Pergamon

Cement and Concrete Research, Vol. 26, No. 8, pp. 1179-1187, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00103-2

HYDRATION CHARACTERISTICS OF β-C_2S IN THE PRESENCE OF SOME ACCELERATORS

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(Refereed)
(Received November 2, 1994; in final form June 6, 1996)

ABSTRACT

β-dicalcium silicate (β-C_2S) is present in portland cement as belite stabilized by some impurities. The hydration of β-C_2S is similar to that of C_3S but with slower rate. Extensive investigation had been done on the effect of $CaCl_2$ as accelerator on the hydration of C_3S but meager work had been done on belite (β-C_2S). The aim of the present work is to investigate the effect of some accelerators such as $CaCl_2$, $Ca(NO_3)_2$, $Ca(CH_3COO)_2$ and K_2CO_3 on the hydration of B_2O_3 stabilized β-C_2S. The results show that the hydration of pure β-C_2S liberates $Ca(OH)_2$ up to 28 days which is consumed within 90 days. The hydration products are mainly tobermorite like phase with some $CaCO_3$. On the other side, the effect of accelerators consumes the liberated $Ca(OH)_2$ and accelerates the hydration of β-C_2S.

1. Introduction

Dicalcium silicate is mostly present in portland cement as the metastable β-form, (belite) which is stabilized by the presence of impurities [1,2]. Fewer studies on the hydration behaviour of C_2S have been performed (than on C_3S) because of its much lower rate of hydration. More interest has been shown in C_2S in recent times because of its lower temperature of formation, resulting in lower energy requirement and lesser formation of calcium hydroxide during hydration, which could give a higher strength portland cement, as compared with C_3S. The hydration of β-C_2S shows broad similarities to that of C_3S [3]. The slower rate of hydration of β-C_2S is due to its different crystalline structure [4]. This has been attributed to the higher thermodynamic stability of β-C_2S. Moreover, the lons in β-C_2S are densly packed whereas the presence of holes in the structure of C_3S makes it easily attacked by water [5]. The C-S-H formed is similar to that obtained from C_3S in terms of overall composition and morphology [6].

Compared to the extensive investigations on the hydration of C_3S in presence of $CaCl_2$, only meager work has been done on the effect of $CaCl_2$ on the hydration of C_2S [7–10]. Calcium chloride accelerates the hydration of C_2S [8]. The C_2S paste containing $CaCl_2$ and hydrated to 1–3 months may show negligible amounts of $Ca(OH)_2$, compared to the paste hydrated without $CaCl_2$ [11]. This indicates that a higher C/S product is formed with $CaCl_2$. Complexes such as calcium oxychloride hydrates are not formed at normal concentration of $CaCl_2$. A combination of $Ca(OH)_2$ + $CaCl_2$ retards the hydration of C_2S [12].

Skalny, Phillips and Cahn [13] who studied the hydration of C_3S in the presence of K_2CO_3 concluded that K_2CO_3 acts as an accelerator.

The hydration of the β-C_2S paste accelerated by the addition of Na_2SO_4 + $NaNO_3$ was studied [14]. The strength of the hardened paste increased with increasing complex-salt additive content owing to the formation of increased amounts of fine-grained C-S-H phase. The plasticizer did not significantly improve the hydration of the C_2S paste. The effect of Ca-formate (I), NaF, and $Al_2(SO_4)_3$ on β-C_2S mortar were also studied by Valenti et al. [15]. All the 3 agents increased the compressive strength, especially the early strength, the most favorable concentrations being 0.25 NaF, 2 $Al_2(SO_4)_3$, and 2.5% I based on mortar weight. The $Al_2(SO_4)_3$ accelerated the hydration rate, NaF to a hydration degree of only 15%, whereas I induced higher compressive strengths at the same hydration degree from the very beginning.

