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Highly reactive dicalcium silicate synthesised by hydrothermal processing

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Abstract

The paper brings information concerning the synthesis and reactivity of a highly reactive dicalcium silicate using calcium silicate hydrates as precursors. The calcium silicate hydrates were prepared by hydrothermal treatments of mixtures consisting in CaO, amorphous SiO_2 (ROMSIL) and water, under various hydrothermal conditions. C_2S was obtained by thermal treatment – at low temperatures (700–800°C) – of these silicates hydrates. Due to this way of processing (hydrothermal synthesis and low temperature treatment), the dicalcium silicate obtained is very reactive and develops good compressive strengths in pressed mortar specimens even after one day of hardening.

Keywords: Highly reactive β-C_2S; Hydrothermal processing; Low temperature treatment; Highly specific surface

1. Introduction

Considering that the low hydration rate of β-C_2S – one of the most important components of Portland cement – is partially due to its well-crystallised structure, the possibility to obtain β-C_2S, at low temperature treatment has received wide attention in recent years. In this context two processing techniques, i.e., sol–gel and hydrothermal treatment, have been recently developed.

Literature data [1–6] suggest the possibility to synthesise β-C_2S at low temperature (less than 900°C) by hydrothermal processing of starting materials, in two different conditions:

- at temperatures ranging from 90°C to 100°C and normal pressure;
- at high pressures ($\leqslant 40$ atm) and temperatures ($\leqslant 250$°C).

The hillebrandite [$Ca_2(SiO_3)(OH)_2$], α-dicalcium silicate hydrate [$Ca_2(SiO_4H)(OH)$] and dellaite [$Ca_6(SiO_4)(Si_2O_7)(SiO_4)(OH)_2$] can be obtained by hydrothermal treatment of an aqueous suspension with $CaO/SiO_2 = 2$. The formation of one or other of these three hydrates is related to the reactivity and homogeneity of the starting materials mixture, as well as the concentration of the aqueous suspension. By thermal dissociation of any of the above-mentioned calcium silicate hydrates, at temperatures ranging from 500°C to 700°C, β-C_2S can be obtained which is stable at room temperature and highly reactive [2–4]. It is assumed that its high reactivity is due to a poor symmetry of $[SiO_4]^{4-}$ tetrahedra in β-C_2S, a very fine grain size and according to some researchers [6], to the absence of any foreign ions as stabiliser.

This paper brings information concerning the influence of some processing parameters in the hydrothermal synthesis of β-C_2S and about its binding properties.

2. Experimental

2.1. Materials

The raw materials were: (i) CaO – obtained by the decarbonatation of $CaCO_3$ (chemical reagent) at 1050°C; (ii) SiO_2 – in vitreous state and characterised by a high specific surface – an industrial product (ROMSIL).

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2.2. Methods

These materials were dosed corresponding to the CaO/SiO_2 molar ratio 2/1 and mixed with water (water/solid ratio 7).

The suspensions were hydrothermally processed in two different ways:

(A) At 95°C and 1 atm for 10 h.

(B) At 195°C and 16 atm for 10 h.

After hydrothermal treatment, the products were dried at 50°C in the presence of NaOH, to avoid carbonatation of the samples. These samples were burned at temperatures ranging from 700°C to 900(1000)°C for 1 h, with rapid cooling to room temperature.

The formation of β-C_2S, in the above-mentioned condition, was studied using XRD, DTA–TG and chemical analysis. The β-C_2S reactivity was assessed by the variation of the concentration of Ca^{2+} in liquid phase, pH and electrical conductivity measurements in aqueous suspensions and by XRD analysis on hydrated pastes.

Mechanical strengths determinations were made on mortar cylinders ($d = h = 20$ mm) with binder/sand ratio 1/3 and water/binder = 0.8 (by weight), compacted at 40 MPa. The compressive strengths of C_2S synthesised by hydrothermal processing were considered comparatively with those of the reference – β-C_2S synthesised by solid state reaction, for which the mechanical strengths were determined on the pressed samples from mortar with binder/sand ratio 1/3 and water/binder ratio = 0.4.

