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Author statement

Mohamed Elkarim Bouarroudj : Conceptualization, Methodology, Acquisition, Writing original draft. **Sébastien Rémond**: Methodology, Funding, Acquisition, Supervision, Writing-review and editing. **David Bulteel** : Funding, Acquisition, Writing-review and Editing. **Guillaume Potier**: Data curation, Resources. **Frederic Michel**: Writing-review and editing. **Zengfeng Zhao**: Writing-review and editing. **Luc Courard**: Funding, Acquisition, Writing-review and Editing

Use of grinded hardened cement pastes as mineral addition for mortars

Mohamed ElKarim Bouarroudj[a,b*], Sébastien Rémond[c], David Bulteel[a], Guillaume Potier[a], Frederic Michel[b], Zengfeng Zhao[b], Luc Courard[b]

[a] Univ. Lille, IMT Lille Douai, ULR 4515 - LGCgE, Laboratoire de Génie Civil et géo-Environnement, F-59000 Lille, France

[b]University of Liège, Urban and Environment Engineering, ArGEnCo Department, GeMMe Building Materials, Liège, Belgium

[c]Univ Orléans, Univ Tours, INSA CVL, LaMé, EA 7494, France

E-mail : bouarroudj.mohamedelkarim@gmail.com
Postal address : 764 Boulevard Lahure, 59500 Douai

Abstract

Recycled Concrete Aggregates (RCA) are not enough used in the construction sector due to their high porosity and water absorption capacity. Fine particles which are composed of large amounts of attached hardened cement paste are even more difficult to valorize, while they could be used as mineral admixture in mortar or concrete. The objective of this work is to find a recovery track for this material as mineral addition. The use of a porous powder as mineral admixture in cementitious mortars raises the question of the effective water definition in such systems. Two powders are used, the first one is a grinded hardened cement paste (porous), and the second one is a limestone filler (non-porous). A comparison of the hydration degree, porosity, fresh, and hardened behaviors between cement pastes and mortars manufactured with the two powders is carried out. The results show that the porosity of the grinded hardened cement paste has an impact on the properties of cementitious materials. Depending on the studied properties (fresh or hardened properties), the substitution of cement by the porous powder could be done with, or without taking into account the water absorption. Taking into account the water absorption allows maintaining the fluidity of the mixture but decreases significantly the compressive strength for cement replacement percentages larger than 20%.

Keywords : Effective water, mineral addition, Recycled concrete aggregates, water absorption, and porosity

1. Introduction

In the last decades, reducing the CO_2 emissions has become a challenge to face. The construction sector is responsible for 25% of the total CO_2 emissions, amongst which no less than 5-8% come from the manufacture of cement [1]. The CO_2 emissions produced during the cement fabrication are caused not only by the energy needed for the calcination of the raw material (40% of the total emission) but also by the decarbonation of calcite [2]. Replacing part of the clinker by mineral additions such as limestone filler,

fly ash… can be a good way to reduce CO_2 emissions. Substituting part of cement by industrial by-products in the manufacture of concrete also reduces CO_2 emissions[3,4].

Using construction and demolition wastes (CDW) as a substitution of clinker can be a good way to reduce CO_2 emissions and can be also an alternative material in the construction sector to preserve natural resources. Recycled concrete aggregates (RCA) represent a significant part of the CDWs. Comparing to natural material, RCAs have a higher water absorption (between 4 and 12%) and a lower density (between 2.1 and 2.5 g/cm^3) [5] due to the adherent hardened cement paste. The coarse fraction of RCA is easier to valorize than the finer one in the construction sector. Up to now, research on RCA has been more focused on using RCA as aggregates in concrete production [6-8] than for manufacturing cement [9,10] or as a mineral addition in concrete production [11,12].

Oksri-Nelfia et al. [11] studied the influence of partial substitution of cement by grinded recycled concrete aggregate on mortar and concrete properties. The results show that the volume of cement could be replaced up to 25% without altering the properties of mortars. In a similar study, Bordy et al. [12] made a substitution of Portland cement by grinded recycled cement paste. The results show that the substitution does not provide any additional filler effect and nucleation sites in comparison to limestone filler. Neither Oksri-Nelfia et al.[11], nor Bordy et al.[12], take into consideration the eventual water absorption of the grinded recycled fine aggregate.

Many research works quantified the water absorption (WA) coefficient of the coarse fraction of RCA [13-15].But none of them were interested to measure the WA of the finer fraction of RCA (<500µm). De Juan et al.[16] showed that when the size of RCA decreases, the content of attached cement paste increases. Due to the fact that the attached cement paste is porous, the WA in RCA is proportional to that hardened cement paste content. Zhao et al. [17] and Le et al.[18] showed that standard EN 1097-6 [19] or IFSTTAR protocol [20] to measure the WA can only be used for particles larger than 0.5mm, due to agglomeration effects between the finer particles [21,22]. Up to know only Bouarroudj et al.[23,24] proposed a method to estimate the WA of finer particles (< 500µm) based on a theoretical approach. This method takes into account the particle size distribution of the powder and the pore size distribution of the monolith (the coarse material before grinding into a powder) by mercury intrusion porosimetry. According to the size of pores and the size of grains, the theoretical model computes the remaining porosity of the powder.

Effective water in concrete is generally defined as the quantity of water that is present in the cement paste, that is to say the amount of water that will be available for cement hydration[25,26]. However, this definition can be questioned if a porous powder is added or substituted to cement in the paste. In that case, the quantity of water present in the paste includes the water that might be absorbed by porous particles. However, it is no more equivalent to the amount of water that will be available for cement hydration, as the water absorbed in the fine particles will not be available (or much less available) than the one present in the intergranular space. The main goal of this paper is to study the effect of the porosity of a grinded hardened cement paste (GHCP) on the hydration and the fresh and hardened behaviors of a cementitious material. Cement pastes and mortars are manufactured by substituting a given volume of cement by a corresponding volume of GHCP. The latter corresponds either to the absolute volume of GHCP (i.e. the solid volume only, excluding any accessible pore inside the powder) or the envelop volume of the GHCP (i.e. the solid volume and the volume of intra granular porosity). A comparison is made with limestone filler (LF), which is considered as a non-porous powder.

The paper is organized as follows. First the preparation of GHCP and its characteristics are presented in part 2. The comparison between the hydration degree and porosity of hardened cement pastes manufactured with GHCP and LF is presented in part 3. In part 4, the mortars composition and the fresh and hardened properties of mortars are presented. Finally, the conclusions and perspectives are formulated in part 5.

2. Materials characterization

2.1 Materials

The used cement is a CEM I 52.5N from CBR Belgium, complying with standard EN 197-1. The LF is provided by Carmeuse Belgium. According to the technical document provided by the manufacturer, the porosity of the original limestone from which the LF is produced is 1% (measured on the monolith limestone according to standard EN 1097-6 [19]). So, in this research the LF is considered as a non-porous powder. The GHCP is produced from a cement paste having a water to cement ratio of 0.5. To insure a good homogenization during the fabrication of cement paste, the half quantity of cement is first added to the water and mixed for 90 seconds, after that the second part is added and 90 seconds of mixing are performed. Thereafter, the fresh cement paste is poured in 1 liter hermetic plastic bottles. The cement paste is gently vibrated to minimize the presence of air bubbles. In the end, the fresh cement paste is sealed and rotated during 6 hours in order to avoid segregation and bleeding during setting. The hardened cement paste (HCP) is hydrated during 90 days in closed containers to insure a high hydration degree as reported in the literature [27].