Hydration of β-C_2S with K_2SO_4, Na_2SO_4, K_2CO_3 and Na_2CO_3 additions was studied [16]. The degree of hydration of β-C_2S phase as well as the liquid phase composition in suspensions of water/solid ratio = 50 were determined. All the additions accelerated β-C_2S hydration at early ages owing to faster leaching and consumption of Ca^{2+} ions from the liquid phases as a result of hydration.

Taha et al. [17] studied the rate of three concrete admixtures on the hydration of β-C_2S. Two of them acted as water reducers whereas the third acted as a set accelerator as followed by DTA and TG techniques. The kinetics of hydration were followed by the estimation of free calcium hydroxide as well as the combined water contents. The results revealed that the rate of hydration of β-C_2S generally increases in the presence of water reducers to a varying extent. The results with the set accelerator are not conclusive.

The aim of the present work was to study the effect of some accelerators such as $CaCl_2$, $Ca(NO_3)_2$, $Ca(CH_3COO)_2$ and K_2CO_3 on the hydration characteristics of β-C_2S. The hydration rate was measured by determining the free lime as well as chemically combined water contents. The hydration products were investigated using DTA and XRD techniques.

2. Experimental and Methods

β-dicalcium silicate was synthesized from reagent grade $CaCO_3$ and silica in the proper molar ratio by firing the mixture twice at 1450°C for two hours using B_2O_3 (0.5%) as stabilizer. The C_2S, with free lime content lower than 0.15%, was ground to a Blaine fineness of about 3000 cm^2/g.

Mixtures of β-C_2S with 1% K_2CO_3, 2% $CaCl_2$, 2% $Ca(NO_3)_2$ and 2% $Ca(CH_3COO)_2$ by weight of β-C_2S was separately mixed with 30% distilled water in a porcelain mortar for 2 min., then left under 100% relative humidity and covered with moistened cotton. The hydration was stopped after one, 3, 7, 14, 28 and 90 days using the technique described elsewhere [18]. The rate of hydration was measured by the determination of free lime [19] and the combined water contents as calculated from the ignition loss minus the water held by free $Ca(OH)_2$.

The development of hydration products were followed using DTA and X-ray diffraction techniques. A Philips Pw 1373/90 diffractometer with Ni-filtered Cu-k_α radiation at 40 kV and 25 mA was used throughout. DTA was also carried out using DT-30 Thermal Analyzer (Shimadzu Co., Japan). A 50 mg (-63 μm) sample placed in a small platinum-rhodium crucible was heated at rate of 20°C/min.

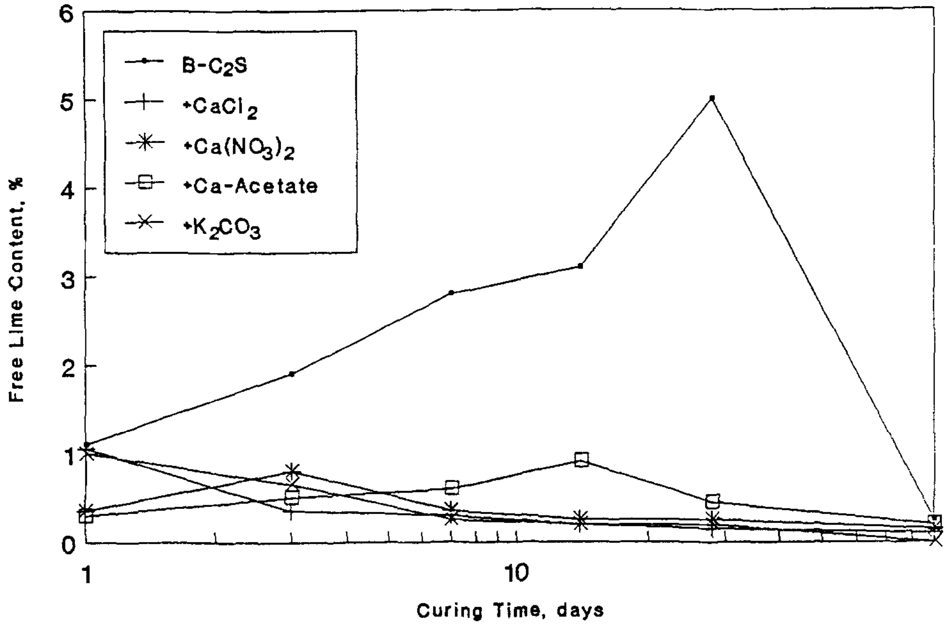

FIG. 1.