3. Results and discussions

3.1. The formation of C_2S from calcium silicate hydrates obtained by hydrothermal processing

XRD and DTA–TG analysis, made on the samples obtained by the drying of A and B suspensions, suggest a quasi-total consumption of initial reagent – $CaO(Ca(OH)_2)$ through the reaction with SiO_2 and H_2O. The main reaction products are the silicates hydrates, which coexist with small quantities of $CaCO_3$ formed by the carbonatation of $Ca(OH)_2$ during the processing of the mixtures. The endotherm from 462°C determined by $Ca(OH)_2$ dehydration which appears only on DTA curve of sample A (Fig. 1) may suggests an incomplete reaction and/or a different basicity of the calcium silicate hydrates formed by hydrothermal processing at normal pressure (A) and those formed by hydrothermal processing at high pressure (B). The presence of the endotherm from 63°C to 100°C on the DTA curves of both samples, corroborated with literature data [2,3] suggest a low structuration degree of formed calcium silicates hydrates. Furthermore, the identification of calcium silicates hydrates by XRD was also difficult due to the presence of $CaCO_3$, whose very intense XRD peaks overlap the less intense peaks, belonging to the calcium silicates hydrates (Figs. 2 and 3).

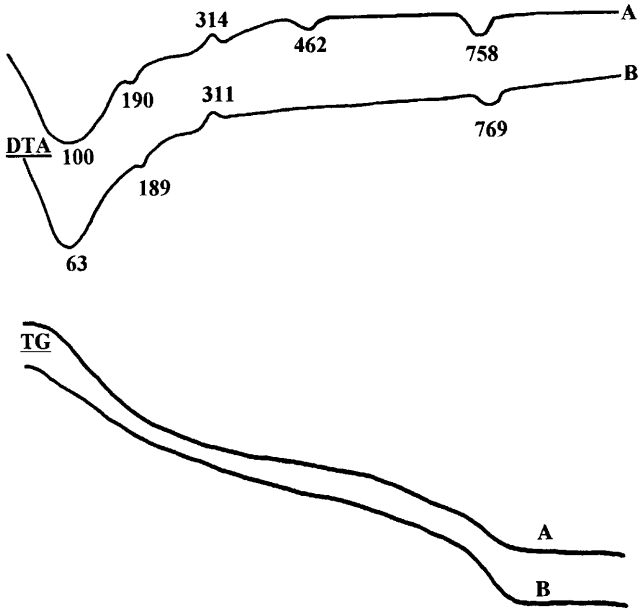

Fig. 1. DTA and TG curves of A and B, respectively, dried calcium silicate hydrates.

The reduction of the free CaO content (Fig. 4) correlated with XRD suggest the formation of β-C_2S even in the samples burned at 700°C. This compound has a very low crystallisation degree (see Figs. 2 and 3).

When the hydrothermal processing is made at high pressure (B), the values of the free CaO content determined in the samples burned at 700°C are smaller and decrease with the increase of the temperature (Fig. 4). This evolution correlated with the DTA-TG data (Fig. 1), suggest an intensification of the β-C_2S formation process when the hydrothermal processing is made at high pressure. It may also be assumed that the amount of minor phases, i.e., $CaCO_3$, $Ca(OH)_2$ formed in these conditions (B) was smaller compared with the amount of these phases formed in normal pressure conditions (A).

The increase of burning temperature from 700°C to 900°C determines the increase of the crystallization degree of β-C_2S shown by the appearance of numerous XRD specific peaks on the spectra of samples burned at 800°C and 900°C (see Figs. 2 and 3).

