Belite cements and their activation

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Abstract.

Belite cements, BCs, containing mainly belite, alite and calcium aluminates, are currently used as low heat cements. These binders produce high amounts of C–S–H gel and have very good durability properties which are reviewed. Additional advantages include: (i) lower limestone demand, with lower associated CO_2 emissions; (ii) lower energy demand; (iii) lower kiln operating temperature, which means lowering CO_2 and NO_x emissions from fuel burning; and (iv) lower temperature increase at early hydration age. However, early-age strength developments are not competitive with those of Portland cements. Hence, to improve their early-age strength developments is a research priority known as activation. This enhancement can be attained by three compatible approaches: (i) chemical, (ii) physical; and (iii) admixture activations. The current research status for BCs activation is reviewed including: cost-effective element substitutions to stabilize high-temperature forms; fast cooling, milling and mild temperature hydration as physical activation; and the use of C–S–H seeds as admixture activation. After discussion of the resulting microstructures, a research outlook is exercised.

Keywords: Sustainability; durability; CO2 footprint; Portland cement; active belite cements; dicalcium silicate activation; amorphous materials; polymorphism

1. Introduction: cement industry and sustainability.

Portland cements (PCs) world production is ~4 Gt/yr, viz. 4.6 Gt in 2015 [1], being the main product for the fabrication of mortars and concretes in the building industry [2]. PC production is expected to be 4–8 Gt/yr by 2100 depending upon the Shared Socioeconomic Pathways [3]. In spite of its ubiquitous usage, PC is a quite environmentally contentious material. On average, for every ton of Portland clinker produced, ~0.87 CO_2 tones are released to our atmosphere [4], that includes emissions from limestone decomposition and burning fuel. This translates into ~7% of the total anthropogenic CO_2 emissions [5].

Concrete, made from Portland cement, water, aggregates, additions and admixtures, is the most manufactured world product, 2.3 t/person/yr, or ~7 km^3/yr or ~18 Gt/yr [1]. The estimated world concrete stock is 315 Gt which currently results in 0.3 Gt/yr of concrete demolition waste (CDW) [6]. A new model [3] predicts a sharp increase of CDW to 20–40 Gt/yr by 2100, i.e. 100-fold. This could not be processed as aggregates within concrete as it will be more than two times the predicted need. This could be a second huge sustainability challenge.

CO_2 footprint reduction has been identified as a core need in the mitigation of the consequences of climate crisis [1,5,7,8]. Producing infrastructures with longer service life [9,10] would also contribute to overall CO_2 footprint decrease, as less cement will be needed, and it would also reduce the future production of CDW. For these endeavors, it will be needed (i) more durable cements with lower embodied carbon content, (ii) novel techniques to quantify short- and long-term hydration chemistry and meso- and micro- structure developments [11], and (iii) original data correlation tools [12] for better prediction(s). The remaining part of this contribution focuses on (i). The CO_2 footprint should be accounted from the embodied carbon content of every infrastructure as it does not help to decrease the CO_2 footprint of a cement if higher amounts are needed per cubic meter of concrete with given performances. Furthermore, in the future, the embodied carbon content should be averaged over the expected service life as again it does not help to produce infrastructures of lower embodied carbon content if they last less as it will result in more CDW in the future, plus the use of additional cement and resources.

Concrete production sustainability [13] has to be framed within the cement industry perspective. Codes of practice and cement standards [14,15] must be taken into account as this industry should ensure very long service lives, at least larger than a century. A recent work [1], identified clinker substitution [16,17] and concrete mixture proportioning [18] as the most favorable approaches for lowering embodied carbon content in concrete fabrication. In the next years, the use of supplementary cementitious materials (SCMs) is undoubtedly the strategy with the lowest economic and performance impacts [1,8,16,17,19]. Typical SCMs used by the cement industry are industrial by-products such as blast furnace slags, fly ashes and silica fume. The long term availability of the industrial by-products will decrease [17] as it is the case of fly ash in the United States and Europe today. Fig. 1 shows the average composition of globally produced cements including SCMs materials. It shows that the use of SCMs in the period 2010-2016 seems to be stagnated [8]. Here, limestone calcined clay cements, LC^3 [20], have a promising future as the availability of medium grade kaolinite-containing clays and limestone seems to be guaranteed. The approach of radically changing cement chemistry, for instance with calcium sulphoaluminate cements, Belite-Ye'elimite-Ferrite cements or alkaline activation [7,21–23] faces tremendous challenges for world-wide adoption mainly due to codes of practice, raw materials availability and costs.
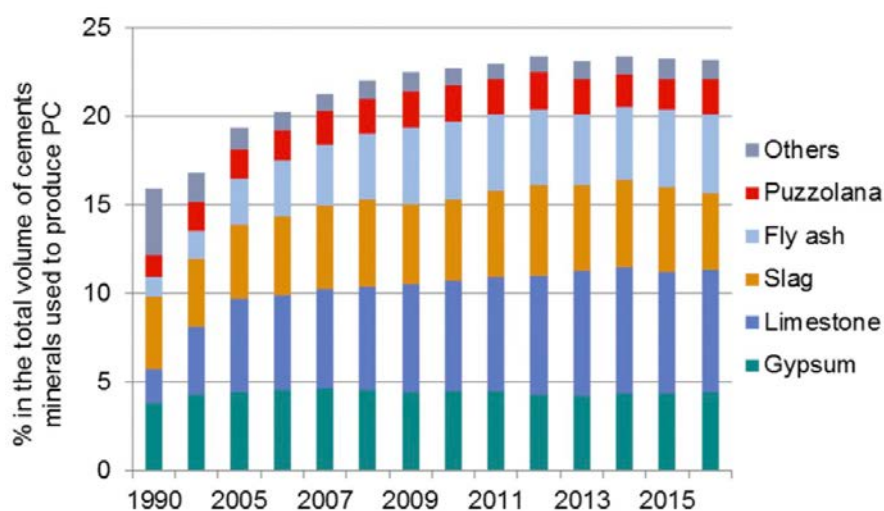

Figure 1. Global composition of cements. Reproduced from [8] with permission from Elsevier.

One way to make compatible the codes of practice with fabricating concretes with likely longer service lives and (slightly) lower CO_2 footprints, allowing also SCMs usage, consists in cements with main components similar to those of PC, but with lower limestone demand: **belite cements (BCs)**. There are many investigations dealing with belite binders containing high amount of ye'elimite. These binders are mainly ettringite-based and they are not reviewed here. This contribution focuses on ordinary and active, C–S–H gel-based, belite binders.

From a point of view of international standards, it can be highlighted that BC clinkers are covered by the existing European standard EN 197/1 as long as their chemical compositions comply with $SO_3 <$ 3.5% or 4% if $Cl^-<0.1\%$, and the mineralogical compositions with $C_2S + C_3S > 66$ wt%. Moreover, there are also standards in China: GB/T 200-2017, Japan: JIS R 5210-2014 and USA: ASTM C150 Type IV.

This paper reports an overview of recent developments of C–S–H gel-based BCs. The first part, section 2, provides a background of ordinary BCs including the advantages and drawbacks when compared to Portland cements. Some key differences in the hydration behavior of BCs and PCs are noted. Durability studies for BCs are also highlighted as this is another key motivation driver in addition to CO_2-footprint reduction. The second part, section 3, focused on single phase belite. After analyzing its polymorphism, the current theoretical studies are discussed. Then, its hydration characteristics are thoroughly treated and compared to those of much better studied, alite. In section 4, we cover belite activation and associated reactivity. Activation is defined as early-age hydration rate enhancement. Activation is being carried out through three different ways during clinkering and hydration stages: (i) chemical, (ii) physical; and (iii) by admixtures. Recent works for single phase and BCs activations are scrutinized. Then, section 5 deals with the microstructural characterization of these binders. Finally, sections 6 and 7 discuss future research needs and some conclusions, respectively.

2. Ordinary belite cements.

Commercial PCs are fabricated from clinker, obtained at 1450-1500 °C, grinded with the setting regulator and in many cases with inorganic addition(s): fillers and SCMs. Alite and belite, the two main clinker phases, are calcium silicate solid solutions based on, Ca_3SiO_5 (tricalcium silicate, simplified C_3S) and Ca_2SiO_4 (dicalcium silicate, simplified C_2S), respectively. Tricalcium aluminate ($Ca_3Al_2O_6$ or C_3A) and ferrite (Ca_2AlFeO_5 or C_4AF) are also generally present in PCs. A typical grey Portland clinker mineralogical composition is close to 65 wt% of C_3S, 10 wt% of C_2S, 15 wt% of C_4AF, 5 wt% of C_3A and ~5 wt% of other minor phases (lime, periclase, alkaline sulfates, etc.) with some regional variability.

One way to decrease the cement environmental CO_2 footprint and to increase its durability is to replace most of alite by belite, see for instance [5,13,24]. There are five main motivation drivers: (i) lower limestone demand with slightly lower associated CO_2 emissions; (ii) lower energy demand as the enthalpy of formation for alite and belite are ~1810 and ~1350 kJ/kg, respectively [25]; (iii) lower maximum kiln operating temperature, ~1200-1350°C, which means additional lowering CO_2 and NO_x emissions from burning and less demanding kiln liner maintenance; (iv) lower temperature increase at early hydration age and chemical shrinkage which minimizes thermal cracking; and (v) last but not least, longer service life, due to the relatively larger fraction of C–S–H gel per unit volume (or mass) of binder. However, there is currently one showstopper and two drawbacks: (i) the lower reactivity of ordinary belite with water results in slow early-age strength developments not meeting current standards (showstopper or a drawback depending upon the application); (ii) high-belite clinkers may require more grinding energy (drawback) [26]; and (iii) higher cooling velocities are likely needed which result in a slightly higher energy demand and higher investment [8]. One concern in the production of BCs is the use of alternative fuels. It is currently not known if the lower burning temperature will allow the massive use of alternative fuels as it is the case today for PCs. It should be pointed out that BCs have other advantages like: allowing the use of lower grade limestone and improving rheology features of the resulting mortars and concretes because the rounded size of belite particles and their lower early age reactivity when compared to that of alite [27]. However, it is acknowledged that workability of belite mortars can be quite variable depending on the burning conditions and cooling characteristics. The aluminate phases (C_3A and C_4AF) formed during belite clinker burning are characterised by relatively small crystal sizes and high porosities. C_3A is well known as a reactive phase at early hydration ages. Due to the higher surface of C_3A in industrial BCs,

its reactivity increases which may cause potential workability loss which would need to be corrected with admixtures.

For an overview of the BC development, production and characterization prior to 2000, the interested reader is addressed to the excellent ninth chapter "the production of low energy cements" [28], in the *Lea's Chemistry of Cement and Concrete* book, and some early reviews [24,29,30]. Belite clinkers usually contain low amounts of alite (10–30 wt%) and high amount of belite (40–60 wt%). The expected direct CO_2 footprint reduction of BC is modest, ~10-12%. A theoretical 9.5% decrease is obtained when comparing a PC mineralogical composition (C_3S, 80; C_2S, 5; C_3A, 5 and C_4AF 10 wt%) with a belite counterpart (C_2S, 80; C_3S, 5; C_3A, 5 and C_4AF 10 wt%) just from limestone decomposition. The expected decrease from lower kiln fuel consumption could be counterbalanced by higher demands in grinding and fast cooling. Therefore and chiefly, a move from PCs to BCs is justified if longer service lives can also be firmly proved (or if lower heat of hydration is required).

2.1. Industrial belite cements. Belite-based low heat cement (LHC) were used in Hoover Dam (finished in 1936), Grand Coulee dam (completed in 1942), and several other dams in the United States and Mexico to reduce the temperature rise of concrete. In these dams, LHC were used together with PC to guarantee the early strength of concrete. Since 1960s, PCs blended with fly ash started to be used to reduce the temperature rise of concrete. However, belite cements are being used nowadays, particularly in China, as they are one of the most effective methods to decrease the thermal stresses and cracking risk in very large structure including dam concrete. A very recent work [31] has reported long-term hydration heat of LHC binders, up to 360 days, as well as drying shrinkage, initial cracking times, cumulative pore volumes and compressive strength developments of four-graded concrete. This BC (44 wt% of C_2S and 30 wt% of C_3S) were mixed with fly ashes and their performances reported and compared to those of neat PC (63 wt% of C_3S and 11 wt% of C_2S) which was used as reference. Moreover, this type of ordinary industrial BC, mainly used for low heat applications, have been widely studied showing very good mechanical values at late ages and also very good durability performances [32]. Most of the reported industrial LHCs / BCs have a belite content close to 40-50 wt% and an alite content ranging 25-30 wt% to ensure relatively good early age mechanical performances [33]. Hereafter, the term ordinary/typical BC is used to distinguish them from active BC.

