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Influence of Triethanolamine on the Hydration Characteristics of Tricalcium Silicate

by
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L'Influence du Triéthanolamine sur les Caractéristiques d'Hydratation du Silicate de Tricalcium

Sommaire

L'auteur étudie les caractéristiques d'hydratation du $3\text{CaO} \cdot \text{SiO}_2$ ou $\beta 2\text{CaO} \cdot \text{SiO}_2$ par l'addition de 0.0%, 0.1%, 0.5% ou 1.0% de triéthanolamine (TEA). La quantité de $\text{Ca}(\text{OH})_2$ qui se forme en 1, 3, 7 ou 28 jours était de l'ordre de $\text{C}_3\text{S} + 0\% \text{ TEA} > \text{C}_3\text{S} + 0.1\% \text{ TEA} > \text{C}_3\text{S} + 0.5\% \text{ TEA} > \text{C}_3\text{S} + 1.0\% \text{ TEA}$, peu importe que la chaux ait été évaluée au moyen de rayons X, de l'analyse thermique différentielle, de l'analyse thermogravimétrique ou de l'analyse chimique. Le taux d'hydratation, c'est-à-dire de disparition du $3\text{CaO} \cdot \text{SiO}_2$, indique que l'hydratation se produit plus rapidement en présence du TEA après un jour. L'addition de TEA prolonge la période d'induction, favorise la formation d'un C-S-H ayant un taux plus élevé de CaO/SiO_2 , augmente la formation de $\text{Ca}(\text{OH})_2$ non cristallin et accroît l'aire du produit de silicate hydraté.

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Influence of Triethanolamine on the Hydration Characteristics of Tricalcium Silicate^a

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The hydration characteristics of $3\text{CaO} \cdot \text{SiO}_2$ or $\beta\text{2CaO} \cdot \text{SiO}_2$ are studied by an addition of 0.0, 0.1, 0.5 or 1.0% triethanolamine. The amount of $\text{Ca}(\text{OH})_2$ found at 1, 3, 7 or 28 days was in the order $\text{C}_3\text{S} + 0\% \text{ TEA} > \text{C}_3\text{S} + 0.1\% \text{ TEA} > \text{C}_3\text{S} + 0.5\% \text{ TEA} > \text{C}_3\text{S} + 1.0\% \text{ TEA}$, irrespective of whether lime was estimated by X-ray, DTA, TGA or chemical analysis. The rate of hydration, in terms of the disappearance of $3\text{CaO} \cdot \text{SiO}_2$, showed that hydration proceeded faster in the presence of TEA after 1 day. Additions of TEA increase the induction period, promote the formation of a C–S–H with higher CaO/SiO_2 ratio, increase the formation of non-crystalline $\text{Ca}(\text{OH})_2$ and enhance the surface area of the hydrated silicate product.

1. Introduction

Certain admixture formulations used in concrete practice as water reducing–accelerating agents contain small amounts of triethanolamine (TEA). The amine reduces excessive retardation effect of the water-reducing admixture. TEA is generally preferred to CaCl_2 in these formulations because in large amounts CaCl_2 may promote corrosion of the embedded metals in concrete. TEA is also used as a grinding aid.¹

The action of TEA in the hydration of cement is not understood. It is not yet even resolved whether it is an accelerator or a retarder.^{1–3} It is quite possible that the amount of admixture and the chemical composition of the cement dictate its final action as retarder or accelerator. A direct study of the influence of TEA on the hydration of cement, although a useful approach from the practical point of view, is not easy to interpret because the admixture may act in a complex way to affect the hydration of the individual phases and their hydration products. Initially it seems essential to gain an understanding of the role of TEA on the hydration of the individual, binary and ternary systems before extending the study to the cement itself. So far, however, no systematic investigation seems to have been done on the kinetics of hydration of the individual phases of portland cement using different amounts of TEA. Ciach and Swenson, basing their observations on the transmission electron micrographs of C_3S pastes, reported that TEA acts as an accelerator.⁴

^a Presented at the Annual Meeting of the American Ceramic Society, Washington, May 1972.

Portland cement contains 70 to 80% tricalcium silicate (C_3S)^a and di-calcium silicate (C_2S). In pastes the hydrolysed products of the silicates predominate and influence many properties of concrete. As the first part of the investigation the hydration characteristics of C_3S were therefore studied sequentially for periods ranging from a few hours to a month in the presence of different amounts of TEA.