The HCP is crushed in two phases, firstly with a jaw crusher with an opening size of 8mm and secondly with a ball mill in order to obtain a fine powder with dimensions lower than 200 µm, and having a close particle size distribution to that of LF. Several crushing steps of 15 minutes with the ball mill have been done. The PSD has been controlled after each step using laser granulometry in liquid phase with ultra-sonic (to avoid agglomeration). This method allows controlling the $d_{10\%}$ and $d_{50\%}$ (diameter of 50% and 10% passing). Sieving particles at 200 µm allows controlling the $d_{90\%}$ (diameter of 90% passing).

Having close particle size distributions between the two powders (LF and GHCP) facilitates the comparison by limiting the geometric differences.

2.2 Characterization protocol

The characterization procedure is carried out in two steps: firstly, on the monolithic material (particle sizes between 4mm and 20mm), and secondly on the grinded material.

Two characterization tests are carried out on the crushed HCP (4/20 mm):

- First, the water absorption is determined according to standard EN 1097-6 [19]. For this test, the aggregate is immersed in water for 24 hours, after that the surface water is removed with dry paper, and the surface dry mass of the aggregate is recorded (M_{ssd}). The aggregate is placed in an oven until constant mass (M_{dry}). For each sample, this test is carried out five times to assure a good repeatability. The water absorption (WA) is computed with (eq.1). The drying temperature for HCP is reduced to 60°C, in order to avoid an excess drying, which would lead to a partial dehydration of hydrates and overestimate the water absorption.

$$WA = \frac{M_{ssd} - M_{dry}}{M_{dry}} \ldots\ldots\ldots\ldots(1)$$

- The pore size distribution is then measured using Micrometritics autopore IV with a mercury pressure between 0 and 200MPa. Five tests are performed with samples of approximately 1x1x1 cm^3. For HCP, the sample is taken in different parts of the material, to verify that HCP is homogenous.

For the grinded powder, the following tests are done:

- The particle size distribution is determined with laser diffraction granulometer (Mastersizer 2000). Because of the anhydrous particles eventually present in GHCP, the laser granulometer test is made with ethanol for both GHCP and LF.

- The remaining intra granular porosity (ϕ_r) of the powder has been computed with the theoretical model developed by Bouarroudj et al. [23,24]. This model is presented with (eq.2) where R_j corresponds to the radius of grain, r_i is the pore radius, ϕ is the initial porosity, x_i is the volume fraction of each size of pore, y_j corresponds to the volume fraction of each size of grain, and $R_{5\%}$ coresponds to the radius of 5% of the passing particles.

$$\phi_r = \phi \times \sum_{j=0}^{k} y_j \times \left\{ \sum_{i=0}^{m} x_i + \sum_{i=m+1}^{n} x_i \times \left(1 - 3\left(\frac{r_i}{R_j}\right) + 3\left(\frac{r_i}{R_j}\right)^2 - \left(\frac{r_i}{R_j}\right)^3 \right) \right\} \dots\dots\dots\dots (2)$$

$$\text{With} \quad \begin{array}{l} r_i < r_{i+1}, for\ i = 1\ to\ i = n \\ r_m < 0.1547 \times R_{5\%}\ and\ r_{m+1} \geq 0.1547 \times R_{5\%} \end{array}$$

- The absolute density (ρ_a) is measured with helium and water pycnometers. The water absorption of the powder is then computed with (eq.3), and the real density (ρ) is obtained with (eq.4).

$$\text{WA} = \frac{\phi_r}{\rho_a \times (1 - \phi_r)} \dots\dots\dots (3)$$

$$\rho = \rho_a \times (1 - \phi_r) \dots\dots\dots (4)$$

- The water demand comparison between GHCP and LF is carried out by making different slump flow tests (S) using different water to powder ratios [28] (mini-cone, h=60 mm, d= 70 mm, and D= 100 mm). The results are presented by plotting the relative flow (R) calculated from (eq.5) as a function of the ratio of the effective water and the volume of powder $\frac{V_w}{V_p}$ (for GHCP, the volume of powder is presented with and without considering the intra granular porosity). [28] demonstrated that, for pastes made with any particular powder, the water to powder volume ratio and the relative flow are linear and can be presented with (eq.6). Where β_p is considered as comprising the water needed to fill the voids in the powder system and provide sufficient disposal of the particles(water demand), and E_p is the deformation coefficient depending on the used powder.

$$R = \frac{S^2 - D^2}{D^2} \dots\dots (5)$$

$$\frac{V_w}{V_p} = \beta_p + R.E_p \dots\dots\dots\dots (6)$$

2.3 Experimental results and discussion

Table 1 presents the initial porosity, absolute density (ρ_a), and real density (ρ) obtained with the MIP on the monolith HCP. In the same table, the water absorption obtained according to the EN 1097-6, and the absolute density obtained with the helium and water pycnometers are also presented.

The absolute density measured with helium pycnometer is higher than the one measured with MIP, this difference is due to the fact that the absolute density with helium is measured on a grinded material, which is not the case with MIP. A small difference is observed between the absolute density measured with helium and water, which could mean that almost all the porosity present in the material is accessible to water.

The porosity and absolute density measured with water are higher than those measured with MIP. This can be explained by the fact that the porosity accessible to water is larger than the one accessible to mercury (with a maximum pressure of 200MPa).

Table 1: Absolute density (with helium and water), Water absorption, average porosity computed and measured using MIP, and real density. Standard deviations are computed from 5 replicates on HCP or GHCP.

ρ_a helium (g/cm^3)	ρ_a water (g/cm^3)	WA EN 1097-6 (%mass)	Water accessible Porosity (%vol)	ρ water (g/cm^3)	ρ_a MIP (g/cm^3)	Porosity MIP (%vol)	ρ MIP (g/cm^3)
2.4 ±0,01	2.39 ±0.02	30 ±0.4	42 ±1.1	1.4	2.12 ±0.01	25.9 ±0.8	1.57

