

## HYDRATION OF DICALCIUM SILICATE IN THE PRESENCE OF CONCRETE ADMIXTURES

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### ABSTRACT

The role of three concrete admixtures on the hydration of  $\beta$ -dicalcium silicate ( $\beta$ -C<sub>2</sub>S) is studied. The admixtures are produced commercially under different trade names; two of them are in the liquid form and act as water reducers and strength improvers whereas the third is a solid powder and acts as a set accelerator. The hydration products of  $\beta$ -C<sub>2</sub>S with and without admixtures were investigated by DTA and TG techniques. The kinetics of hydration were followed by the estimation of free calcium hydroxide liberated during hydration as well as by the chemically combined water contents. The results reveal that the rate of hydration of  $\beta$ -C<sub>2</sub>S is generally increased in the presence of admixtures 1 and 2 to a varying extent. The results with admixture 3 are not decisive. The chemically combined water contents were found to increase with the rate of hydration.

### INTRODUCTION

Dicalcium silicate is one of the most important components of portland cement clinker in which it usually exists as the metastable  $\beta$ -polymorph and is stabilized by the presence of impurities. The rate of hydration of  $\beta$ -dicalcium silicate ( $\beta$ -C<sub>2</sub>S) is known to be slow compared with that of the alite phase. Therefore, it does not play a large part in the development of the properties of cement paste during the early stages of hydration. However, its hydration products play an important role in the development of the ultimate engineering properties of hardened cement and concrete. The hydration of dicalcium silicate polymorphs has been reviewed [1–3].

Tong and Young [3] showed that during the hydration of  $\beta$ -C<sub>2</sub>S, the rate of release of the ionic species Ca<sup>2+</sup> and SiO<sub>4</sub><sup>4-</sup> into solution is slow and

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results in a subsequent low degree of supersaturation. It is also assumed that the degree of supersaturation is a function of the nucleation of  $\text{Ca}(\text{OH})_2$  and calcium silicate hydrate phases. The small supersaturation observed for  $\beta\text{-C}_2\text{S}$  will mean a slow rate of its hydration.

In the last few decades, concrete admixtures have become universally widely used. Different types are employed to produce certain effects on the physical and/or mechanical properties of fresh or hardened cement and concrete. Admixtures are classified into water-reducing, retarding, accelerating, water-reducing and retarding and water-reducing and accelerating agents [4].

Owing to the importance of  $\beta\text{-C}_2\text{S}$  as a clinker mineral, the aim of this work was to study its hydration under the influence of concrete admixtures. Because of the sluggish rate of hydration of this mineral, it was more conclusive to chose concrete admixtures from the types which accelerate setting and hardening of the hydrated paste. The hydration reactions of  $\beta\text{-C}_2\text{S}$  with and without admixtures were followed using DTA and TG techniques. The kinetics of hydration were also followed between 3 h and 150 days by determining the chemically combined water and the  $\text{Ca}(\text{OH})_2$  liberated during hydration. The hydration products were identified by DTA.

## EXPERIMENTAL

The  $\beta\text{-C}_2\text{S}$  used in this investigation was prepared from chemically pure calcium carbonate and silica flour and stabilized by 0.5%  $\text{B}_2\text{O}_3$  added as boric acid. The required proportions were thoroughly mixed in a porcelain ball mill and then moulded into briquettes. These were fired twice at  $1450^\circ\text{C}$ . The completion of the reaction was checked by X-ray diffraction (XRD) and chemical methods. The fired product was ground in an agate mortar down to two surface areas, namely, 2770 and  $7800\text{ cm}^2\text{ g}^{-1}$  as determined by the Blaine air-permeability apparatus.

Three concrete admixtures were used: the first acts as a water-reducer and strength improver (admixture 1); the second is a strength improver and set accelerator (admixture 2); and the third is an antifreeze and set accelerating agent (admixture 3). Admixture 1 is an aqueous solution of the modified salts of hydroxylated carboxylic acids and amine salts with a chloride content of 8%–9%. Admixture 2 is a mixture of solutions of inorganic and amine salts and having a chloride content of 11%–12%. Admixture 3 is a chloride-free solid powder of complex organic compounds which readily dissolves in water. These admixtures were supplied by the Grace Co., Italy.