When comparing ordinary PCs and BCs, clearly, at early hydration ages, the compressive strength of PC surpass that of BC, see Fig. 2 [34]. However, it is equally evident that under similar hydration conditions and rheological properties of the initial fluid mass, the compressive strengths at late hydration ages, after about 100 days, of BCs are larger than those of PCs, see Fig. 2. The evolution of the strength development with hydrating temperature is also worth noting. Fig. 3 displays the compressive mechanical strength as function of time and temperature for two BCs (neat and blended) and two PCs [35]. It can be seen that higher temperatures accelerates the hydration of belite without yielding poorer mechanical performances, at least up to the reported hydration age, 28 days. The compressive strength for BC mortars at 28 days of hydration increased from 58 to 74 MPa, i.e. +28%, when the temperature increased from 20 to 70 °C. The corresponding values for PC mortars decreased from 58 to 46 MPa, or -21%. The mechanical strength measurements for specimens hydrated for 28 days at 60 °C indicated that the value for PC was 25% lower than that of BC. This intriguing result is backed by an earlier report [36] and it has been reproduced by the authors of this review, 23% for our two cements. This means that there is a profound difference between BCs and PCs hydration with temperature and its mechanistic explanation, including the microstructural differences, has still to be found. The tensile mechanical properties of concretes derived from BCs and PCs have been compared [37] for samples having the same w/c ratios but the rheological properties were not reported/compared. The mineralogical composition for BC was 53.0 wt% of C_2S, 24.7 wt% of C_3S, 3.3 wt% of C_3A and 15.7 wt% of C_4AF, and the corresponding one for PC was 52.4 wt% of C_3S, 24.5 wt% of C_2S, 8.4 wt% of C_3A and 10.4 wt% of C_4AF. The splitting and axial tensile strengths were reported at 28, 90 and 180 days of hydration. The tensile strength values were invariably larger for

BC concrete when compared with the PC one. Furthermore, the interfacial transition zones (ITZ) were also studied by microhardness measurements and scanning electron microscopy. The thickness of the ITZ for BC concrete was reported to be ~20 μm smaller than that of PC and the microhardness value of the BC concrete ITZ ~9 MPa harder. The origin of this difference is not currently known but it could be likely due to the larger fraction of C–S–H gel in the BC hydrated products.
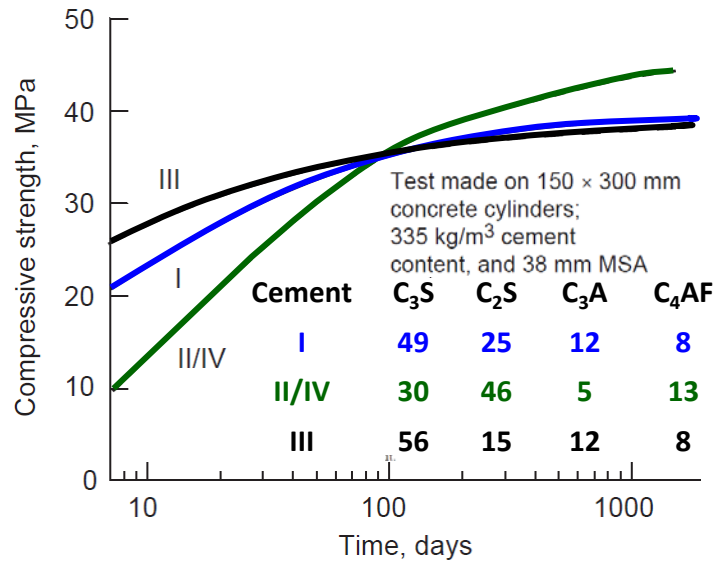

Figure 2. Compressive strength development with time for three concretes from cements with different phase assemblages. Adapted from [34] with permission from McGraw-Hill Education.
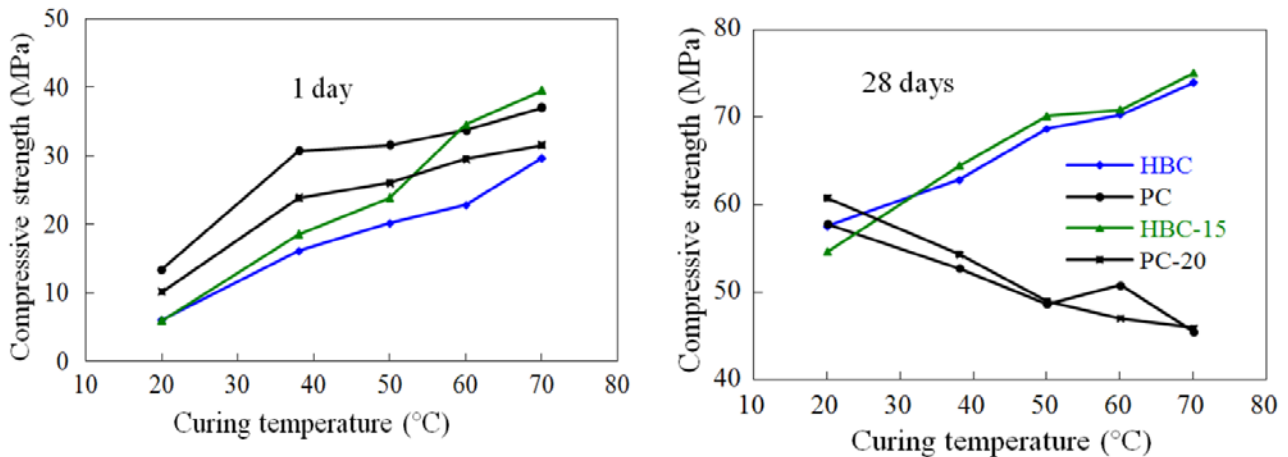

Figure 3. Compressive strength development as function of temperature for mortars fabricated from an industrial High Belite Cement (HBC) and a PC at 1 day (left panel) and at 28 days (right panel). HBC-15 and PC-20 stand for blends of HBC and PC with 15% of slag (Blaine value of 493 m^2/kg) and 20% of fly ash (Class I with Blaine value of 533 m^2/kg), respectively. Reproduced from reference [35] with permission from David Publishing Company.

Some interesting details concerning the early age hydration behaviors of commercial BCs have also been reported. The rheology of a BC was characterized by using different types of water reducer agents with water-to-cement (w/c) mass ratios ranging 0.30 to 0.36 [27]. The results were compared to those obtained for an ordinary PC. The BC displayed lower shear-thickening response regardless of the used admixture and the w/c ratio. However, this effect could also be partly due to the different C_3A contents, 7.0 and 3.0 wt% for PC and BC, respectively. C_3A consumes larger amount of water in the formation of ettringite. Thus, comparative studies are required where the C_3A content is similar and the main variable parameter is just the C_3S/C_2S ratio.

At this stage, three works dealing with the hydration of industrial BCs should be discussed. Firstly, the compressive strength results for a Low Heat Cement (~52 wt% of C_2S and ~30 wt% of C_3S) were

correlated to the bound water as determined by quasi-elastic neutron scattering between 15 hours and 7 days [38]. It was reported that the compressive strength of the mortars was directly proportional to bound water index in the studied period. Secondly, the hardening mechanisms and mechanical properties of a polymer-modified BC binder, produced by carbonation of an industrial BC (~51 wt% of C_2S and ~32 wt% of C_3S) has also been reported [39]. The resulting composite binders display much higher bending strength with an improved toughness by carbonation. Thirdly, it has been also shown that carbonation curing induces the dissolution of the belite phase into the pore solution and the crystallization of calcite in the pore solution saturated with CO_3^{2-} [40]. The polymorphism of the precipitated $CaCO_3$ was not studied, just the presence of calcite was established. This precipitating reaction is very effective to densify the microstructure improving the mechanical strength performances of the corresponding mortars as the compressive strength at 28 days increased from 57 to 98 MPa when comparing normal and 5% CO_2 curing, i.e. 72% increase. For the reference PC, the compressive strength at 28 days increased from 61 to 75 MPa, or +23%. This seems to be another important unexplained different behavior between BCs and PCs.

Durability performances of ordinary BCs are acknowledged as very good [2,34,41,42]. For instance, a recent study [43] has reported durability data for concretes prepared from a BC produced in an industrial scale trial project. The results for this BC (64.4 wt% of C_2S and 17.3 wt% of C_3S) were compared to that of a reference PC (62.1 wt% of C_3S and 17.9 wt% of C_2S). The concretes were designed to have 80 MPa at 28 days which was achieved with w/c ratio of 0.34 for both cements with moderate additions of fly ash, slag and silica fume (w/b mass ratio of 0.23). The results of standardized tests for compressive strength, drying shrinkage, creep, chloride ion penetration, carbonation, water penetration and freezing and thawing were reported. It was also reported that the drying shrinkage of this BC concrete was slightly higher than that of the PC concrete during the duration of the tests, 90 days. On the other hand and for the remaining assays, the belite concrete showed the same, or better, performances than the Portland counterpart.

BCs develop less water demand for normal consistency, slightly better compatibility with superplasticizer, lower drying shrinkage and excellent resistance to sulfate attack [35]. The compressive strength of a belite mortar reached 98 MPa at 180 days of hydration meanwhile the equivalent value for an ordinary Portland mortar was 77 MPa. Chemical corrosion resistance comparison between BC and PC was carried out using three corrosive media: (i) 5% of $MgCl_2$; (ii) 3% of Na_2SO_4; and (iii) artificial sea water with 3 times the concentration of ions of natural sea water. The bending strength results after 3 months indicated that BC exhibits better resistance to the corrosion for the three employed solutions. It is worth noting that for the sulfate 'attack', the bending strength increases, +8%, for the exposed belite-based binder, conversely to the Portland behavior where a drop, -56%, was measured. Durability studies of high-performance BC concretes were also published in a related paper [36]. The resistance to sulfate and chloride migratio of BC (53 wt% of C_2S and 25 wt% of C_3S) concretes were better than those of PC (52 wt% of C_3S and 25 wt% of C_2S) concretes studied under identical conditions. BC with 25 wt% of fly ash and w/s=0.32 showed a chloride permeability value 14% lower than that of the reference PC. Furthermore, both concretes showed very good resistance to freezing and thawing with air-entraining agents.

The long term durability, up to 180 days, of a BC mortar exposed to sulfate attack was studied at 40 ºC [44]. The flexural strength of the binder immersed in Na_2SO_4 solution doubled after 90 days, reaching values ~9 MPa; the reference samples (immersed in plain water) stayed approximately constant, ~5 MPa. Therefore, these BCs were tagged as resistant to the aggressive sulfate solution. The behavior of this BC was better than that of a reference PC in spite of its high Al_2O_3 content, 15.2 wt%. This was justified two-fold: (i) a small fraction of ettringite was detected in the sulfate exposed samples that it did not provoked expansion and it decreased porosity; and (ii) the sulfate exposed belite samples developed a white coat layer, powder diffraction showed that it was mainly composed by ettringite and calcite, which likely minimized further sulfate ingress. Unfortunately, it was not discussed the role of portlandite in this type of attack which has been shown to be important.

2.2. Laboratory belite cements. Several laboratory BCs have been prepared by specialized ways (combustion synthesis, hydrothermal methods, etc.) and they are not reviewed here. Selected studies reporting laboratory BCs prepared by high temperature firing and including hydration measurements are briefly described next. Firstly, five sources of inorganic wastes (oyster shell ash, rice husk ash, water-treatment-plant sludge, basic-oxygen-furnace slag and electroplating sludge) were employed as raw materials to fabricate laboratory BCs [45]. In a second example, ceramic waste was used as raw material by firing using the fluxing/mineralized pair $CaF_2/CaSO_4$ [46]. Furthermore, belite cements have been prepared at temperatures as low as 1100-1150 ℃ by using four mineralizers (2% NaF; 2% LiF; 1% NaF+1% $CaSO_4$; 1% LiF+1% $CaSO_4$) [47]. Moreover, two belite clinkers with no mineralization were also fabricated, one fast-cooled and another slow-cooled to contribute to the understanding of the cooling role on the hydration rate of belite cements. The compressive strengths of BCs with no mineralization were low even when cooled quickly. However, the use of mineralizers improved the belite reactivities as it stabilized high temperature forms with optimized (small) particle sizes. Compressive strengths at 7 days of hydration were 7, 13 and 23-26 MPa for slow-cooled, fast-cooled and several mineralized BCs, respectively. BCs have also been prepared from a number of alternative raw materials like natural zeolites [48] or agricultural waste ashes [49,50]. Finally, β-C_2S was prepared from lime sludge, a waste from the pulp and paper industry, and silica fume. This belite was mixed in different ratios with a reference PC to investigate the changes in performances of the resulting binders [51].

3. Dicalcium silicate.

3.1. Dicalcium silicate polymorphism. Stoichiometric Ca_2SiO_4 has a rich crystal chemistry with five crystalline phases described in the literature as function of temperature, see Fig. 4 [2,52]. Furthermore, the existence of a sixth crystalline phase, x-C_2S, has been reported from the thermal decomposition of α-C_2SH [53]. The crystal structure of this new phase was solved from synchrotron powder diffraction data [54]. It has been recently reported that x-C_2S hydrates very fast but slower than amorphous-C_2S [55]. This work reported the dehydration of α-C_2SH between 400 and 800 °C which led to a multiphase binder consisting of an amorphous dicalcium silicate, x-C_2S, γ-C_2S. Annealing α-C_2SH at 420 ℃ yielded the highest content of amorphous-C_2S.
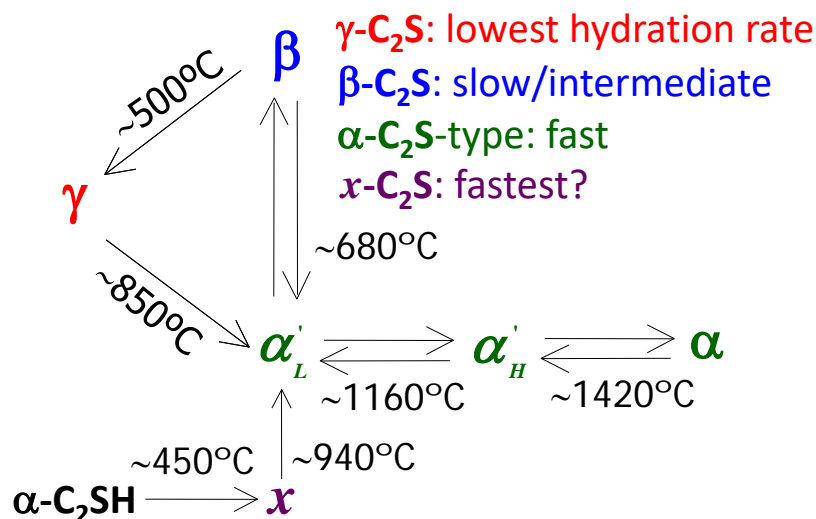

Figure 4. Polymorph relationships for stoichiometric Ca_2SiO_4. Amorphous Ca_2SiO_4 is not included. Qualitative hydration rate sequence is also shown. *Own elaboration.*

The hydration rates are different for the different polymorphs as γ-C_2S has the lowest hydration rate followed by β-C_2S. α-type-C_2S seems to have faster hydration kinetics and x-C_2S the fastest. However, very much care has to be exercised when comparing reactivities as there are a number of factors strongly affecting the dissolution rates including: i) particle size distribution, ii) surface defect

concentration and types, iii) element substitution used to stabilize the 'polymorph', iv) pH of the hydrating solution, and v) temperature of the hydration reaction.

The role of defects in general, and dislocations in particular, has been studied for different polymorphs of dicalcium silicates. Edge dislocations were studied experimentally by high-resolution transmission electron microscopy and computationally by simulation using the cluster embedded atom model [56]. The authors reported that γ-C_2S and α-C_2S polymorphs are the most favorable polymorphs for dislocations in belites. Etch pit formation, and hence early age hydration rate, mainly depends on the amount and properties of defects including density of dislocations. This work also reported that the dislocation core energies, for similar core radius of ~14 Å, were 0.18, 0.46 and 0.53 eV for γ-C_2S, β-C_2S and α_L-C_2S, respectively. Hence, it seems that dislocation core energy is more important than density of dislocations for early age hydration reactivity of belites. In this context, α-C_2S was found to be the most reactive and β-C_2S the most brittle polymorphs.

