

Hydration Properties and Physical Characteristics of Belite Cements

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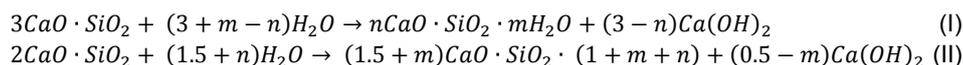
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In 2019 global cement production has been estimated at 4.1 billion tonnes and CO₂ emissions from cement plants were nearly 3.0 billion tonnes. Belite-rich Portland cements (BPCs) have been suggested as innovative environmentally-friendly materials, inasmuch as they can allow a reduction of CO₂-emissions up to 35% with respect to ordinary Portland cements (OPCs); in fact, the manufacturing process of BPCs, compared to that of OPCs, is characterized by reduced limestone requirement, lower synthesis temperatures and decreased specific fuel consumption. The peculiar composition of BPCs can be also exploited for achieving valuable technical properties (e.g. better durability against sulfate and carbonation attacks as well as low heat of hydration).

This paper examined the hydration behaviour and the physical characteristics of a pilot-scale industrial belite cement hydrated with different water/cement ratios (w/c=0.35 and 0.50) for curing times comprised in the interval 2-90 days; an OPC (class 52.5 R), hydrated with a w/c=0.5, has been employed as a reference term. The experimental findings showed that BPCs systems had better performances, especially at the longest curing periods.

1. Introduction

In 2019 about 8% of all anthropogenic carbon dioxide emissions was generated by the cement industry (IEA, 2020). Ordinary Portland cement (OPC) is the most used binder in the world; it is a mixture of clinker (about 95% by mass) and gypsum. OPC clinker is mainly obtained by heating a raw meal (a blend of limestone, L, (Tregambi et al., 2018) and clay in a 4:1 mass ratio) in a rotary kiln at about 1500°C. The production of 1 tonne of OPC generates about 830 kg of CO₂ deriving from both L thermal decomposition (about 60% of the total CO₂ emissions) and fuel combustion (Xu et al., 2015, Telesca et al., 2020). OPC is mainly constituted by alite (3CaO·SiO₂, 50-60% by mass) and belite (2CaO·SiO₂, 15-25% by mass) both responsible for the mechanical strength of hydrated cement pastes. Alite and belite react with water according to the following reactions:



Global growing concerns over climate change due to greenhouse gas emissions (mainly CO₂) from the concrete industry have strongly stimulated the development of eco-binders as a way of cutting the carbon footprint of OPC manufacture; in this regard, Mg-based cements, alkali-activated, calcium sulfoaluminate (CSA) and belite-rich binders are particularly worthy of consideration (Canonico, 2018, Chaunsali and Vaishnav, 2020, Gastaldi et al., 2021, Marroccoli et al., 2009, Marroccoli et al., 2010a, Marroccoli et al., 2010b, Paul et al., 2021, Pimraksa et al., 2009, Staněk and Sulovský, 2015, Telesca et al., 2016, Telesca et al., 2017, Telesca et al., 2019a, Telesca et al., 2019b). Furthermore, the production of concrete structures with

longer service life can further reduce the CO₂ footprint (Cuesta et al., 2021). Belite Portland cements (BPCs) satisfy both aspects since they can allow a significant decrease in CO₂-emissions (e.g. 10% for belite-Portland cements and 35% for belite-CSA binders) besides having excellent durability properties. The manufacturing process of BPCs, compared to that of OPC, is characterized by (I) reduced L requirement, (II) lower burning temperature (1250°-1350°C instead of about 1500°C) and (III) decreased specific fuel consumption (Cuesta et al., 2021). The peculiar composition of BPCs can also be exploited for achieving valuable technical properties such as low heat of hydration as well as better resistance against sulfate and carbonation attacks (Cuesta et al., 2021). However, a massive application of these binders unavoidably requires the overcoming of some drawbacks, such as the low hydration rate of 2CaO·SiO₂ which doesn't significantly contribute to the mechanical strength at very early age of hydration; this disadvantage has led to efforts to produce hydraulically active forms of belite with properties like those of standard "alite" (Boháč et al., 2019, Cuberos et al., 2009, Cuesta et al., 2012, Liu and Zheng, 2013).

