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Characterisation and hydration kinetics of β-C_2S synthesised with K_2SO_4 as dopant

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ABSTRACT

In this study, a protocol for synthesising β-C_2S using K_2SO_4 as a dopant has been reported. Quantitative X-Ray diffraction was used to characterise synthesised samples. It was observed that it is possible to synthesise β-C_2S with high purity (>96 wt%) and limit the formation of free lime to below 0.5 wt% using this protocol. Unreactive γ-C_2S was the main secondary phase present in the sintered samples. Isothermal calorimetry studies were conducted to understand the reaction kinetics which showed that β-C_2S reacts slowly but produces similar calorimetric curve profiles as that of C_3S. The C-S-H formed from the hydration of C_2S was observed to be morphologically and compositionally identical to the C-S-H produced from the hydration of C_3S. The hydration kinetics of β-C_2S was seen to be affected by the presence of aluminosilicate pozzolan, such as calcined clay, which can have practical implications while producing blended cements with belitic clinkers.

1. Introduction

Alite (C_3S with minor inclusions of Mg, Al, Fe, and other elements) and belite (β-C_2S, stabilised with minor inclusions of Mg, Al, or others) are the main calcium silicate phases present in Portland cement. Significant efforts have been made over the years to understand the hydration mechanisms of alite as it is the primary phase present in Portland cement systems [1–3]. However, only a limited number of studies are available on pure belite systems, most likely due to the reaction rate of belite at room temperature being extremely slow compared to other clinker phases [4]. Hence, strength development during the early ages of cement hydration is controlled by the reaction of alite, making studies on alite systems more relevant and interesting for the research community.

Recently, there has been a renewed interest in developing belite-based binders [5–7]. Production of belitic cements is less energy-intensive since belite sinters at a lower temperature than alite. Belitic cements can be produced using limestone with lower calcium carbonate content, which is beneficial from the view of raw material conservation [8]. In literature, high belite cement/low heat cement/belitic cements are generally defined as cements having belite as the major phase (40 to 50 %). They also usually contain sufficient alite (20 to 30 %) to ensure adequate development of early-age mechanical properties. However, ordinary Portland cements produced in several countries (e.g., India) contain higher belite contents (25 to 30 %) than are common elsewhere (10 to 15 %) but may not be classified as high belite cements [9].

Five polymorphs (α, α'_H, α'_L, β, and γ) of C_2S are known to exist, of which only the least reactive γ-C_2S is stable below 500 °C [4]. However, the reactive β polymorph is generally observed in industrially produced clinkers due to the presence of substituent ions (such as Al^{3+}, Fe^{3+}), which prevents the $\beta \rightarrow \gamma$ transformation. Therefore, selecting a suitable dopant is critical during the laboratory-scale synthesis of β-C_2S. Several studies have reported using boron-bearing dopants (H_3BO_3, $Na_2B_4O_7.10H_2O$) for synthesising β-C_2S [10–12]. The α'_H polymorph also exhibits good reactivity and has been stabilised at room temperature after thermal treatment of hydrated cement paste at 700–800 °C [13].

The main hydration products of alite and belite are C-S-H and portlandite (Eqs. (1) and (2)). Belite hydration produces more C-S-H per unit volume than alite, indicating that belitic cements may perform similarly to conventional alitic cements using lower cement content. However, it is also important to note that the total volume of all the

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hydration products (not just C-S-H) contributes to strength development. Studies also suggest that the belite produces a more durable matrix of hydration products than alite [8,14].

$$C_3S + (3 - x + y)H \rightarrow C_x - S - H_y + (3 - x)CH \quad (1)$$

$$C_2S + (2 - x + y)H \rightarrow C_x - S - H_y + (2 - x)CH \quad (2)$$

Widespread adoption of belitic cements is still limited due to the slower hydration rate of belite compared to alite, leading to low early-age strength. Belitic cements may also not be suitable for producing blended cements that incorporate supplementary cementitious materials (SCMs) due to a lack of sufficient portlandite, which limits the extent of the pozzolanic reaction possible in these systems. More importantly, studies indicate that the long-term hydration of belite appears to be inhibited in blended cement systems with aluminosilicate pozzolans such as calcined clay [15,16]. This is a critical issue since partial clinker replacement using calcined clays has emerged as the most promising solution for producing sustainable cements [17]. A higher sensitivity of the hydration of belite to temperature has also been suggested [18]. Therefore, a better understanding of belite hydration is essential not just for developing more practically viable belitic cements but also to better optimise the use of SCMs with clinkers containing a higher belite content.

In this study, as a first step towards solving the challenges discussed above, it is attempted to better understand the reaction mechanisms of belite by conducting studies on model systems. The objective of this study was to develop a methodology for producing belite (specifically the reactive β polymorph commonly found in commercial Portland cements) in significant quantities at a laboratory scale and to provide new insights into its hydration kinetics, microstructure development and interaction with SCMs.

2. Synthesis protocol and experimental methods

2.1. Synthesis of β-C_2S

The experimental protocol reported by Li et al. (2018) [19] for the laboratory synthesis of large quantities of alite was modified to produce β-C_2S in this study. The raw materials ($CaCO_3$, dopants, and nano-silica) were initially homogenised in a ceramic ball mill for 24 h. Potassium sulfate and alumina were used as dopants to stabilise the β-C_2S polymorph at room temperature. Wet-milling process was preferred over dry milling to ensure sufficient homogenisation of the calcium carbonate and nano-silica. The raw meal was then transferred to cylindrical moulds and dried at 105 °C for 48 h to remove the excess moisture. The dried cylinders were then placed over ceramic crucibles in the high-temperature furnace for the sintering reaction at a maximum temperature shown in Table 1. A fixed ramp rate of 7 °C/min was used for the sintering process. The cylinders were immediately removed from the furnace after sintering and air-quenched with the help of a table fan. This procedure makes it possible to synthesise relatively higher quantities of pure clinker phases compared to the other methods reported in the literature [19]. The details of the mix design and the sintering parameters are shown in Table 1.

2.2. Experimental methods

2.2.1. Preparation of paste samples

The sintered belite clinker was initially ground in a laboratory ball mill for 30 min. A vertical shaft, high-shear mixer operating at 1600 rpm was used for preparing the paste samples, with a mixing time of 2 min. Paste studies were conducted only at 40 °C as it was observed that the pastes prepared at 20 °C did not harden even after 28 days (also see the isothermal calorimetry results, Fig. 6). The belite powder and water were conditioned at 40 °C for 24 h before mixing. A water-to-binder ratio of 0.5 was used for all the experiments. The paste specimens were then transferred to sealed plastic cylinders and stored at 40 °C. Additionally, the paste sample of C_3S was also prepared using the same protocol to understand the similarities/differences between the hydration products of C_3S (T_1 polymorph) and β-C_2S. Additional information regarding the C_3S used can be found in the study of Zunino and Scrivener [20].

2.2.2. Isothermal calorimetry

Hydration kinetics studies were conducted on an 8-channel TAM-air isothermal calorimeter from TA instruments. Approximately 10 g of the freshly prepared paste was sealed in a glass ampoule and placed in the calorimeter to monitor heat evolution. Deionised water (with a specific heat capacity ±10 % of the sample) was used as a reference. The calorimetry tests were conducted in temperature controlled room to ensure stable measurements. A commercially available PCE-based superplasticiser (0.5 % of the weight of solids) was used to prepare pastes for calorimetry studies. Calorimetric studies were conducted at two temperatures, 20 °C and 40 °C.

2.2.3. X-ray diffraction

X-ray diffraction (XRD) experiments were conducted on a Panalytical X'Pert Pro diffractometer operating at 45 kV and 40 mA with a Cu source and Bragg-Brentano configuration. Sample spinning was used to improve the particle statistics. For anhydrous specimens, the diffractograms were recorded between 5° and 70° 2Θ in approximately 30 min. For hydrated specimens, fresh slices were removed from the hardened paste cylinder using a diamond saw for the XRD analysis. The diffractograms were recorded between 5° and 70° 2Θ for approximately 15 min. A shorter scanning time was used for hydrated specimens to prevent carbonation and drying. Rietveld quantitative phase analysis was carried out using Bruker TOPAS v5 software. Rutile (Kronos 2300 – titanium oxide) was used as the external standard for estimating the phase quantities in hydrated systems.