Finally, high-temperature belite forms can be (meta)stabilized at room temperature by elemental substitution, particle size management, fast cooling and combinations of these approaches. These works will be reviewed in fourth section, belite activation, as they improve belite hydration rate.

3.2. Theoretical studies. Belite polymorphism has been theoretically investigated upscale from the nanoscale using density functional calculations in atomistic models. Polymorphism of stoichiometric C_2S is studied at length in a recent publication for the five temperature-dependent polymorphs [57]. The order of stability in polymorphs is studied using the Gibbs-free energy, which takes into account entropy terms due to temperature. The temperature-stability between phases in our DFT calculations mostly agrees with the experiment reports. Using phonon dynamics data, it was found that the key polymorphs involved in water hydration, such as γ-, β- and α'_L- C_2S, have positive phonon frequencies indicating that the relaxed structures are indeed metastable structures. An important detail is that other polymorphs found at higher energies have imaginary frequencies indicating that either modulations can exist in bigger unit cells or different structures have to be considered, because they are doped to fix their high-temperature structures to perform X-ray experiments. Strain or pressure allows to stabilize some high temperature polymorphs like the β-C_2S as shown in Fig. 5 (a). This study [57] reported structural, electronic and phonon dynamics data, being a necessary (first) step to understand the behavior with water of relevant element-substituted C_2S, i.e. chemical activation. The relationship between belite polymorphs and the role of element substitution were studied by force field calculations and density functional theory (DFT) [58] and water reactivity was study using the idea of frontier orbitals as in previous works for other clinker components [59].

The structural relaxations provide information concerning bonds and reactive sites in the C_2S polymorphs [57]. The Si-O bonds remain nearly the same for all polymorphs while the largest changes correspond to Ca-O bonds and Ca-Ca interactions, which are deemed critical with respect to the hydraulic activity. The two Ca ions increase the number of coordinated O ions when going along γ-, α'_L-, and β- C_2S polymorphs. The existence of phases having over six Ca-O bonds indicates enhanced water reactive, i.e. with deviations from the octahedral value for Ca ions. Those are accompanied by an increase on the number of Ca-Ca units and a decrease in the average distance between Ca-Ca pairs in the β and α' polymorphs, about 0.1-0.25 Å shorter values, with respect to the γ phase. Further aspects have to be considered for the water dissolution of C_2S, such as the electronic description and kinetic issues on surfaces. First principles calculations were used to prove the relationship between the reactivity of calcium silicates and their electronic structures [60,61].
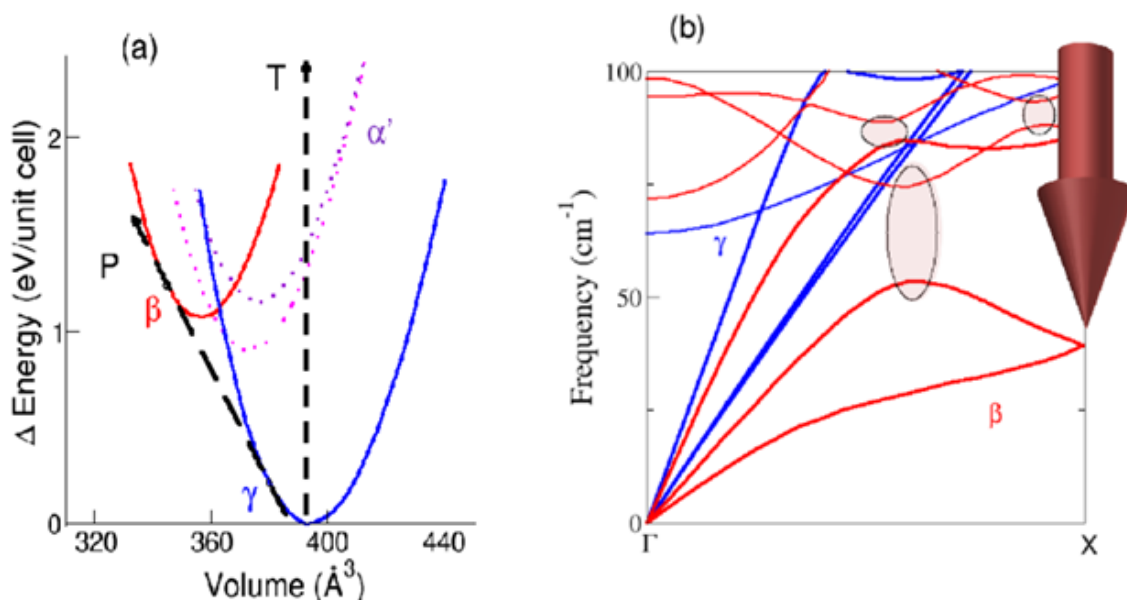
Figure 5. (a) Scheme of the energies between polymorphs using data from [57]. Note that C_2S polymorphs can be reached by temperature and pressure following a different order. (b) Phonon frequencies along (110) direction. There are large optical-acoustic couplings for the β polymorph indicating large structural softening near the zone edge, which are going to be chemically active with temperature and/or even light. *Own elaboration.*

Reactivity properties along the different crystalline directions change with temperature, and they can be linked to the elastic properties and phonons. The acoustic phonon energies along (110) direction have the smaller values for the polymorphs near the edge zone in reciprocal space. The differences between two polymorphs in the phonon spectra along (110) direction are shown in Fig. 5 (b). Phonon slopes in the limit of q~0 are related to sound velocities and lattice anisotropies. In this way, it is possible to explain the brittleness of β-C_2S mentioned above. More importantly, at long q values, phonon curves show not only a softening as in the β phase near the edge zone, but phonon frequencies are imaginary, especially for the α' polymorphs indicative of modulations. Furthermore, the coupling between optical and acoustic modes suggests that using light, it could be possible to locally induce the softening, a fact that has to be experimentally tested. It is noteworthy that deformations induced by surfaces and long q modulations can be behind the large water reactivity in the β and α' polymorphs at long hydration times.

Moreover, the role of selected C_2S surfaces for the onset in the water adsorption has been studied by computational tools [62–64]. Surfaces in water have to be considered explicitly when studying water reactivity. The orientation of surfaces can be an issue concerning water reactivity, for instance, a clear variable is the ratio between exposed areas of Ca ions and silica tetrahedra. Note that surface energies are not indicative because the bond saturation in liquids, or even air due to humidity, in any case takes place. The multiple configurations that a water molecule adopts on surfaces has been discussed in two ways: (i) repeating numerous adsorptions in a fine grid and starting from multiple configurations [64], and even more appropriated (ii) performing ab initio molecular dynamics simulations at room temperature [62]. The second approach has an added value because is the key to sample the energy landscape of the claimed ground state configurations, and additionally it can include temperature related effects. The basic physisorbed mechanism behind water saturation is that water molecules join the O atom with Ca^{2+} ions exposed at the surface, and a H atom makes a H-bond with an O ion from a silicate tetrahedron. Furthermore, there is a state with chemically dissociated water, in which the O ion in the near silica tetrahedron becomes protonated, and the Ca^{2+} ions get compensated with a hydroxyl group.

Although it is tempting to ascribe reactivity to water adsorption energies, it is necessary to go beyond the adsorption of a single water molecule and few layer coverage to understand the dissolution of

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belite polymorphs. On one hand, once water is dissociated, the proton exchange to other O in the tetrahedron, the process continues all the way to form $Si(OH)_4$ units in water [62]. On the other hand, the [OH] concentration is increasing near the Ca^{2+} ions so that they can get into the water solution. Hydroxylation and surface calcium leaching seems key to the hydration process of cement mineral components. When a large amount of OH groups are in solution, it is expected that Ca^{2+} ions would be released into the solution in contact with the mineral surface. Ca^{2+} ions relaxation several tenths of Å above the surface, when water coverage increases, can be considered an initial stage that can lead to leaching from surfaces [63]. Then, acid silicic tetrahedra get into solution at a lower rate. In solution, the $Si(OH)_4$ units suffer silica tetrahedra condensation to start forming C–S–H gel [65] aided by Ca^{2+} ions in a self-assembly process [66]. In other words, the exothermic condensation process of silica tetrahedra can happen already between the $Si(OH)_4$ units in solution or below the initial grain surface to form inner and outer C–S–H gels, respectively. A word of caution has to be given to all the atomistic simulations performed this far. Molecular dynamics results show that water is highly nanostructured around 15 Å above C–S–H surfaces [67] which can be the case of water on calcium silicates. Furthermore, C–S–H gel is a granular [68,69] mesoporous material made of nanoparticles with ~5 nm diameter size that pack to form several nanoporous structures difficult to simulate just starting from atoms. Other soft matter methods of simulations, such as kinetic Monte Carlo models [70], phase fields [71] and Brownian cluster dynamics [72], have to be used to dealt with large length and longtime scales in belite hydration, whose discussion is beyond the scope of this work.

Although there are many theoretical reports, an atomic deep understanding of belite water reactivity has not yet been achieved. High reactivity of C_3S is mainly due to its largely-ionic isolated oxygen atoms that act as the source of hydroxyl groups in solution at early times. C_2S does not contain isolated oxide anions but polymorphism [57,61,73] may improve the hydration rate because water attack is enhanced at low symmetric sites due to dislocations and modulations in undoped high temperature polymorphs.

3.3. Dicalcium silicate hydration. The heterogeneous calcium silicate hydration can be described by a set of processes including, but not restricted to, *dissolution, mass transport and precipitation/crystallization*. Additional involved processes, at constant temperature, are surface hydroxylation of the pristine solids and chemical speciation equilibria in (pore) solution. A key first process is the dissolution step, and a good knowledge of the dissolution kinetics is key for implementing computational models for cement hydration [74]. Dissolution kinetics of β-C_2S has been measured in pastes [75], ultra-diluted stirred powder suspensions [76] and on sintered and polished pellets [77].

From stirred ultra-diluted powder suspensions [76], the true experimental solubility products of triclinic-C_3S, monoclinic-C_2S and CaO were determined, being $K_{sp}= 9.6\cdot10^{-23}$, $4.3\cdot10^{-18}$ and $9.17\cdot10^{-6}$, respectively. Hence, it was possible to compare the free enthalpy of dissolution deduced from the dissolution rates with the values calculated from the free enthalpies of formation. The difference was huge for C_3S [56.8 vs. 125.7 kJmol^{-1}] and CaO [-27.8 vs. 28.8 kJmol^{-1}] and small for C_2S [95.7 vs. 99.2 kJmol^{-1}]. These discrepancies were explained by the formation of hydroxylated surfaces immediately after being in contact with water, which also explained the low experimental solubility products. Depending upon the experimental hydration conditions, the dissolution rates (flux) were determined to range between -74.0 and -114.7 μmolm^{-2}s^{-1} for C_3S and between -17.5 and -18.4 μmolm^{-2}s^{-1} for C_2S. Additionally, it was established that, in these bulk suspensions, the C_3S and C_2S dissolutions are congruent, see Fig. 6. Furthermore, C_3S and C_2S dissolutions in lime solutions were also measured, as it is known that the higher the $Ca(OH)_2$ concentration, the lower the calcium silicate dissolution initial rate. Fig. 7 displays the C_3S and C_2S dissolutions, expressed as the silicate concentration, as function of time for three lime concentrations. It can be seen that, under these conditions, the decrease of the dissolution rate with the calcium hydroxide concentration is more pronounced for C_2S than for C_3S. Finally, the energy for the opening of the etch pits was determined to be ~31 kJmol^{-1} both for triclinic C_3S and monoclinic C_2S.
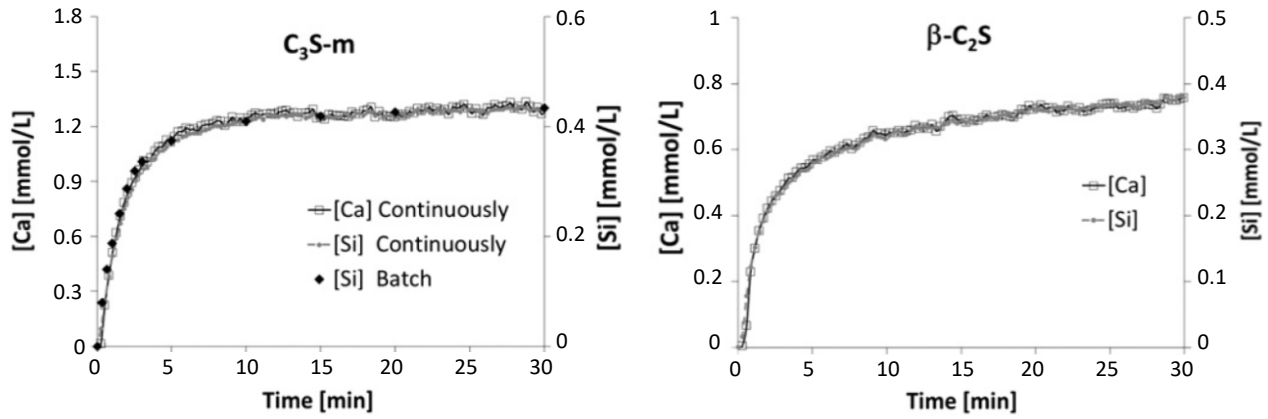
Figure 6. Evolution of Ca and Si concentrations during the dissolution of monoclinic C₃S and C₂S in distilled water (w/s=10⁴, stirring rate=500 rpm, T=25 °C). The Y-curves [Ca]=f(t) and [Si]=f(t) are superimposed, when properly scaled, to clearly show the congruent dissolution. Adapted from [76] with permission from Elsevier.
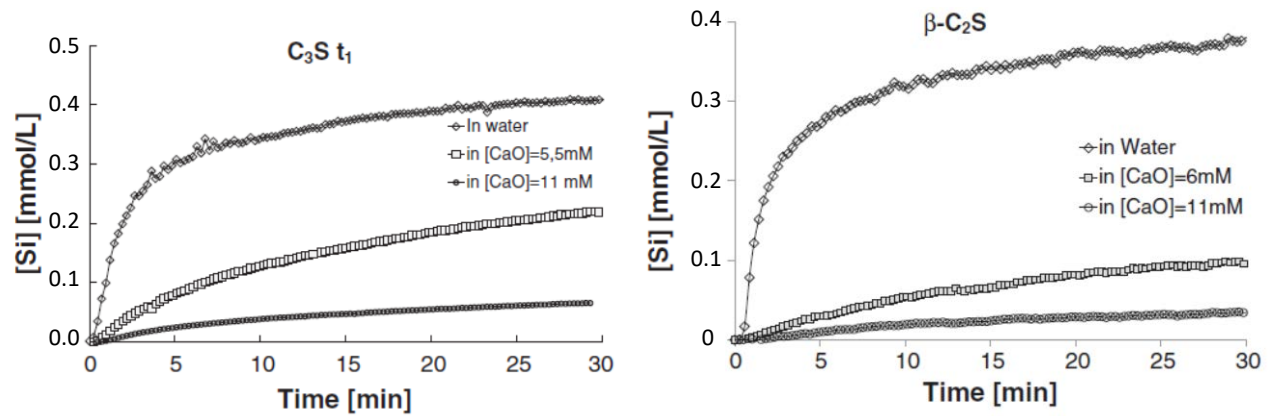

Figure 7. C₃S and C₂S dissolutions in different initial lime solutions as a function of time (w/s=10⁴, stirring rate=500 rpm). Adapted from [76] with permission from Elsevier.