This paper aimed to investigate the hydration behaviour and the physical characteristics of a pilot-scale industrial belite cement hydrated with different water/cement ratios (w/c=0.35 and 0.50) for curing times up to 90 days. An OPC (w/c=0.5) has been employed as a reference term. The hydrated cements were investigated using differential thermogravimetry (DTG), X-ray diffraction (XRD), mercury intrusion porosimetry (MIP) analyses as well as shrinkage/expansion and compressive strength measurements.

2. Experimental Section

A pilot-scale industrial belite cement clinker (BCli) and an industrial CEM I class 52.5 R (OPC) were supplied by Buzzi UNICEM cement company. The chemical composition of BCli and OPC, determined through X-ray fluorescence (Bruker Explorer S4 apparatus) together with the loss on ignition (l.o.i.) values, evaluated at 950±10°C, are reported in Table 1. For the identification of the main mineralogical phases of cements a Bruker D4 Endeavor diffractometer (CuK α radiation and 0.02°2 θ , time/step 0.5 s) was employed. A belite cement (BC) was prepared mixing 2.5% of natural anhydrite (containing about 96% by mass of CaSO₄) with BCli. Cement samples were tested both as mortars and pastes for curing periods ranging from 2 to 90 days. BC was hydrated at two different water/cement (w/c) mass ratios, namely 0.35 (BC 035) and 0.50 (BC 050), while OPC only at 0.50. Mortar prisms were prepared according to the European Standard EN 196-1 and cured, after demoulding, under water at 20±1°C. A water-reducing admixture was used for the preparation of BC-based mortars with 0.35 w/c ratio.

Cement pastes were cast into small plastic cylindrical moulds and placed inside a thermostatic bath at 20°C. At the end of each aging period, cylinders were broken in half: one part was submitted to mercury intrusion porosimetry (MIP) measurements, the other pulverized (grain size <63 μ m) for DTG (Netzsch TG/SDTA tasc 414/3 apparatus operating in air in the temperature ranges 20°–1000°C, at a heating rate of 10°C/min) and XRD analyses. Specimens were treated with acetone (to stop hydration) and diethyl ether (to remove water); they were subsequently stored in a desiccator containing silica gel-soda lime (to ensure protection against H₂O and CO₂). Porosity measurements were executed with a Thermo Finnigan Pascal 240 Series porosimeter (maximum pressure, 200 MPa; resolution 0.01 MPa up to 100 MPa and 0.1 MPa up to 200 MPa) equipped with a low-pressure unit (140 Series) able to generate a high vacuum level (10 Pa) and operate between 100 and 400 kPa. Cement pastes were also submitted to dimensional stability test; in this regard, eighteen prisms (15X15X78mm) were first cured in air at 20°C for 24 hours and then demolded. Three samples per each system were aged at 20°C under tap water; the other three samples were stored at the same temperature in a climatic chamber at 50% relative humidity (R.H.). The length changes were determined as average values of three measurements taken with a length comparator apparatus.

3. Results and Discussion

The chemical and mineralogical compositions for BC and OPC are reported in Table 1. OPC, compared to BC, is higher in CaO and lower in SiO₂. From XRD analysis, it can be easily argued that alite is the main component for OPC, while belite for BC.

The compressive strength development for OPC, BC 050 and BC 035 mortars as a function of curing time is presented in Figure 1. At two days of curing, OPC exhibits the greatest compressive strength value due to the higher hydration rate of 3CaO·SiO₂ compared to that of 2CaO·SiO₂; so, BC samples, even the one with low w/c ratio, doesn't reach comparable strength results. On the contrary, after 7 days of curing, the BC 035 sample, exhibits the highest compressive strength value (51.4 MPa), about 17% and 37% higher than those for OPC and BC 050 mortars, respectively. At longer curing periods, the lowest and the highest compressive strength values have always been found for OPC-based and for BC 035-based mortars, respectively.

Table 1: Chemical and mineralogical composition for BC and OPC, wt%

Chemical composition (wt%)	Mineralogical phase composition (wt%)		ICDD Ref. Number			
	BC	OPC				
CaO	60.4	65.9	3CaO·SiO ₂	14.2	63.7	31-0301
SiO ₂	23.0	21.6	α -2CaO·SiO ₂	5.8	-	23-1042
Al ₂ O ₃	5.0	5.6	β -2CaO·SiO ₂	60.1	14.0	33-0302
Fe ₂ O ₃	2.8	1.9	3CaO·Al ₂ O ₃	2.8	11.6	38-1429
TiO ₂	0.2	-	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	7.9	5.8	30-0256
K ₂ O	0.9	0.3	Others	9.2	4.9	
MnO	-	-				
Na ₂ O	0.2	0.3				
MgO	2.5	1.0				
Cl ⁻	0.1	-				
SO ₃	4.0	2.5				
P ₂ O ₅	0.2	-				
l.o.i.	0.4	0.4				
Total	99.7	99.5	Total	100.0	100.0	
Specific gravity (g/cm ³)	3.11	2.57				
Specific surface (cm ² /g)	4500±50					