Free lime content of β-C_2S in the presence of some accelerators as a function of curing time.

3. Results and Discussion

The measurement of free lime content can be considered as an indirect method for estimating the degree of hydration of β-C_2S. The free lime of β-C_2S in the presence of 2% $CaCl_2$, 2% $Ca(NO_3)_2$, 2% $Ca(CH_3COO)_2$ and 1% K_2CO_3 as a function of curing time up to 90 days are graphically plotted in Fig. (1). The β-C_2S without any accelerator hydrates at a slow rate liberating $Ca(OH)_2$ which increases up to 28 days then decreases sharply and completely disappears at 90 days. The disappearance of free lime at this age may be due to the formation of $CaCO_3$ and calcium silicate hydrate with higher C/S ratio [20] as shown from the following sequence:

$$C_2S \rightarrow C_2S\ aq \rightarrow CSH\ (I)\ \text{with C/S: } 0.2\text{–}0.62 \rightarrow CH + CSH\ (II)$$

having C/S = 1.56 → CSH (II) with C/S = 1.56–1.88.

The addition of accelerators to β-C_2S tends to consume the $Ca(OH)_2$ and decreases with time. The effect of Ca-salts may be due to the formation of hydration products with the ratio C/S > 2, which is different from the tobermoritic phase which forms when C_3S is hydrating without accelerators [11 & 13]. It may be assumed that Cl^- introduced by $CaCl_2$ is "built in" in the calcium hydro-silicates lattice. There is evidence that the hydration of β-C_2S with some chloride is bound rigidly [21].

The accelerating mechanism of K_2CO_3 is attributed to its reaction with $Ca(OH)_2$ which comes from the hydration of C_3S. The potassium part of K_2CO_3 forms KOH which decreases the solubility of $Ca(OH)_2$ due to the common ion effect, which in turn diminishes the retarding effect of $Ca(OH)_2$. The carbonate ion reacts with the $Ca(OH)_2$ forming $CaCO_3$ and thus decreasing the concentration of $Ca(OH)_2$ in the solution. This results in an increase in the hydration of alite. K_2CO_3 acts also as an accelerator for the hydration of β-C_2S.

The actual degree of hydration of β-C_2S can be measured from the amounts of combined water at any given time of hydration. The combined water contents of pure β-C_2S and with accelerators are graphically plotted as a function of curing time in Fig. (2). It is evident that the amounts of combined water of β-C_2S with accelerators are higher than that of the admixture free β-C_2S. The addition of Ca-salt accelerators increases the rate of hydration as indicated from the amounts of combined water at all ages of hydration. The disappearance of $Ca(OH)_2$ in the β-C_2S paste containing $CaCl_2$ and hydrated up to 3 months may be due to the formation of a higher C/S product. It has been evidenced that in the hydration of β-C_2S some chloride, nitrate or acetate is bound rigidly. The accelerating effect of the Ca salts as shown from the combined water content is of the order Ca-acetate > nitrate > chloride (Fig. 2). This may be due to the decrease of the acidic character of the acid producing salts. The C/S ratio depends on the amount of $CaCl_2$ and degree of hydration. Collepardi and Massida [22] also observed that at early age addition of 2% of $CaCl_2$ accelerates the formation of low C/S ratio product in C_3S.