2. Experimental

2.1. Materials

The tricalcium silicate used in this work contained 99.33% C_3S , 0.21% tricalcium aluminate and 0.46% free lime. It had a Blaine surface area of 3310 cm²/g. Triethanolamine of certified grade was supplied by Fisher Scientific Co. Some experiments were carried out using βC_3S having a Blaine surface area of 2770 cm²/g.

2.2. Methods

Differential thermal analysis (DTA) was carried out in air or in a flow of N_2 using a Du Pont-900 thermal analyser at a heating rate of 20 °C/min. In the thermograms the exothermal effects are shown upwards and endothermal curves downwards with respect to the base line. Surface area was obtained using N_2 as the adsorbate by a Numinco-Orr surface area-pore volume analyser. Free lime in the samples was estimated by the solvent variation method. Thermogravimetric analysis (TGA) was carried out using a sensitive Cahn balance. The rate of heat development during the hydration of C_3S was determined by means of a conduction calorimeter containing six chambers and supplied by the Institute of Applied Physics, Delft. Although the chambers were coated with Teflon, the hydrated products tended to stick to the surface and polyethylene liners were therefore necessary. Sensitivity of the calorimeter was 20 mV/W. The temperature of the water bath was kept at 25 °C.

X-ray diffractograms were obtained by a Hilger and Watts unit using a $CuK\alpha$ source. Each of the samples was mixed with 20% $Mg(OH)_2$ used as an internal standard. The relative amounts of calcium hydroxide formed at different times were determined in terms of the ratio of the intensities of peaks at 4.77 and 4.90 Å to the peak at 2.36 Å. Two peaks for $Mg(OH)_2$ at 4.77 and 2.36 Å were used to counteract the interference effects at 4.77 and 4.90 Å.¹² The unhydrated C_3S was expressed as a ratio of the intensity of the peak at 2.18 Å to that at 2.36 Å.

2.3. Preparation of samples

The hydration of C_3S or C_2S was studied by mixing with double-distilled water at a water to silicate ratio of 0.5. Hydration was carried out in tightly covered polyethylene containers rotated continuously over rollers. At specified intervals of time, varying from 15 min to 1 month, each sample was ground in cold ethyl alcohol, placed in a desiccator and continuously evacuated for 24 h using liquid air in the trap. Care was taken throughout to prevent contamination with CO_2 .

^a The following nomenclature is adopted: C_3S = tricalcium silicate; C_2S = dicalcium silicate; H = H_2O ; MH = magnesium hydroxide; TEA = triethanolamine; CH = calcium hydroxide; DTA = differential thermal analysis; TGA = thermogravimetric analysis.

A similar method was followed for hydration experiments in the presence of 0.1, 0.5 or 1.0% TEA with respect to the silicate. The solution-silicate (volume/weight) ratio was kept at 0.5.

3. Results and discussion

3.1. DTA results

Differential thermograms were obtained for C_3S and C_2S hydrated for periods of 5 min to 28 days and containing 0.0, 0.1, 0.5 or 1.0% TEA. Only representative thermograms are included in Figures 1, 2 and 3.

Figure 1. Thermograms of $3CaO.SiO_2$ hydrated to different periods. (In this and subsequent thermograms, exotherms are shown in an upward direction.)

Figure 1 presents the thermal curves of C_3S hydrated for 5 and 30 min, for 1, 3, 4, 6, 8 and 10 h, and for 1, 3, 7 and 28 days. At very early periods there is an almost complete absence of any endothermal effect at temperatures below 300 °C. It can be discerned at 8 h, however, and its intensity increases continuously to 28 days. At low temperatures a small endothermic peak also appears in some of the samples at about

260 °C. An endothermal valley is evident between 340 and 380 °C and is more pronounced at 28 days. An unmistakable endothermal effect appears in all samples at about 480 to 500 °C, but it is better defined at 1 h and later. The rate of increase of this peak is substantial between 3 and 4 h and continues to grow throughout the period of hydration studied. The peak temperature of this effect shifts slightly towards higher temperatures with the progress of hydration. There are also irregular, poorly defined thermal effects of small magnitude between 640 and 680 °C. In addition, two endothermal effects are registered in all samples at 930 and 980 °C, the former being of higher intensity. Both peaks decrease in intensity as hydration proceeds.

Figure 2. Thermograms of $3\text{CaO} \cdot \text{SiO}_2$ hydrated to different periods in presence of 0.5% TEA.