The first two solution mixtures were added to the mixing water at a dose of 0.2 wt.% of the dried material. The third (solid) admixture was dissolved in the mixing water at a dose of 2.0 wt.%. Throughout this study, a water to solid ratio of 0.30 was used.  $\beta\text{-C}_2\text{S}$  was mixed with the appropriate amount

of water to which the required admixture (or none at all) was pre-added. Mixing was continued for 3 min in a porcelain mortar and the pastes were kept in an air-tight container for the first day and then under water until the time of the test. The hydration was followed after periods of between 3 h and 150 days at room temperature. After the prescribed period, a representative piece of the hydrated sample was taken and its hydration was stopped using the technique described elsewhere [5].

The kinetics of hydration were studied by DTA and TG methods using a thermal analyzer of the type DT-30 (Shimadzu Co., Japan) at a heating rate of  $10^{\circ}\text{C min}^{-1}$  from the ambient temperature up to  $700^{\circ}\text{C}$ . The TG runs were carried out in a nitrogen atmosphere. The degree of hydration at any given age is defined as the ratio of the chemically combined water of the paste to the corresponding value at complete hydration; the latter is reported to be equal to  $0.1840\text{ g g}^{-1}$  for  $\beta\text{-C}_2\text{S}$  [6].

## RESULTS AND DISCUSSION

Table 1 lists the calculated values for the chemically-combined water and the free  $\text{Ca(OH)}_2$  of hydrated  $\beta\text{-C}_2\text{S}$  pastes having a Blaine surface area of  $7800\text{ cm}^2\text{ g}^{-1}$  with and without admixture 2 as a function of curing time. The results for the combined water  $w_n$  and for the  $\text{Ca(OH)}_2$  with admixtures 1 and 3 generally show the same trend but differ in detail. It is seen from the data of Table 1 that the presence of 0.2% of admixture 2 begins to influence the rate of hydration of  $\beta\text{-C}_2\text{S}$  after about 24 h from the beginning of hydration. At a given age, the  $\text{Ca(OH)}_2$  and combined-water contents steadily increase at a higher rate for the admixture-containing samples, e.g., values of 1.02% and 3.55% for  $\text{Ca(OH)}_2$  and combined water respectively are given after 3 days of curing of the control samples. The corresponding values for the admixture-containing samples are 1.31% and 3.92%. After 150

TABLE 1

Effect of concrete admixture 2 on the combined water and calcium hydroxide contents of hydrated  $\beta\text{-C}_2\text{S}$

Curing time	Pure $\beta\text{-C}_2\text{S}$		$\beta\text{-C}_2\text{S} + 0.2\%$ admixture 2	
	Combined $\text{H}_2\text{O}$	$\text{Ca(OH)}_2$	Combined $\text{H}_2\text{O}$	$\text{Ca(OH)}_2$
6 h	1.8	Nil	2.11	Trace
1 day	3.0	Nil	3.20	0.42
3 days	3.55	1.02	3.92	1.31
7 days	4.50	2.06	6.20	2.35
28 days	9.75	3.38	11.78	3.71
150 days	13.25	4.11	14.20	4.98

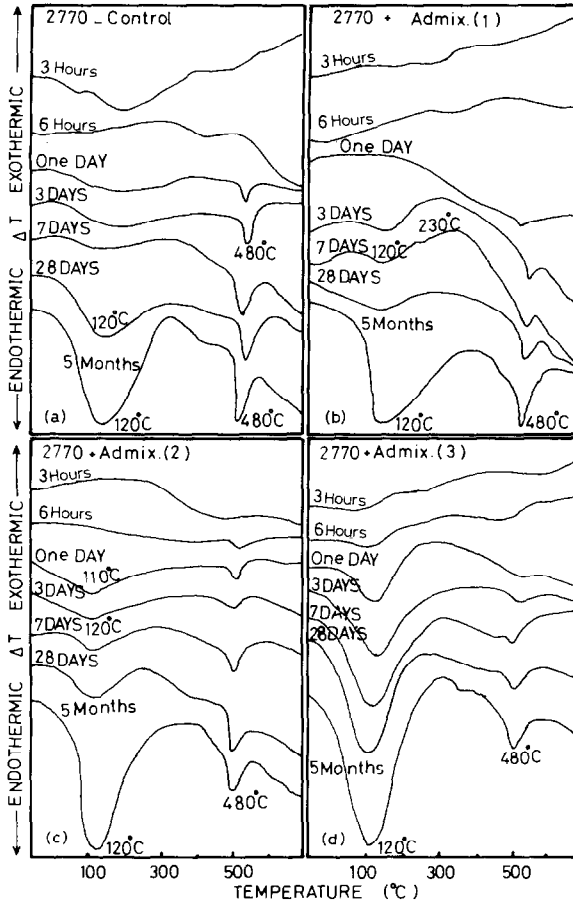


Fig. 1. DTA thermograms of hydrated  $\beta$ - $C_2S$  of surface area  $2770 \text{ cm}^2 \text{ g}^{-1}$  with and without admixtures 1, 2 and 3.