2.2.4. Scanning electron microscopy

The microstructural development was studied using scanning electron microscopy (SEM) on an FEI Quanta 200 microscope. Element distribution maps were collected from polished sections of hydrated belite paste embedded in resin, using an accelerating voltage of 12 kV, a working distance of 12.5 mm and a spot size adjusted to obtain about 0.9 nA of current over the sample. The maps were collected at 2000× magnification in 30 scans with a dwell time of 512 μs, resulting in a total measuring time of approximately 8 h per map. The data was then quantified using a calibration database acquired under the same

Table 1
Details of the raw meal/sintering parameters used for the synthesis of β-C_2S.

S No	Name	$CaCO_3$ (g)	Nano-silica (g)	K_2SO_4 (g)	Al_2O_3 (g)	Sintering temperature (°C)	Sintering time (h)	CaO/SiO_2 (molar)
1	1300C-KS-A-3h-2.13	266	75	4.5	5.4	1300	3	2.13
2	1200C-KS-A-3h-2.13	266	75	4.5	5.4	1200	3	2.13
3	1300C-KS-3h-2.07	266	77	4.5	0	1300	3	2.07
4	1300C-KS-3h-1.93	262	81.5	4.5	0	1300	3	1.93
5	1300C-KS-3h-1.90	258	81.5	4.5	0	1300	3	1.90
6	1300C-KS-3h-1.86	254	82	4.5	0	1300	3	1.86

conditions. Afterwards, the *edxia* image analysis framework was used to process the hyperspectral maps and obtain phase distribution masks [21]. The results were used to assess the composition of the hydrates formed and their distribution in the microstructure in relation to the anhydrous C_3S/C_2S grains.

3. Results and discussion

3.1. Optimisation of belite synthesis

The first objective of this study was to develop a methodology for producing high-purity belite (>96 % β-C_2S) and to minimise the formation of other reactive phases, such as free lime (f-CaO) and C_3S. This was an important consideration since these fast-reacting phases may interfere with the comparatively slower hydration process of belite. Three critical parameters (sintering temperature, dopant type, and CaO/SiO_2 ratio) were investigated for optimising the raw meal to produce β-C_2S clinker having the desired composition (see Table 1). Quantitative XRD analysis was used for the characterisation of the synthesised clinker. Several studies have reported the successful synthesis of β-C_2S at temperatures ranging from 700 °C to 1550 °C [22,23]. However, significant amounts of free lime (>15 %) were also observed at temperatures below 1000 °C. At higher sintering temperatures (above 1450 °C), there is a high possibility of the formation of tricalcium silicate. Therefore, two temperatures, i.e. 1300 °C and 1200 °C, were initially used for the sintering process, with a residence time of 3 h.

As boron-bearing dopants are relatively expensive and typically not observed in the C_2S formed in commercial clinkers (Table 1.2, Page 8 in Ref. [4]), the feasibility of using alternative dopants was investigated in this study. Belites formed in commercial clinkers contain nearly 4 to 6 % of substituent oxides (mainly Al_2O_3 and Fe_2O_3). Higher belite contents have also been reported in clinkers with higher SO_3 contents, most likely due to the coupled substitution of $2Al^{3+}$ and S^{6+} substitution for $3Si^{4+}$ [4,24]. Hence, alumina (Al_2O_3) and potassium sulfate (K_2SO_4) were used initially as the dopants for these mixes. Table 2 shows the phase assemblage of the synthesised clinkers estimated using Rietveld analysis. The phase compositions of the clinkers were similar at 1200 °C and 1300 °C, with <90 % β-C_2S forming in both the clinkers. A slight decrease in the free lime content was observed at 1300 °C (1.48 % to 0.76 %). It has been reported that higher sintering temperatures lead to a reduction of f-CaO content [25,26]. Therefore, it was decided to use 1300 °C as the standard sintering temperature for the remainder of the study. The formation of tricalcium aluminate (C_3A) was also observed (Fig. 1), which is undesirable due to its rapid hydration reaction. As the source of alumina for the C_3A was most likely the dopant added to the raw meal, the possibility of using only K_2SO_4 as the dopant was explored. Although this resulted in an increase in the β-C_2S content (89.35 % to 93.08 %), a significant increase was also observed in the free lime content (0.76 % to 4.92 %) (Fig. 2). More importantly, no C_3A formation was observed once the alumina (Al_2O_3) was removed as a dopant from the raw meal (Table 2). The belite synthesised using only K_2SO_4 was considerably softer than the one synthesised using Al_2O_3 and K_2SO_4 as dopants, with a higher apparent grindability. The role of minor elements on the hardness of clinkers was beyond the scope of this study but merits further investigation due to its practical implications.

Higher f-CaO content in the sintered clinker (1300C-KS-3H-2.07) suggests that the raw meal has higher lime content than required. The molar ratio between CaO and SiO_2 in the raw meal was varied from 2.07 to 1.86 by adjusting the proportions of limestone and nano-silica. Fig. 3 shows the effect of varying the CaO/SiO_2 molar ratio on the clinker phase assemblage. A clear increase in the β-C_2S content was observed as the CaO/SiO_2 molar ratio was reduced. It was possible to reduce the f-CaO content to <0.1 % when the CaO/SiO_2 ratio was 1.86. The approximate expected solid solution composition of the sintered belite was $(CaO)_{1.86}\cdot(K_2O)_{0.02}\cdot(SiO_2)\cdot(SO_3)_{0.02}$. Similar observations were reported by Koutnik [22], where nearly 4 % f-CaO remained after sintering a raw meal having a CaO/SiO_2 molar ratio of 2. No clear trends were observed for the formation of γ-C_2S. One possible reason for this could be the variable cooling rates, which could not be controlled precisely due to the variations in the ambient temperature of the room in which the furnaces were located. Still, the formation of γ-C_2S is not as problematic as f-CaO due to its unreactive nature; as long as the sintered clinkers are well-characterised to quantify the reactive β-C_2S and the unreactive γ-C_2S. Therefore, it was decided to use the 1300C-KS-3h-1.86 mix to synthesise the β-C_2S clinker for further investigation since this study aims to develop a protocol for producing β-C_2S with minimum free lime content. Fig. 4 shows the Back-scattered Electron (BSE) microscopy image of β-C_2S clinker where the hexagonal grains of belite is clearly visible. The XRD and particle size distribution of the sintered 1300C-KS-3h-1.86 mix are shown in Figs. 5 and 6, respectively.

The composition of the β-C_2S was computed based on elemental composition data collected by SEM-EDX. Over 400 points were collected from three different specimens from the same batch of β-C_2S for the analysis. The mean $(Ca + K)/(Si + S)$ ratio of the synthesised β-C_2S was 1.91. Increasing the molar ratio above 1.86 resulted in residual free lime in the clinker.

3.2. Hydration of belite

The isothermal calorimetric curves of the β-C_2S hydrating at 20 °C and 40 °C are shown in Fig. 7(a) and (b), respectively. The deceleration part of the main hydration curve of β-C_2S is not completely observed even after 50 days of hydration at 20 °C, indicating a very slow reaction rate compared to that of β-C_2S generally found in Portland cement. It is also important to note that it is difficult to distinguish between the signal and noise in the calorimetry curve due to the extremely slow reaction kinetics of the sintered β-C_2S at 20 °C. A significant reaction acceleration was observed upon increasing the temperature to 40 °C, but the main hydration curve's duration was still longer than 16 days. It is important to note here that the peak value of the hydration curve at 40 °C is nearly ten times the order of magnitude of the peak value at 20 °C. The profile of the belite hydration curve appears to be very similar to alite hydration curve, with the reaction kinetics being the most important differentiator. The observed results reaffirm that the main hydration curve of Portland cement systems is controlled by the reaction of alite [4]. It has been suggested that the presence of C_3S can inhibit the reaction of β-C_2S in Portland cements. In real cement systems, the reaction of belite has been observed from 7 days onwards. The present results indicate that β-C_2S is an inherently slow-reacting phase irrespective of the presence of C_3S.