Figure 2 shows the thermal behaviour of C_3S hydrated in the presence of 0.5% TEA. The low-temperature endothermal effect below 300 °C is generally of greater amplitude than the corresponding effect in samples of C_3S hydrated without TEA (Figure 1). A distinct characteristic of thermograms of TEA-treated samples is the sudden emergence of a sharp exothermal peak after 6 h at a temperature of about

400 °C. It is absent below 6 h. This peak is evident for up to 1 day of hydration but is not clearly seen at later periods. A small endothermal effect occurs at about 475 °C after 10 h and increases in intensity with the progress of hydration. In this series the endothermal effect observed in the range 720 to 760 °C is generally of higher intensity than that at 640 to 680 °C for C_3S hydrated without TEA. Thermograms of C_3S hydrated with 1.0% TEA are somewhat different from those hydrated with 0.5% TEA. With 1.0% TEA the exothermal effect at about 400 °C is of higher intensity, whereas the endothermal effect at about 475 °C is lower. The sample containing 0.1% TEA shows an exothermal effect of lesser magnitude than that with 0.5% TEA.

Figure 3. Thermograms of $2CaO \cdot SiO_2$ hydrated alone (a), and (b), in the presence of triethanolamine (obtained in an N_2 atmosphere).

The hydration of C_2S with 0.5% TEA may be followed by the thermograms presented in Figure 3. The endothermal peaks at 450 to 480 °C are generally of larger intensity in the sample containing 0% TEA.

3.2. Hydration of C_3S , 0% TEA

The hydration of C_3S may be followed by different methods such as the determination of the amounts of non-evaporable water, calcium hydroxide, residual C_3S , and by measurements involving electrical conductivity, heat of hydration or strength. The amount of calcium hydroxide liberated at different times of hydration may be estimated by chemical, DTA, TGA or X-ray techniques. Amounts determined by these techniques seem to differ so that caution should be exercised in the interpretation of results. In conjunction with the conduction calorimetric technique, however, these techniques serve as useful tools for investigating the influence of different amounts of TEA on the hydration of C_3S .

Thermograms of pure C_3S and C_3S cured at earlier times indicate three endothermal peaks at 640 to 680 °C, 930 °C and 970 to 980 °C (Figure 1). They may represent $Triclinic\ I \rightleftharpoons Triclinic\ II$, $Triclinic\ II \rightleftharpoons Triclinic\ III$ and

Triclinic III $\rightleftharpoons$ Monoclinic transformations in the C_3S sample.⁵ As hydration proceeds, the intensity of these peaks diminishes because of progressive depletion of C_3S .

The two endothermal effects below 300 °C, which seem to merge in many cases, denote the removal of loosely- as well as firmly-bound water from the C-S-H product. Increase in the intensity of this effect with time is due to the formation of larger amounts of C-S-H as hydration progresses.

An endothermal valley between 340 and 480 °C, more evident in some samples than in others, may represent the dehydration effect of $Ca(OH)_2$ present in non-crystalline form. The evolution of H_2O from the C-S-H phase is also possible⁶ in this temperature range.

The very small endothermal effect at about 480 °C was evident at 1 h but more pronounced at 4 h, and may be attributed to the dehydration of $Ca(OH)_2$. The intensity of this peak is proportional to the amount of $Ca(OH)_2$ and may be used to follow the kinetics of hydration of C_3S . Figure 4 shows the amounts of $Ca(OH)_2$

Figure 4. Estimation by DTA of $Ca(OH)_2$ at different periods of hydration of $3CaO \cdot SiO_2$ containing triethanolamine: (—) none; (·····), 0.1%; (---), 0.5%, and (— · — ·), 1.0%.

formed at different times in terms of the endothermal areas for the $Ca(OH)_2$ decomposition. A rapid increase in the quantity of $Ca(OH)_2$ between 3 and 4 h represents an increase of 200%. Accordingly, the first 3 h should be termed the dormant period during which only very small amounts of $Ca(OH)_2$ are produced. The period between 3 and 8 h may be termed the acceleratory period, because it accounts for about 25% of all the $Ca(OH)_2$ produced for up to a month. After 8 h $Ca(OH)_2$ continues to form but at lower rates.