days of hydration, the control samples give 4.11% and 13.25% for  $\text{Ca}(\text{OH})_2$  and the combined water respectively compared with 4.98% and 14.20% when admixture 2 is employed.

Figure 1 illustrates the DTA thermograms of hydrated  $\beta$ - $C_2S$  of surface area  $2770 \text{ cm}^2 \text{ g}^{-1}$  with and without admixtures 1, 2 and 3 for periods between 3 h and 150 days. The results show the endothermic peaks of hydrated calcium silicates and of  $\text{Ca}(\text{OH})_2$  in the temperature range  $100\text{--}130^\circ\text{C}$  and at about  $470^\circ\text{C}$  respectively. It is clear that the presence of concrete admixtures generally enhances the rate of hydration of  $\beta$ - $C_2S$ , though at different rates. This is indicated by the intensity of the peaks on the DTA thermograms. In addition to the first two endothermic effects, Fig. 1(d) shows an endotherm in the range  $300\text{--}400^\circ\text{C}$  given by some samples to which admixture 3 has been added. This endotherm can probably be attributed to the oxidation of the organic constituents of this admixture.

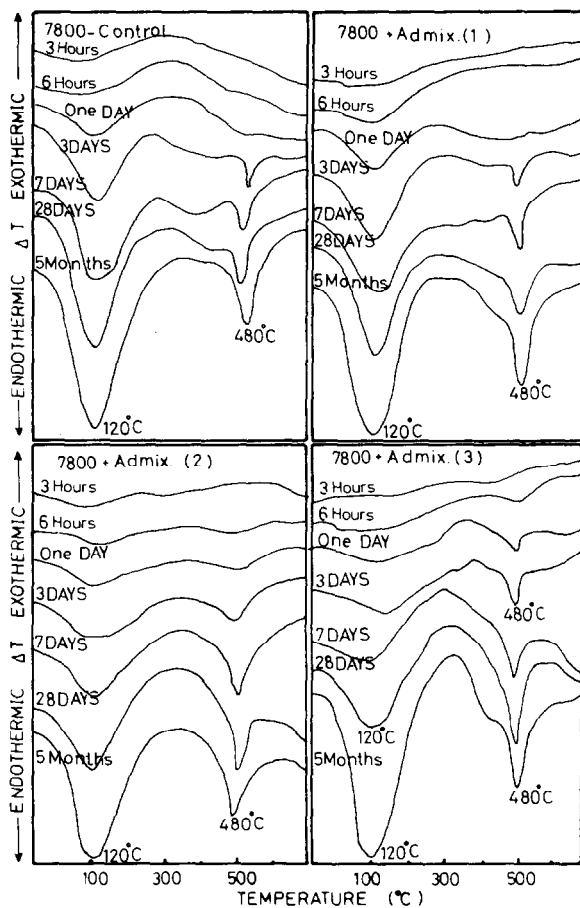


Fig. 2. DTA thermograms of hydrated  $\beta$ - $C_2S$  of surface area  $7800 \text{ cm}^2 \text{ g}^{-1}$  with and without admixtures 1, 2 and 3.

Another endothermic effect is apparent on the runs of some samples at about  $350^\circ\text{C}$ . This effect has been reported to be due to the formation of  $C-S-H(II)$  [7].

The influence of concrete admixtures 1, 2 and 3 on the hydration of  $\beta$ - $C_2S$  having a surface area of  $7800 \text{ cm}^2 \text{ g}^{-1}$  was studied. Figure 2 represents the DTA thermograms of the hydrated samples with and without admixtures as a function of curing time. It is seen from the intensity of the peaks that the addition of the admixtures generally enhances the rate of hydration of  $\beta$ - $C_2S$  to various extents. A comparison of the results of Figs. 1 and 2 indicates that, for a given admixture and a given curing time, the rate of hydration is faster the finer the starting material. The fine material presumably has a larger surface area and hence the points of contact between water and solid particles are increased. Accordingly, the rate of hydration is increased.

