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Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/0008-8846(76)90026-0
Cement and Concrete Research, 6, September 5, pp. 623-631, 1976-09-01

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by

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Reprinted from

CEMENT AND CONCRETE RESEARCH

Vol. 6, No. 5, September 1976
9 p.

DBR Paper No. 688
Division of Building Research

Price 25 cents

OTTAWA

NRCC 15423

CEMENT and CONCRETE RESEARCH. Vol. 6, pp. 623-632, 1976. Pergamon Press, Inc.
Printed in the United States.

HYDRATION OF CEMENT -- ROLE OF TRIETHANOLAMINE

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(Communicated by F. D. Tamas)
(Received Feb. 24, 1976)

ABSTRACT

Following addition of 0.1, 0.25, 0.35, 0.5 and 1.0 per cent triethanolamine, studies have been made of the hydration and hardening characteristics of (a) tricalcium aluminate, (b) tricalcium aluminate + gypsum, (c) tricalcium silicate, (d) dicalcium silicate, and (e) portland cement. Triethanolamine (TEA) accelerated the hydration of $3CaO.Al_2O_3$ and $3CaO.Al_2O_3$-$CaSO_4.2H_2O$ systems and extended the induction period of the hydration of $3CaO.SiO_2$. In portland cement paste TEA decreased the strength at all ages and setting characteristics were drastically altered, especially at higher TEA contents. Evidence was obtained also of the formation of a complex of TEA with the hydrating silicate phase.

On a étudié l'hydratation et les caractéristiques de durcissement a) de l'aluminate tricalcique, b) de l'aluminate tricalcique + gypse, c) du silicate tricalcique, d) du silicate bicalcique, et e) du ciment portland, après l'addition de 0.1, 0.25, 0.35, 0.5 et 1.0 pour cent de triéthanolamine (TEA). La TEA accélère l'hydratation des systèmes de $3CaO.Al_2O_3$ et de $3CaO.Al_2O_3$-$CaSO_4.2H_2O$ et prolonge la période d'induction de l'hydratation de $3CaO.SiO_2$. Pour ce qui est de la pâte de ciment portland, la TEA réduit sa résistance pour tous les degrés de vieillissement et modifie profondément ses caractéristiques de durcissement, surtout pour les teneurs plus élevées en TEA. On obtient également des indications de la formation d'un complexe de TEA avec la phase de silicate en hydratation.

Presented at the VIth International Congress on the Chemistry of Cement, Moscow, September 1974.

Introduction

Triethanolamine (TEA) is used as a grinding aid in cement manufacture and is a constituent in certain admixture formulations in concrete practice. Its addition in hydrating cements is thought to reduce the excessive retarding action of water reducing admixture. Part or complete replacement of $CaCl_2$ by TEA is also favoured because, unlike $CaCl_2$, TEA does not promote corrosion of embedded metals in reinforced concrete.

The exact mechanism of the action of TEA in hydrating cements is not known. It seems to be complex, and it is not even certain whether it acts as an accelerator or as a retarder (1-5). Practically no work has been published of a systematic investigation of the effect of TEA on the hydration of different phases of cement or of cement itself (5,6).

From a practical standpoint a study of the action of TEA on the hydration behaviour of cement would be useful, but the admixture may act in a complex way on the hydration of the individual phases and their hydration products. It seems more meaningful, therefore, to study the role of TEA in the hydration of individual, binary, and ternary systems before extending the study to cement itself. This paper briefly describes the effects of different amounts of TEA on the hydrating characteristics of C_3A, C_3A + gypsum, βC_2S and C_3S (C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O). It also attempts to extend this knowledge to the role of TEA on the hydrating and hardening behaviour of portland cement.