Figure 1 presents the particle size distributions (PSD) of GHCP and LF, and figure 2 presents the pore size distribution of HCP, both figures have the same x-axis scale. The average diameter of pores for HCP is 0.07µm. The crushing procedure of HCP allows a close PSD between LF and GHCP. The average diameter of the GHCP and LF is about 20µm.
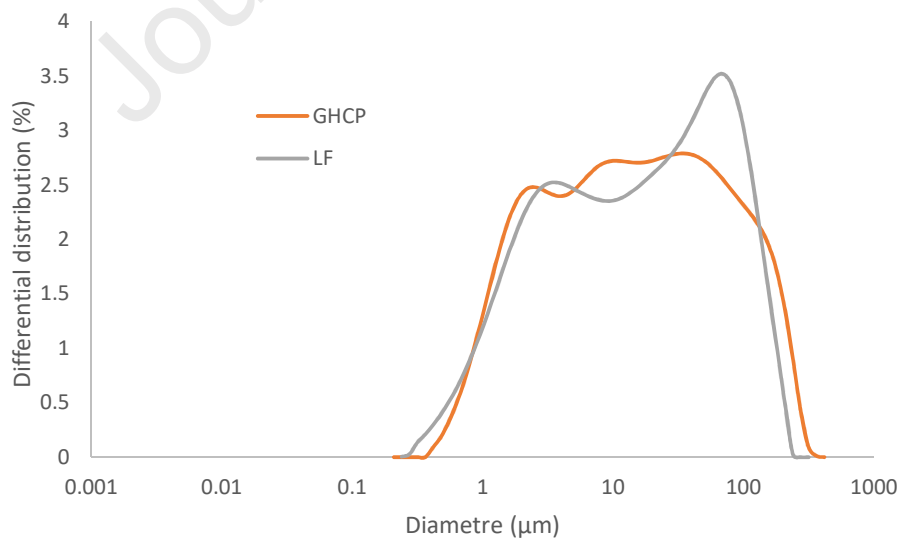

Figure 1: Particle size distributions of GHCP and LF determined by laser diffraction.
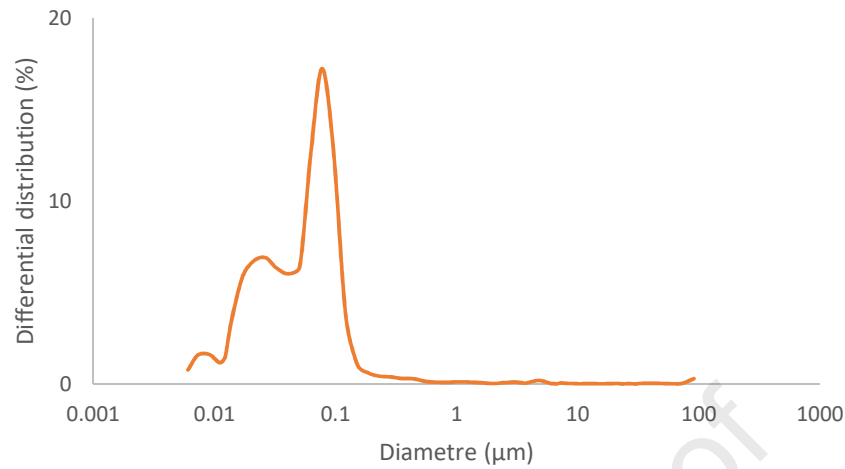
Figure 2: Pore size distribution of the HCP determined by MIP.

Table 2 presents the characteristics of GHCP and LF. The porosity of GHCP is computed with (eq.3). A small difference is observed between the porosity obtained in HCP and the one computed for GHCP. This result is attributed to the fact that the size of particles is much higher than the size of pores (comparison between figure 1 and figure 2). The WA and the real density are computed respectively with (eq.4) and (eq.5).

Table 2: Absolute density, computed porosity, water absorption and real density of GHCP and LF

	ρ_{app}(g/cm^3)	ρ(g/cm^3)	WA(%mass)	ϕ_r(%vol)
GHCP	2.4	1.4	28.5	40
LF	2.72	2.72	0	0

Figure 3 presents the relative flow (R) as function of the water to powder volume ratio made with LF and GHCP with and without considering the intra granular porosity of GHCP. The β_p (water demand) for LF, GHCP and GHCPWA are respectively 0.71, 0.23 and 1.12. It's shown that when the porosity is not considered for GHCP the β_p (water demand) is higher than the one of LF. However, the water demand of LF is higher than the one of GHCPWA. Given the close PSDs and morphological characteristics of the two powders, the difference on the water demand can be attributed mainly to the agglomeration.
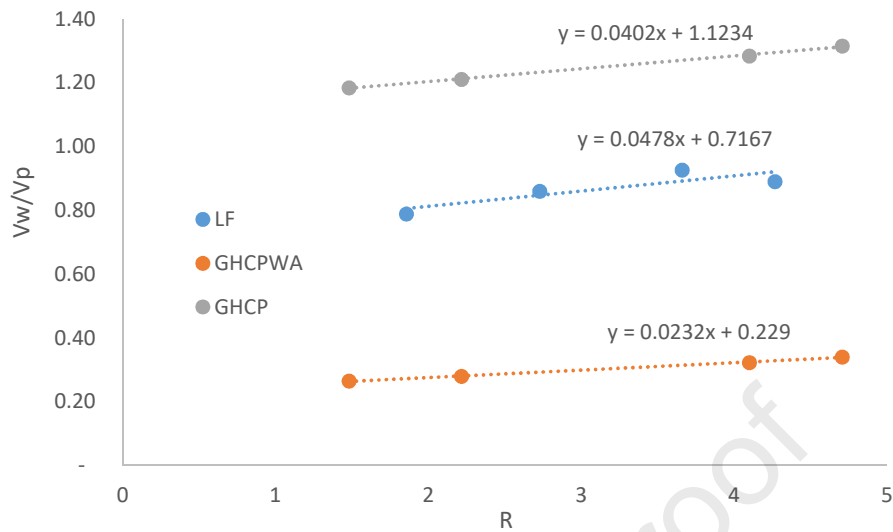
Figure 3: comparison between β_p (water demand) of pastes made with GHCP and LF. GHCP WA presents the result where the intra granular porosity is considered.

3. Hydration degree and porosity of cement pastes with GHCP and LF

3.1 Methodology and experimental procedure

To identify the influence of GHCP and its porosity on cement hydration in comparison to LF, cement pastes are manufactured with LF and GHCP. This part is carried out on pastes to simplify the studied systems.

Figure 4 presents the principle adopted for cement pastes composition. The mixes with mineral addition (LF and GHCP) are manufactured by adding the later with a volume corresponding to 50% of the cement volume of the reference mix. For the pastes made with GHCP, the addition is carried out in two different ways. Firstly, the envelope volume of grains is considered, and the added volume is computed with the real density (the porosity and water absorption of the powder are considered here). Secondly, the absolute volume is considered, where the porosity and the WA are not taken into consideration (only the solid volume). These different mixtures are prepared in order to study the impact of the mineral addition porosity on the hydration of cement.