The thermal effects discernible between 640 and 800 °C, especially at longer periods of hydration, represent the decarbonation of very small amounts of $CaCO_3$ as well as the loss of small amounts of H_2O from the C-S-H phase.⁷

The TGA method was applied in calculating the amount of $Ca(OH)_2$ by determining the quantity of H_2O evolved during the decomposition of $Ca(OH)_2$ in the

temperature range 450 to 550 °C. Weight loss was calculated between the temperature at which the TGA curve showed deviation from linearity and the temperature at which it almost levelled off, generally between 450 and 550 °C. The method is not expected to be very accurate because deviations in the curve are not sharp and, in addition, some water is lost by the C-S-H phase in the temperature range 450 to

Figure 5. TGA estimation of Ca(OH)_2 at different periods of hydration of $3\text{CaO} \cdot \text{SiO}_2$, (—) no TEA, and (.....) with 0.5% TEA.

Figure 6. Amounts of Ca(OH)_2 estimated by S.V.M. method in $3\text{CaO} \cdot \text{SiO}_2$ pastes (ignited basis) in the presence of (—), no TEA and (.....), 0.5% TEA.

550 °C. It is useful, however, for evaluating marked changes in the relative weight losses occurring at different times and in the presence of different amounts of TEA in the hydrating C_3S . In general, the relative amounts of Ca(OH)_2 determined by DTA and TGA for C_3S samples hydrated in the absence of TEA are similar (Figures 4, 5). Figure 6 shows the amounts of Ca(OH)_2 estimated by chemical analysis. The shape of the curve suggests that the relative amounts of Ca(OH)_2 determined by DTA, TGA and chemical analysis follow nearly the same trend. The X-ray diffraction method was also used to estimate Ca(OH)_2 (each sample is mixed with 20% magnesium hydroxide). The ratio of the peak intensity for $\text{Ca(OH)}_2 + \text{Mg(OH)}_2$: Mg(OH)_2 represented as $(I_{4.90} + I_{4.77})/I_{2.36}$ gave an approximate estimation of the

relative amounts of Ca(OH)_2 formed at different periods (Figure 7). The curves in Figure 7 show some variance from those of TGA, DTA and chemical analysis, but the X-ray method estimates only crystalline Ca(OH)_2 .

Figure 7. Relative amounts of crystalline Ca(OH)_2 formed at different periods of hydration of C_3S : (○), no TEA; (●), with 0.1% TEA; (△), with 0.5% TEA, and (▲), with 1.0% TEA.

Isothermal conduction calorimetry provides information on the rate of heat development in hydrating C_3S . In the C_3S sample hydrated without TEA, there was little heat development in the first few hours, representing the dormant period. This was also observed in the differential thermograms. The curve starts to rise steeply at about 2½ to 3 h, denoting the beginning of the acceleratory period (Figure 8). Maximum heat development occurs between 7 and 8 h and thereafter there is a decrease in the rate of heat evolution.

Figure 8. Conduction calorimetric curves of $3\text{CaO} \cdot \text{SiO}_2$ with different amounts of added triethanolamine.

3.3. Hydration of C_3S +TEA

The comparative rates of hydration of C_3S with or without TEA may be evaluated from Figures 1, 2 and 4 to 7. With TEA certain features were observed that have not been reported in the literature.

If, in the hydration of C_3S with or without TEA, it is assumed that the chemical composition of the C-S-H phase does not change with time, then the amounts of $Ca(OH)_2$ estimated at different times should provide data on the relative rates of hydration of C_3S . The amounts of $Ca(OH)_2$ estimated by DTA, TGA, X-ray and chemical analysis are shown in Figures 4 to 7. Irrespective of the method adopted to estimate $Ca(OH)_2$, the presence of TEA leads to a decrease of $Ca(OH)_2$ at any stage of hydration. One may conclude that the rate of hydration is retarded during the whole course of hydration. There is, in fact, a clear indication that TEA enhances the rate of hydration of C_3S at 1 day, 7 days or 28 days (Figure 9). Data indicate that

Figure 9. The relative amounts of C_3S present at different periods of hydration: (○), with no TEA; (△), with 0.1% TEA; (●), with 0.5% TEA and (▲), with 1.0%.

between 1 day and 28 days more C_3S remains unhydrated in samples lacking TEA. Conduction calorimetric work also reveals that although there is a long induction period in the presence of TEA, once the acceleratory stage has been reached the samples containing TEA generate large amounts of heat (Figure 8). The formation of lower quantities of $Ca(OH)_2$ and an increase in the rate of consumption of C_3S in the presence of TEA can be explained by the formation of a C-S-H product with a CaO/SiO_2 ratio higher than that normally formed in C_3S pastes hydrated without the admixture.