Experimental

Materials

Tricalcium aluminate of high purity was prepared by calcination of $CaCO_3$ and Al_2O_3. The Blaine surface area was 4350 cm^2/g. Tricalcium silicate and β dicalcium silicate prepared by calcination of $CaCO_3$ and SiO_2 had a Blaine surface area of 3310 cm^2/g and 2770 cm^2/g, respectively. Reagent grade gypsum and triethanolamine were used. The portland cement, type 1, used in this work had the following characteristics:

Chemical Analysis = SiO_2 = 21.38 per cent; Fe_2O_3 = 1.91 per cent;
Al_2O_3 = 4.91 per cent; CaO = 64.42 per cent;
MgO = 4.0 per cent; SO_3 = 1.86 per cent;
Na_2O = 0.13 per cent; K_2O = 0.59 per cent;
Free lime = 0.10 per cent;
Insoluble residue = 0.10 per cent;
Loss on ignition = 0.78 per cent

Potential Composition = C_3S = 54.22 per cent C_2S = 20.68 per cent
C_3A = 9.99 per cent C_4AF = 6.11 per cent

Fineness (Blaine) = 3100 cm^2/g

Soundness (Autoclave expansion) = 0.46 per cent

Hydration

C_3A, C_3S, C_2S, C_3A + gypsum, and portland cement with and without TEA in amounts varying between 0.1 and 1.0 per cent were each mixed with double distilled water at a water/solid ratio of 0.5 or 1.0 and placed in a tightly covered polyethylene container and rotated continuously over rollers. At specified intervals varying between a few minutes and 28 days each sample was placed in an excess of cold acetone, washed with cold acetone, and subsequently evacuated for 24 hours using liquid air trap.

Methods

Differential thermal analysis was carried out in N_2 or air using a DuPont-900 thermal analyser. A Cahn balance was used for thermogravimetric analysis. Surface area values were obtained, with N_2 as the adsorbate, with a Numinco Orr surface area-pore volume analyser. Free lime was estimated by the solvent variation method, and TEA in solution by Perkin-Elmer UV-VIS-NIR 350 spectrophotometer. The rate of heat development during hydration was determined by a conduction calorimeter having a sensitivity of 20 mV/W. X-ray diffraction patterns were obtained by a Hilger and Watts unit using Cuk_α source. Scanning electron microscopic work was carried out with the Cambridge steroscan Mark 2A unit.

Details of all these techniques are available in other publications (7,8). The time of initial and final setting of mortar specimens was carried out according to ASTM test method C403-70 (9); and compressive strengths were determined using ASTM C109-70 (10).

Results and discussion

A brief discussion of the effect of TEA on the hydration behaviour of C_3A, C_3A + gypsum, C_3S, C_2S and cement systems follows.

Hydration of C_3A and C_3A + gypsum in presence of TEA

Without TEA, C_3A hydrates initially to the hexagonal aluminate hydrate before it transforms to the cubic form. With TEA, in additions of 0.5, 1.0 or 5.0 per cent, a larger amount of hexagonal hydrate forms at a given time and conversion to the cubic form is accelerated. Conduction calorimetric curves in Figure 1 illustrate these effects clearly.

Hydration of C_3A with 5 or 25 per cent gypsum, with or without 1 per cent TEA, shows some differences. In the absence of TEA gypsum reacts initially to form ettringite; with TEA the formation of ettringite is accelerated (5,7).