Thermo Gravimetric Analyses (TGA) and mercury intrusion porosity tests (MIP) have been carried out on the different pastes at different ages (1, 2, 7 and 28 days) in order to identify the hydration degree and the porosity of the different pastes, and make the comparison between the one manufactured with GHCP and LF with those manufactured without mineral addition (reference mix). Table 3 presents the compositions of the manufactured cement pastes.
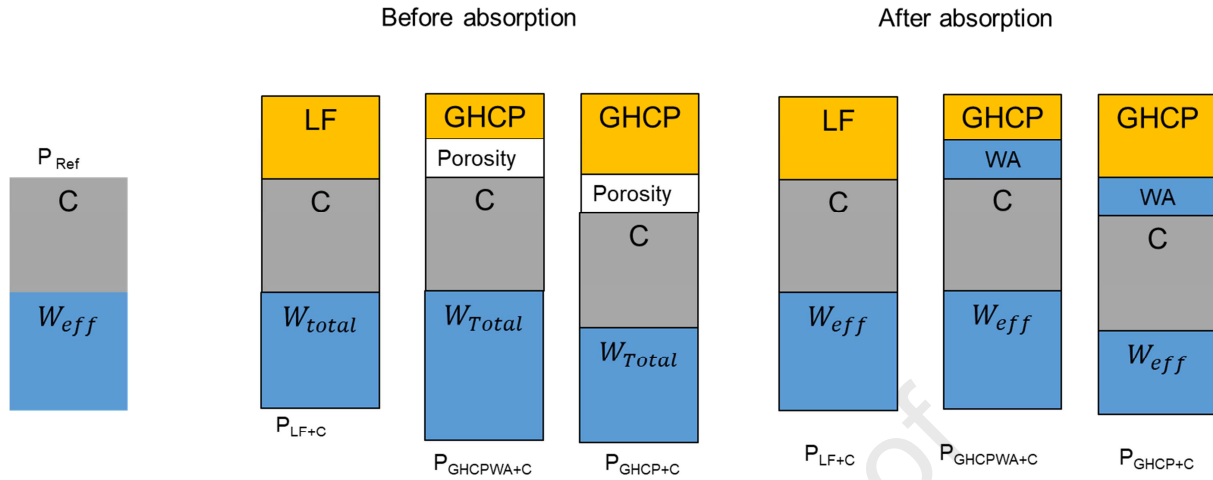
Figure 4: Illustration of the different mixes

Table 3: Paste compositions

	Cement (g)	Powder (g)	Total water (g)	Absorbed water (g)	W_{eff} (g)	W_{eff}/C
P_{Ref}	77.50	0	38.75	0	38.75	0.5
P_{LF+C}	77.50	68.00	38.75	0	38.75	0.50
$P_{GHCPWA+C}$	77.50	36.25	48.75	9.97	38.78	0.50
P_{GHCP+C}	77.50	60.00	38.75	16.5	22.25	0.29

To ensure a good homogeneity for the pastes, a mini mixer where only 200 ml can be produced is used. The followed steps are:

- Add all the amount of water in the mixer,
- Add the first half of the powders (cement + mineral addition),
- Mix for 90 seconds,
- Stop the mixer for 30 seconds, and add the second part of the powders,
- Mix for 90 seconds.

The paste is poured into small hermetic containers (15ml). Each container is rotated for 6 hours in order to avoid segregation and bleeding of cement pastes during setting [29]. The obtained paste is stored in hermetic containers at 20°C for 1, 2, 7 and 28 days. Then, the hardened paste is cut into small pieces (1x1x1 cm^3) and immersed in isopropanol for 1 week to stop the hydration of cement[30,31]. After that, the paste is dried at 40°C until constant mass and put in sealed bottles to avoid any carbonation or rehydration.

3.2 Hydration degree
To estimate the hydration degree of the cement mixtures, the quantity of Portlandite produced at a given time and the maximum quantity of Portlandite that can be produced during the complete hydration of the cement are needed.

3.2.1 Quantification of Portlandite produced for total hydration of the cement

According to [32-38] the simplified reactions that produce Portlandite from ordinary Portland cement (OPC) are presented in (eq.7), (eq.8), (eq.9), (eq.10) and (eq.11). The amount of Portlandite formed is identical for the 3 hydration equations of C_4AF.

$$C_3S + 5.3H \longrightarrow C_{1.7}SH_4 + 1.3 \ CH \ \ldots\ldots\ldots \ (7)$$

$$C_2S + 4.3H \longrightarrow C_{1.7}SH_4 + 0.3CH \ \ldots\ldots\ldots (8)$$

$$C_4AF + 3C\bar{S}H_2 + 30 \ H \longrightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \ \ldots\ldots\ldots\ldots.(9)$$

$$2C_4AF + C_6A\bar{S}H_{32} + 12H \longrightarrow 3C_4A\bar{S}H_{12} + 2CH + 2FH_3 \ \ldots\ldots\ldots.(10)$$

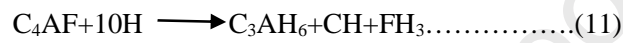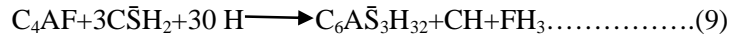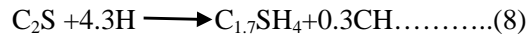$$C_4AF + 10H \longrightarrow C_3AH_6 + CH + FH_3 \ \ldots\ldots\ldots\ldots.(11)$$

Table 4 shows the composition of the used cement obtained by XRF combined with Bogues method. The percentage mass of Portlandite produced for each phase is calculated. The total amount of obtained Portlandite for the total hydration of the cement is equal to 0.294g/g of anhydrous cement.

Table 4: Portlandite production for a complete hydration of cement

Anhydrous phases	Mass content in cement (%)	CH mass per unit of anhydrous phase (g/g cement)	CH mass for 1 gram of anhydrous cement (g/g cement)
C3S	61.9	0.42	0.261
C2S	11.2	0.13	0.014
C3A	6	0	0
C4AF	12	0.15	0.018

3.2.2 Portlandite quantification for the different mixes at different ages

TGA analysis is used in order to quantify the Portlandite produced in the different mixes. The samples are heated up to 1000°C in a platinum crucible at 10°C/min, under argon. The mass variation is due to dehydration of hydrates and decarbonation of calcite.

Figure 5 presents the obtained TGA results for pure GHCP and the different pastes after 1 day of hydration. Three peaks are observed. The first peak corresponds to the dehydration of C-S-H, the second one to the dehydration of Portlandite and the last one corresponds to the decarbonation of $CaCO_3$. It is noted that the $P_{GHCP \ WA+C}$ has the highest peak for Portlandite compared to the other mixtures (pastes manufactured with LF and GHCP). The $P_{GHCP \ WA+C}$ and P_{GHCP+C} mixtures have larger Portlandite amounts than the P_{LF+C} mixture. A peak of $CaCO_3$ is also observed for the different mixtures. The P_{LF+C} mixture has a large $CaCO_3$ peak compared to the GHCP, P_{GHCP+C} and $P_{GHCP \ WA+C}$ due to the fact that LF is essentially composed of $CaCO_3$. A small peak of $CaCO_3$ is obtained for GHCP, this can be explained by the fact that a part of the cement paste has been carbonated. The carbonation of the different pastes has been limited by making the TGA tests directly after stopping hydration. The obtained peaks of $CaCO_3$ in P_{GHCP+C} and