The degree of hydration of pure β-C_2S is shown in the DTA and XRD patterns in Fig. (3). The distinct peaks of $Ca(OH)_2$ with CSH and residual β-C_2S at 28 days are observed. The

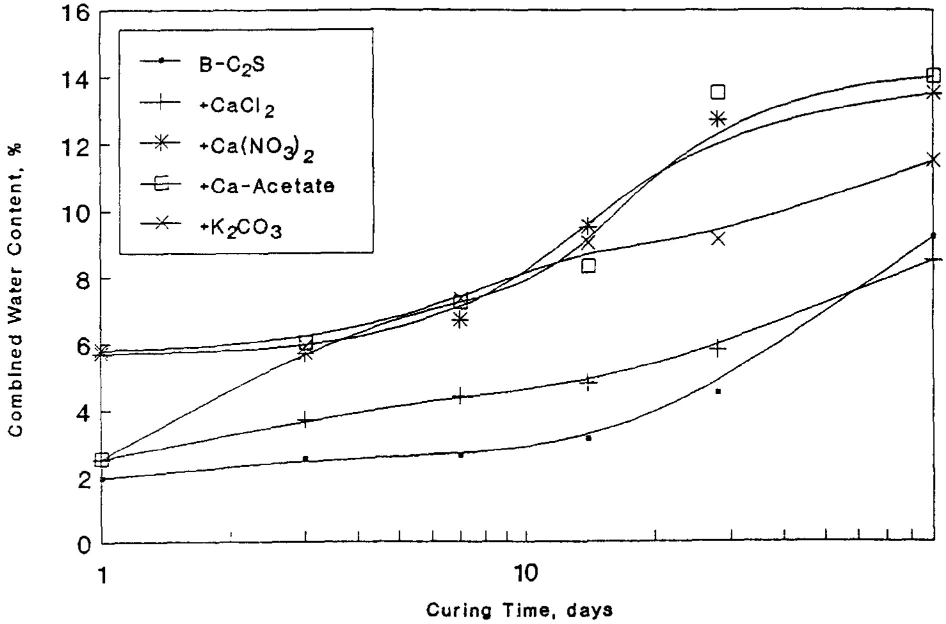

FIG. 2.
Combined water content of β-C_2S with accelerators in relation with curing time.

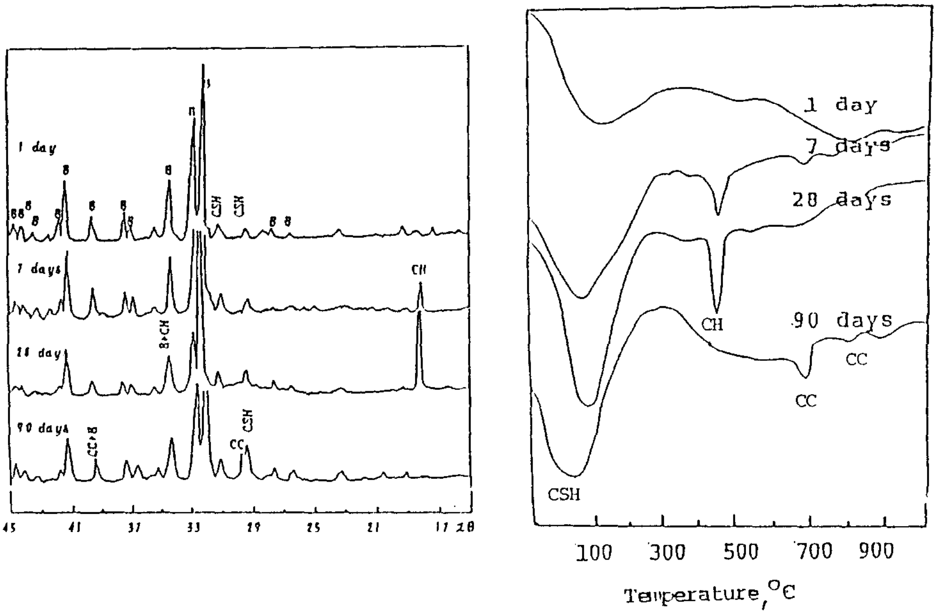

FIG. 3.