The surface normal dissolution rate of a flat surface of β-C₂S has been very recently quantified using *in situ* digital holographic microscopy [77]. The determined macroscopic dissolution flux, −1.0 $\mu mol\,m^{-2}s^{-1}$, was about 20 times lower than the dissolution rates reported above, −18 $\mu mol\,m^{-2}s^{-1}$, for stirred powder suspensions. The observed (large) difference was justified based on the different microstructure of the specimens. Powders (composed of 3D microparticles) have more kink sources at corners and edges than a flat surface, and likely more defects for instance due to milling. Therefore, it is expected that microparticles will inherently dissolve more quickly than an equal area of a large two-dimensional surface. Because of this, it is also possible that two powders with the same average particle size may exhibit different *surface normalized* dissolution rates. This work also reported clear evidences of dissolution etch pits for β-C₂S, see Fig. 8. Furthermore, *ex situ* laboratory X-ray photoelectron spectroscopy indicates that the Ca/Si ratio at the surface of the β-C₂S specimen was lower than 2.0, i.e. 1.6 in agreement with a previous publication [78], and it decreases by 10% after exposure to flowing water solution for 30 min. Hence, the hydroxylate layer formed in contact with water seems to be (Si,Al)-rich with dimensions of a few nanometers. The β-C₂S used had the following stoichiometry, 2CaO-0.94SiO₂–0.03Al₂O₃, and the regions with greatest local dissolution fluxes, yielding deep and irregular etch pits, were aluminum rich which again highlights the role of defects in dissolution kinetics. Finally, we speculate that bulk β-C₂S congruent dissolution, see right panel of Fig. 6, could not necessarily be in contradiction with this depleted Ca-layer as very different volumes are interrogated in the two set of measurements. In bulk, β-C₂S dissolves congruently, within

the errors of the measurements, but at the nanoscale, there is a Ca-depleted dissolution layer. Spatially resolved measurements are needed to clarify the dissolution mechanism at the nanoscale.
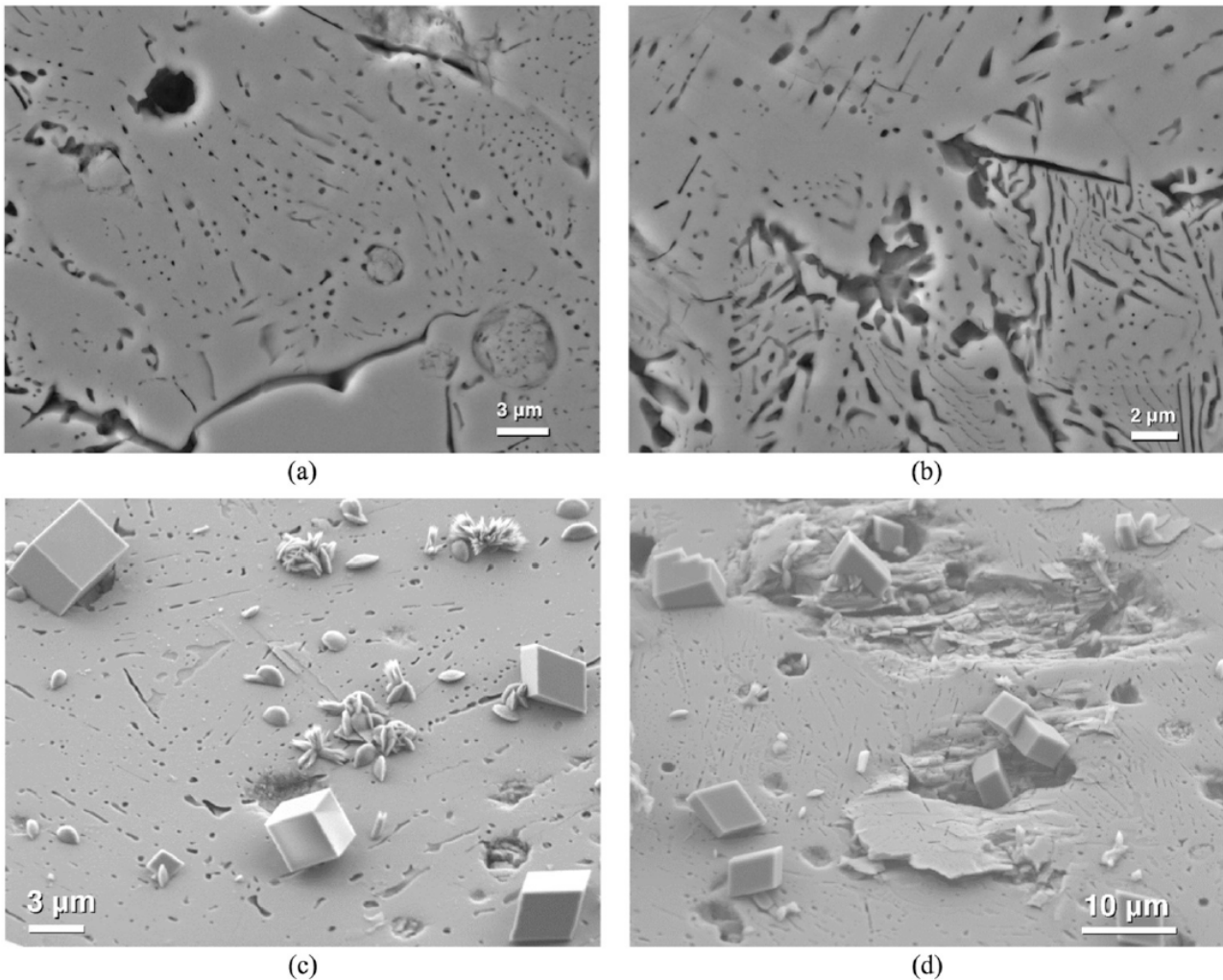

Figure 8. β-C$_2$S surface morphology under contact with water. (a,b) After 30 min water exposure, undersaturated conditions respect to C–S–H gel. (c,d) After a 30 min sessile drop of deionized water exposure, supersaturated conditions respect to C–S–H gel. Etch pits are clearly visible in all microphotographs, but there are precipitates only in supersaturated conditions. More details in the original publication. Reproduced from [77] with permission from Elsevier.

The dissolution of belite has also been studied at later ages, up to one year, in neat Portland binders and composite cements from thermodynamic analysis of pore solution data [79]. The analysis of the compiled pore solution data indicated that saturation indexes of belite decrease over the hydration time. For neat Portland cements, belite phase is supersaturated up to about 1 day of hydration showing that C$_2$S will probably not dissolve during that time. Subsequently, its saturation indexes decrease. Belite in slag-containing composite cements displays more negative saturation indexes which means that the pore solutions are more undersaturated with respect to belite. Furthermore, the belite reaction is usually retarded in blended cements when compared to the neat PCs. This can be, at least in part, justified because aluminate ions bind to (hydroxylated) calcium silicate surfaces and inhibit their dissolution [80]. However, these reactions are pH, and undersaturation, dependent and hence, belite reactivity can be relatively fast depending upon the local hydration conditions. Concerning the precipitation of C–S–H gel, the pore solution is invariably supersaturated respect to this phase. It was reported in [79] that at relative humidity of 100%, quite low supersaturation levels are needed to allow the precipitation of particles smaller than 10 nm given the reported values of interfacial energies. Crystallization pressure theory dictates that saturation indexes must increase if pore sizes decrease. It is highlighted here that the published values for C–S–H are 12 and 55 mJ/m^2 in these two publications

[81] and [82], respectively. Given the local heterogeneities in cement paste hydration including the presence or reaction rims, today, it is not known if the interfacial energy for C–S–H gel precipitated out of belite is similar to that formed from alite hydration. These type of time-dependent pore studies are needed for BCs and active BCs including a deeper study of the resulting C–S–H gel(s) and it is acknowledged that interfacial energy is not the only parameter at stake.

At this stage, it is important to compare the (heterogeneous) hydrations of alite and belite. The current most accepted hydration reactions are given in equations (1) and (2) for neat alite and belite, respectively. The densities for the different phases have been taken from [83] unless for C–S–H gel where the latest value for its density and water content is adopted here [84,85]. The chemical reaction for belite is much less studied than that of alite and current knowledge, in the absence of dedicated studies, accepts that the C–S–H gel composition and microstructure from belite does not differ too much from that of alite. Keeping in mind the simplifications taken in these chemical reactions (elemental substitutions in the phases which may slightly alter the compositions and densities are not considered), some valuable information can be drawn: (i) for the reported stoichiometries, full alite hydration requires a water-to-solid (w/s) mass ratio of 0.41, meanwhile belite seems to require w/s=0.44. This difference is small but not negligible and it would mean that the standard w/s employed ratio, 0.50, will lead to (slightly) lower residual porosities in belite pastes or mortars; (ii) the theoretical chemical shrinkage, which slightly depends upon the calcium silicate densities (polymorphism) and C–S–H micrometer density (which itself slightly depends on the w/c ratio used, through the gel water content), is smaller for belite than for alite; and (iii) a fully hydrated alite paste contains 72.5 vol% of C–S–H gel and 27.5 vol% of portlandite, meanwhile, the corresponding belite paste has 94.4 vol% of C–S–H gel and 5.6 vol% of portlandite. Qualitatively, the "ultimate strength" (i.e. strength at a time allowing full hydration) of belite should be higher than that of alite as it develops less calcium hydroxide which mainly acts as a diluent.
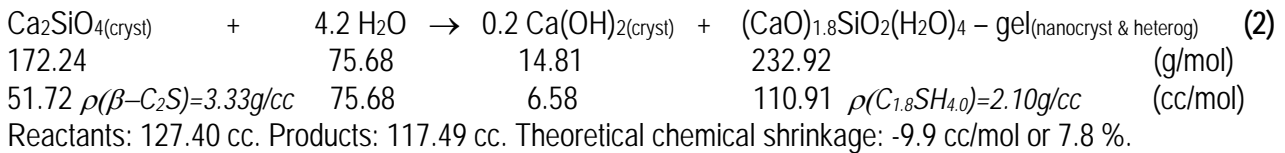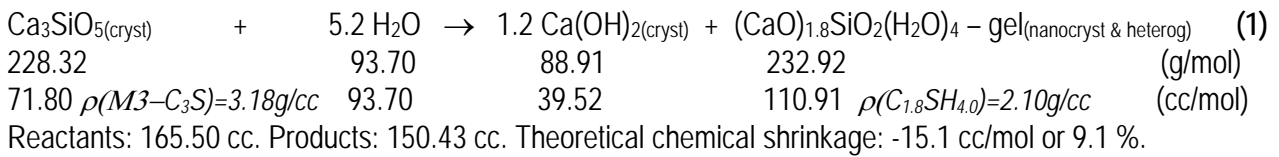
$$Ca_3SiO_{5(cryst)} + 5.2\,H_2O \rightarrow 1.2\,Ca(OH)_{2(cryst)} + (CaO)_{1.8}SiO_2(H_2O)_4 - gel_{(nanocryst\ \&\ heterog)} \quad (1)$$

228.32   93.70   88.91   232.92   (g/mol)

71.80 $\rho(M3–C_3S)=3.18g/cc$ 93.70   39.52   110.91 $\rho(C_{1.8}SH_{4.0})=2.10g/cc$ (cc/mol)

Reactants: 165.50 cc. Products: 150.43 cc. Theoretical chemical shrinkage: -15.1 cc/mol or 9.1 %.

$$Ca_2SiO_{4(cryst)} + 4.2\,H_2O \rightarrow 0.2\,Ca(OH)_{2(cryst)} + (CaO)_{1.8}SiO_2(H_2O)_4 - gel_{(nanocryst\ \&\ heterog)} \quad (2)$$

172.24   75.68   14.81   232.92   (g/mol)

51.72 $\rho(\beta–C_2S)=3.33g/cc$ 75.68   6.58   110.91 $\rho(C_{1.8}SH_{4.0})=2.10g/cc$ (cc/mol)

Reactants: 127.40 cc. Products: 117.49 cc. Theoretical chemical shrinkage: -9.9 cc/mol or 7.8 %.