The reactivity of such β-C_2S appears to be dependent on the

Table 2
Effect of temperature and dopant type on the phase assemblage.

Phase (%)	1300C-KS-A-3h-2.13	1200C-KS-A-3h-2.13	1300C-KS-3h-2.07	1300C-KS-3h-1.93	1300C-KS-3h-1.90	1300C-KS-3h-1.86
β-C_2S	89.35	87.82	93.08	97.15	98.20	97.85
γ-C_2S	3.31	0.98	0.71	0.64	0.47	1.51
C_3A cubic	6.48	7.4	0	0	0	0
C_3A monoclinic	0.05	0.45	0	0	0	0
f-CaO	0.76	1.48	4.92	1.55	1.10	0.09
K_2SO_4	0.04	1.85	1.27	0.56	0.23	0.55

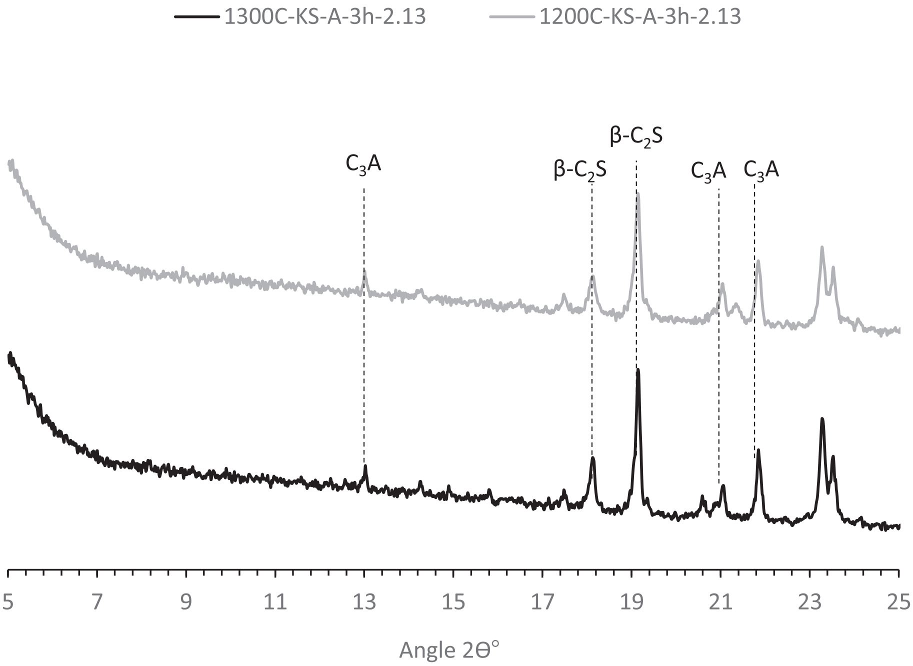

Fig. 1. The effect of sintering temperature on the synthesised belite clinker.

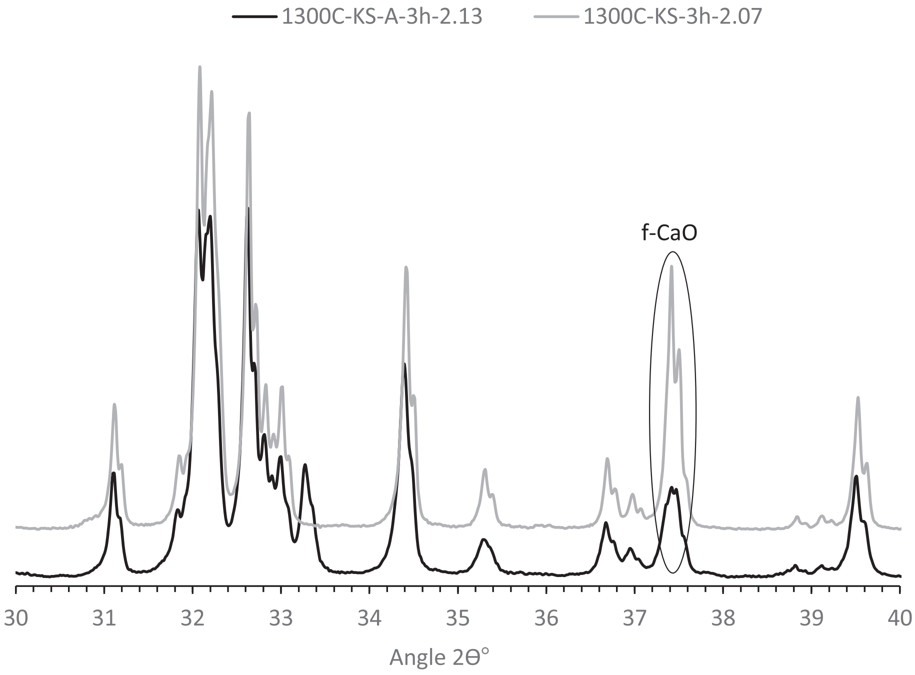

Fig. 2. The effect of dopants on synthesised belite clinker.

parameters like the type of doping ions, their concentration, sintering temperature and the crystallite size [27–29]. Due to this, there is disagreement in the studies of the reactivity of laboratory-synthesised belite in the literature. Park [12] investigated the influence of different dopants (B_2O_3, K_2O and SO_3) on the β-C_2S hydration and reported that the main hydration curve was complete by 30 h in all the systems. Kim and Hong [30] suggest that Al^{3+} and B^{3+} increase the reactivity while K^+ and S^{6+} decrease the reactivity of β-C_2S. In this study, K_2SO_4 was used as a dopant for stabilising the β polymorph, which could explain the slow reaction rate observed for the belite. There appears to be little consensus regarding the exact role of the different synthesis parameters on the reactivity of the β-C_2S. Due to the slow reaction rate of the β-C_2S synthesised in this study, the remaining investigations were only carried out on the sample cured at 40 °C.

Fig. 8a) compares the diffractograms of hydrated C_3S and β-C_2S after 28 days at 40 °C. Due to its nano-crystalline nature, the diffractogram of the C-S-H gel presents as a hump (between 25° and 35°) rather than distinct peaks. The C-S-H amorphous bands were seen to be similar in both systems. Approximately 70 % of the β-C_2S and 85 % of the C_3S react by 28 days of hydration (Fig. 8b). As expected, the portlandite peak intensities were lower in the β-C_2S system compared to the C_3S system. The portlandite contents in the β-C_2S and C_3S systems are shown in