$P_{GHCPWA+C}$ are therefore caused by the former carbonation of GHCP and not by the carbonation of newformed hydration products.
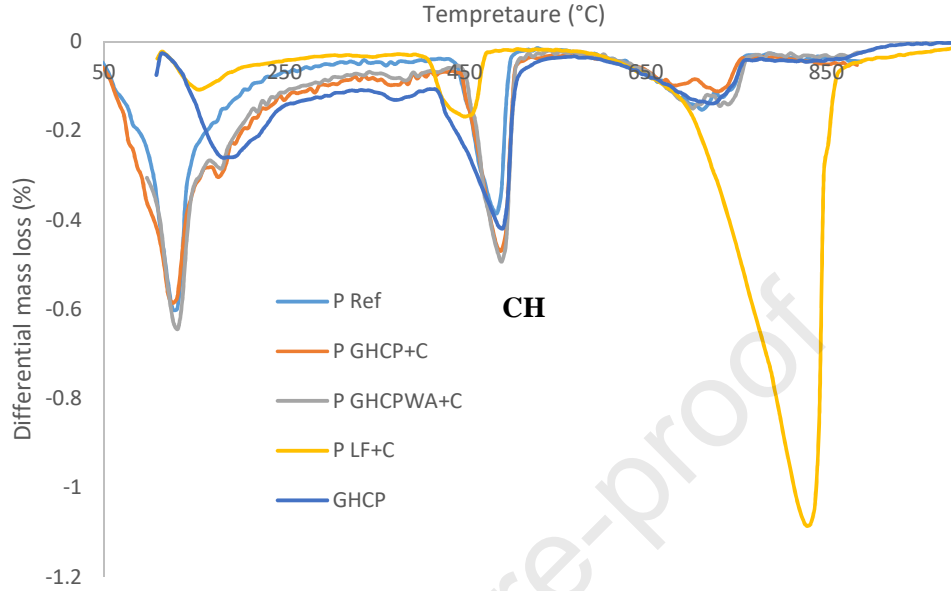

Figure 5: TGA results for GHCP and different mixtures after 1 day of curing

Equation 12 (eq.12) is used in order to calculate the Portlandite quantity $(CH(t)_{total})$ for the different mixtures. Where $\Delta m_{405°C-560°C}$ (%) is the mass loss of samples between 405°C and 560°C obtained with TGA results. M_{CH} is the molar masse of Portlandite (74.09 g/mol) and M_{H2O} is the molar mass of water (18g/mol).

$$CH(t)_{total} = \frac{\Delta m_{405°C-560°C} \times M_{CH}}{M_{H2o}} \ldots\ldots (12)$$

For the $P_{GHCP\ WA+C}$ and P_{GHCP+C} mixtures, the amount of Portlandite brought by the GHCP is subtracted from the total quantity in order to only take into account the neo-formed Portlandite (CH $(t)_{neo-formed}$) (eq.13) where m_{GHCP} and m_C are respectively the mass of GHCP and cement. (eq.14) is used to compute the quantity of neo-formed Portlandite for 1 gram of cement $(CH(t)_{neo-formed/g\ cement})$.

$$CH(t)_{neo-formed} = CH(t)_{total} - CH_{GHCP} \times \frac{m_{GHCP}}{m_{GHCP}+m_C} \ldots\ldots\ldots\ldots\ldots(13)$$

$$CH(t)_{neo-formed/g\ cement} = CH(t)_{neo-formed} \times \frac{m_C + m_{mineral\ addition}}{m_C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

3.2.3 Degree of hydration

The calculation of hydration degree is presented according to the cement quantity in the mixture and is computed with (eq.15), where CH $(t)_{neo-formed/gcement}$ corresponds to the quantity of neo-formed Portlandite produced at time t (1, 2, 7 and 28 days) for 1 g of cement. $CH_{C\ total}$ is the amount of total Portlandite that can be produced if 1 gram of cement is 100% hydrated [36-38].

$$\alpha = \frac{CH(t)_{\text{neo-formed/gcement}}}{CH_{Ctotal}} \dots\dots\dots\dots\dots\dots\dots(15)$$

The results of the degrees of hydration are presented in figure 6. The reference mixture presents a lower degree of hydration at early ages compared to those made with GHCP and LF. Thus, the addition of GHCP and LF accelerates the hydration of cementitious pastes. The $P_{GHCP\ WA+C}$ mixture has a lower hydration degree at 1, 2, 7 and 28 days than P_{LF+C}. The P_{GHCP+C} presents a high hydration degree at 1 day, but its further hydration is less compared to other cement pastes, which can be explained by the fact that the P_{GHCP+C} mixture has a low W_{eff}/C ratio (0.27).
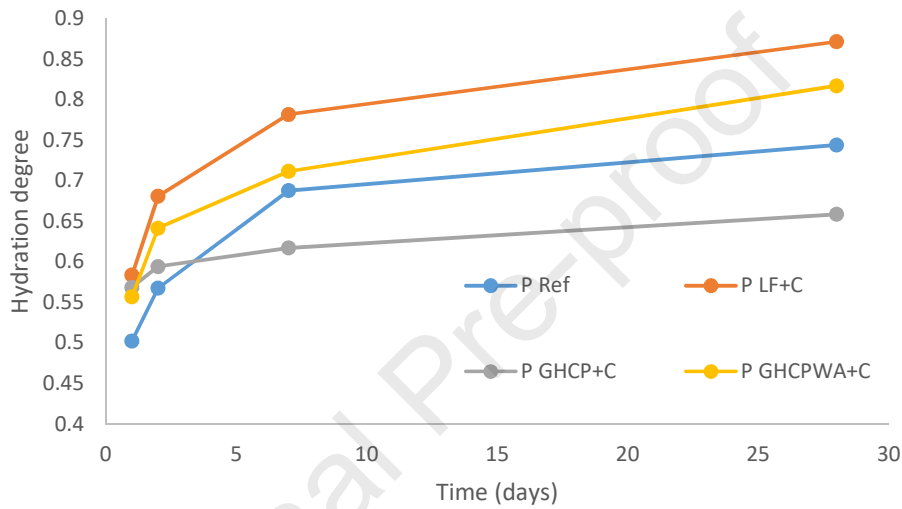

Figure 6: Hydration degree of the different mixes

3.3 Porosity measurement

The porosity of the different mixes is measured by Mercury Intrusion Porosimetry (MIP) at 1, 2, 7 and 28 days. Table 5 presents the obtained results. The porosity has been corrected for the different mixes in order to compute the porosity of the neo-formed cement paste, excluding that of the mineral addition. (eq.16) is used to make the porosity corrections, where $\varphi_{\text{neo-formed}}$ presents the porosity of the neo-formed cement paste, P_{Total} is the total porosity obtained with MIP , φ_{powder} is the porosity of the mineral addition, and V_{powder}, V_{Weff} and V_{cement} are respectively the volume of mineral addition, effective water, and cement.

$$\varphi_{\text{neo-formed}} = (\varphi_{\text{total}} - \varphi_{\text{powder}} \times \frac{V_{powder}}{V_{powder}+V_C+V_{W_{eff}}}) \times \frac{(V_{powder}+V_C+V_{W_{eff}})}{(V_{powder}+V_C)} \dots\dots\dots\dots\dots(16)$$

Table 5: Porosity of the different mixes

	Total porosity (%vol)				Porosity of the neo-formed paste (%vol)			
	P_{Ref}	P_{LF+C}	$P_{GHCPWA+C}$	P_{GHCP+C}	P_{Ref}	P_{LF+C}	$P_{GHCPWA+C}$	P_{GHCP+C}
1 day	40.0	28.0	35.5	24.4	40.0	38.8	39.8	24.1
2 days	38.2	23.5	28.2	22.2	38.2	32.7	29.6	20.0
7 days	26.8	14.7	23.7	19.0	26.8	20.5	23.3	14.0
28 days	24.2	12.2	18.3	18.0	24.2	17	15.8	12.1

It is noted, for the mixtures before correction, that the reference mixture and $P_{GHCP\ WA+C}$ present the highest porosity whatever the ages. The lowest porosity is obtained for P_{LF+C}.

