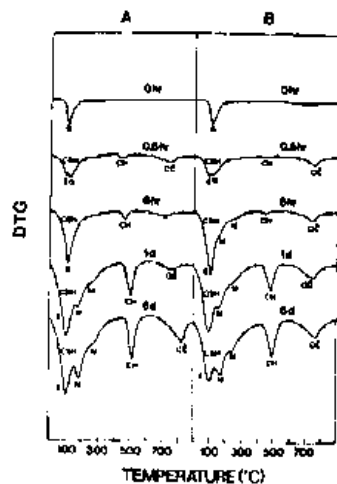


Fig. 4 DTG curves of mixes of  $C_3S-NC_3A-CSH_2$  (A) and  $C_3S-NC_3A-CSH_2 + TEA$  (B) hydrated from 0.5 hours to 7 days. The top curve refers to the anhydrous mix. G = gypsum; E = ettringite; M = monosulfate; CH = calcium hydroxide; CC = calcium carbonate; CSH = calcium silicate hydrate.

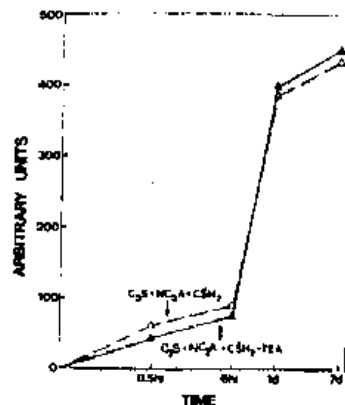


Fig. 5 Amount of  $Ca(OH)_2$  produced by  $C_3S$  hydration as a function of time for the  $C_3S-NC_3A-CSH_2$  and  $C_3S-NC_3A-CSH_2 + TEA$  systems.

All these results demonstrate that in the presence of  $C_3A$  or  $NC_3A$  the retarding effect of TEA on  $C_3S$  hydration decreases (8). This could be attributed to the adsorption of TEA molecules on the hydration product of  $C_3A$  (ettringite) so that the concentration of TEA in mixing water is reduced and consequently the retarding effect on the  $C_3S$  hydration also decreases.

In order to verify this hypothesis a sample of 25 g of ettringite was left in contact with 1 liter of aqueous solution containing 2000 mg of TEA per liter of water. The amount of TEA which remained in solution after different times is reported in Fig. 6. Triethanolamine is gradually removed from the aqueous solution, and during the first 6 hours, the ettringite adsorbs about 50% of TEA molecules originally present. This experiment seems to confirm that ettringite is responsible for the reduction in the retarding effect of TEA on  $C_3S$  hydration. On the other hand TEA accelerates the ettringite production. Therefore the retarding effect of TEA on the  $C_3S$  hydration in Portland cement could depend on the  $C_3A$  content in Portland cement. The higher the  $C_3A$  content, the weaker the retarding effect on the  $C_3S$  hydration. It does not seem that the alkali content in  $C_3A$  affects the influence of TEA on the  $C_3S$  hydration.

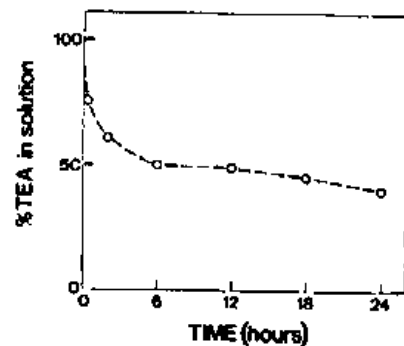


Fig. 6 Amount of TEA remained in solution after different times of contact with ettringite.

#### CONCLUSION

Addition of TEA (0.1%) to a  $C_3S$  paste slightly retards the early hydration process during the first 6 hours.

This retarding effect is almost eliminated when  $C_3S$  hydrates in the presence of  $C_3A$  (or  $NC_3A$ ) and  $CSH_2$ . Addition of TEA accelerates the early production of ettringite and its conversion into monosulfate. It seems that adsorption of TEA molecules on ettringite can remove the admixture from the aqueous phase and reduce the retarding effect on the  $C_3S$  hydration.

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