Thermograms also suggest the existence of a C-S-H product with a higher CaO/SiO_2 ratio. Larger endothermic peaks below 300 °C for the TEA-treated C_3S are the result of larger amounts of H_2O in the C-S-H phase. It has been shown that a higher CaO/SiO_2 based C-S-H has also a higher H_2O/SiO_2 ratio.⁸ Larger endothermal effects are observed at 720 to 760 °C in samples containing TEA (Figure 2). This is also typical of the high C/S ratio, hydrated product of C_3S . Similar results have been obtained with C_3S hydrated in the presence of 4 to 5% $CaCl_2$.⁹

Figure 10 examines the relative amounts of CH formed at different degrees of hydration of C_3S with 0 or 0.5% TEA. For the same degree of hydration the sample treated with TEA shows lower values of CH and there is indication that the proportion of CH formed in the TEA-treated C_3S decreases as hydration progresses.

Figure 10. A comparison of the amount of $Ca(OH)_2$ with the amount of unreacted C_3S at different periods of hydration of $3CaO \cdot SiO_2$: (○), with no TEA; (●), with 0.5% TEA.

As has already been stated, the amount of CH formed in the presence of TEA is always less, whatever the method employed or period of hydration. The percentage decrease in CH estimated for $[(C_3S + 0\% \text{ TEA} - C_3S + 0.5\% \text{ TEA}) / (C_3S + 0\% \text{ TEA}) \times 100]$ differs from one technique to another (Figure 11). The largest difference is shown by the X-ray technique and the least by chemical analysis. The X-ray technique estimates only the crystalline CH; the chemical method, the total amount of free CH. TEA seems to discourage the development of crystallised CH. The relative amounts

Figure 11. The percentage difference in the amounts of $Ca(OH)_2$ estimated by different methods: (●), by X-ray; (○), by DTA; (△), by TGA and (▲), by chemical analysis.

of CH, expressed as a ratio $(C_3S + 0\% \text{ TEA}) / (C_3S + 0.5\% \text{ TEA})$ by chemical analysis, show lower values than those shown by the X-ray technique. There is thus a probability that TEA promotes the formation of non-crystalline CH (Table 1). There is some evidence of this effect in the hydrated products of C_2S . Figure 3 presents thermograms of C_2S hydrated to different periods with 0.5% TEA. The intensity of the endothermal peak for the dehydration of $Ca(OH)_2$ in the sample hydrated without TEA is much larger. The sample containing TEA exhibits two endothermal peaks, probably indicating the amorphous and crystalline forms of $Ca(OH)_2$.

TABLE 1. Relative amounts of crystalline and non-crystalline $Ca(OH)_2$

Type of $Ca(OH)_2$	$(C_3S + 0\% \text{ TEA}) / (C_3S + 0.5\% \text{ TEA})$		
	1 day	7 days	28 days
Crystalline (X-ray)	1.73	1.55	1.86
Non-crystalline + crystalline (chemical analysis)	1.13	1.11	1.30

The amounts of CH determined by DTA or TGA compare well for the hydration of $C_3S + 0\% \text{ TEA}$. In the presence of TEA, however, larger variations occur, especially at 1 day of hydration (Figure 11). At earlier periods of hydration the large exothermal effect occurring in the vicinity of the CH peak in the C_3S -TEA- H_2O system may partially mask the endothermal effect of CH hydration. This results in the assigning of lower values for CH peak areas. The masking effect may be eliminated by carrying out DTA in an N_2 atmosphere. In adopting this procedure it was observed that a TEA-treated C_3S , after 1 day's hydration, gave nearly the same amount of CH as the TGA method. At 28 days both TGA and DTA gave the same values for CH because the interfering exothermic effect is absent. DTA and TGA methods seem to estimate both crystalline and amorphous $Ca(OH)_2$, but how quantitative the results are would need a more exhaustive study.