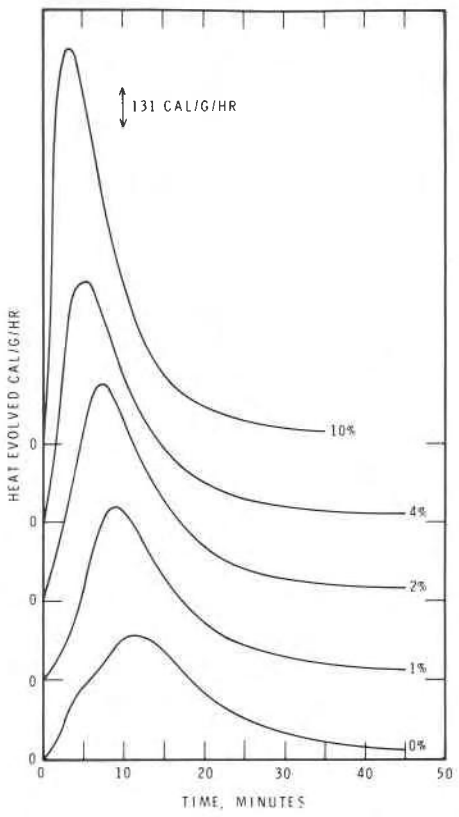

FIG. 1
Conduction calorimetric curves of $3CaO.Al_2O_3$ with different amounts of added TEA.

Hydration of C_3S and C_2S in the presence of TEA

In the presence of TEA the hydration characteristics of C_3S and C_2S are significantly altered. DTA curves in Figures 2(a) and 2(b) illustrate the thermal characteristics of C_3S hydrated with and without TEA. The change in the intensities of the initial endothermal peaks below 200°C correspond to the expulsion of H_2O from the C-S-H phase; the endothermal effect between 480 and 500°C represents decomposition of $Ca(OH)_2$; and the emergence of an exothermic effect in the region of 400°C and an endothermal effect in the region of 720 to 760°C are evident in TEA-treated samples. The amount of $Ca(OH)_2$ found at 1, 3, 7 or 28 days was in the order C_3S + 0 per cent TEA > C_3S + 0.1 per cent TEA > C_3S + 0.5 per cent TEA > C_3S + 1.0 per cent TEA, independent of the method adopted for estimation, viz. X-ray, DTA, TGA and chemical analysis. There was an increase in the induction period, probably owing to the formation of a surface complex of TEA on the hydrating C_3S. The N_2 surface areas at 28 days with 0, 0.1 and 1.0 per cent TEA are, respectively, 24.8, 30.9 and 44.6 m^2/g. In addition, TEA promotes the formation of C-S-H with a high CaO/SiO_2 ratio and enhances the formation of non-crystalline $Ca(OH)_2$ (8).

The behaviour of C_2S is similar to that of C_3S except that the reaction proceeds more slowly.

Hydration of portland cement with TEA

Attempts were made to explain the effect of TEA on the hydration and hardening behaviour of portland cement, mainly on the basis of the effect of TEA on the individual phases, viz. aluminate and silicate phases. Portland

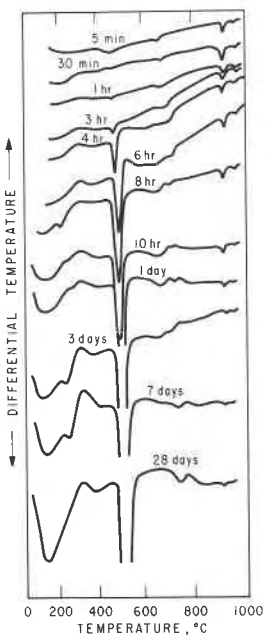

FIG. 2(a)
Thermograms of $3CaO.SiO_2$ hydrated to different periods

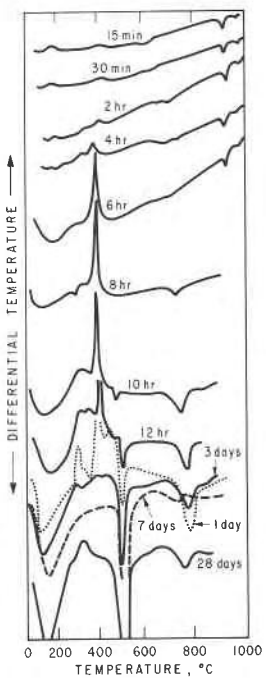

FIG. 2(b)
Thermograms of $3CaO.SiO_2$ hydrated to different periods in presence of 0.5% TEA

cement is, however, a complex mixture of several other components and its behaviour is probably also influenced by the alkali and SO_3 contents.