After correction, the $P_{GHCP\ WA+C}$ mixture has a similar porosity comparing to the P_{LF+C} mixture, which is due to the fact that the W_{eff}/C is similar for the two mixes ($W_{eff}/C=0.5$). Despite the fact that the reference mixture has the same W_{eff}/C ratio than P_{LF+C} and $P_{GHCP\ WA+C}$ mixes, a higher porosity comparing to the P_{LF+C} and $P_{GHCP\ WA+C}$ mixture is obtained. This can be explained by the fact that the hydration degree of the mixes made with LF and GHCP is higher than the reference one. The P_{GHCP+C} presents the smallest porosity. This is due to the W_{eff}/C ratio, which is smaller than the other mixes (0.27). The porosity results are in accordance with the hydration degree results.

Thus, we can conclude that the water present in the paste is not the same as the water available to cement hydration when porous mineral addition are used. Moreover, the addition of GHCP into a cementitious mixture can accelerate the one day hydration of the cement. Also the GHCP has an impact on the hydration degree and the total porosity of the manufactured mixes by decreasing the amount of available water for the cement hydration. The next step of this work is to study the effect of adding GHCP on mortar properties.

4. Fresh and hardened behavior of mortars with GHCP and LF

4.1 Methodology and experimental procedure

In order to identify the effect of the GHCP porosity on fresh and hardened behaviors of mortar, the calculation of the total porosity is needed. The initial porosity of the mixture is presented with (eq.17) in which W_{eff}, V_{pore}, V_{powder}, V_{air} and V_c are respectively the effective water, the pore volume of the powder, the solid volume of the powder, the volume of air in mortar, and the cement volume:

$$P_0 = \frac{V_{void}}{V_{total}} = \frac{W_{eff}+V_{pore}+V_{air}}{W_{eff}+V_{powder}+V_{pore}+V_C+V_{air}} \dots\dots\dots\dots\dots\dots\dots(17)$$

Mortar compositions are made with a volume substitution of cement by GHCP and LF, the following mixes are made:

- M_{LF+C}: volume substitution of the cement by LF at 10, 20, 30 and 40% by using the absolute density
- $M_{GHCP\ WA+C}$: volume substitution of the cement by GHCP at 10 ,20 ,30 and 40% by using the real density

- M_{GHCP+C}: volume substitution of the cement by GHCP at 10, 20, 30 and 40% by using the absolute density.

The mortar compositions are presented in table 6. The reference composition complies with standard EN 196-1. Figure 7 illustrates the followed approach to study the fresh and hardened behavior for the different mortars.
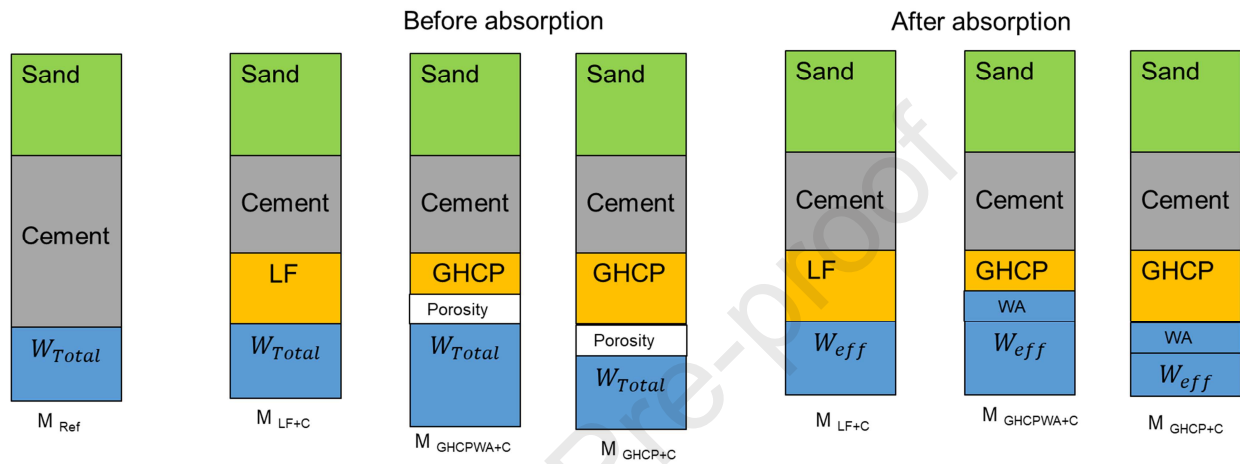

Figure 7: Illustration of the different mixes

Table 6 : Mortar compositions

	Substitution rate (%)	Cement [g]	Addition [g]	Sand [g]	W_{Total} [g]	WA [g]	W_{eff}	W_{eff}/C
M_{Ref}	0	450	-	1 350	225	-	225	0.50
M_{LF+C}	10	405	39.5	1 350	225	-	225	0.56
	20	360	79.0	1 350	225	-	225	0.63
	30	315	118.5	1 350	225	-	225	0.71
	40	270	157.9	1 350	225	-	225	0.83
$M_{GHCP\ WA+C}$	10	405	21.1	1 350	230.8	5.8	225	0.56
	20	360	42.2	1 350	236.6	11.6	225	0.63
	30	315	63.2	1 350	242.4	17.4	225	0.71
	40	270	84.3	1 350	248.2	23.2	225	0.83
M_{GHCP+C}	10	405	35.1	1 350	225	0	215.3	0.53
	20	360	70.3	1 350	225	0	205.7	0.57
	30	315	105.4	1 350	225	0	196	0.62
	40	270	140.5	1 350	225	0	186.4	0.69

Figure 8 presents the initial porosties computed with (eq.17), the air volume is considered equal to 0. The mix M_{LF+C} presents a similar porosity to the mix M_{GHCP+C}. This is due to the fact that in the latter the water absorption is not taken into account, and the solid volume of GHCP is equal to that of LF. A difference is observed between the mix $M_{GHCP\ WA+C}$ and both M_{LF+C} and M_{GHCP+C}. This difference is due to the water absorption which is considered in the added water in $M_{GHCP\ WA+C}$.