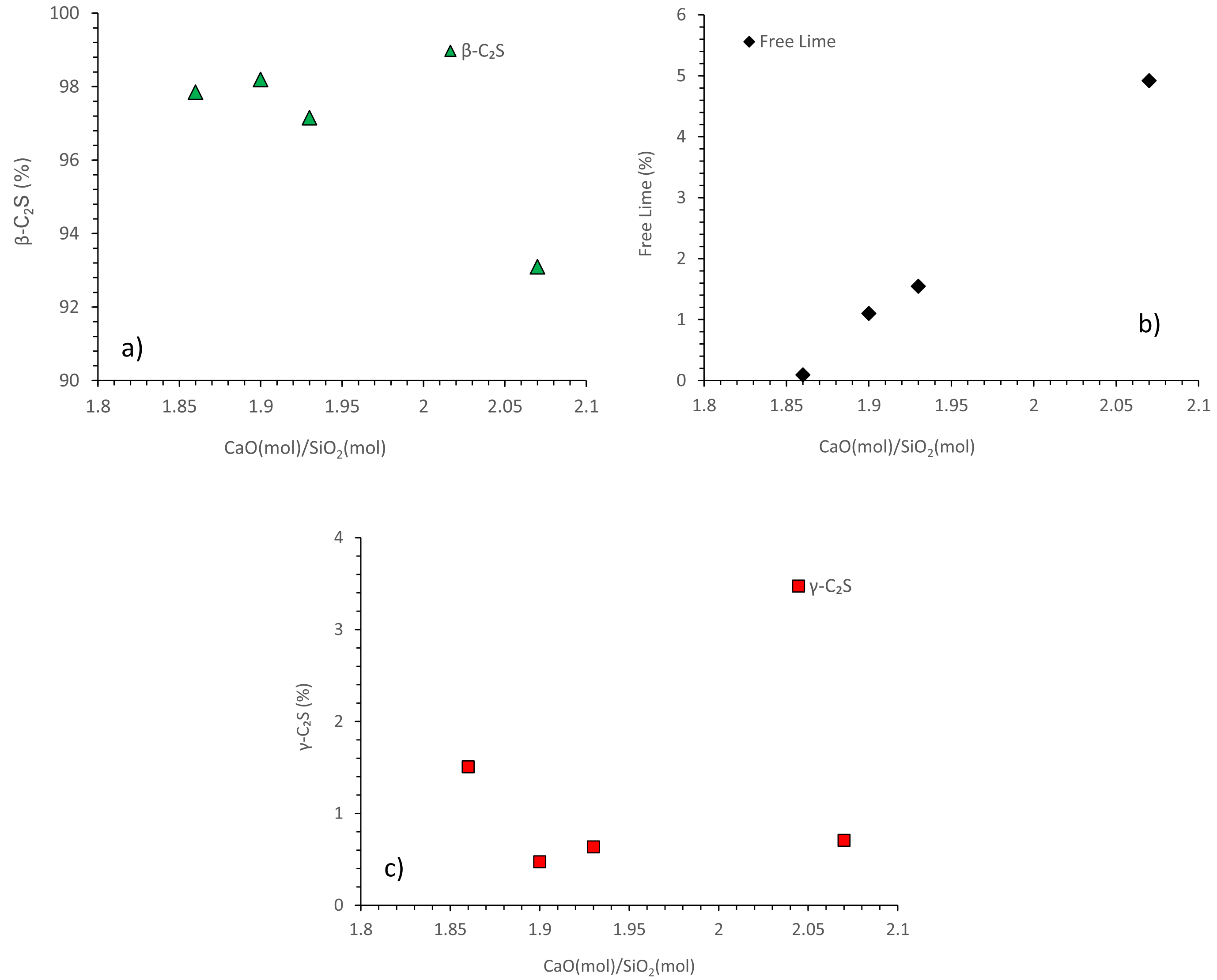

Fig. 3. The effect of the molar ratio between CaO and SiO_2 on the phase composition of sintered clinker. (a) β-C_2S (b) f-CaO and (c) γ-C_2S.

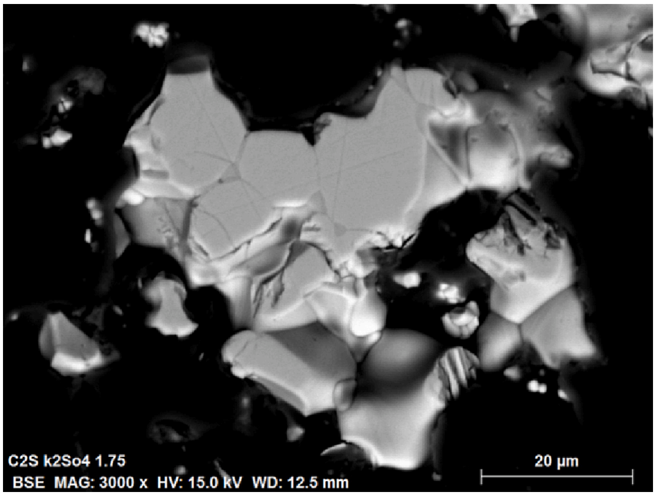

Fig. 4. Back-scattered electron (BSE) micrograph of the β-C_2S (1300C-KS-3h-1.86).

Fig. 9. It is interesting to note that the estimated portlandite contents in the hydrated β-C_2S systems are significantly lower than what would be expected to form in these systems by stoichiometric calculations. While not unexpected, the lower portlandite content in the belite system is an important factor that needs to be considered to optimise blended cements produced with belitic clinkers. The diffractogram of the hydrated β-C_2S after 60 days is shown in Fig. 10.

3.3. Morphology and composition of the C-S-H

3.3.1. Morphology

Several studies have attempted to understand the morphology of the C-S-H formed from the hydration of pure clinker phases and Portland cement systems [31–34]. Based on experimental evidence, it is generally accepted that the C-S-H formed during C_3S hydration has a “needle-like” or fibrillar morphology during the first hours of hydration [3,35,36]. In previous studies on Portland cement paste, the C-S-H formed from the hydration of β-C_2S appeared to have similar morphology as that of the C-S-H from alite hydration [4].

The SEM-BSE images of polished sections of hydrated C_3S and C_2S systems after 28 days are shown in Figs. 11 and 12, respectively. In the C_3S system, a combination of partially and fully reacted C_3S grains was observed, with fibrous or “needle-like” C-S-H growing outwards from

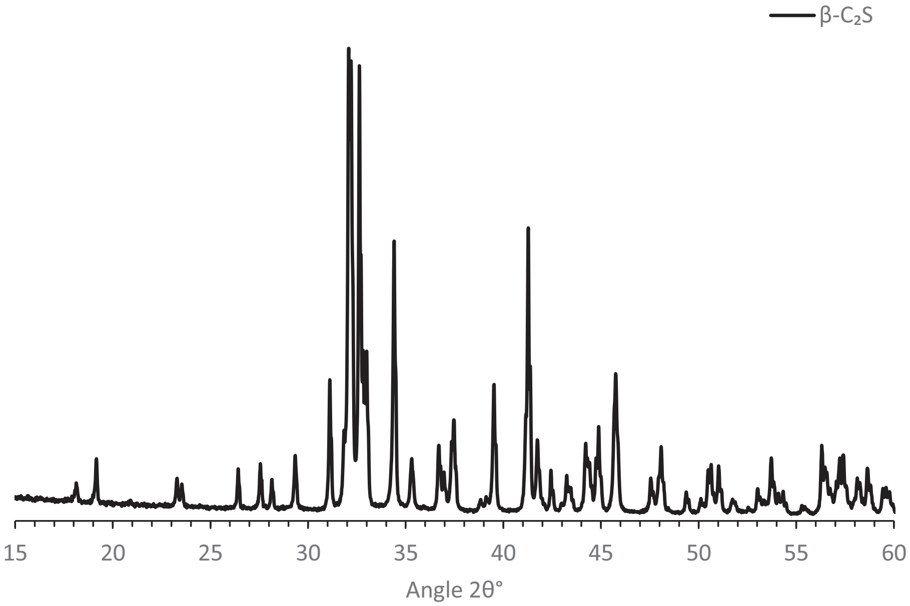

Fig. 5. XRD of sintered β-C_2S (1300C-KS-3h-1.86).