For curing periods longer than 7 days, the compressive strength values for CB 050 mortars are about 19% higher than those for OPC mortars; the compressive strength values for CB 035 mortars are 45% (79.7 MPa), 57% (87.8 MPa) and 65% (94.3 MPa) higher than those for the OPC system respectively at 28, 56 and 90 days of curing.

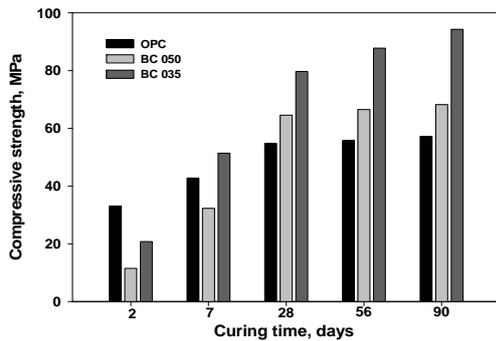


Figure 1: Results of compressive strength measurements for OPC, BC 050 and BC 035 at various curing periods.

Another important observation can be drawn about w/c ratio; it plays an important role in the gain of compressive strength for BC samples, i.e. the samples with a lower w/c ratio had a greater increase in compressive strength. The length change vs. curing time for the three systems is displayed in Figure 2; there are no substantial differences among all the samples both when immersed under water and placed in air.

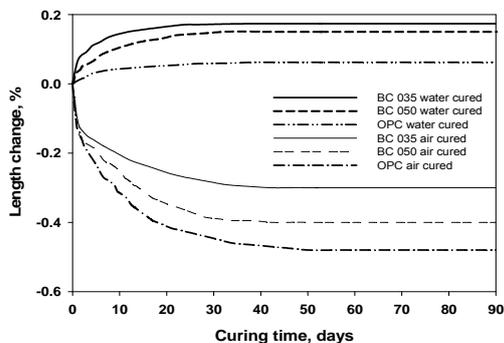


Figure 2: Dimensional stability curves for OPC, BC 050, and BC 035 (air and water cured).

For the samples cured under water the maximum expansion values are comprised in the thin range 0.06 (OPC) - 0.17% (BC 035); these values have been reached after more than 20 days of curing. For the pastes cured in air, a continuous shrinkage can be clearly observed till about 50 days of curing; at that period, a minimum length change has reached (-0.48%, -0.40% and -0.30% for OPC, BC 050 and BC 035, respectively). DTG results for OPC, BC 050 and BC 035 hydrated for 2, 28, and 90 days are displayed in Figure 3. With DTG temperature increase, three endothermic effects have been identified at $146^{\circ}\pm 6^{\circ}\text{C}$, $196^{\circ}\pm 6^{\circ}\text{C}$ and $493^{\circ}\pm 14^{\circ}\text{C}$ (Taylor, 1997).

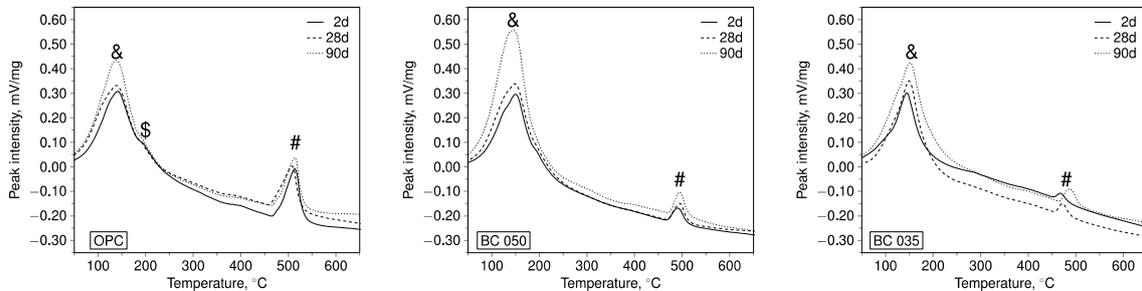


Figure 3: DT results for OPC, BC 050, BC 035 hydrated for 2, 28 and 90 days. &=calcium silicate hydrate+ettringite; \$=monosulfate; #=calcium hydroxide.