In the following, the fresh and hardened behavior comparison is made with M_{LF+C}, $M_{GHCPWA+C}$ and M_{GHCP+C}. Given the porosity of GHCP, the effective water and the solid volume of GHCP between $M_{GHCPWA+C}$ and M_{GHCP+C} are not the same. This procedure allows: first to make a comparison between LF and GHCP using the same effective water and envelope volume and second to make a comparison using the same initial porosity of mortar made with LF and GHCP.
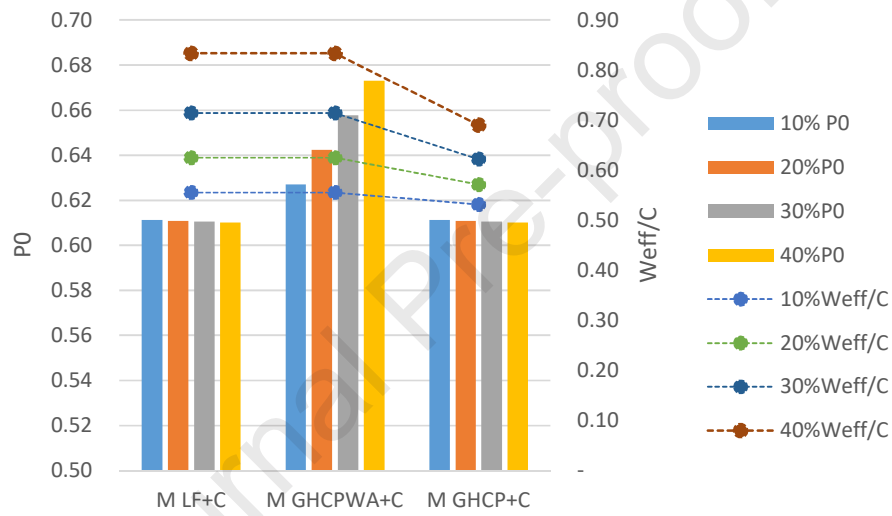

Figure 8: Initial porosity and Weff/C computed with (eq.17)

The mixing of the different mortars is 4 minutes long. The cement, addition and all the water are first mixed at low speed for 30 seconds; thereafter the sand is introduced gradually for 30 seconds. An additional mixing of 30 seconds at low speed is then performed. Subsequently, the bowl is scraped for 15 seconds, followed by 1 minute 15 seconds of rest. Finally, high speed mixing for 1 minute is performed.

The mortar's workability is measured with the MBE cone ("Mortiers de Béton Equivalent'' that can be translated as ''Equivalent Mortars to Concrete'') according to the procedure described in [39]. The cone is filled in 3 layers of equivalent volume and each layer is compacted 15 times with the tamping rod. The upper surface of the cone is leveled to remove the excess mortar. The cone is lifted vertically in 3 seconds. The slump is measured by considering the highest point [39].
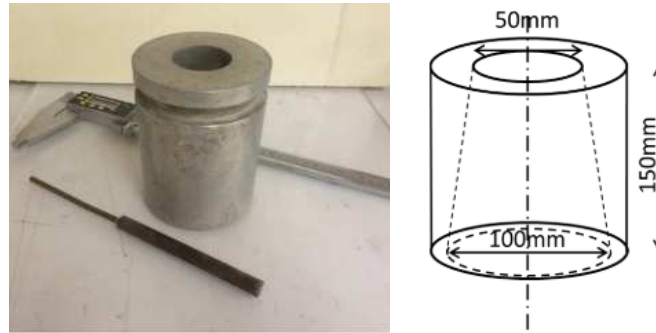
Figure 9: MBE cone [39]

Air content is measured on all mortars with CONTROLS/1L. The compressive strength is determined on $4\times4\times16$ cm^3 samples. The samples are demolded after 24 hours and stored under water at 20°C until the day of the test (28 days). The compressive strength is expressed as the mean value of 6 samples as reported in the standard EN 196-1.

4.2 Fresh properties

Figure 10 presents the workability results of mortars made with LF and GHCP as a function of the cement substitution percentage. The workability of the M_{LF+C} is almost constant regardless of the substitution percentage. For the mix M_{GHCP+C} the slump decreases very rapidly with the substitution rate and becomes null beyond 30% of substitution, which is due to the absorption of water by GHCP. For the mix $M_{GHCP\,WA+C}$, considering the porosity and water absorption of the powder gives a better workability than the mortar made with LF. The increase in workability of $M_{GHCP\,WA+C}$ in comparison to M_{LF+C} can certainly be attributed to different behaviors of the two powders regarding agglomeration (water demand of powders), to physical differences between the powders, and/or to uncertainties in the estimation of the water absorption of GHCP.

Figure 11 shows the results of air content obtained for the different mixtures. It is noted that the air content is slightly higher for mortars made with GHCP compared to those made with LF. However, it can be considered that, considering the water absorption of GHCP does not affect significantly the air content of mortars, but it affects significantly their workability.

These results show that, if the water absorption of the powder is not considered, a sharp decrease in the workability of the mortar occurs as the substitution rate increases, because of the decrease in the interstitial water of the mix. Hence, if one wants to design mixes where GHCP would replace LF without changing too much the workability of the mix, the WA of the substitute powder has to be taken into account.
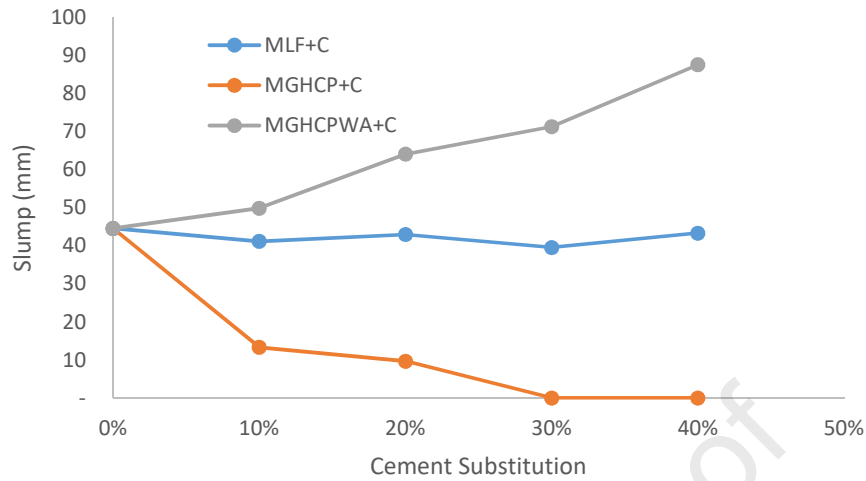
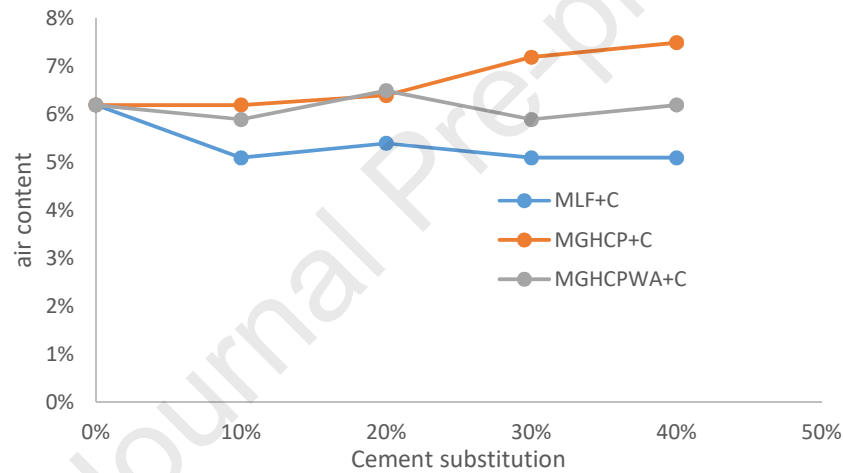**Figure 10:** Slump of the different mixes, in function of the substitution rate

Figure 11: Air content variation in function of the substitution rate for the different mixes

4.3 Hardened properties

Table 7 presents the compressive strengths obtained for the mortars made with LF and GHCP. It's observed that the mechanical resistance decreases when the substitution rate of GHCP and LF increases. The substitution percentages of cement by GHCP and LF in mortar compositions have been made by the solid and envelope volume. In order to have knowledge about the influence of adding GHCP as a mineral addition, the compressive strengths are compared as a function of the total water (effective + absorbed water) to cement ratio.