The sudden emergence in TEA-treated samples of a sharp exothermal peak at 6 h absent at earlier times of hydration, must indicate that it is not caused by free TEA (Figure 2). The exothermic peak was not present when the thermogram was obtained in an atmosphere of N_2 , showing that oxidation causes the peak. Additional evidence suggests that the exothermic peak is caused by a complex of TEA formed on the surface of hydrating C_3S . A sample of C_3S containing 1.0% TEA and hydrated to 3 days was leached with H_2O and ethyl alcohol for several hours. TEA is soluble in both H_2O and ethyl alcohol, but the alcohol leachate did not contain any TEA whereas the water leachate showed that more than 80% TEA was extracted from the sample. DTA of the sample leached with alcohol retained the exothermic peak but leaching with water resulted in the disappearance of this peak (Figure 12). These results resemble those obtained in the hydration of C_3S in the presence of 4 to 5% $CaCl_2$. The exothermal peak due to the complex of chloride on hydrated C_3S could be eliminated by extraction with water but not with alcohol.⁹

The exothermal effect that emerges at 6 h disappears after 3 days of hydration. Similar behaviour is shown by $CaCl_2$ -treated C_3S samples.⁹ The masking effect of the endothermal valley in the temperature region of the exothermal effect does not

seem to be the major cause of its disappearance. It is more probable that as hydration proceeds the surface complex is desorbed and goes into the surrounding solution. Subsequently, it may be trapped in the interlayer positions of the C-S-H phase. As a consequence, the mechanism of decomposition of the TEA complex is modified, with loss of the sharp exothermic peak. A change occurs in the mechanism of decomposition of an organic material in the interlayer spaces of clay minerals.^{10, 11}

Figure 12. Effect of extraction on the exothermic peak of C_3S hydrated with TEA: (A) unextracted, (B) extracted with alcohol, and (C) extracted with water.

In the hydration of C_3S it has been suggested that the C-S-H forming on the surface of C_3S has a high CaO/SiO_2 ratio and retards the reaction in the induction period. It is then converted to a second hydrate with a lower CaO/SiO_2 ratio and a higher permeability. Once the nuclei of the second hydrate are formed the conversion takes place with a higher velocity by an autocatalytic effect.¹² Initially, a surface complex of the amine forms in the presence of TEA. Triethanolamine ($CH_2-CH_2.OH)_3N$ is an aminoalcohol and cation active and it is possible that the cations of the hydrating surface of C_3S are replaced by the amine-containing cation. The complex thus formed

is strongly adsorbed and increases the induction period. Ethanolamine is known to interact with the silica surface and also forms complexes with metal ions.¹³⁻¹⁶ The induction period is increased as the amount of TEA added to C_3S is increased. This may be explained by the formation of a thicker layer of the complex with less permeability. As an admixture, TEA should be termed a retarder, especially in the initial stages of hydration when it would be expected to retard setting. This is in contrast with the behaviour of the $CaCl_2$ accelerator, which not only decreases the induction period but also decreases the setting time. The adsorbed complex is subsequently dissolved by H_2O and hydration proceeds normally because the freshly formed, high-surface-area C-S-H product strongly adsorbs the TEA and retards its further action on C_3S .

The presence of TEA in C_3S results in changes in the surface area of the hydrated product. At 28 days of hydration the N_2 surface areas of $C_3S+0\%$ TEA, $C_3S+0.1\%$ TEA and $C_3S+1\%$ TEA are, respectively, 24.8, 30.9 and 44.6 m^2/g . The C_3S containing $CaCl_2$ also shows an increased area of hydration products. Under electron microscopic examination the hydrated C_3S sample is reported to exhibit striated plate structure, whereas the sample treated with TEA promoted felted and fibrous plates with many formed in an unoriented structure.⁴ The latter type of microstructure may enhance the surface area. It may be envisaged that the chemisorption of TEA on freshly forming C-S-H inhibits the orderly growth of plates in tabular form. The formation of more non-crystalline $Ca(OH)_2$ in the products containing TEA may also contribute, to some extent, to the increase in surface area.

4. Conclusions

Additions of triethanolamine (TEA) increase the induction period for the hydration of tricalcium silicate (C_3S), probably owing to the formation of a surface complex of the admixture on the hydrating surface of C_3S . Thus, TEA acts as a retarder of hydration at early stages. At hydration periods exceeding a day the hydration of C_3S proceeds slightly faster with than without TEA. It promotes the formation of C-S-H product with a higher CaO/SiO_2 ratio. The hydrated C_3S with higher surface area and higher content of non-crystalline $Ca(OH)_2$ results when C_3S is hydrated with 0.1 to 1.0% TEA. The effect of TEA on the hydration characteristics of β -dicalcium silicate is similar to its effect on C_3S , except that the rate of hydration of βC_2S is much slower.

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