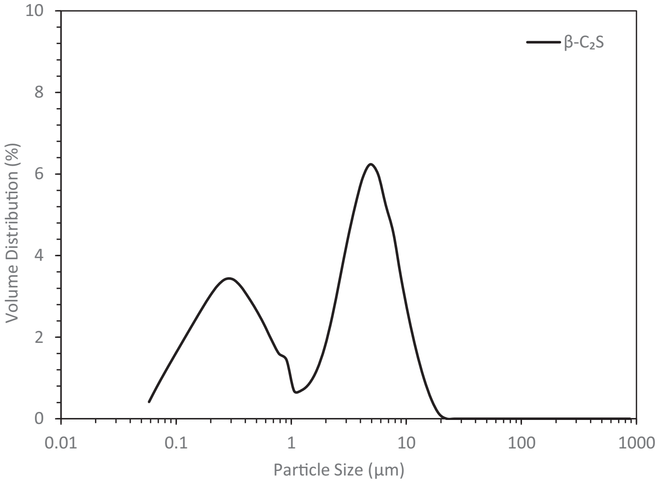

Fig. 6. Particle size distribution of sintered β-C_2S (1300C-KS-3h-1.86).

the outer edges of the C-S-H rims.

Two distinct features can be observed in the SEM-BSE images of the β-C_2S system, i.e. i) partially and fully reacted grains surrounded by C-S-H rims (similar to the C_3S system) and ii) formation of hollow shells or “Hadley grains”, which are a characteristic feature of cement hydration, but are usually not observed in the case of alite [37]. During the early stages of hydration, a thin layer of C-S-H gets deposited along the grain boundary, followed by the “hollowing out” (or dissolution) of the grain, leaving behind a hydrate shell. As the hydration reaction proceeds, these hollow shells gradually vanish after getting filled with the hydration products, but some of these hollow shells may remain unfilled even at later ages depending on the particle size of the initial anhydrous grain (<5 μm) [38]. However, a correlation between the grain size and the final fate of the Hadley grain (i.e. filled vs unfilled) could not be observed in the β-C_2S system. It is also interesting to observe that a significant number of the hollow shells remain unfilled in the β-C_2S system even after 28 days of hydration (DoH ≈ 69 %), whereas much fewer unfilled shells were seen in the C_3S system. These shells remain unfilled even after 60 days of hydration (Fig. 13). However, it has been recently shown that filling these hollow shells with hydrates such as

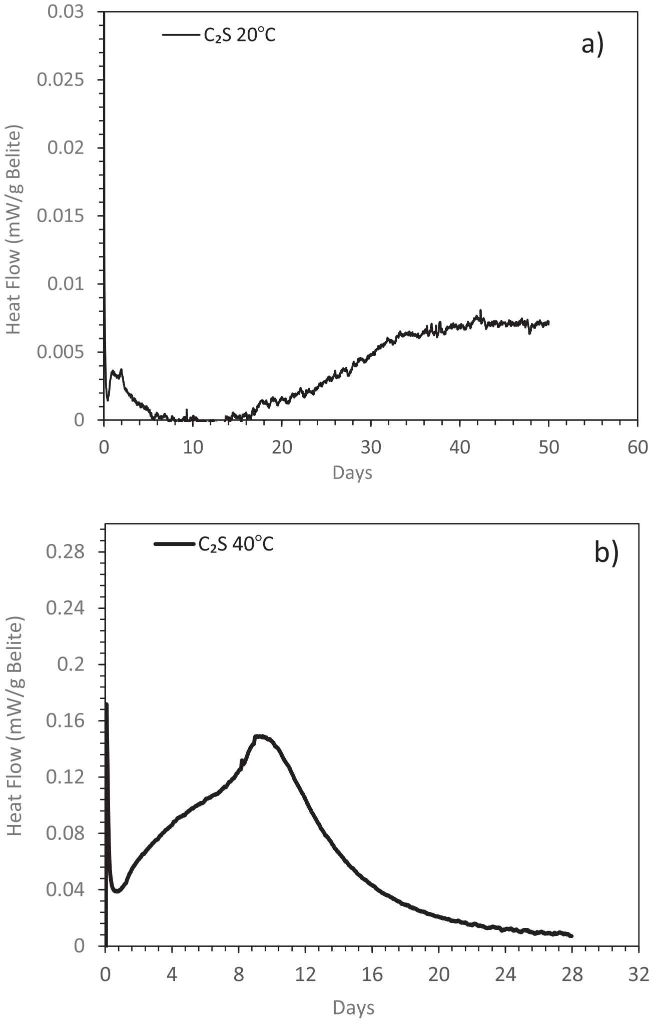

Fig. 7. Isothermal calorimetry curves for β-C_2S at (a) 20 °C (b) 40 °C.

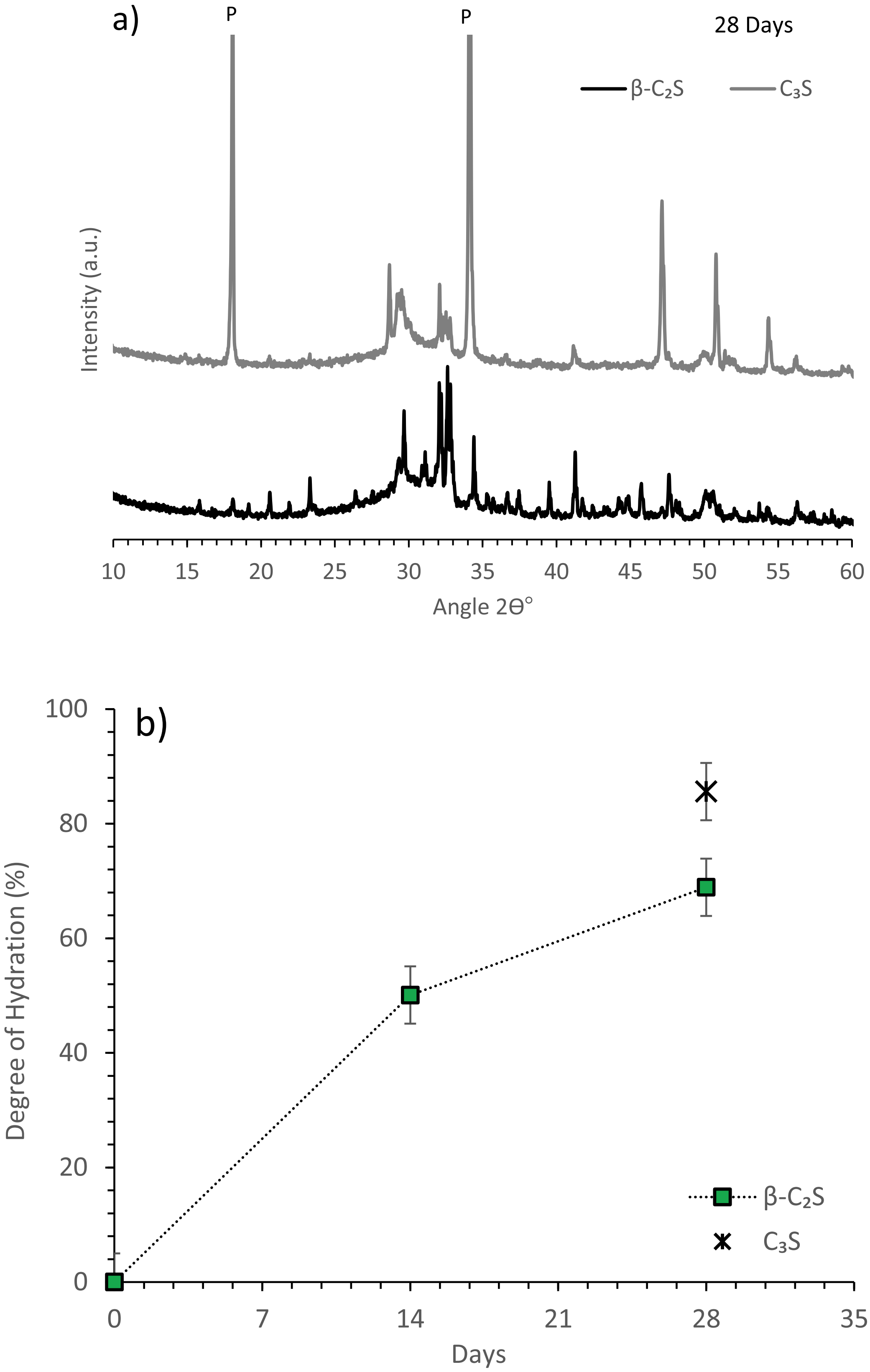

Fig. 8. a) The diffractograms of the 28 days hydrated β-C_2S and C_3S at 40 °C, b) The degree of hydration of β-C_2S and C_3S from QXRD estimated using Rietveld refinement.