Fig. 9a displays the compressive strength development of alite and belite pastes [86]. Clearly, the rate of hydration of C_3S is faster than that of C_2S. Unfortunately, this work did not report the compressive strengths close to full hydration. Fig. 9b shows the evolution of the compressive strengths for the two samples as a function of the gel-space ratio descriptor. It is evident that the C_2S paste exhibits a significantly higher compressive strength than the C_3S paste for the same gel–space ratio. This behavior can be justified because, for the same gel–space ratio, the C_2S paste contained a larger amount of C–S–H gel, highlighting that all hydrates do not equally contribute to compressive strength, which can also be derived from the ultimate compressive strength values of alite and belite, see Fig. 10. The degree of reaction at comparable strength was not directly reported in [86] but this information can be extracted from the graphics. At 14 and 28 days, the C_3S pastes developed a compressive strength of 63 and 74 MPa, respectively. The C_3S reaction degrees at these ages were 74 and 80%, respectively. At 9 months of hydration, a similar C_2S paste developed 69 MPa for a 71% degree of reaction.
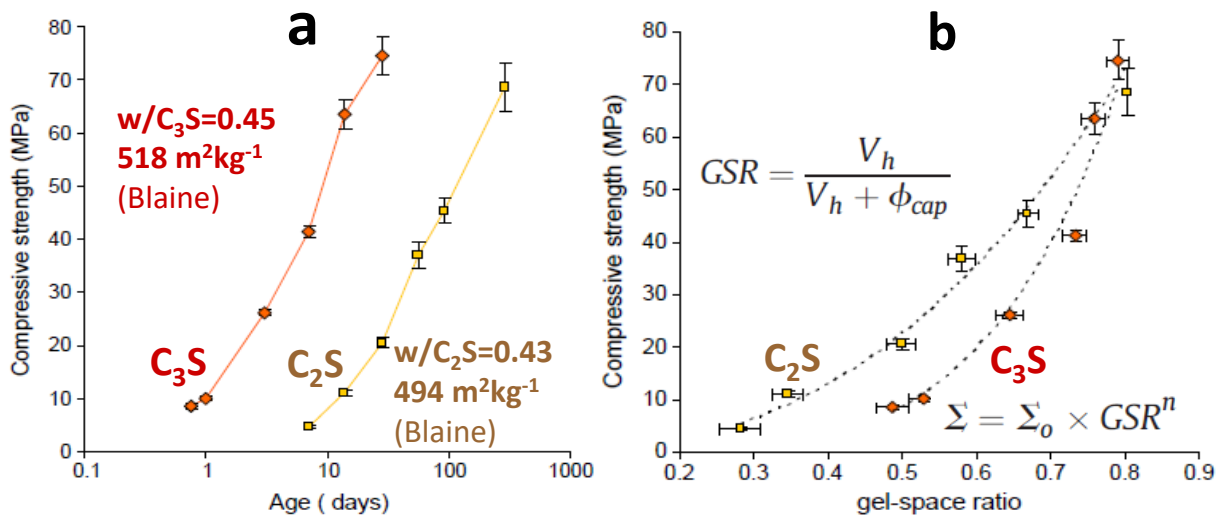
Figure 9. (a) Compressive strength development for C₃S and non-active C₂S. (b) Compressive strength vs. gel-space ratio descriptor for C₃S and C₂S. Adapted from [86] with permission from Elsevier.
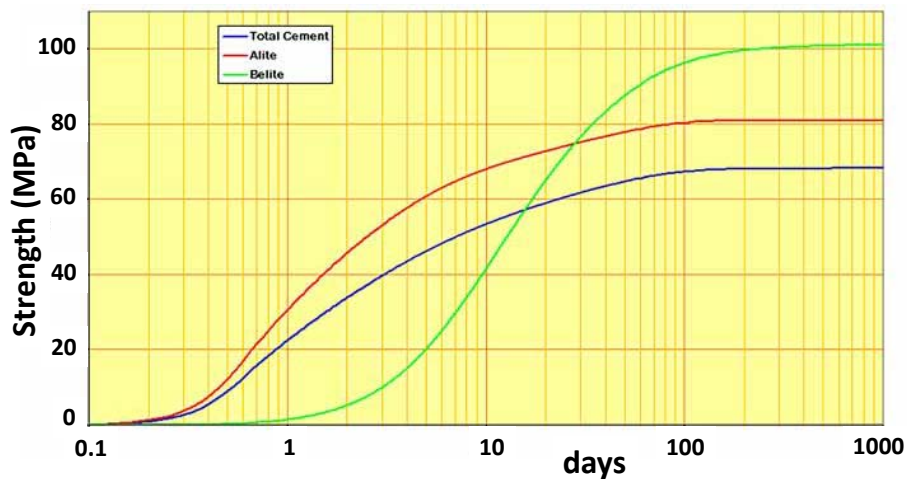
In figure 9b the equations shown are:

$$GSR = \frac{V_h}{V_h + \phi_{cap}}$$

$$\Sigma = \Sigma_o \times GSR^n$$

Figure 10. Qualitative apparent mortar compressive strength development of calcium silicates including "ultimate strength" (final strength after full hydration and before any degradation): alite (red); belite (green); typical Portland cement (blue). Reproduced from www.cementkilns.co.uk (Dylan Moore) with permission.

4. Belite activation and associated reactivity.

It is difficult to extract conclusive information about hydration performances from publications dealing with belite clinkers as there is an interplay between (at least): mineralogical composition; cooling rate; fineness; element substitutions; w/c ratio and hydration temperature. Hence, full experimental information should be provided in the publications to be able to incorporate the local findings within a global landscape. There is a hope that simulation and correlation tools [12] will be helpful here but again this will be only possible if complete sets of information are provided. This section intends to contribute to the knowledge of these relationships and to report the current status, but the situation, as of today, is far from a good understanding.

Belite reactivity can be improved by three compatible approaches: (i) chemical, (ii) physical; and (iii) admixture activations which are discussed next for single phase studies. The reductionist approach is problematic in cement sciences as hydration reactions affect to each other. Hence, it is currently difficult to predict the hydration behavior of a mixture from the studies of the isolated hydration reactions although thermodynamic modelling is helping a lot for well established, thoroughly-studied,

systems [87,88]. Therefore, it is also very important to research the hydration behavior of active, large-scale prepared, BCs.

4.1. Stabilization of high-temperature belite polymorphs. High-temperature belite polymorph stabilization is usually associated with higher reactivity and therefore with activation. However, the hydration kinetics can strongly vary and therefore hydration studies, not always reported, are needed to ensure the activation degree which has taken place. The high-temperature forms of dicalcium silicate can be (meta)stabilized at room temperature by element-substitution. It is appropriated to note that these forms should not be strictly termed as polymorphs because the chemical compositions differ. There are reports about faster hydration by some elemental substitution. Old reports were reviewed in [24] and the main findings were: (i) B_2O_3-doping at 0.5 wt% seems to be as effective as K_2O-substitution at 1 wt%; (ii) Fe_2O_3 and Cr_2O_3 may slightly increase reactivity; and (iii) SO_3 is clearly an activator of belite but its overall role, in cements, is difficult to stablish because it also destabilizes alite in clinkers.

Next, it is reviewed works dealing with cost-effective, not severely toxic, elemental substitutions in belite. There are many reports dealing with exotic dopings, with very little relevance for large-scale BC development, and therefore they are not discussed/reviewed here. β-C_2S (in some cases coexisting with α'-C_2S) was stabilized by Al^{3+}, B^{3+}, P^{5+}, Fe^{3+}, S^{6+} and K^+ substitutions [89]. The employed synthetic method was the Pechini process that consists of the formation of a chelate between the cations and citric acid and ethylene glycol. After the polyesterification process, the resulting resin is calcined at relatively low temperatures which leads to the formation of a powder with a very small average particle size. However, particle size distributions and specific surface areas were not reported which are key to understand hydration rates at early ages. In any case and under the reported hydration conditions, for instance w/c=2.0, some samples showed 100% hydration degree at 28 days. Another work focused on SO_3 doping, up to 4 wt% in SO_3, resulted in β-C_2S stabilization [90]. The resulting solids, obtained by firing at 1350 ºC for 4 h, were characterized by X-ray powder diffraction, infrared radiation and scanning electron microscopy. BaO and MgO independent substitutions seem to stabilized a mixture of α'-C_2S and β-C_2S.

Boron is known to (meta)stabilize high temperature forms of belite at room temperature. The solid solution mechanisms were established for boron and sodium/boron coupled substitutions [91]. For B-doping, it was shown that β-C_2S and α'-C_2S forms were stabilized by the substitution of silicate groups by tetrahedral borate groups with the concomitant substitution of calcium by boron for charge compensation, $Ca_{2-x}B_x(SiO_4)_{1-x}(BO_4)_x$. For B/Na coupled doping, for instance using borax, the study showed that α'-C_2S was stabilized by the following mechanism, $Ca_{2-x}Na_x(SiO_4)_{1-x}(BO_3)_x$, where x may reach values as high as 0.25. Aluminum incorporation in dicalcium silicate has also been studied [92]. A relatively small substitutional range was reported, $Ca_2Si_{0.972}Al_{0.028}O_{3.986}\square_{0.014}$, which stabilized β-C_2S.

To end this section is worth highlighting two studies. One was centered on the role of element substitutions (B, P and S) on the stabilization of β-Ca_2S at RT [93]. The mechanisms of polymorph stabilization were extensively studied by electron microscopies. It was concluded that these elements incorporations produced C_2S lattice parameters modifications and they also induced specific twinning morphologies and surface relief, as well as grain boundaries deformations. However, the hydration characteristics of the resulting solids were not researched. The second work focused on the stabilization of dicalcium silicate forms by micron- and nano-size TiO_2 and MgO oxides [94]. The study showed that nano-sized TiO_2 was more effective stabilizing β-C_2S than micro-sized TiO_2, even when the samples were fired at 1450 ºC for 1 h. This result indicates that diffusion is one of the limiting steps for highly charged activators.

4.2. Belite single phase physical activation. Three main parameters are involved here: cooling rate, milling and hydrating temperature. The first two processes are intended to decrease the average particle sizes and/or to introduce defects. The third process increases reactivity by adding energy to

the system. There is consensus in belite reactivity upswing by rapid cooling. The influence of the cooling rate on the C_2S transitions was extensively studied [95]. Mechanical activation through high-energy milling has been reported for γ-C_2S [96]. Although the hydraulic properties of pristine γ-C_2S were negligible, milling resulted in smaller particle sizes and the development of a large amount of an amorphous component with hydrating behavior. In fact, the activated sample developed 55 J/g of cumulative heat release after 30 hours which indicates an hydration degree close to 20%, under the approximation of considering 262 J/g for its hydration enthalpy [2].

On the other hand, the hydrating temperature plays a very important role in the acceleration of the reactivity of belite. Fig. 11 reports the calorimetric study of four β-belite samples [97]. Two belites were prepared by the standard high-temperature ceramic approach which yielded low reactivities at room temperature but that they were very much enhanced at relatively higher temperatures, see Fig. 11a. Two additional highly-reactive belites were prepared by the Pechini approach and the degree of reaction at one day varied from 8-15% at 30 ºC to 50-90% at 85 ºC, see Fig. 11c and d. This work reported the activation energies for hydration of typical and highly reactive β-C_2S pastes from the calorimetric study. The measured activation energies were 32 and 55 kJmol^{-1}, respectively. This large difference likely indicates a change in the rate-controlling step for hydration from dissolution-limited to nucleation and growth-limited.
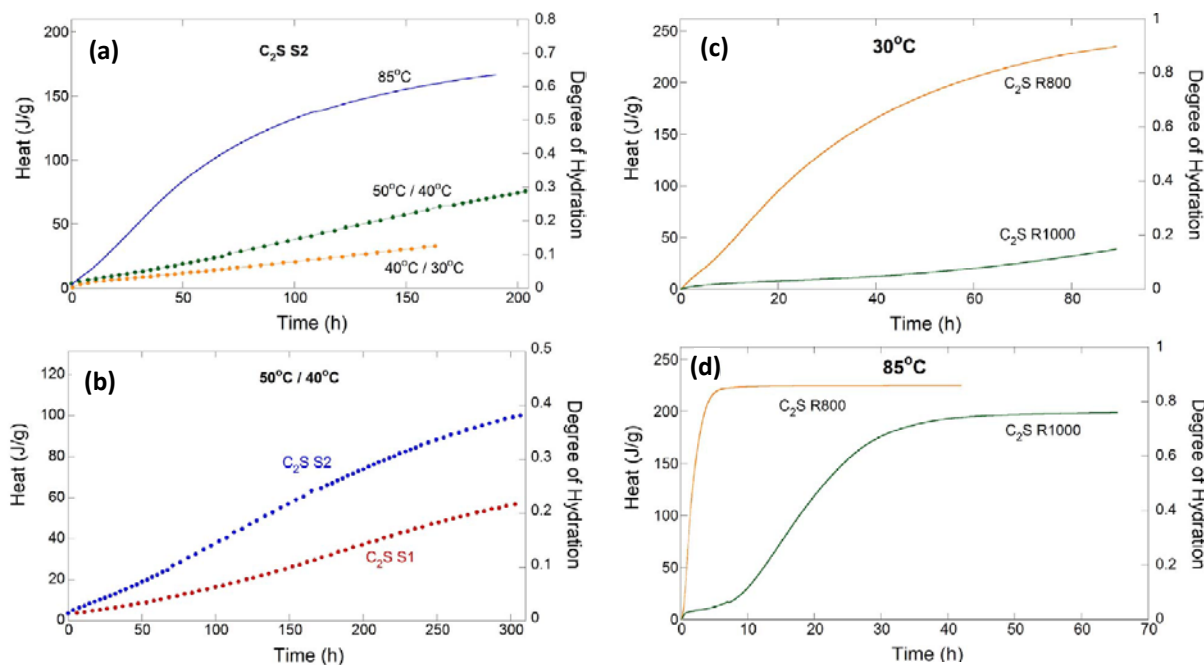

Figure 11. Cumulative heat (left axis) and corresponding degree of hydration (right axis) for neat pastes made with typical β-C_2S powder (a and b panels) and two reactive β-C_2S powders (c and d panels). S1 and S2 stand for typical β-C_2S samples obtained by high temperature firing and grinded to two different particle sizes. S1 passed a 100 mesh (maximum size 100 μm) and S2 passed a 325 mesh (maximum size 45 μm). C_2S R800 and C_2S R1000 highly-reactive belites were prepared by Pechini process and they had BET surface areas of 26.5 and 8.3 m^{2}g^{-1}, respectively. Dual temperature runs indicate hydration with temperature alternating between the two values. Adapted from reference [97] with permission from Elsevier.

4.3. Belite single phase admixture activation. Calcium silicate hydration can also be accelerated by seeding with calcium silicate hydrates which has been recently reviewed [98]. Alite hydration has been accelerated by a number of seedings including amorphous C–S–H gels or crystalline afwillite [99]. The seeding effect by C–S–H gel has also been tested for β-belite with positive results [97].

In addition to seeding, admixture activation can be carried out by alkaline means. For instance, γ-C_2S, which is hydraulically almost inactive with water, has shown to have a reaction degree larger than 90% at 56 days when hydrated with w/s=1.0 in the presence of 10% Na$_2$O activators (in the form of

Na_2CO_3, Na_2SiO_3, and $NaHCO_3$) [100]. β-C_2S hydration has also been accelerated in the presence of 8-*M* NaOH, 4 wt% Na_2CO_3 and 4 wt% Na_2SO_4 with w/s=0.3 [101,102]. In these studies, reaction degrees close to 80% were measured at 28 days.