3.2. Reactivity and binding properties of C_2S synthesised by hydrothermal processing

By physical, chemical and mechanical determinations information was obtained concerning the reactivity of β-C_2S synthesised in two different ways:

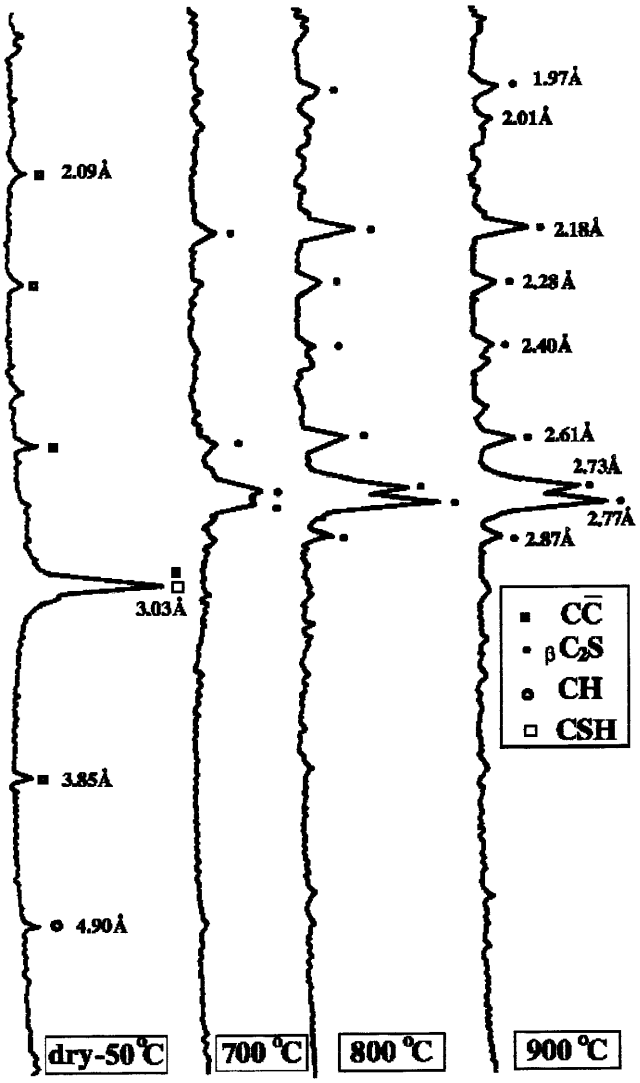

Fig. 2. XRD spectra of A, dried calcium silicate hydrates sample respectively of the samples burned at 700°C, 800°C and 900°C.

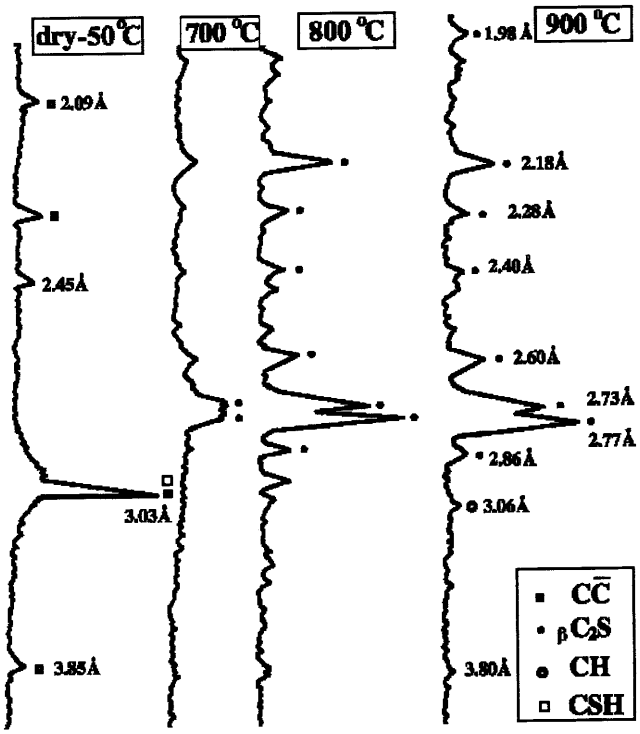

Fig. 3. XRD spectra of B, dried calcium silicate hydrates sample respectively of the samples burned at 700°C, 800°C and 900°C.