It is generally agreed that  $\text{CaCl}_2$  accelerates the hydration of  $\beta\text{-C}_2\text{S}$  to a lesser extent than  $\text{C}_3\text{S}$ . This is due to the assumption that the chloride ions tend to form less soluble complex salts (calcium oxychloride) with the  $\text{Ca}(\text{OH})_2$  that is liberated during the hydration of calcium silicates [8,9]. Therefore, the reaction goes faster. It has been reported that the 28-day strengths of  $\text{CaCl}_2$ -doped dicalcium silicate pastes to be 10%–15% higher than those of chloride-free samples [10], however, Young and Tong [11] did not observe any significant difference in tensile strength.

In this study, it is likely that the effect of admixtures 1 and 2 on the rate of hydration of  $\beta\text{-C}_2\text{S}$  could be due, at least partly, to the presence of chloride ions among their constituents. Admixtures 1 and 2 contain about 9% and 11% chloride ions respectively.

The influence of admixture 3 on the rate of hydration of  $\beta\text{-C}_2\text{S}$  is seen in Figs. 1 and 2. Under the same conditions, the rate of hydration increases with the surface area of  $\beta\text{-C}_2\text{S}$  either in the presence or in the absence of admixture 3. This is indicated by the intensities of the DTA thermograms. However, if one compares the magnitudes of the influence of this admixture, it is concluded that admixture 3 would apparently have a retarding effect on the rate of hydration when used with a material having a surface area of  $2770 \text{ cm}^2 \text{ g}^{-1}$ ; this is indicated by the intensity of the  $\text{Ca}(\text{OH})_2$  peak on the DTA curve at about  $470^\circ\text{C}$ . Also, on increasing the surface area of  $\beta\text{-C}_2\text{S}$  from  $2770$  to  $7800 \text{ cm}^2 \text{ g}^{-1}$ , the extent of hydration between 6 h and 150 days is apparently almost the same with and without admixture 3. This leads to the conclusion that the influence of this admixture as a set accelerator may have a physical rather than chemical effect, i.e., it may increase the

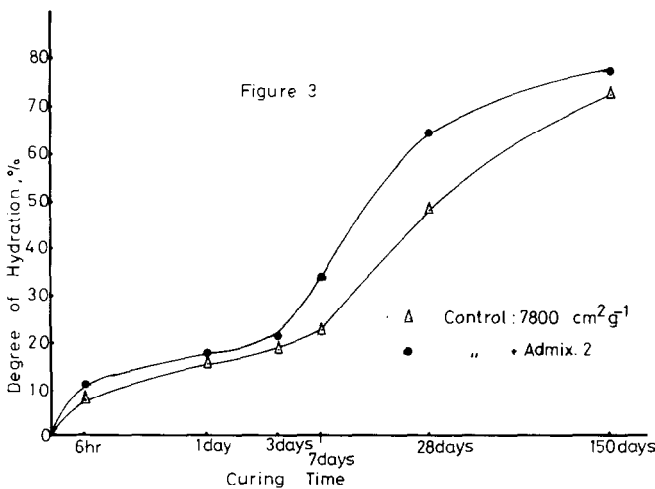


Fig. 3. Effect of admixture 2 on the degree of hydration of  $\beta\text{-C}_2\text{S}$  with a surface area of  $7800 \text{ cm}^2 \text{ g}^{-1}$ .

initial strength by filling up a part of the pore system of the hardened paste or by bridging neighbouring particles by additional bonds. However, the chemical effect exerted by admixture 3 cannot be completely excluded, but this assumption has not been proven owing to the lack of sufficient data.

Figure 3 illustrates the degree of hydration of pure  $\beta$ -C<sub>2</sub>S of surface area 7800 cm<sup>2</sup> g<sup>-1</sup> with and without admixture 2 vs. curing time. It is evident that the presence of 0.20% of this admixture enhances the reaction after as short a time as 6 h of hydration. The magnitude of this enhancement increases with curing time and it reaches a maximum between 7 and 28 days.

A comparison of the results of the present work with previous data obtained on the hydration of alite under the influence of concrete admixtures [12] confirms the findings that the rate of the hydration reaction of  $\beta$ -C<sub>2</sub>S is much slower than that of alite even with fine grinding of  $\beta$ -C<sub>2</sub>S and/or in the presence of accelerating agents.

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