4.4. Laboratory-scale belite cement activation.

4.4.1. Belite clinker activation. BCs reactivity is enhanced by rapid cooling, see [103]. The main element dopings reported for activating belite within clinkers in the last two decades are summarized next: Na_2O-K_2O [89,104–106], SO_3 [89,90,104,107,108] and B_2O_3 [91,109–112]. The belite formation was analyzed *in-situ* by high-energy synchrotron powder diffraction with raw meals in Pt tubes heated up to 1400ºC [113,114]. Most of the works dealing with clinker activation reported the phase assemblage and the hydration behavior but not mechanical/durability data as large amounts of material are needed. It is worth to note here the key work dealing with laboratory activation of belite clinkers by sulfates [115]. In that work, six kilograms of each belite clinker activated with increasing contents of SO_3, from 4 to 8 wt% of SO_3, were produced. Lime saturation factors ranged between 75 and 97 without SO_3 and between 85 and 90 for clinkers containing 4 wt% of SO_3. Many clinkers were described and the compressive strengths of the resulting binders reported. Here, it is highlighted the results for one clinker displaying very competitive properties. For a lime saturation factor of 85 and 4 wt% of SO_3, the clinker had 67 wt% of C_2S, 17 wt% of C_3S, 12 wt% of C_4AF and 2 wt% of C_3A. The compressive strength values, for an active BC fabricated with 3 wt% of gypsum and a Blaine value of 397 m^2kg^{-1}, were 14, 35, 57 and 64 MPa for 2, 7, 28 and 90 hydration days, respectively. This research group has very recently activated C_2S with sulfur and reported the resulting mechanical properties in active belite and belite cement samples [116]. The rheological properties of sulphur-activated belite cements have also been reported with promising performances [117].

Alternatively, boric acid and boron waste were also used to investigate their role in the performances of the resulting active BCs [118]. The compressive strength values for a cement activated with boric acid, 1.1 wt% expressed as B_2O_3, were 2, 3 and 53 MPa at 3, 7 and 28 days of hydration. The reported compressive strengths at very early ages are quite low which seems to indicate that boric acid is not suitable for belite clinker activation. Borax activation seems to have a different role than boron. In this context, it must be discussed the recent results for a borax activated Alite-Belite-Ye'elimite (ABY) clinker [119]. This clinker cannot be classified as typical BC but its reactivity is worth to be discussed. A reference clinker without borax had only β-C_2S meanwhile the clinker activated with borax (0.6 wt% of B_2O_3 and 0.3 wt% of Na_2O) contained a mixture of β- and α'_H-C_2S. Chiefly, as more than 2 kg of each clinker were fabricated, mortars could be prepared and compressive strength values measured and compared to the degree of hydration determined by Rietveld quantitative phase analysis [120]. The binder processing was optimized using a PCE superplasticizer, through rheological measurements, to obtain homogeneous pastes and mortars. The compressive strength values and the reaction degree of every phase were obtained at 1, 7, 28 and 56 days of hydration for several mortars including two prepared with w/c=0.40 and 0.4wt% of superplasticizer. The compressive strengths at 7 and 28 days for reference ABY, with that processing values, were 42 and 45 MPa. The equivalent data for borax activated ABY were 41 and 75 MPa. The hydration degrees of β-C_2S, for reference ABY, at 7 and 28 days were 14 and 31%, respectively. The hydration degrees of β-C_2S and α'_H-C_2S, for borax-activated ABY, at 7 and 28 days were 0 and 25%, and 73 and 88%, respectively. Therefore, the jump in compressive strength with borax activation was explained by improved belite hydration rate of both β- and α'_H- belite forms. However, it is acknowledged that borax/boron roles are different when employed in the raw meals than when used as retarder admixtures in the hydration media. Furthermore, in this second case, it is noteworthy that the compressive strength of cements with borax used as retarder were higher than the strength of the neat cements [121]. The type and amount of retarder could vary the types, amounts and microstructures of the resulting hydrates, which in turn impacts the development of the mechanical strengths.

An active belite clinker was prepared by using mineral waste from iron ore quarry [122] and adding boron oxide as a mineralizer to lower the clinkering temperature and to activate belite. The elemental

and mineralogical analyses were reported but unfortunately the boron oxide dosage was not. The clinker contained α-type C_2S in overall amount larger than 85 wt% and C_3S content lower than 2 wt%. Flexural and compressive strength results, for w/c=0.5, were relatively good with values 1.5 and 5.9, 2.5 and 11.8 and 8.5 and 71.4 MPa at 3, 7 and 28 days, respectively. Arc furnace steel slag was also used to synthesize belite clinkers [123]. The belite cements were activated by fast cooing with blown air and concurrent crushing. The early strength values were low but at 28 days ranged between 43 and 47 MPa.

4.4.2. Belite cement hydration activation. The role of admixture activation (NaOH, KOH and C–S–H seeds) in a BC has been very recently reported [124]. The mineralogical composition of the cement was given but its elemental analysis not. The cement had a Blaine value of 400 m^2kg^{-1} and the pastes were prepared with w/s=0.4. The reference BC developed ~33 J/g at 7 days, meanwhile with 1 wt% of C–S–H seeds (X-seeds, a commercial activator from BASF), the accumulated heat release at that time was ~83 J/g. This acceleration took place after 3 days of hydration. Under the assumption that this excess heat only comes from belite, the measured 50 J/g additional heat release would mean 20% of further belite reaction in the critical 3-7 days period. Another, related, way to activate BCs is by adding commercial oxide nanoparticles [125] which has been tested with relative success but the viability of such approach for large-scale concrete production is quite dubious.

In this context, Fig. 12 displays a calorimetric study of a pilot-scale belite cement hydrated at room temperature with w/c=0.5. Two commercial admixture activators, C–S–H seed-based, were employed: Master X-Seed 100 and Master X-Seed 130 from BASF. X-Seed 130 is formulated with the same patented C–S–H particle suspension but with additional organic alkylamine. As it can be seen, X-Seed 100 was not effective accelerating this active BC but X-Seed 130 hastened early age hydration, see Fig 12(a). Furthermore, the addition of 2 wt% of X-Seed 130 (total weight of admixture including its water content) not only accelerated the early age hydration but the total heat released at 14 days was 10% larger than that liberated by the neat BC paste, see Fig 12(b). The mechanism of this enhancement is under investigation as it is not currently known if the phase which reacts faster is belite, or another phase present in the cement. A synchrotron powder diffraction experiment is already scheduled to decipher this.
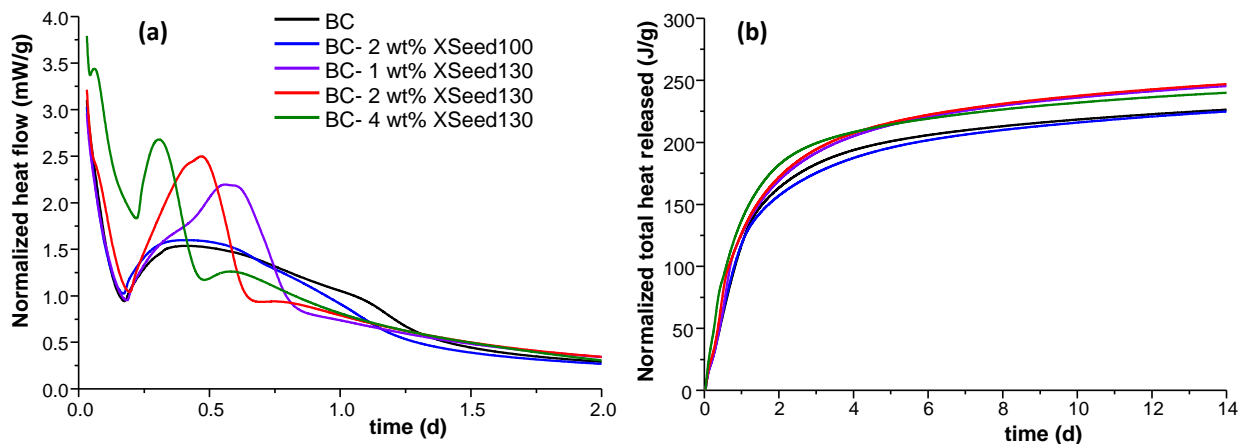

Figure 12. Heat flow at early ages (a) and total heat of hydration (b) for BC pastes hydrated with w/c=0.5 at T=20 ºC. The curve for the neat BC is displayed as reference, which is a pilot-scale industrial cement fabricated by Buzzi Unicem with main mineralogical components (larger than 2 wt%) being, β-C_2S: 50 wt%, α'-C_2S: 4 wt%, C_3S: 20 wt%, C_4AF: 8 wt%, C_3A: 4 wt%, $C\bar{S}$: 3 wt%, $C\bar{C}$: 3 wt%, $C_4A_3\bar{S}$: 2 wt%, and a Blaine value of 502 m^2kg^{-1}. The results of admixture activations are shown for Master X-Seed 100 and Master X-Seed 130. *Unpublished data from University of Malaga.*

Finally, it is highlighted that the *in-situ* hydration study of a class-G HSR Oil Well Cement with synchrotron radiation has recently reported a 43% hydration degree of β-C_2S at 14 h at 150 ºC and 150 bars [126]. A similar study for a BC at 155ºC and 180 bars showed a degree of reaction of belite

of 62% at 14 hours [127]. These studies are not of direct relevance for industrial BCs at room temperatures and pressures but it highlights that there is room for improving belite reactivity.

4.5. Industrial-scale belite cement activation. There are not many recent reports dealing with active belite cements fabricated at industrial-scale. An early work [128] compared the performances of three clinkers: (i) ordinary Portland; (ii) typical belite (with high ferrite content); and (iii) sulphur-activated belite cement containing about 12 wt% of ye'elimite, see Fig. 13. Activation of belite cements with high-contents of calcium sulphoaluminate phase, aluminum-rich, is a timely topic but it is not within the scope of the present contribution. The interested reader is addressed to recent reviews on this [7,21,23,129]. In any case, this seminal work [128] reported the performances of a BC with a compressive strength of 34 MPa at 28 days of hydration. After 100 days of hydration, the compressive strength of the BC surpasses that of the ordinary Portland cement used as reference, see Fig. 13. It is widely reported that ~100 days (see Figs 2 and 13 as independent examples) is the hydration time when the mechanical properties of ordinary BCs surpass those of PCs.
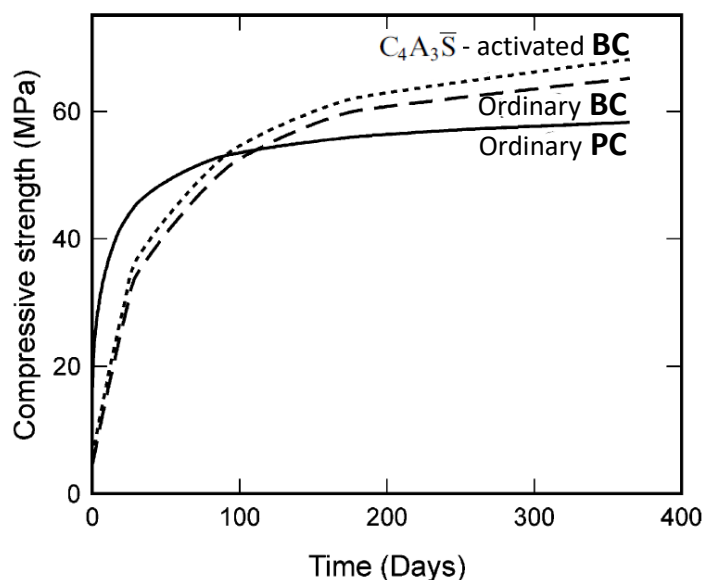

Figure 13. Development of the compressive strength for three industrially-produced cements, PC (65 wt% of C_3S, 7 wt% of C_2S, 15 wt% of C_3A, 12 wt% of C_4AF, Blaine: 315 m^2kg^{-1}), BC (45 wt% of C_2S, 30 wt% of C_3S, 23 wt% of C_4AF, Blaine: 320 m^2kg^{-1}) and ye'elimite-activated BC (61 wt% of C_2S, 26 wt% of C_4AF, 11 wt% of $C_4A_3\bar{S}$, Blaine: 310 m^2kg^{-1}). Adapted from reference [128] with permission from Elsevier.