Figure 12 presents the variation of compressive strength as a function of the total water (effective water + absorbed water) to cement ratio at 7 and 28 days. The results show close variations of compressive strength for the different samples. So, the compressive strength of mortars mainly depends on the amount of cement (reactive phase of the binder), and initial porosity of the mixes, including the internal porosity of the GHCP. Considering the water absorption in the mix design to compensate for a loss of workability (as stated in the previous section), leads to a decrease in the compressive strength of mortars.

Table 7: Compressive strength (Cs) result of mortars made with LF and GHCP (with and without considering the WA) at 7 , and 28 days

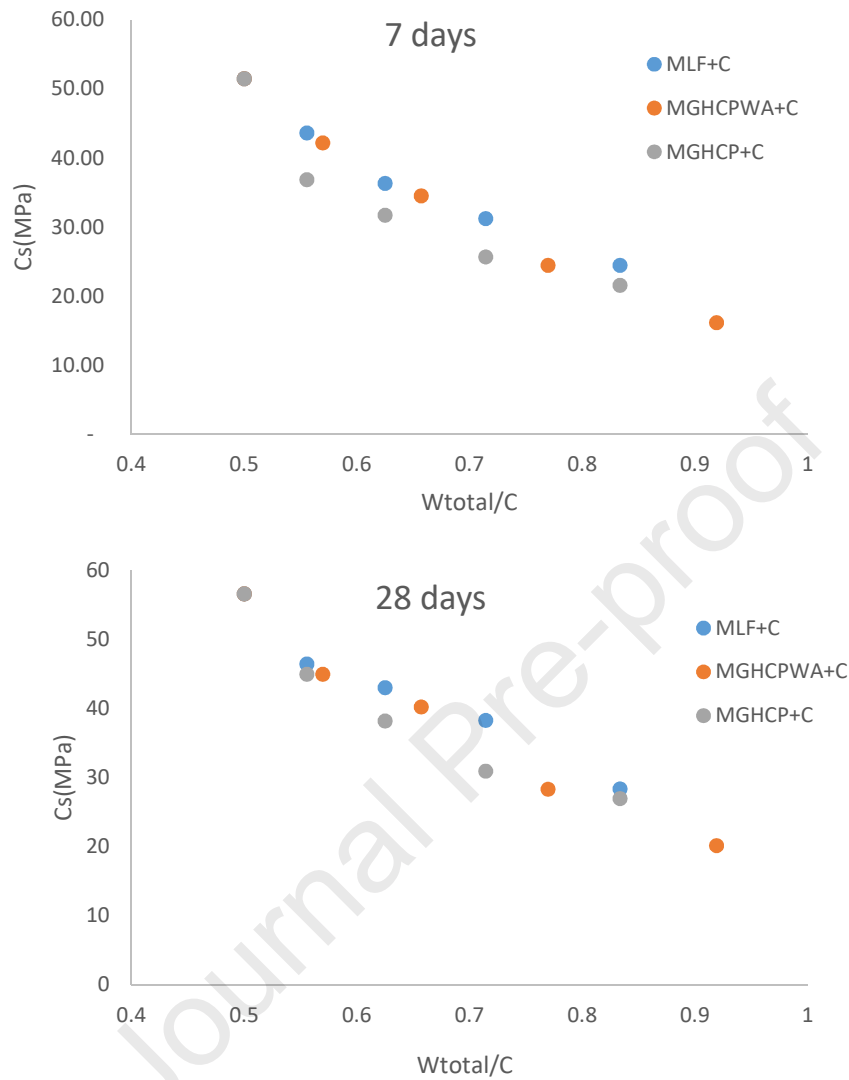|	Volumique substitution rate (%)	Cs 7 Days (MPa)	Cs 28 Days (Mpa)
MRef	0	51.5	56.6
MLF+C	10	43.6	46.5
	20	36.3	43
	30	31.2	38.3
	40	24.5	28.3
MGHCP	10	42.2	45
WA+C	20	34.5	40.2
	30	24.4	28.3
	40	16.1	20.2
MGHCP+C	10	39.9	45
	20	31.7	38.2
	30	25.7	30.9
	40	21.6	26.9

Figure 12: Compressive strength (Cs) results expressed as function of the total water to cement ratio for mortar made with GHCP and LF.

5. Conclusion

Cementitious mixes manufactured with the grinded hardened cement paste (GHCP) have been compared with others containing limestone filer (LF). The TGA and MIP analyses on pastes showed that both GHCP and LF allow the acceleration of the cement hydration. Also, when using the GHCP, the water present in the paste (effective water) is not the same as the one available for cement hydration due to the absorption of part of the water by fine particles.

Using a constant total porosity makes it possible to obtain equivalent mechanical strengths between the mixtures manufactured with LF and the GHCP. But a worse workability is obtained for the mixes with GHCP. However, if the water absorption is taken into consideration when the cement substitution is proceeded, the workability increases and the mechanical resistance decreases. The decrease of the

mechanical strength is caused by the porosity present in GHCP. In fact, the neo-formed porosity of the paste of both $M_{GHCP\ WA+C}$ and M_{LF+C} are identical, but the total porosity of the $M_{GHCP\ WA+C}$ increases due to the porosity of the mineral addition, which makes the compressive strength decrease. Taking into consideration the envelope volume with the absorbed water of GHCP when manufacturing a mortar or concrete seems to be the best recommended procedure. It means moreover that, when using that GHCP in mortar or concrete production, the mixing water should include the effective water (the needed water to hydrate the cement), and the absorbed water by aggregate and GHCP.

In the standard EN 206-1, the limestone filler can be used as a mineral addition to replace cement. The former can be used at a maximum substitution rate of 20% by weight, which corresponds to 23% by volume substitution. If its water absorption is taken into consideration, the use of the GHCP, with similar volume substitution, is clearly possible.

The recycled fine powders from RCA do not contain 100% of hardened cement paste. Other non-porous materials (natural aggregates) that can significantly decrease the porosity are present in RCA. Thus, if the recycled powders from RCA are well characterized, they can be incorporated as a mineral addition in the manufacture of mortar or concrete and the fresh and hardened behaviors of mortar or concrete can be controlled.

Acknowledgment

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Conflicts of interest:

The authors declare that they have no conflicts of interest .