A sequential study of the hydration characteristics of cement was carried out by DTA and TGA. Cements containing 0, 0.1, 0.25, 0.35 and 0.5 per cent TEA were hydrated for periods varying from 6 hours to 28 days. Thermograms indicated that samples containing TEA formed ettringite and that this converted to monosulfate at an increasing rate as the amount of TEA was increased. Figure 3 illustrates that at any period of hydration less $Ca(OH)_2$ is formed in TEA-treated samples (presumably for the same degree of hydration), suggesting that TEA promotes formation of C-S-H with a higher C/S ratio. TGA curves showed a generally higher initial loss of water for samples treated with TEA. This may be due to the higher amounts of H_2O contained in the C-S-H phase with a higher C/S ratio (11). There is evidence that TEA forms a complex with the hydrating cement. Water extracts 80 per cent TEA, but with ethyl alcohol none can be extracted from the hydrated sample.

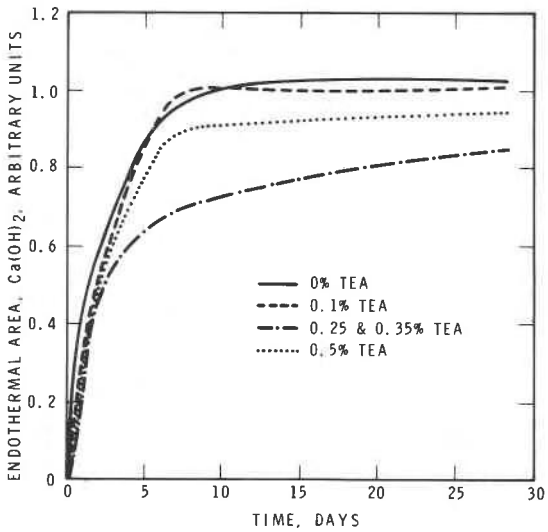

FiG. 3
DTA estimation of lime in cement pastes hydrated with triethanolamine

Figure 4 shows the conduction calorimetric curves of cement containing 0, 0.25, 0.35 and 0.5 per cent TEA. Immediately on contact with water each sample evolves heat (not shown in the figure) that may be ascribed to the heat of wetting, hydration of free lime and reaction of C_3A with gypsum to form ettringite. The magnitude of the heat developed increases with amount of TEA, indicating that TEA accelerates the reaction between C_3A and gypsum in forming ettringite.

The second peak, occurring after 9 to 10 hours in cement without additive, is mainly caused by hydration of C_3S. A small hump at about 22 hours denotes the formation of low sulfoaluminate from the reaction between ettringite and excess C_3A. In samples treated with TEA, the pattern of the curves (Figure 4) suggests that dual peaks appear between 10 to 15 hours. One of them represents the ettringite-monosulfate reaction, which appears to be accelerated by TEA. The other peak may represent the hydration of a small amount of C_3S, triggered by the heat developed by the aluminate-gypsum reaction. DTA examination of the samples, carried out at different periods of hydration, shows that below 20 hours some hydration of C_3S has proceeded in all samples, although it is less than in the sample containing 0 per cent TEA. The peak resulting from C_3S hydration is extended in the presence of TEA. For example, the peak at 27 to 28 hours for C_3S + 0.5 per cent TEA represents the heat from C_3S hydration, indicating that hydration of C_3S is retarded in the presence of higher amounts of TEA.

Calcium chloride is widely used as an accelerating admixture in concrete. It acts by accelerating the hydration of the C_3S phase. Figure 5 gives the conduction calorimetric curves for cement containing different

amounts of $CaCl_2$. The curves are different from those obtained with cement-TEA mixtures. Calcium chloride mainly accelerates the hydration of C_3S, as is evident from the appearance of a peak at earlier periods. At C_3S + 0 per cent $CaCl_2$ the peak appears at 9 to 10 hours, whereas with C_3S + 5 per cent $CaCl_2$ the peak appears as early as after only 2 hours. The thermograms demonstrate that the action of TEA is not similar to the action of $CaCl_2$.