A Boron-activated BC was produced in the Göltaş cement Plant in Turkey in 2009. Several papers have reported different properties of the resulting pastes, mortars and concretes. A first work reported the chemical analysis of the cement as well as the compressive and tensile strength data for a concrete fabricated with a cement content of 385 kgm^{-3}, w/c=0.55, up to one year [130]. Furthermore, mechanical data were also reported after treatment with sulfate solution and they were compared to the performances of an ordinary PC. Finally, this study also included the mechanical performances at 28 days of hydration at different temperatures ranging from 20 to 80 °C. In a second independent work [131], the compressive strengths (at 2, 4, 7, 14, 28, 90, 180 and 365 days) were reported for four boron-activated cements with Blaine values ranging 356-427 m^2kg^{-1}. For the cement with the smaller particles, the corresponding compressive strengths were: 17, 34, 44, 55, 61, 67, 70 and 72 MPa. Furthermore, for concrete specimens, the compressive strengths at 7, 28 and 90 days were reported as a function of the cement content, for two different slump values. Fig. 14 displays compressive strengths for boron-activated belite concretes which are compared to those obtained for PC concretes. It can be seen that at 7 days the compressive strength for the active belite concretes are smaller than those of the PCs but at 28 the values are reversed. Furthermore, at 90 days of hydration, the compressive strength values for the active BC concretes are much larger than those of PC

concretes. In a third work [132], variable fly ash contents up to 30% were studied and the compressive and flexural mortar strength values were compared to those obtained for equivalent Portland samples. It is worth to highlight that for the Boron-active BC mortar with w/c=0.5 (without superplasticizer), the compressive strength values were 28, 41 and 52 MPa at 7, 28 and 90 days, respectively. It is also noteworthy that the flexural strengths at 90 days for active BC and PC were 7.8 and 10.0 MPa for the mortars having 52 and 47 MPa, respectively. Finally, the mechanical strength values for samples heated up to 900 ºC were also published. Interestingly and somehow unnoticed, a G-mark standard describing a "Boron modified active Belite cement" was adopted in 2008 in Turkey (TS 13353).
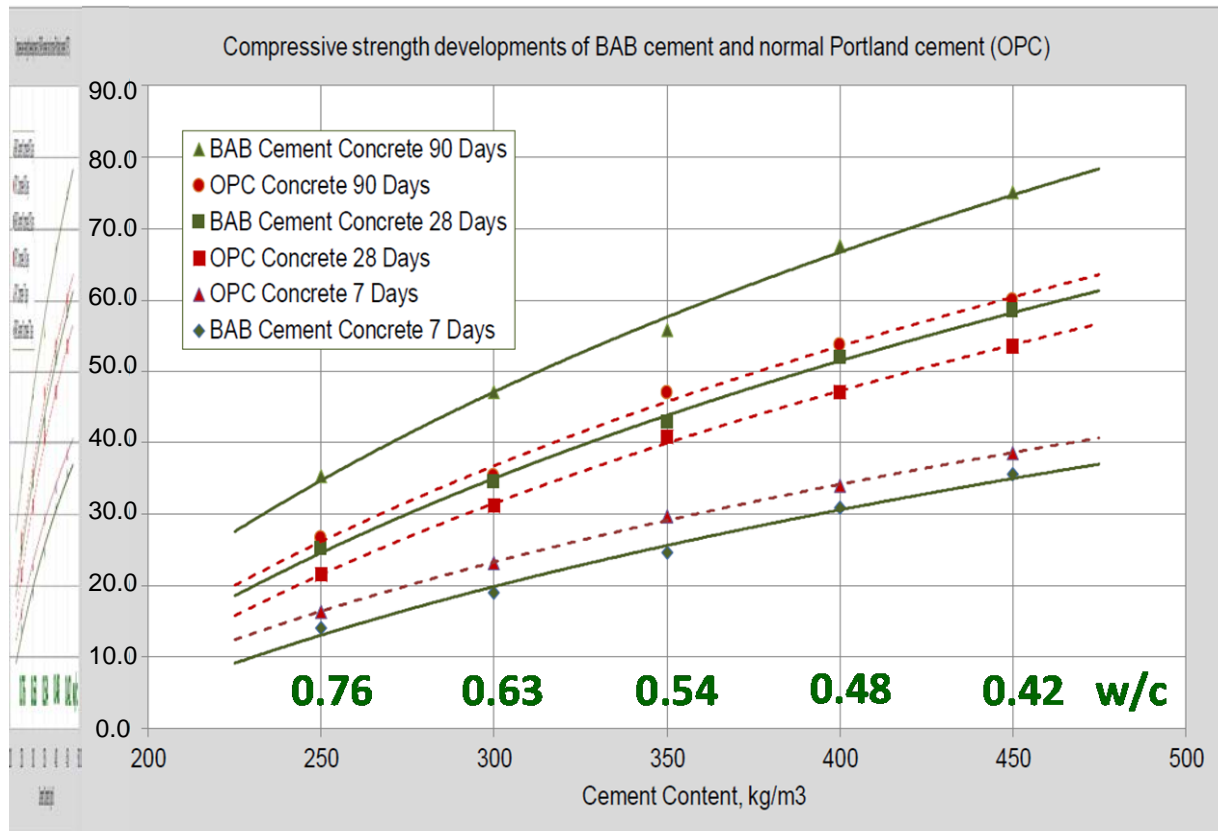

Figure 14. Compressive strength development at 7, 28 and 90 days for concretes with increasing amounts of boron-activated belite cement (BAB). The results are compared to those obtained for Portland cement (OPC) with the same dosages. All concretes were prepared with slump value of 10 cm and the water to cement ratio evolving from 0.76 to 0.42. Adapted from reference [131] with permission from the author.

Durability studies of boron-activated BC from Göltaş have also been very recently reported [131]. Water permeability tests, according to EN 12390-8 standard, and chloride penetration tests, according to ASTM C1202 (in fact, total charge passed: ionic movement), were carried out at 28 and 90 days of hydration and the results compared to that obtained for a reference PC. The concretes were fabricated with cement dosages ranging from 250 kgm^{-3} to 450 kgm^{-3} and slump values of 10 and 15 cm. Compressive strength development data were reported between 2 and 365 days of hydration. The water permeability tests were carried out according to EN 12390-8 Standard and they indicated much better performances of active belite concretes when compared to PC I 42.5R concretes with the same cement dosage, see Fig. 15. Penetration depths as low as 22 mm were measured for an active BC concrete with 350 kgm^{-3} of cement dosage and a w/c ratio of 0.57, which resulted in a slump value of 15 cm. The corresponding depth for the PC concrete with the same cement dosage was 35 mm, hence, the water penetration was 59% larger. The same active BC content but with a w/c ratio of 0.54, resulting in a slump value of 10 cm, yielded a concrete with a water penetration depth as low as 18 mm. Furthermore, active BC concretes were more resistant towards chloride ion penetration than the reference PC concrete. For instance, for concretes fabricated with w/c=0.50, 400 kgm^{-3}, and

slump values of 15 cm, the charge passed after 28 and 90 days for active BC were 3588 and 2525 Coulombs, respectively. For the corresponding PC concrete, the measured charge moved was 4833 and 4100 Coulombs, respectively.
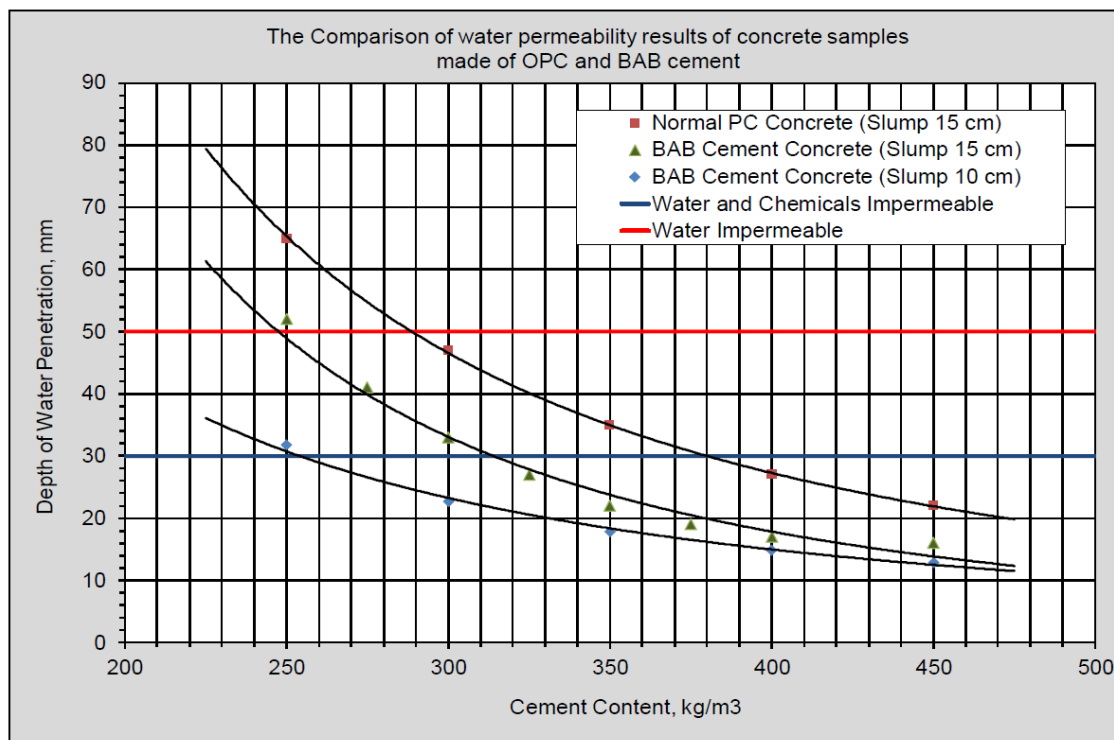

Figure 15. Water permeability results for concrete samples fabricated with increasing contents of boron-activated belite cement (BAB) and Portland cement. BAB cement concrete –slump 10 cm–, BAB concrete –slump 15 cm–, and PC concrete –slump 15 cm– cured for 7, 90 and 28 days, respectively. Reproduced from reference [131] with permission from the author.

Buzzi Unicem has an ongoing set of research activities in BCs and active B. Selected details of recently industrially-produced belite high-content cements have been reported [133]. The grinding energy needed was slightly higher than that required for a PC clinker. The industrial grinding trials performed at Trino plant showed an increase of ~15% (35 KWh/t for BC vs. 30 KWh/t for PC). A BC with an overall amount of C_2S of 65 wt% and a Blaine value of 400 m^2kg^{-1} developed 137 J/g at 7 days and mechanical strength values, as determined employing EN 196-2, of 11, 24, 48 and 65 MPa at 2, 7, 28 and 90 days of hydration, respectively. The durability performances of BC concretes exposed to severe environmental conditions have also been published [134]. Concrete prepared using 420 kgm^{-3} of BC or PC plus 100 kgm^{-3} of class F fly ash were compared to the corresponding binders where 35 % of the cements were replaced by Dyckerhoff Mikrodur® R-U, based on ultrafine ground blast furnace slag; and hence the concretes had 275 kgm^{-3} of cement, 145 kgm^{-3} of Mikrodur® and 100 kgm^{-3} of fly ash. These concretes were prepared with w/c=0.36 and an aggregate to cement mass ratio of 4. The aggregates were sand and gravel, fraction of 0/16 mm. A PCE based superplasticizer was used to adjust and maintain the consistency. Chloride migration tests were carried out according to the German BAW code of practice, freeze thaw resistance tests according to the RILEM recommendations, TC 117-FDC, and accelerated acid resistance tests were performed with sulfuric acid at a constant pH value of 2 according to the pH-stat method. All values were lower than the threshold of 5×10^{-12} m²/s set by the German BAW code for exposure class XS3. The chloride migration coefficients were significantly improved by the addition of the ultrafine powder. Furthermore, BC showed an extraordinarily high resistance to attack from sulfuric acid. Finally, it is worth noting the two European patents very recently granted to Buzzi Unicem S.p.a. related to belite high-content cement [135,136] where selected mechanical performances were stated. The first patent deals with a very low heat of hydration cementitious binder composed by a mixture of active belite

clinker and fly ash. The binder contains variable amounts of belite clinker, between 25 and 75 wt%, which has a mineralogical composition with a β-C_2S content > 65 wt%, a $C_4A_3\bar{S}$ content < 3 wt%, a C_3S content < 10 wt% and a SO_3 content > 4 wt% [135]. The second patent focuses on the production of sulfur-activated belite clinker from the fine fraction of CDW with a β-C_2S content > 60 wt%, a $C_4A_3\bar{S}$ content < 5 wt% and a C_3S content < 15 wt% [136].

5. Microstructural characterization of belite binders.

There are much less microstructural studies reported for belite single phase and belite cement hydrations than for the alite counterparts. Next, it is summarized the most recent findings for medium and late hydration stages. For very early belite hydration, etch pit development was already discussed in section 3.3.

5.1. Dicalcium silicate hydrated microstructures. The hydration products from β-C_2S and α'-C_2S have been recently characterized using scanning transmission soft X-ray microscopy coupled with ptychographic imaging [137]. The low energy of the synchrotron X-rays imposed severe constraints to the thickness of the samples that can be analyzed. As a consequence, the hydration reactions took place at a w/s mass ratio of 10, which means that a lot of space is available for the hydrates to growth. Under these special hydration conditions, the local degree of silicate polymerization and calcium coordination were reported. Ptychographic imaging showed, for this very high w/c ratio, that the outer hydration product of α'-C_2S displayed coarser fibrils than those of β-C_2S.

A very relevant report has been recently published [138]. These authors studied C–S–H gel formed by the hydration of very reactive, *x*-C_2S and amorphous C_2S, the belite sample in turn being prepared from gentle calcination of α-C_2SH, see section 3.1. Because these belite samples have very high surface areas, they had very high water demands. Therefore, a commercial superplasticizer (BASF ACE 30) was used to decrease the water-to-binder (w/b) ratio from 0.8 to the target values of 0.50, 0.40 and 0.35. The microstructure of the hydrated binders was studied by backscatter scanning electron (BSE) microscopy, see Fig. 16, and mercury intrusion porosimetry among other techniques. The BSE images on polished surfaces, for a binder hydrated for 14 days with w/b=0.4, showed a very dense microstructure where inner C–S–H could not be observed likely due to full reaction, see Fig. 16. The light areas represent inert impurities particles which accounted by ~ 18 wt% of the initial binder. The chemical composition of C–S–H gel showed a systematic variation with an increase of the Ca/Si ratio from 1.67, for the system with w/b ratio 0.8, to almost 2.0, for the binder with w/b ratio 0.35 and 0.4. This approach is very relevant as it allows to obtain samples with very high ratios of C–S–H gel in short hydration times and in fact, for a low w/b ratio of 0.35 and after full hydration (in less than two weeks), crystalline portlandite was not observed. To end this discussion, it is acknowledged that a different belite hydration pathway could take place in these systems due to their very small crystals sizes. This merits further investigations.