DTA and XRD patterns of pure β-C_2S as a function of curing time. B = β-C_2S; CSH = Calcium silicate hydrate; CH = $Ca(OH)_2$ and CC = $CaCO_3$.

$Ca(OH)_2$ is completely consumed at 90 days with the appearance of $CaCO_3$. The DTA endothermic peaks at 100–150, 350–450 and 800–900°C are due to CSH whereas the peaks at 770 and 830°C are attributed to amorphous $CaCO_3$ and CSH.

The hydration of β-C_2S with accelerators is shown on XRD patterns as a function of curing time in Fig. (4). The pastes show the disappearance of $Ca(OH)_2$ at any time of hydration. This is also confirmed from the results of the chemical analysis of free $Ca(OH)_2$. In general, the intensity of the peaks of β-C_2S decreases with curing time from one up to 90 days. The intensity of the peaks of β-C_2S with 2% Ca-nitrate is lower than those in the presence of $CaCl_2$, Ca-acetate and K_2CO_3. Also, the peak of the CSH increases with progressive hydration. This is also shown from the values of the combined water. The addition of accelerator activates the hydration of β-C_2S as compared with the XRD patterns of β-C_2S without accelerators as shown in Fig. (3). It may be concluded that $Ca(NO_3)_2$ has the higher accelerating effect than $CaCl_2$ and a small difference with $Ca\ (CH_3COO)_2$ whereas K_2CO_3 shows the lowest accelerating effect.

The degree of hydration of β-C_2S with accelerators and its hydration products were studied from DTA (Fig. 5). The sample with 1% K_2CO_3 (Fig. 5a) hydrated for one day shows two endothermic peaks at 120 and 200°C due to the dehydration of C-S-H. The peak at 770°C is due to $CaCO_3$ dissociation. After 7 days of hydration, two additional exothermic effects at 360°C and 480°C appeared. These exothermic peaks may be due to the chemisorbed carbonates on the C-S-H surface. Samples hydrated for 28 and 90 days show the appearance of a new endothermic