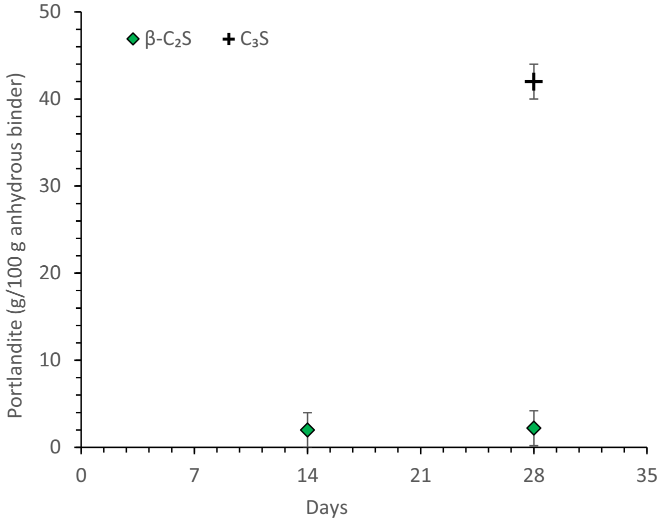

Fig. 9. The estimated amount of portlandite formed in the hydrated β-C_2S and C_3S systems from Rietveld refinement.

carboaluminates contributes significantly to the early-age strength and porosity refinement of blended cements [39]. Fibrous or needle-like growth of C-S-H from the C-S-H rims was also noticeable in the β-C_2S system (Figs. 12 and 13).

3.3.2. C-S-H composition

The SEM-EDS analysis results of the C-S-H formed from the hydration of β-C_2S at 14, 28 and 60 days are shown in Table 3. No significant variations in the Si/Ca and Al/Ca elemental ratios could be observed. Table 3 also shows the SEM-EDS analysis of the C-S-H formed from the hydration of C_3S after 28 days, which confirms that there is no noticeable difference in the composition of the C-S-H formed from the hydration of C_3S and C_2S.

The composition of the C-S-H formed in a paste sample containing 50 % C_3S and 50 % C_2S hydrated for 28 days at 40 °C was studied by EDS mapping. Fig. 14 shows a composite micrograph where the unreacted C_3S and belite grains are identified, along with portlandite and C-S-H. As observed, the same features typically observed in pure C_3S/alite pastes are observed. In agreement with the point analysis results (Table 3), a single cluster of C-S-H was identified with a uniform chemical composition. Clustered precipitation of portlandite was observed. Most of the unreacted alite grains are large. On the other hand, a significant amount of unreacted small belite grains is observable.

The results presented show that hydration of belite contributes to space filling in the same manner as alite, and the observed differences are then related to a difference in the reaction rate of these phases rather than a different morphology/distribution of the hydrates formed.

3.4. Influence of reactive alumina on C_2S hydration

Recent studies have suggested that the long-term hydration of belite appears to be retarded in blended cement systems containing reactive alumina [9,15,16]. Several hypotheses have been proposed to explain the apparent inhibition effect of aluminium on the silicate reaction. One possibility is that the alumina gets bound on the silicate surface, preventing further dissolution [40,41]. The pH of the system also appears to be critical in this regard. At higher pH values, the detrimental effect of Al ions on the silicate dissolution seems to reduce [42]. It has also been suggested that the formation of aluminium hydrates reduces the space available for the growth of C-S-H, resulting in an overall reduction of silicate hydration [43]. To verify this retardation effect of reactive alumina on pure β-C_2S, isothermal calorimetry experiments were carried out on two additional systems in which ground quartz (inert filler) and metakaolin were used to replace 30 % of β-C_2S, Fig. 15.

The calorimetry results appear to confirm the inhibiting effect of aluminosilicate pozzolans like calcined clays on the hydration of β-C_2S. Clear exothermic reactions were observed in the C_2S, and C_2S-quartz systems, whereas little to no reaction could be observed in the C_2S-metakaolin system. The system with 30 % quartz replacement shows a higher reactivity during the first week of hydration due to the filler effect. However, at later ages, this effect is less significant, indicating that

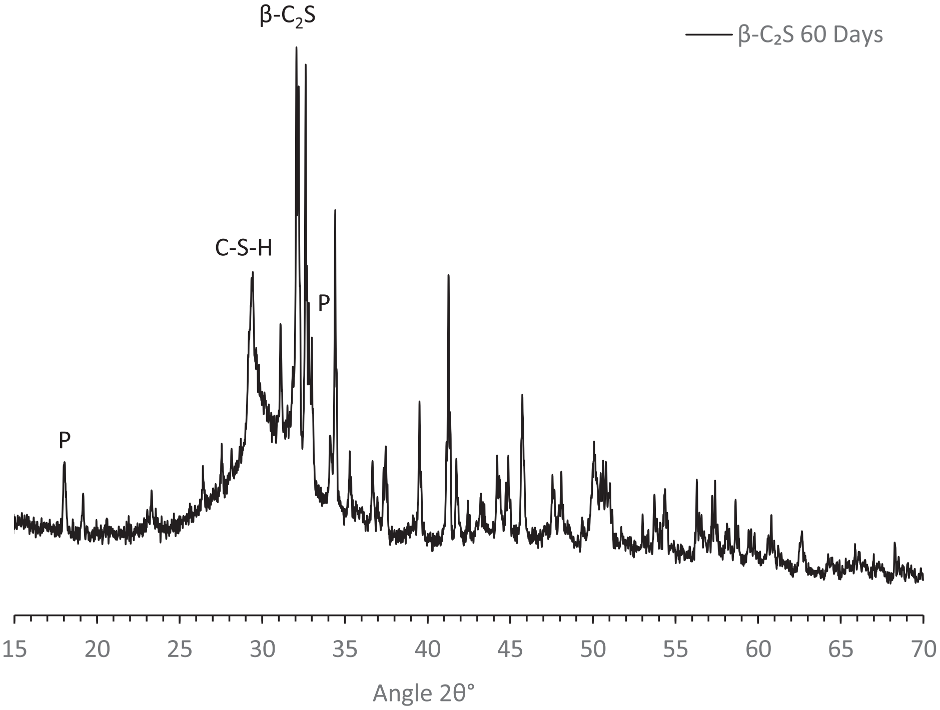

Fig. 10. The diffractogram of β-C_2S after 60 days. P – Portlandite, the amorphous band corresponding to C-S-H formation, is visible.