TABLE I

INITIAL AND FINAL SETTING CHARACTERISTICS OF CEMENT MORTARS WITH ADDED TEA

No.	Per Cent TEA	Initial Setting Time	Final Setting Time
1	0	4.3 hr	8.3 hr
2	0.01	4.7 hr	8.1 hr
3	0.025	4.9 hr	8.1 hr
4	0.05	4.8 hr	8.4 hr
5	0.1	~ 2 min	24 hr
6	0.5	~ 6 min	-

The initial and final setting characteristics of portland cement treated with 0, 0.01, 0.025, 0.05, 0.1 and 0.5 per cent TEA are shown in Table I. With up to 0.05 per cent TEA the initial setting time is retarded slightly and there is an accompanying slight extension in the induction

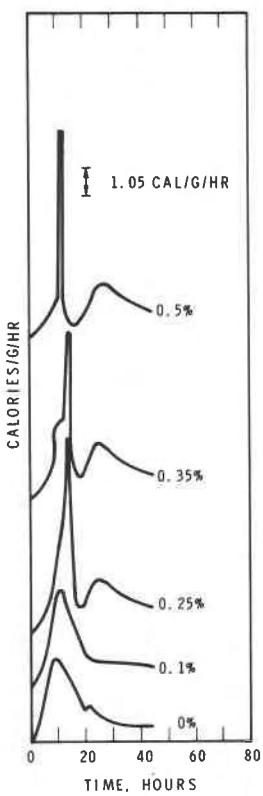

FIG. 4
Conduction calorimetric curves of cement hydrated in the presence of triethanolamine

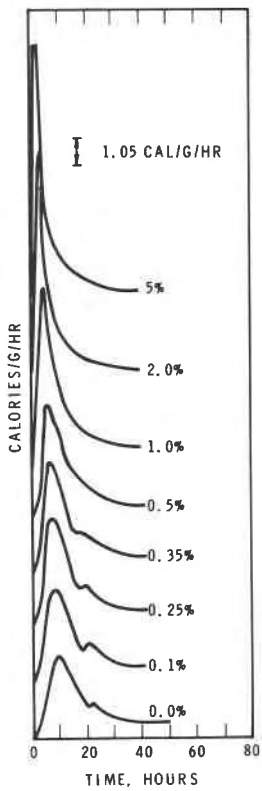

FIG. 5
Conduction calorimetric curves of cement hydrated in the presence of calcium chloride

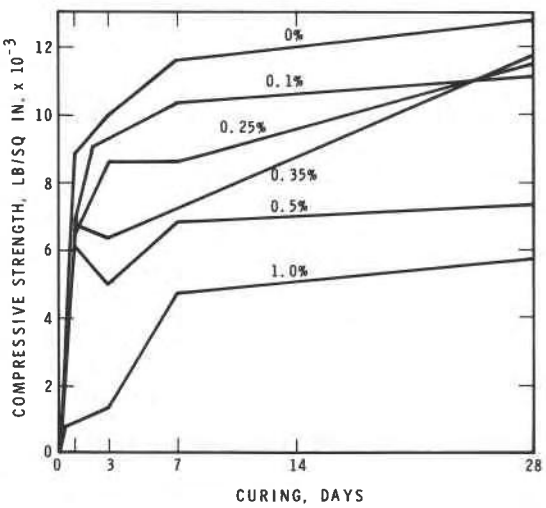

FIG. 6
Compressive strengths of cement pastes containing triethanolamine

period of the hydration of C_3S. At 0.1 and 0.5 per cent TEA, however, rapid setting occurs. During the calorimetric studies a considerable amount of heat is registered in the first few minutes in those mixtures containing more than 0.1 per cent TEA. Thermograms also indicate more intense endothermal peaks below 150°C at higher TEA concentrations. These results suggest that the rapid setting phenomenon may be associated with the accelerated formation of the ettringite phase in the presence of TEA. In the C_3A + gypsum system small amounts of TEA have practically no effect on the rate of hydration, whereas in larger amounts TEA accelerates the reaction between C_3A and gypsum.

