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# Multiscale investigation of cement pastes with low and high-grade calcined clays and slag at early and advanced ages

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## ABSTRACT

Clays are abundant materials worldwide, but the massive demand for pure kaolinitic clays in multiple fields could reduce the availability of high-grade calcined clay. For this reason, the properties of cementitious materials with low-grade calcined clays should be seriously investigated. In this work, binary and ternary binders composed of high-grade or low-grade calcined clays and slag, replacing 30% of Portland cement, are studied using nanoindentation, standard strength measurement, MIP, and SEM in order to demonstrate the impact of calcined clay composition on the microscale and macroscale properties of cementitious materials during both early and mature ages. Results show that in binary binders, low-grade calcined clay leads to reduced porosity and enhanced elastic and viscoelastic properties, as probed by means of nanoindentation, while high-grade calcined clay results in a high amount of low-density calcium silicate hydrate (LD CSH). Moreover, in the ternary binder, a synergistic effect has been highlighted between low-grade calcined clay and slag through the improvement of compressive strength at early age, as well as a refinement of the pore structure. From this study, it can be concluded that low-grade calcined clays give rise to good micromechanical properties and can be particularly effective in ternary blends when associated with slag.

**Keywords:** Nanoindentation, Micromechanical Properties, Creep, Microstructure, Calcined Clay, Blast Furnace Slag.

## 31 **Summary of abbreviations**

### **Mineral additions**

SCMs	Supplementary cementitious materials
CC	Calcined clay
GBFS	Granulated blast furnace slag

### **Pastes' phases**

LD CSH	Low-density CSH
HD CSH	High-density CSH
CH	Portlandite/calcium hydroxide
UC	Unhydrated cement
Q	Quartz
M	Muscovite

### **Atomic species**

Al	Aluminium
K	Potassium
Ca	Calcium
Si	Silicon

### **Experimental and numerical techniques**

XRD	X-ray diffraction
SEM	Scanning electron microscope
EDS	Energy dispersive spectroscopy
BSE	Backscattered electrons
MIP	Mercury intrusion porosity
TGA	Thermogravimetric analysis
GMM	Gaussian Mixture Model

## 32 **1. Introduction**

33 Cement production is a highly CO<sub>2</sub>-emitting process. Its main constituent, clinker, is obtained by  
34 limestone and natural clays being fired at 1,450°C, which requires fossil fuels for heating and induces  
35 limestone decarbonation. To reduce this substantial environmental impact, supplementary  
36 cementitious materials (SCMs) can partially replace cement in concrete. Commonly used SCMs  
37 include fly ash, silica fume and granulated blast furnace slag; however, these are only available in  
38 limited supplies. Fine limestone and natural pozzolans are also employed, but their reactivity remains  
39 low when used alone. The introduction of calcined clays in cement blends has thus received great

attention of late due to their smaller carbon footprint, widespread availability [1] and potential to improve cementitious material properties.

Replacing a portion of Portland cement with calcined clays results in several changes in the cement paste hydration products. In addition to calcium-silicate-hydrate (CSH), calcium hydroxide (CH) and ettringite, which are the main hydration products of a Portland cement paste, other products may be formed depending on the raw clay composition. For instance, the alumina-rich amorphous phase of metakaolin (MK) triggers the formation of calcium aluminosilicate hydrates (CASH), CAH, strätlingite  $C_2ASH_8$ , and hydrogranet  $C_3AH_6$  or  $C_4AH_{13}$ , depending on both the  $AS_2/CH$  ratio ( $AS_2$  stands for  $Al_2O_3 \cdot 2SiO_2$ ) and reaction temperature [2]. In the presence of reactive calcite, calcium hemicarboaluminate hydrates (Hc) are also formed as a consequence of ettringite conversion [3]. The hydration kinetics are also modified with calcined clay incorporation, since they accelerate the hydration of clinker minerals, with ettringite being formed faster [4], which also increases the heat of hydration, as reported in [5]. Moreover, calcined clays are pozzolanic materials, which results in calcium hydroxide consumption inside the cement paste after several days/weeks [6].

Overall, it has been proven that incorporating calcined clays is beneficial to cementitious materials, as regards the majority of their properties. It has also been shown that compressive strength increases relative to pure cement reference samples, especially at early ages, given that the filler effect is immediate [7], as is the elastic modulus [8,9]. Durability properties may actually be enhanced with calcined clay incorporation through pore size refinement [10]. In their study, Dwivedi *et al.* pointed out that a 20% replacement of cement by metakaolin in mortars reduces the number of capillary pores, thus leading to decreased permeability [11]. Chloride ion ingress is also reduced [12,13], as is the resistance to freeze-thaw cycles [14].

However, the use of calcined clays in cementitious systems also has some drawbacks, such as a loss of workability due to its high specific surface area [15]. The use of other SCMs with calcined clays can serve to overcome these obstacles and enhance other properties. Recently, several studies have demonstrated the efficiency of using calcined clays with limestone in  $LC^3$  binders, in improving chloride resistance [16,17] and preventing the alkali-silica reaction [18]. Similarly, the use of calcined clays with slag improves fluidity of the cement blend [19] as well as compressive strength [20]. Even though several works have studied the hydration and macromechanical properties of calcined clay-based cementitious blends, their micromechanical properties are rarely addressed, especially at an early age. In addition, the effect of the calcined clay grade on several properties of cementitious materials was studied, such as rheology [21], hydration and mechanical performance [22–24],

72 printability [25], but there is no such study to determine its effect on micromechanical properties,  
73 namely elastic modulus, hardness, and contact creep modulus, of the cementitious materials phases,  
74 which is of huge importance to understand the observed behaviors at the macroscale.