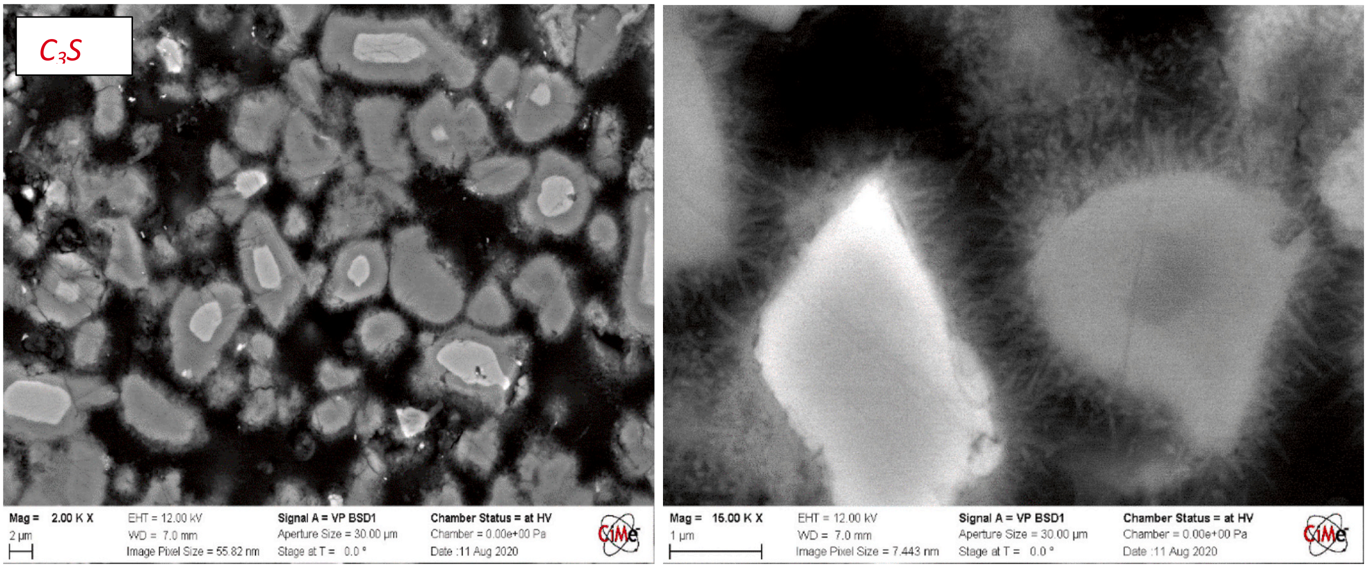

Fig. 11. SEM – BSE images of C_3S after 28 days of hydration.

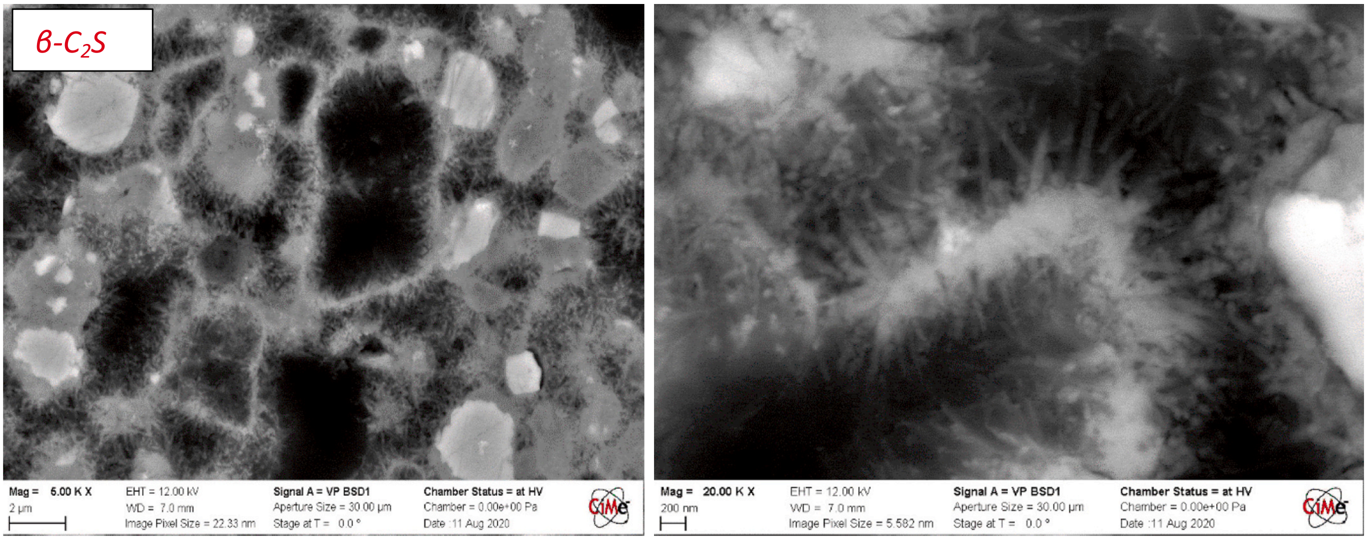

Fig. 12. SEM – BSE images of β-C_2S after 28 days of hydration.

kinetics are likely controlled by the reactivity of the belite itself. The long-term reduction in the hydration of belite in the presence of aluminium can result in lower DoH (and the expected consequences in strength and durability) of cements with high contents of this phase when blends incorporating reactive aluminosilicates such as metakaolin are designed. It is also interesting to note that since the hydration of belite is inhibited from the start, this inhibition may not be due to the consumption of CH by metakaolin and the reduction in pH that may result from this consumption.

4. Conclusions

In this paper, a methodology has been developed for producing β-C_2S (>96 % purity) at a laboratory scale. The hydration characteristics and the nature of the C-S-H formed from the hydration of the β-C_2S were investigated. From the results obtained, the following conclusions could be drawn:

- Selection of suitable dopants is important for producing high-purity belite, and preventing the formation of unwanted minor phases. The addition of the Al_2O_3 as a dopant resulted in the formation of C_3A in the clinker, which can potentially affect the reaction of belite. It is possible to produce belite using only K_2SO_4 as the dopant.
- The free lime formation during the synthesis could be controlled by varying the molar ratio between CaO and SiO_2 in the raw meal.
- The sintered β-C_2S showed low reactivity at 20 °C compared to the β-C_2S found in Portland cements.
- The C-S-H formed from C_3S, and β-C_2S were indistinguishable in terms of morphology and composition. This suggests that both minerals contribute to space-filling and strength development similarly.
- Persistence of hollow hydration shells or “Hadley grains” were observed during the hydration of β-C_2S even after 60 days of hydration.
- Reactive alumina from metakaolin appears to have a retardation/inhibiting effect on the hydration of pure belite as observed from the isothermal calorimetry results. This can have practical implications on the clinker reaction in blended cements containing aluminosilicate pozzolans.

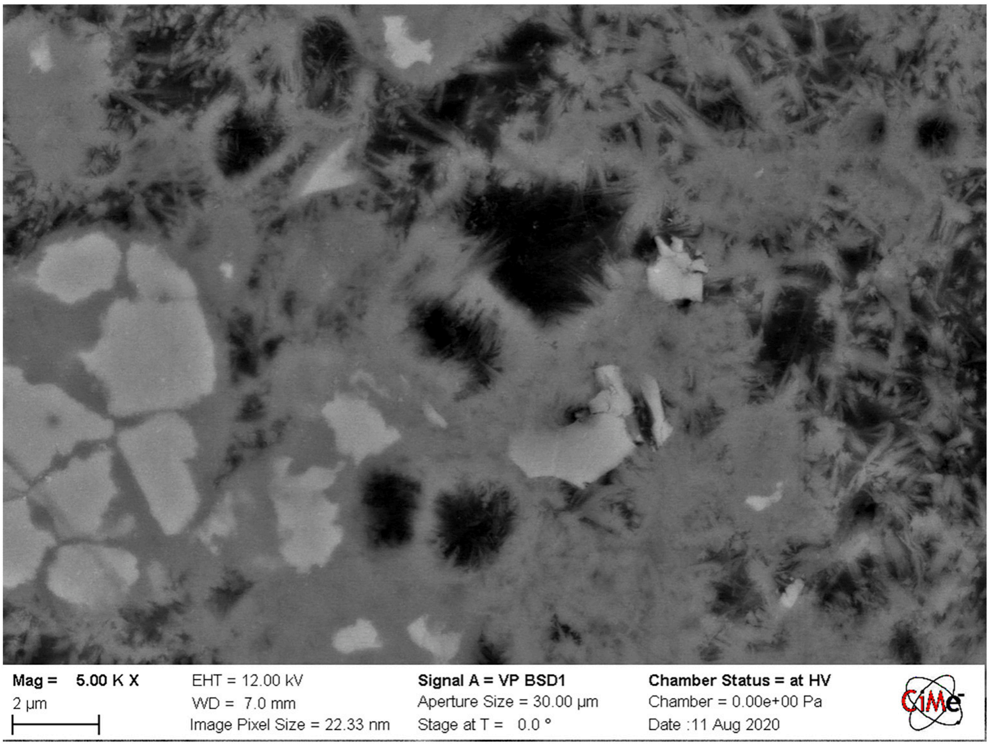

Fig. 13. The SEM – BSE image of β-C_2S after 60 days of hydration.