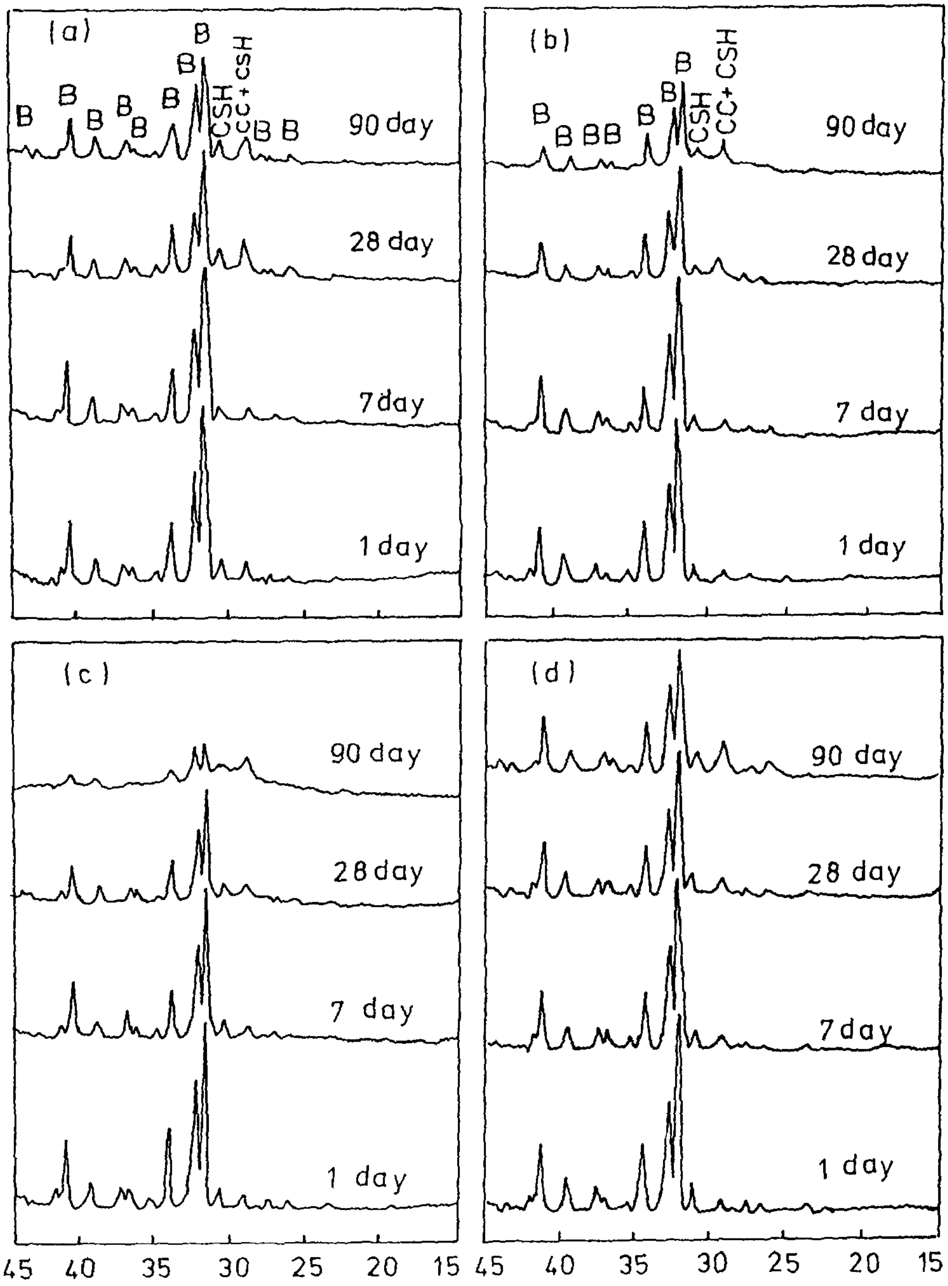

FIG. 4.

XRD patterns of β-C_2S in the presence of some accelerators. a = 1% K_2CO_3; b = 2% $Ca(CH_3COO)_2$; C = 2% $Ca(NO_3)_2$ and d = 2% $CaCl_2$.