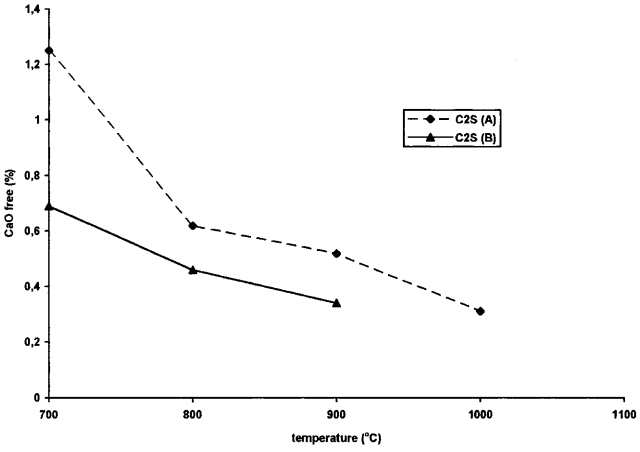

Fig. 4. Free CaO content vs. the burning temperature of calcium silicate hydrates.

(I) Hydrothermal processing at normal pressure and thermal treatment at 800°C.

(II) Hydrothermal processing at high pressure (16 atm) and thermal treatment at 700°C.

Fig. 5 shows the variation of the pH and the electrical conductivity values for suspensions made with three types of C_2S and with water/solid ratio 50, respectively, the Ca^{2+} concentration in the liquid phase. C_2S obtained by hydrothermal processing ((I) and (II)) exhibits a better reactivity than the one conventionally obtained (E), i.e., by burning of $CaO + SiO_2$ mixture at 1400°C with B_2O_3 as stabiliser. On the other hand, the C_2S (II) obtained by hydrothermal processing at high pressure and burned at lower temperature – 700°C seems to be more reactive than C_2S (I) obtained at normal pressure.

The evolution of the concentration of Ca^{2+} in the liquid phase, respectively the electrical conductivity of C_2S suspensions presents specific features in correlation with the kinetic of hydration – hydrolysis process.

In the case of reference suspension (E) in the first seven days a slow continuous increase of the Ca^{2+} concentration in the liquid phase and of the electrical conductivity occurred, due to the slow evolution of the C_2S hydrolysis process. In the case of suspensions C_2S (I) and C_2S (II) – obtained by burning at – 800°C and 700°C, the electrical conductivity and the concentration of Ca^{2+} in liquid phase show an important increase in