Table 3
The elemental ratios of the C-S-H formed estimated using SEM-EDS.

±0.015	Si/Ca	Ca/Si	Al/Ca
β-C_2S – 14 days	0.67	1.49	0.02
β-C_2S – 28 days	0.65	1.53	0.02
β-C_2S – 60 days	0.69	1.45	0.02
C_3S – 28 days	0.67	1.49	0.02

CRediT authorship contribution statement

Sreejith Krishnan: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Franco Zunino:** Investigation, Methodology, Writing – review & editing, Visualization. **Shashank Bishnoi:** Conceptualization, Writing – review & editing. **Karen Scrivener:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sreejith Krishnan reports financial support was provided by Federal Commission for Scholarships for Foreign Students (FCS). Editorial Advisory Board of Cement and Concrete Research - SB Honorary Editorial Board of Cement and Concrete Research – KS.

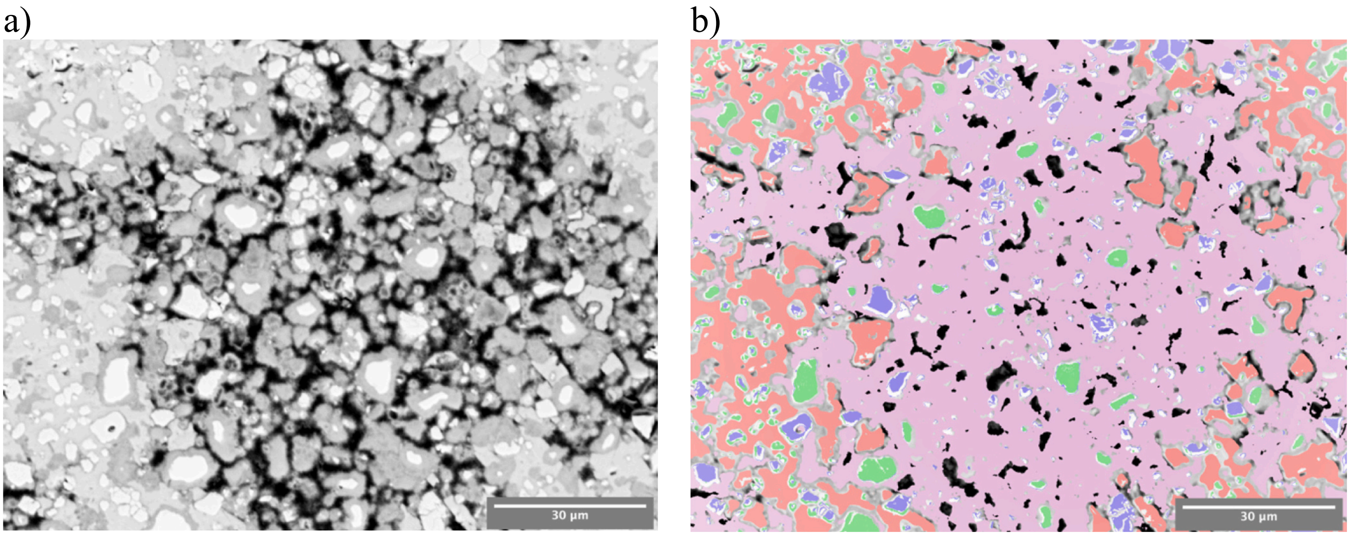

Fig. 14. BSE (a) and composite phase map (b) of a polished section of a 50/50 C_3S/C_2S paste sample hydrated for 28 days at 40 °C. C-S-H is shown in pink, CH in red, C_3S in green and C_2S in blue.

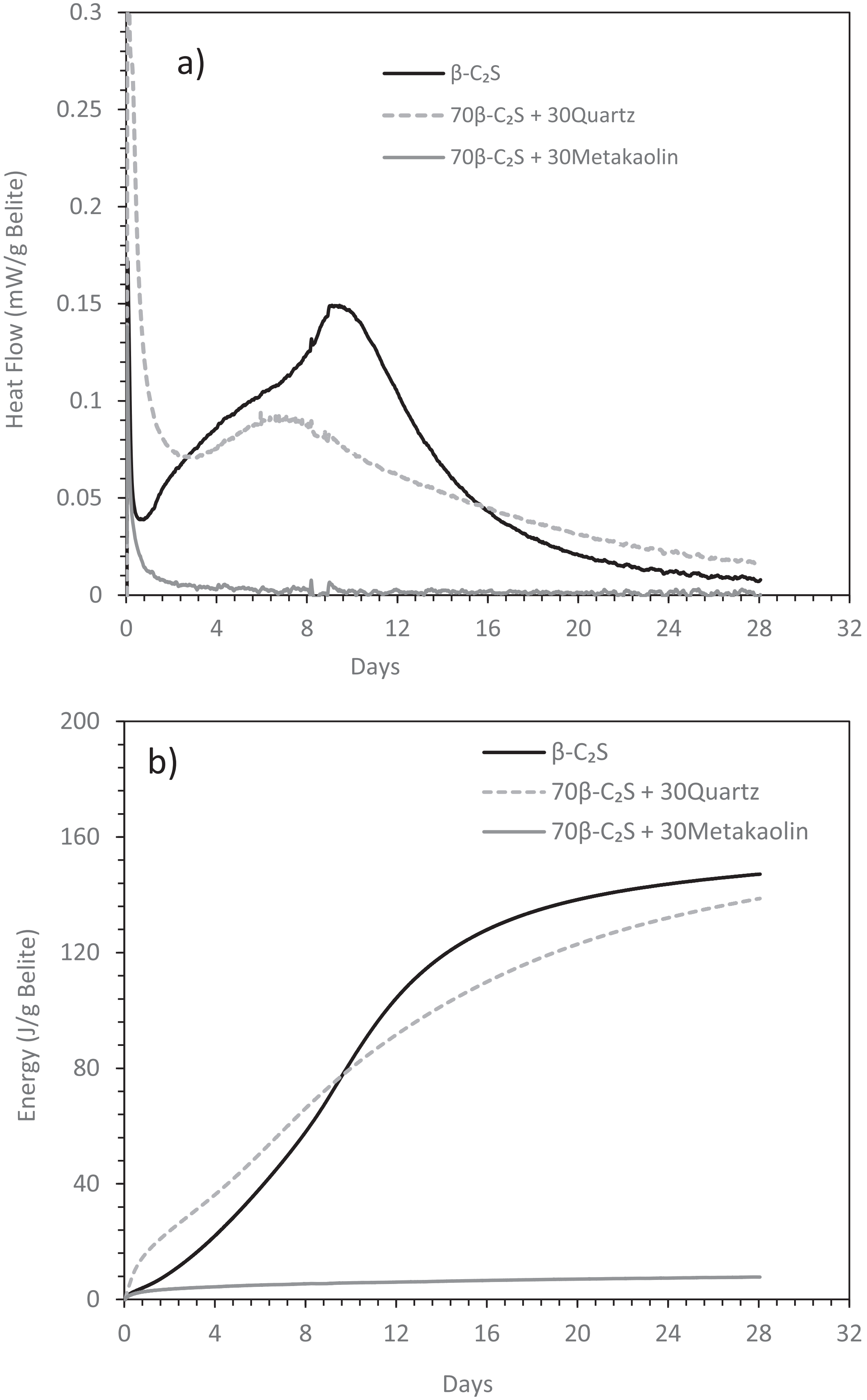

Fig. 15. Influence of metakaolin on the hydration of β-C_2S. A w/b ratio of 0.5 and PCE based superplasticiser were used to prepare the paste. a) Heat flow b) Total heat released.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cemconres.2023.107119.

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