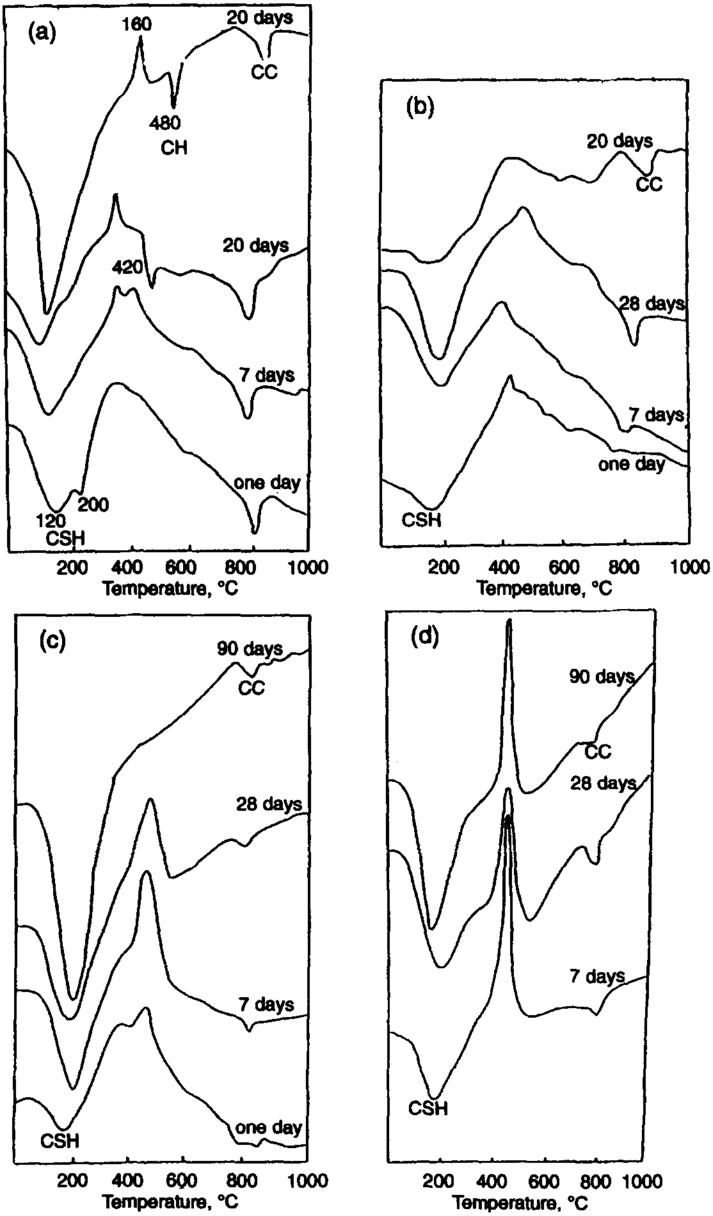

FIG. 5.

DTA thermograms of β-C_2S with. a = 1% K_2CO_3; b = 2% $Ca(CH_3COO)_2$; C = 2% $Ca(NO_3)_2$ and d = 2% $CaCl_2$, as accelerators.

peak at 480°C due to the decomposition of the KOH which is formed from the reaction of K_2CO_3 with $Ca(OH)_2$ as in the equation.

$$Ca(OH)_2 + K_2CO_3 \longrightarrow CaCO_3 + 2KOH \quad (1)$$

As the hydration proceeds for example, at 90 days, the intensity of the endothermic peak at 120°C increased due to the acceleration of K_2CO_3. This is confirmed from the XRD and combined water content. The pH of the system most likely increases and the reaction accelerates. Also, the $CaCO_3$ formed affects the hydration and crystallization of CSH [23].

From the DTA thermograms of β-C_2S with 2% $CaCl_2$ (Fig. 5b), the sample hydrated for one day illustrates the presence of CSH, $Ca(OH)_2$ and $Ca(CO_3)_2$. As the hydration proceeds the CSH increases. Sample hydrated for 90 days shows two endothermic peaks at 220 and 640°C which are due to the CSH and the complex of the $Ca(OH)_2$ with $CaCl_2$. The peak at 770°C due to amorphous $CaCO_3$ is present at all ages. Sample hydrated with 2% $Ca(NO_3)_2$ for one day also developed endothermic peaks at 130, 770, and 840°C. The two exothermic peaks in the range 300–500°C may be due to the chemisorbed nitrate of CSH. As the hydration proceeds the intensity of the low endothermic peak of CSH increases due to the accelerating effect of NO_{3-}. At 7 days one exothermic peak of the nitrate silicate remains. After 90 days, there is an intense endothermic peak of the CSH at 140°C with two other endothermic peaks at 770, 840°C and an exothermic peak in the range 800–900°C [24].

The DTA thermograms of β-C_2S with 2% Ca-acetate with curing time are illustrated in (Fig. 5d). The pattern shows two endothermic peaks at 135, 770°C due to the CSH and $CaCO_3$ respectively. $Ca(OH)_2$ does not appear. The exothermic peak at 430°C may be due to the oxidation of Ca-acetate. As the hydration progresses (90 days) the amount of CSH increases as evident from the low endothermic peak. The acceleration of β-C_2S may be due to the consumption of $Ca(OH)_2$.

The action of these accelerators involves the formation of insoluble compounds by reaction of $Ca(OH)_2$ formed during the hydration of β-C_2S [25]. Some suggestions imply that these accelerators act catalytically.

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