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Limestone fillers cement based composites: Effects of blast furnace slags on fresh and hardened properties

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HIGHLIGHTS

- The use of limestone fillers in substitution of cement has a low impact on fresh properties of mortars.
- Limestone fillers have an impact on the dormant period of the cementitious mixes.
- The use of blast furnace slags induces a lower open porosity.
- Durability generally decreases when limestone filler is used.
- Total and autogenous shrinkage decrease when limestone substitution rate increases.

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ABSTRACT

Limestone filler is a raw material that is already used in several applications like paints, bricks, and bituminous mixtures. Moreover, and particularly in Belgium, classical additions for concrete like fly ashes and granulated blast furnace slags are becoming rare; there is a need for new additions that could have a positive effect on the properties of the fresh and hardened cementitous composites.

Substitution of limestone filler in Portland cement and Granulated blast furnace slag cement has been realized between 15% and 27% in mass. In addition to the characterization of the powder itself – specific mass, specific surface and laser granulometry – the problem of the water demand has been analysed: it seems that it remains constant with the substitution rate. Electric conductivity has also been performed in order to study the evolution of the "dormant" period. Tests on hardened mortars were performed with regard to mechanical properties and evolution of the porosity. Test results indicate that the porosity seems to be finer in the case of granulated blast furnace slags cements, partially due to a very low diameter of the slags particles. Oxygen permeability does not seem to be influenced by the filler while capillary absorption increases with substitution rate. Finally, carbonation rate, sulphate resistance and chloride penetration show quite interesting behaviours, leading to the conclusion that limestone fillers maybe a good substitution material.

1. Introduction

Common additions such as fly ashes and granulated blast furnace slags are widely used in Belgian cement industry. On the other hand, limestone fillers are quite abundant and already used in several applications [1]: they are actually cheaper and more "sustainable" than cement. This is the reason why limestone fillers for cement substitution were investigated, specifically for Self Compacting Repair Mortars [2] but also classical Self Compacting Concrete (SCC) [3].

Mineral filler are usually defined as an "inert material that is included in a composition for some useful purpose" [4]. It can be added to compounds to fulfil a large variety of final results or to improve specific characteristics like hardness, brittleness, impact strength, compressive strength, softening point, fire resistance, surface texture, electrical conductivity, etc. [5,6]. These effects are the result of the properties of the fillers, including chemical activity, hardness, particle size, shape and distribution, surface structure, colour, density and refractive index [7,8].

Limestone fillers are notably used as cement replacement materials (cement additions); they are well-adapted, specifically for Belgian market, because of their local availability [9]. As the behaviour of fresh and hardened concrete depends on the intrinsic properties of fines [10], the use of these by-products requires a thorough characterization [11]. Rheological problems may be solved usually by means of admixtures and viscosity agents [12].

Durability of limestone cement based mixtures has been studied, specifically for Self Compacting Concrete [13,14]. Results do

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not show clear impact of limestone fillers on carbonation depth even if SCC generally presents an improved behaviour with regard to ordinary concrete [15]. Resistance to chloride diffusion and freeze–thaw cycles are mainly dependent on pore size distribution and connectivity of pores: as limestone fillers may partially fulfil capillary pores, some improvement is expected [16].

This research project tends to quantify limestone fillers effects on the durability of limestone fillers cement based composites.

2. Experimental program

2.1. Tests for durability

Three levels of investigations have been selected: fine material, slurries and mortars. The characterization of fine materials is based on sieving and specific surface [7]. The modified cement paste was also analysed with regards to its water demand and its electric conductivity: these results gave us information about fresh behaviour and hydration process. Afterwards, tests were carried out on fresh and hardened mortar in order to determine consistency [17], mechanical characteristics [18], shrinkage [19], porosity [20], capillary absorption [21] and permeability to oxygen [22]. Durability of mortars was finally evaluated through their resistance to carbonation [23], sulphates and chloride ingress [24].

The strength activity indexes at 28 days, determined in accordance with French standard NF P18-508 [25], have been evaluated: strength activity index is defined as the ratio between compressive strength measured at the same age on specimens prepared with 75% reference cement and 25% limestone filler, by mass, and 100% reference cement, respectively.

2.2. Materials

Two cements (Portland cement and granulated blast furnace slag cement) and four rates of substitution (0%, 15%, 23% and 27% by mass) of limestone filler were tested, i.e. eight mixtures: these very high limestone filler contents were selected in order to promote concrete with lower CO_2 footprint. A normalized sand (EN 196-1) and water tap were used. The Portland cement was of CEM I 42.5 R HES type: this is a 100% Portland clinker which is characterized by a high early strength (www.holcim.be). Binary cement was artificially but precisely composed with 65% (by mass) of Portland cement and 35% of Granulated Blast Furnace Slag (bfs) directly obtained from producer. The filler comes from a local limestone quarry [26].