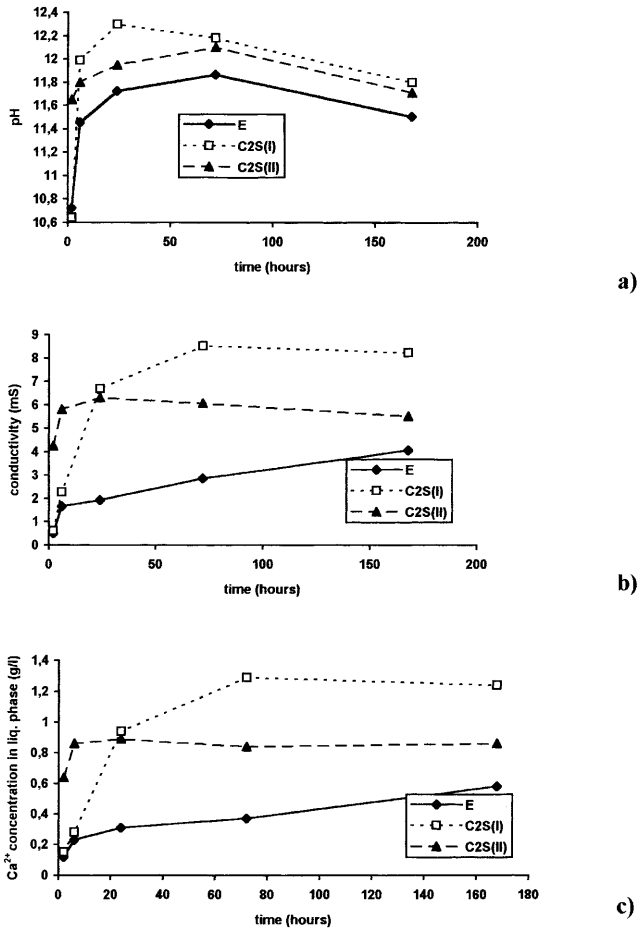

Fig. 5. Evolution vs. time for: (a) pH of suspensions; (b) electrical conductivity of suspensions; (c) concentration of Ca^{2+} in liquid phase.

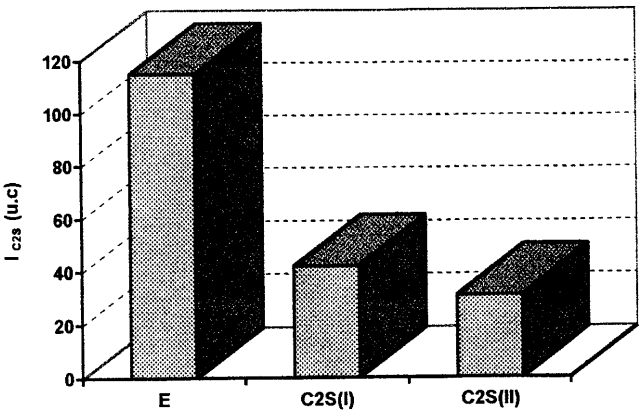

Fig. 6. Variation of the crystallinity degree (the crystallinity degree was appreciated by the intensity of 277 A peak on XRD spectra) for reference (E), C_2S (I) and C_2S (II) samples.

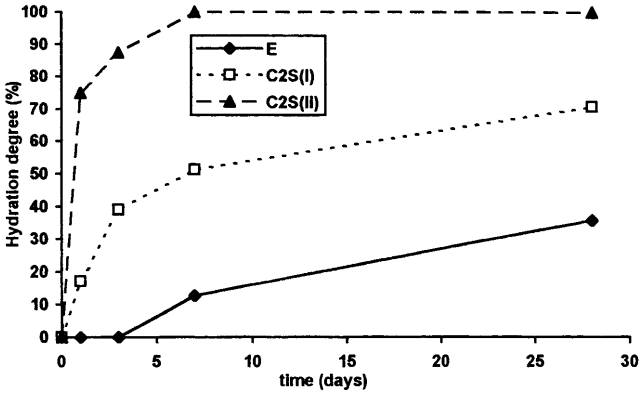

Fig. 7. Hydration degree (H_d) ($H_d = [(I_0 - I_t)/I_0 \times 100$ (%), were I_0 = the intensity of 277 A peak on XRD spectra of anhydrous sample; I_t = the intensity of 277 peak on XRD spectra of samples hydrated t days) of C_2S vs. time for reference (E), C_2S (I) and C_2S (II) samples.

the first day and three days, respectively. At later hydration periods the decrease of Ca^{2+} ions in solution is due to their consumption in the formation process of calcium silicate hydrates with variable CaO/SiO_2 ratio.

The higher hydrolysis rate in the case of C_2S (II) may be explained, considering also literature data, [2,5] by its very poor crystallinity (see Fig. 6) and its high specific surface area (SSA = 8–10 m^2/g – for C_2S (I) and C_2S (II) and SSA = 0.31 m^2/g – for (E)). According to Ishida et al. [5] the increase of the burning temperature of calcium silicates hydrates from 600°C to 800°C determines a very important reduction of C_2S specific surface area.