The first peak (&) refers to both calcium silicate hydrate ($3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$) and ettringite ($3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), namely the hydration products of calcium silicates (a process that gives $\text{Ca}(\text{OH})_2$ as secondary product) (Telesca et al., 2021) and of calcium aluminate together with calcium sulfate, respectively (Taylor, 1997). The second peak (\$), detected only in OPC-hydrated systems, is related to the presence of monosulfate ($3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{CaSO}_4\cdot 12\text{H}_2\text{O}$) coming from partial decomposition of ettringite (Tregambi et al., 2018); finally, the third peak (#) reveals the presence of calcium hydroxide. From the first peak of DTG curves it can be noticed that, at 2 days of curing, OPC generates a calcium silicate hydrate amount higher than that of BC thanks to the high reaction rate of $3\text{CaO}\cdot \text{SiO}_2$ (Cuesta et al., 2021). At longer hydration periods, the height of this peak results almost equal for the three systems; this is due to the slower hydration reaction of $2\text{CaO}\cdot \text{SiO}_2$ (Staněk and Sulovský, 2015). Moreover, Figure 3 clearly shows that the peak of $\text{Ca}(\text{OH})_2$ is much higher for OPC than for BC 050 and BC 035 pastes inasmuch as, according to the reaction (I), the amount of calcium hydroxide generated by the hydration of $3\text{CaO}\cdot \text{SiO}_2$ is significantly higher. The hydration evolution for the three systems was also evaluated in terms of both bound water (Figure 4, left), calculated considering the mass loss values up to 650°C from DTG analyses, and calcium hydroxide concentration (Figure 4, right). Furthermore, the chemically bound water for the sample BC 035 reaches values very close to that of the initially added water.

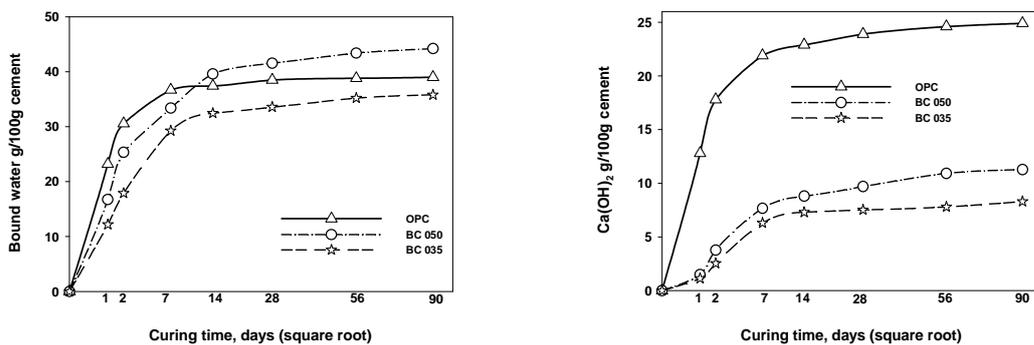


Figure 4: Bound water (left) and calcium hydroxide concentration (right) from TG data (normalized to 100 g of anhydrous cement) vs. curing time for OPC, BC 050 and BC 035.

The results reported in Figure 4 are in accordance with the outcomes of DTG analysis; these findings are also confirmed by XRD investigations. The porosimetric curves for the hydrated cement pastes (cured at 2, 28 and 90 days) of the OPC, BC 050 and BC 035 are displayed in Figure 5; the cumulative and derivative plots of intruded Hg volume are respectively located in the left and right side of the Figure. At all the investigated curing periods, a trimodal pore size distribution is observed for OPC pastes while BC systems show a different

trend, being bimodal for BC 050, and unimodal for BC 035 (Figures 5a, 5b, and 5c right). Moreover, as curing time increases, the cumulative pore volume of the OPC system reduces, passing from about 175 mm³/g (at 2 days) to 89 mm³/g (at 90 days).