Finally, the hydration of activated β-C_2S, by nano-TiO_2 and nano-MgO, was studied in the presence of 1M solutions of $CaCl_2$, NaCl, NaOH and compared to that underwent in distilled water [94]. As expected, $CaCl_2$ accelerated belite hydration at early ages. Powder diffraction and thermal data indicated that $CaCl_2$ activation reduces the crystallization of portlandite and it increased the Ca/Si ratio in the resulting C–S–H gel. Furthermore, the morphologies of the formed products were studied by field emission scanning electron microscopy. It was concluded that morphology of the C–S–H gel strongly depends on the solutions used for the hydration being fiber-like in the presence of $CaCl_2$ and plate-like for the remaining three hydration media.
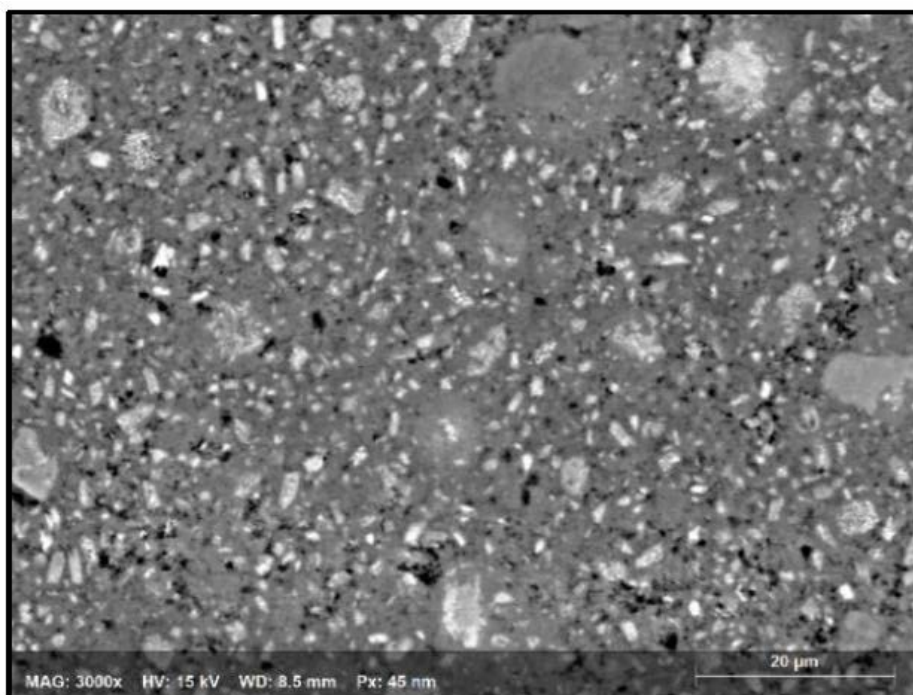
Figure 16. BSE image of a polished surface of a very highly reactive C_2S sample after 14 days of hydration with w/b=0.40. Reproduced from reference [138] with permission from the authors.

5.2. Microstructural studies of belite cement binders. There are very few recent microstructural studies for belite cements. To the best author's knowledge, three are no publications of belite cement paste microstructure studied by BSE neither by X-ray tomography. As a matter of fact, the very recent review on X-ray tomographic studies of cement binders [139] reports more than a hundred of studies but none for belite-based binders.

Here, it is highlighted two studies dealing with mercury intrusion porosimetry (MIP) for ordinary BCs. A first work [31] reported mechanical properties (splitting tensile and compressive strength), autogenous shrinkage, adiabatic temperature rise and crack resistance of four-graded concretes (cement, fly ash, sand and coarse aggregate) based on BCs. Furthermore, hydration heats (dissolution and semi-adiabatic methods) and MIP studies were carried out for BC pastes (w/b mass ratio of 0.40). Fig. 17 shows the cumulative entry pore volume curves and differential entry pore size distribution curves of hydrated BC and reference PC. In the original publication, it can be found additional MIP data for the blended cements with fly ashes. As expected, the cumulative pore volumes decrease with hydration age. From the comparison of both data sets, and also as expected, ordinary BC pastes showed larger pore fraction than the PC pastes for hydration ages of 28 days or younger. On the other hand, at late hydration ages, 180 days or older, the BC pastes showed lower cumulative pore volume than the PC pastes. These is also reflected in the average entry pore diameters where at late hydration ages, the BC pastes showed a slightly more refined porosities.

A very related study by the same research group [140] reported the mechanical properties for three-graded concretes (cement, sand and coarse aggregate) with w/b ratios of 0.40 and 0.50. In addition to the characterization discussed just above, abrasion resistance tests were also reported. The MIP study of the BC and PC pastes showed above was complemented with results for a moderate heat Portland cement showing a mineralogical composition in between the previously discussed cements. The cumulative pore volume at 180 hydration days for this cement was ~0.075 cm^3g^{-1}, which was in between the values for the BC and the PC pastes at that hydration time.
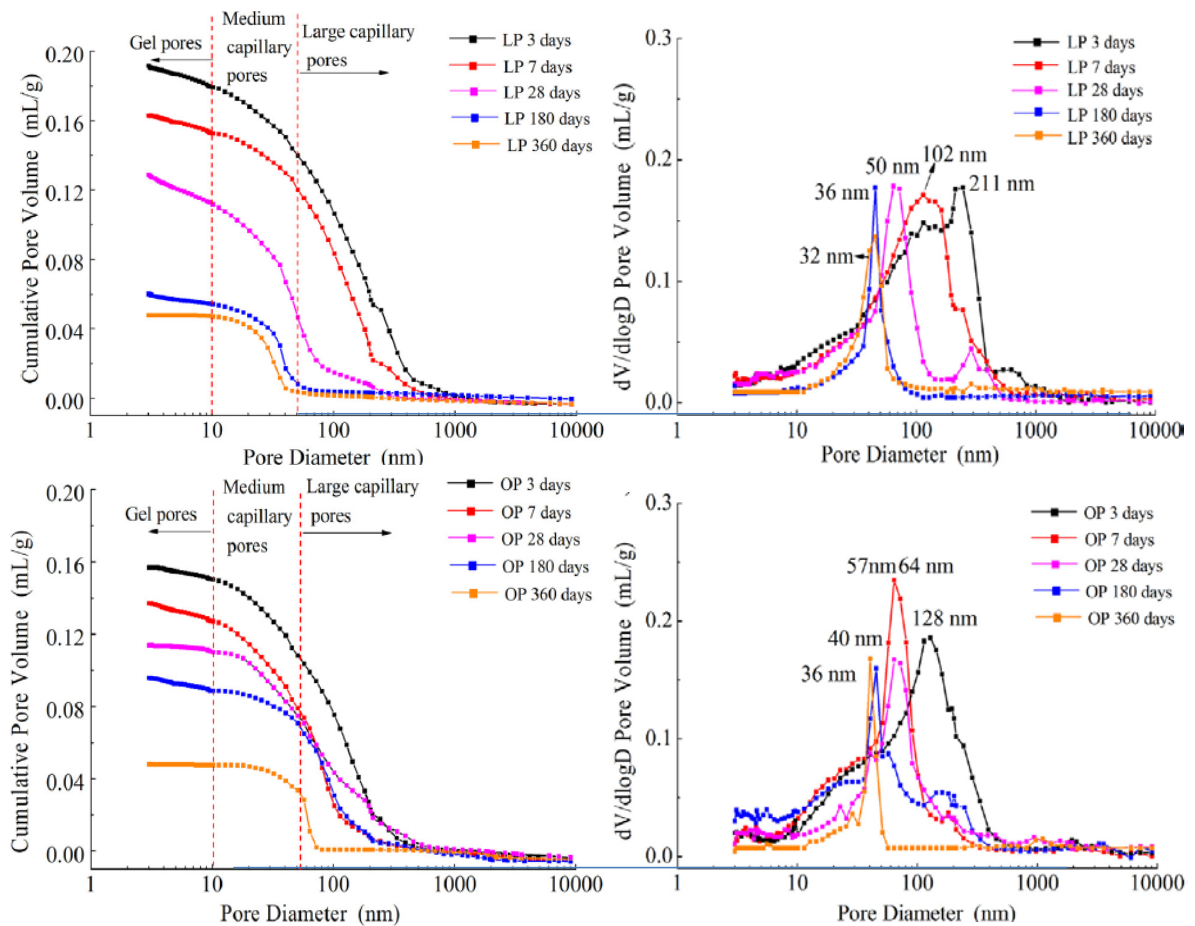
Figure 17. Mercury intrusion porosimetry results as a function of hydration time for pastes fabricated with w/c ratio of 0.40. (Left) Cumulative entry pore volume curves for belite pastes (top) and Portland pastes (bottom). (Right) Differential entry pore size distribution curves for belite pastes (top) and Portland pastes (bottom). Adapted from reference [31] with permission from Elsevier.

6. Research needs and outlook.

Initially, it should be distinguished the research needs for typical belite binders from those in active belite cements. The properties and performances of ordinary BCs mortars and concretes are well established. The influence on their performances of fly ashes, for low heat applications, is also thoroughly reported. However, little effort has been dedicated to the performances of BCs with other SCMs. This is understandable as SCMs will likely results in further decrease of the hydration rate. Furthermore, and to the best of our knowledge, there are not recent work dealing with the processing of recycled aggregates in belite concretes. This is less easy to understand as the amount of construction and demolition wastes can only increase in the future and the denser microstructure of belite-based binders could be more adequate for hosting such materials/wastes. Works are needed in this subfield. It is also noted here that BCs seem to show improved performances, compared to PCs, when hydrated at relatively high temperatures, low water-to-cement ratios and under CO_2 exposure. These behaviors should be clarified and the detailed mechanisms established.

Now, we will focus on activation of belite clinkers and cements to improve the early-age mechanical strength without degrading final strength neither the durability performances. Here a word of caution is required. Increased hydration rates of belite do not necessarily results in improvements in mechanical strength performances at later ages. Therefore, thorough works describing both the early age hydration rates complemented with mechanical and durability values at relevant ages, for the same mixtures and hydrating conditions, are the works that will make durable impact.

All considerations discussed above, for ordinary BCs, apply to active belite binders but many other specific issues appear. Firstly, an optimum chemical activation has still to be found/agreed. It is becoming clear that sulfur-activation will be key at the clinkering stage but other elements may play an important (additional) role at lower dosages like B, Na and K. Furthermore, the capacity of flux/mineralizers to low the operating temperature has still to be fully explored. This could have additional beneficial consequences in the cement milling step. Secondly and concerning physical activation, the roles of (i) cooling rate; (ii) milling; and (iii) temperature of hydration; have to be established for optimum chemically-activated BCs. Moreover, active belite clinkers produced at lower temperature and faster cooling contain smaller crystal size for the aluminate phases when compared to typical C_3A and C_4AF phases in PC. Therefore, more research will be needed for tailoring the admixtures and setting regulators in active belite mortars and concretes. In the context of physical activation, power ultrasound has been applied to the acceleration of early-age alite reaction in PC and their applications to cementitious materials have been very recently reviewed [141]. This application is interesting for PCs but it could become more relevant for BCs. Unfortunately, we are not aware of any report, so far, dealing with the use of power ultrasound for activating belite binders. Thirdly and concerning admixture activation, more studies are required for investigating the role of C–S–H nanoparticle seeds, and other chemical activators, for belite binders. It is important not only to report the acceleration in the early-age hydration rate of belite, before the first hydration week, but also to state their consequences in the early and late- age mechanical strength developments as well as on the durability performances. With the present knowledge, it is not known in CO_2 exposure can be considered as activation but more research in needed based on the reports showing improved mechanical properties.

As discussed above, the parameter space to be investigated in active belite binders is huge. Scattered investigations will require several decades to bring the active BC knowledge close to that we have today for PCs. Scientific research has proven that point collaborations between a few research groups could help to advance scientific discoveries. Moreover, collaborative experiences for very complex endeavors have been already established with success. The case of high energy physics and genomics are the paradigms here. It could be that active belite research may self-organize in a collaborative way approaching a few selected compositions to be activated by several compatible procedures as discussed above. A unified way of presenting results in a very detailed and systematic way will undoubtedly help AI software to profit from all the investigations to advance in the understanding of these binders. To this end, a Belite Research Alliance first step could take shape. The researchers interested to know more about this initiative could visit https://sites.google.com/view/cementscience-uma/home/belite-research-alliance.

The current accepted knowledge states that C–S–H gel from belite would be similar to that of alite. However, it has been shown that the hydration behavior of belite pastes, mortars and concretes at temperatures higher than room temperature is very different from that of alite binders. Therefore, intensive research on belite-originated C–S–H gel, including chemistry, local structure and microstructure(s) at the relevant length scales, is strongly needed. Furthermore, the role of hydration temperature on local structure and microstructure of belite C–S–H gel(s) must be determined. It is also important to extend the service life modelling and prediction tools already being developed for PCs [10] to the reinforced concrete structures fabricated from active belite cements.

Finally, much more emphasis should be placed in researching and reporting CO_2 emission concrete fabrication decrease. It is not enough to state the CO_2 footprint of cements but the relevant parameters are: (i) embodied carbon content in a given concrete, for instance the standard 45 MPa concrete, from cradle to site of use; and (ii) the expected durability (service life) of the resulting structure because if the structure will stand much longer, the overall CO_2 footprint will be accordingly reduced. The really relevant parameter is the embodied carbon of a given structure/infrastructure as measured from cradle to grave. This includes the extraction of every raw material, transport at all stages, processing/firing,

assembly, uses and finally to dismantle it including the emissions related to the processing of the resulting CDWs. We acknowledge that this is a complex issue, common to PC research, and efforts are being placed here. Initiatives like 'Embodied Carbon in Construction Calculator - EC3' https://buildingtransparency.org, will allow not only to estimate the CO_2 emissions related to a material, like a given cement, but also to a final product like a given concrete. These approaches could/will be upgraded in the future to account for the total (expected) live service which will be a more rational way to deal with total embodied carbon in our constructions. When adopting a long-term approach, belite binders will have a brighter role to play. Research from motivated scientists should pave this way.

7. Conclusions.

This review highlights the main differences in the hydration behavior of belite cements when compared to that of Portland cements. The behaviors of both type of binders with hydration temperature seem to be quite different. The mechanical strengths of BC concretes increase with hydrating temperature and the opposite behavior is shown by PCs. This may reflect a different local structure and/or microstructure of C–S–H gel from BCs which merits investigation. Other differences are highlighted like the mechanical strength evolution on carbonation. For a number of reasons, compiled in this review, BCs could be an attractive alternative to PCs taking into account the durability and CO_2-footprint perspectives. However, belite reactivity at early ages is low and therefore, activation of BCs, i.e. affordable, sustainable and safe early age hydration rate enhancement, is strictly required for wide usage.

Faster hydration rates are attained by three approaches: (i) chemical, (ii) physical; and (iii) admixture activations, which have been reviewed. So far, research on BC activation centered on one mechanism but here it is proposed an integrated way, performing compatible activations which are not being pursued so far. Chemical activation is carried out at the clinkering stage by stabilizing high temperature belite polymorphs plenty of defects from widely-available non-problematic element substitutions, f.i. sulfur and boron species. However, an optimum element dosage has still not been achieved. Physical activation can be carried out both at clinkering and hydration stages. Fast clinker cooling and harder cement milling are being explored at the cement fabrication stage. Mild temperature hydration is one option at the concrete preparation phase with some possibilities unexplored like power ultrasound enhancement. Admixture activation could enhance belite reactivity at the hydration stage by using chemicals like C–S–H seeds. Finally, it is worth underlining that neither BCs nor active BCs have been researched for incorporating construction and demolition wastes. The high C–S–H gel content and its dense microstructures make belite cements good candidates for incorporating recycled aggregates.

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