Table 1 shows the mineralogical composition, the specific mass and the specific surface of the three powders used for composing the binders. Particle Size Distributions (PSD) of blast furnace slags (bfs), limestone filler and cement were performed by means of laser diffraction while specific surface area was measured according to Blaine method [7,26]. The characteristic percentile diameters d_{50} is reported. Fig. 1 shows that Granulated Blast Furnace Slags (bfs) offer the finer particle but a less continuing gradation. Limestone fillers are fine products but coarser with d_{50} = 12.60 μm. The cement is well graded with the smallest amount of fine particles (around 27% of particles smaller than 5 μm). Blaine specific surface areas are ranging from about 2700 to 3090 m^2/kg; the highest value is obtained for cement particles.

Recent studies [27,28] have shown that limestone filler particles (LF) have a lower bluntness in comparison with cement grains. This may be due to longer crushing process for limestone (from meter level) than for clinker (from centimeter level). Blending cement with fillers can effectively improve the packing density of the binder (Fig. 2). Dry packing methods are conventionally performed according to standard code BS 812-2 [29]; in this case, conventional dry packing method has been modified by introducing vibration and compaction in order to reduce the influence of inter-particle forces [28]. The higher amount of limestone fillers in mixes can result in a higher packing density of solid particles, which is favourable for durability and strength behaviour.

Table 1
Chemical composition and physical characteristics of materials.

	Portland cement	Granulated Blast Furnace Slag (bfs)	Limestone filler
CaO	62.8	38.46	98.1 ($CaCO_3$)
SiO_2	19.3	35.08	0.533
Al_2O_3	5.1	13.47	0.166
Fe_2O_3	3.1	0.51	0.082
MgO	0.8	8.5	0.35
SO_3	3.1	0.1	0.085
Specific mass (kg/m^3)	3090	2890	2700
Specific surface (m^2/kg)	385	440	305

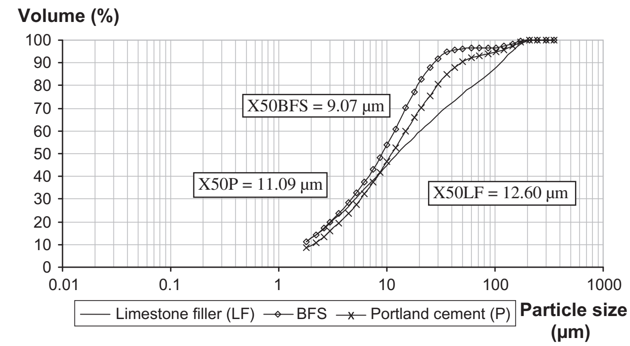

Fig. 1. Particle size distribution of Portland cement (P), granulated blast furnace slag (BFS) and limestone filler (LF).

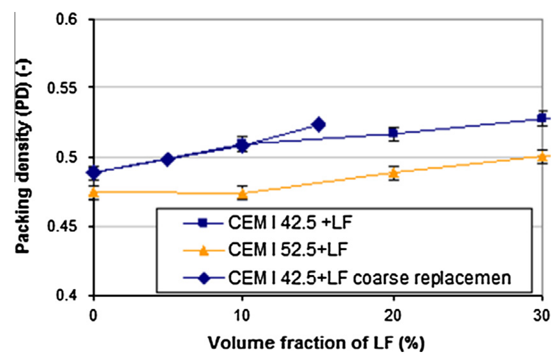

Fig. 2. Dry packing density of limestone filler blended cement (error bars indicate the variance for three tests).

2.3. Mortar compositions

The different compositions are characterized by the same sand and water contents. Water demand and consistency tests showed indeed that these two properties remained constant whether limestone filler was incorporated or not. It was then decided to work with a constant water-to-binder ratio of 0.45 (by mass) for all the mixtures. Four substitution rates were tested with the two cements (0%, 15%, 23% and 27% by mass). Table 2 presents the eight compositions tested, as well as air content (EN 1015-7) [30].

Mortars are referred by M–P when cement is 100% Portland cement and M-BFS when cement is composed of 65% Portland cement and 35% Blast Furnace Slags. Mortars were prepared in accordance with European Standard EN 196-1 [18]. Water was first introduced in the mechanical blender. The dry mix solids (cement + filler) were then added to the water solution and mixed for 30 s at low speed; sand was added and mixed for 30 s. Then the mixing proceeds in a sequence of three steps: 30 s mix at high speed, 90 s in rest, 60 s mix at high speed. After casting, the samples were covered with wet burlap and a polyethylene sheet for 24 h. They were then stored for 27 days at (20 ± 2) °C and (90 ± 10) % R.H.

3. Results and discussions

3.1. Tests on cement paste and fresh mortars

3.1.1. Evaluation of water demand

The water demand (Fig. 3) is characterized by the β_p factor (expressed by mass) [31]. Beta *P* tests [26,32] are performed in order to quantify water demand β_p of the mixture corresponding to a paste without spreading. The test involves the measure of the spreading of a paste for different water contents and the determination of a factor *R* from the spreading diameter *D* (mm), according to (Eq. (1)):

$$R = \left(\frac{D}{100}\right)^2 - 1 \quad (1)$$