Information concerning the reactivity of C_2S synthesised from calcium silicate hydrates precursors was obtained by quasi-quantitative processing of the XRD data (Fig. 7). The values of the hydration degree after one day are 17% for C_2S (I), 75% for C_2S (II) and practically 0% for reference. After seven days C_2S (II) seemed to be fully hydrated and the hydration degree of C_2S (I) is 50% and only 13% for reference (E). These data suggest a decrease of the reactivity in the series: C_2S (II) > C_2S (I) > E.

The identification of the calcium silicate hydrates by XRD was rather difficult due to the $CaCO_3$ presence in the hydrated samples. It has already been mentioned that XRD peaks corresponding to $CaCO_3$ overlap those corresponding to calcium silicate hydrates. Also considering literature data it may be assumed that especially calcium silicate hydrates with a CaO/SiO_2 molar ratio less than 2 are formed during the hydration of pastes. $Ca(OH)_2$ was not identified. However, according to [1], $Ca(OH)_2$ possibly formed might be convert into $CaCO_3$.

The mechanical strengths of C_2S synthesised by hydrothermal processing, where assessed in comparison with those of C_2S synthesised by solid state reaction.

The high reactivity of β-C_2S obtained from calcium silicate hydrate precursors leads to measurable strengths on pressed mortar samples, even after one day of hydration, see Fig. 8.

The compressive strengths of C_2S (I) burned at 800°C increase continuously in time. In the case of C_2S (II)

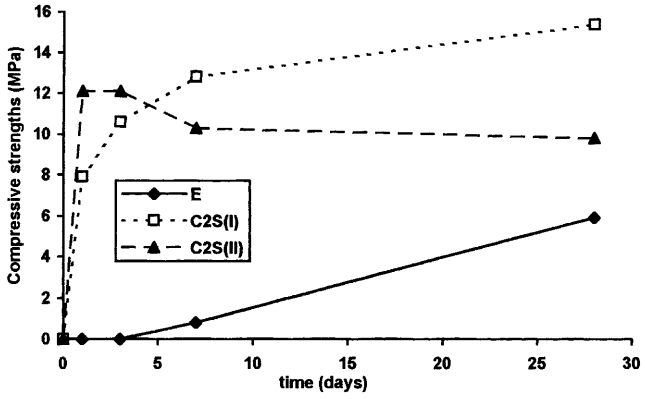

Fig. 8. The evolution of compressive strengths vs. time.

obtained at lower temperature (700°C) the compressive strength increase at early ages and then decrease after longer hardening period. The decrease may be due to a very high hydration rate (Fig. 7) which determines the apparition of internal tensions, with a negative influence on mechanical strength.

4. Conclusions

β-C_2S obtained by burning at 700°C of calcium silicate hydrates formed at 195°C and saturated steam pressure is highly reactive; it is almost completely hydrated after seven days.

β-C_2S obtained by burning at 800°C of calcium silicate hydrates formed at 95°C and normal pressure is also very reactive; its hydration degree is 50% after seven days hydration.

Good mechanical strengths, in pressed mortars specimens, even at early ages of hydration (one day) were developed by the C_2S obtained from calcium silicate hydrates formed at 195°C under saturated steam pressure; after three days of hydration a reduction of mechanical strength occurred and this may be correlated with the very high hydration rate of this compound.

The mechanical strengths developed by the C_2S synthesised by hydrothermal processing at normal pressure increase continuously with time.

Taking into account the hydration reactivity and the development of mechanical strengths as well as the technological features of the hydrothermal processing, the synthesis of the C_2S from calcium silicate hydrates obtained at normal pressure, seems to be more favourable, than synthesis from calcium silicate hydrates formed under high pressure conditions.

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