The final setting times vary between 8.1 and 8.4 hours for TEA contents between 0 and 0.05 per cent. At 0.1 per cent TEA, however, the final setting occurs at about 24 hours and the cement with 0.5 per cent TEA does not show the final setting time (corresponding to a penetration resistance of 4000 lb/sq in.) even after a day. The weaker cement structure produced in the presence of larger additions of TEA may be due to quick initial setting, change in composition, surface area and morphology of the hydrated products.

Compressive strength of cement pastes and mortar cubes with and without TEA is shown in Figures 6 and 7. At all periods of curing all samples containing TEA show lower strengths than the standard specimen; strengths decrease as TEA is increased. There is a particularly steep drop in strength in the sample with 1.0 per cent TEA, notably at early periods. Very low amounts of TEA (<0.1 per cent) do not significantly alter strength.

Portland cement is a multi-component system and the addition of TEA significantly alters the rate of reaction of individual components and the nature of the hydration products. It is not easy to assess the

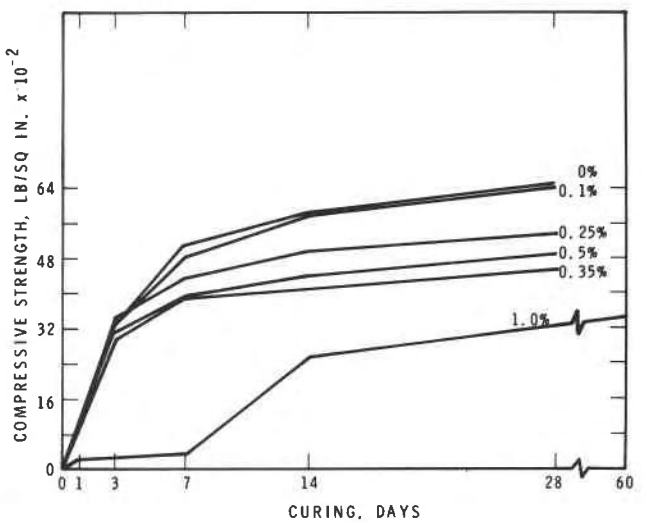

FIG. 7
Compressive strengths of cement mortars containing triethanolamine

relative influence of the factors responsible for the slow development of strength in samples containing TEA. Formation of C-S-H with higher C/S ratio, retardation of hydration of C_3S, and rapid initial setting followed by development of a large amount of heat may be some of the important factors.

Pastes prepared at a higher initial temperature and autoclaved cement pastes are also known to yield lower strengths. Some of the explanations offered for the low strengths in pastes containing large amounts of TEA may be applicable to these systems also. They include:
(1) Rapid early hydration may create a dense zone of hydration product around the grains and retard subsequent hydration.
(2) Formation of hydration product with higher density may promote a more porous structure.
(3) Cement that has set in a few minutes has obviously not been thoroughly mixed, and consequently there will be a non-uniform distribution of hydration products within the structure that will prevent the development of full strength.
(4) Rapid formation of ettringite may alter the initial matrix and disturb subsequent bonding characteristics.
(5) Rapid setting may promote initial cracks; heat development and cooling may also initiate shrinkage cracks.
(6) Evaporation of water due to heat may be a factor for low strengths.

Conclusions

In very small amounts triethanolamine has practically no effect on the setting, hydration, heat development and strength development of portland cement pastes. In amounts greater than 0.1 per cent it has significant influence. TEA acts as a retarder in the hydration of the silicate phases and as an accelerator in the hydration of the aluminate phase. The mechanism of this action may be traced to a complex formed between TEA and the hydrating components of portland cement.

Acknowledgements

The author wishes to thank G.M. Polomark, R.E. Myers, J.P. Lefebvre and R. Lacroix for experimental assistance. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

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