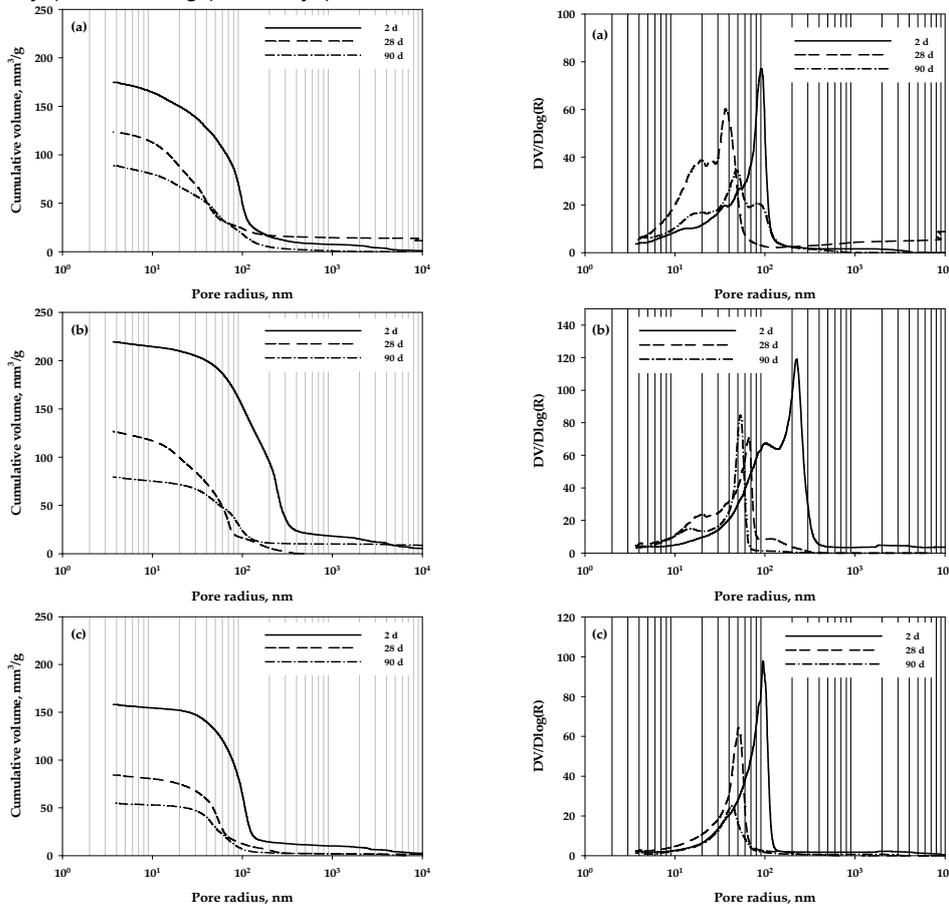


Figure 5: Cumulative (left) and derivative (right) Hg volume vs. pore radius for OPC (a), BC 050 (b), and BC 035 (c) pastes cured a 2, 28 and 90 days.

At 2 days of curing, the cumulative pore volume of BC 050 is 25% higher than that of OPC due to the lower hydration rate of belite; at the same curing period, the cumulative volume for BC 035, owing to its lower w/c ratio, is about 10% and 30% lower than that for OPC and BC 050, respectively. Finally, at longer curing periods, OPC and BC 050 have almost the same cumulative volume, while that for BC 035 is always lower, particularly at 90 days when it results equal to 55 mm³/g (about 40% and 30% lower than that of OPC and BC 050, respectively).

4. Conclusions

In this paper, the hydration behaviour and the physical characteristics of a pilot-scale industrial belite cement (BC), hydrated with different water/cement (w/c) ratios (0.35 and 0.50) up to 90 days, were evaluated. BC is mainly composed of β -2CaO·SiO₂ which, combined with water, can generate, at longer curing periods, high amounts of hydration products (calcium silicate hydrates) characterized by high-density microstructures; as a consequence, low porosity values allow obtaining high compressive mechanical strength and durability properties. From the experimental findings it has been found that, compared with a class 52.5 ordinary Portland cement (OPC), the investigated BC systems showed lower mechanical properties at the shortest curing periods (2 days); on the contrary, at longer hardening periods, the compressive strength values of BC-based mortars were always greater than those for OPC mortars. Moreover, shrinkage tests on cement pastes displayed that BC systems were more stable than OPC in air, while presented almost the same behaviour under water. In addition, through mercury intrusion porosimetry, X-ray diffraction as well as thermal analyses, the best hydration behaviour, in terms of both lower porosity value and calcium hydroxide content, were shown by the BC-based pastes, especially at the longest curing periods (90 days). Moreover, as expected, the best results were obtained with the BC system hydrated with the lowest w/c ratio.

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