75 Microindentation and nanoindentation were applied as local mechanical investigation techniques in  
76 order to assess the mechanical properties of cementitious materials [26]. Some studies used these  
77 techniques to investigate localized phenomena, such as the interfacial transition zone (ITZ) [27,28]  
78 and carbonated areas [29], while others targeted specific phases of interest in a heterogeneous material  
79 [30]. Nonetheless, since cementitious materials exhibit heterogeneous features, the majority of studies  
80 performed a large number of indentations in the regular grid forms so as to study the cement pastes;  
81 the properties of the various phases were determined by means of different clustering methods,  
82 namely least-square estimation (LSE) and maximum likelihood estimation (MLE). [31–33]. A number  
83 of studies on pure cement mixes were conducted according to these techniques [34–36], then  
84 extending to mixes containing SCMs to assess their effect on micromechanical properties. The elastic  
85 modulus of the CSH phase was indeed found to be 10% lower when silica fume and fly ash were  
86 incorporated [37], while another study demonstrated that the elastic properties did not change with  
87 fly ash incorporation [38]. Instead, the fractions of portlandite decreased and those of high-density  
88 CSH increased [37,38], which was explained by the pozzolanic reaction. Evidence of the pozzolanic  
89 reaction has also been proven in the presence of metakaolin [39] and slag [40]. The incorporation of  
90 pure metakaolin (96.4% amorphous phase) and slag resulted in an increase of CSH porosity at 7 days  
91 [41].

92 Over the last two decades, a study of the viscoelastic behavior of materials subjected to  
93 microindentation and nanoindentation techniques has been added as well. These techniques have  
94 speeded the characterization of creep properties of cementitious materials by applying a constant load  
95 for several tens of seconds on the tested materials; in contrast, measuring creep properties typically  
96 takes weeks to years at the scale of concrete laboratory samples or actual structures [42,43]. Although  
97 the creep mechanism of cementitious materials has yet to be well understood, it is generally agreed  
98 that CSH acts as the primary cause. In [44,45], the authors proved that CSH exhibits logarithmic  
99 creep properties that depend solely on CSH packing density. Several studies were subsequently  
100 conducted to investigate the creep properties of cementitious materials [43-45]. Li and colleagues  
101 have examined the effect of various cement paste phases on cement paste creep properties and  
102 underscored the importance of considering the actual pore creep modulus instead of 0 GPa, as well  
103 as the possibility of considering all unhydrated particles, despite a wide range of creep property  
104 variation, as a single phase in homogenization schemes [49]. The impact of SCMs on viscoelastic

properties has rarely been assessed although they may play a significant role in the modern green concrete creep phenomenon. Li *et al.* have shown that a 10% cement replacement with silica fume was found to enhance the CSH creep modulus [50]; but to the best of the authors' knowledge, no such studies on calcined clay binary or ternary blends have yet to be conducted, especially at an early age.

In this study, the micromechanical properties of binary and ternary calcined clay-blended pastes at both early and advanced ages will be investigated, and the advantage of using low-grade calcined clays in terms of performance will be demonstrated, along with their availability, lower environmental impact (due to lower calcination temperatures) and lower cost. To this end, a comprehensive comparison of the pastes microstructure and nanoindentation-inferred micromechanical properties will be drawn between low-grade and high-grade calcined clay-based cement pastes. Next, the effect of slag addition on the Portland cement / low-grade calcined clay system will be discussed and the synergistic effect of slag and low-grade calcined clay highlighted.

## 2. Materials and methods

### 2.1 Materials and sample preparation

The materials used in this study are Portland cement CEM I 52.5 N, two distinct calcined clays CC1 and CC2, respectively originated from "Charentes" and "Mairiais" extraction sites in France, and granulated blast furnace slag (GBFS). The chemical composition and physical properties of the binders are given in

Table 1.

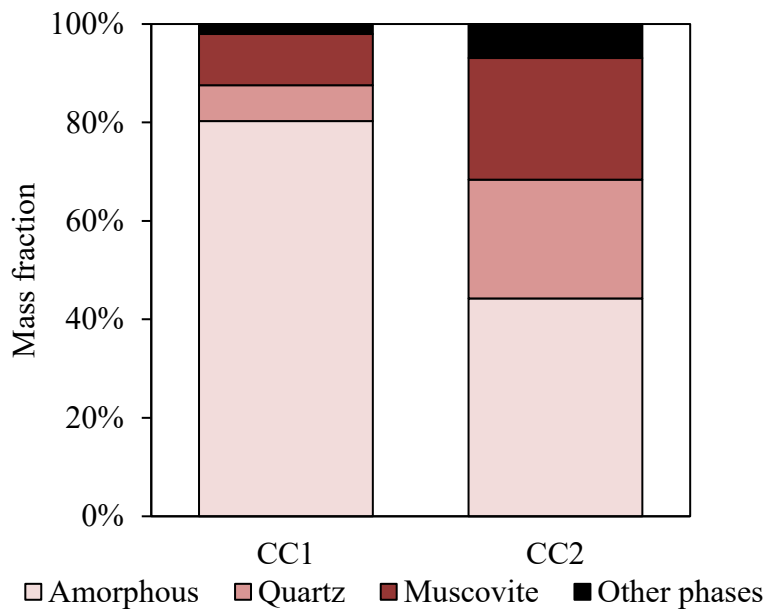


Fig. 1 shows the mineralogical composition of the studied calcined clays obtained by means of XRD and quantified by Rietveld analysis using the external standard method. According to the figure, CC1 and CC2 are mostly composed of amorphous phase (80.2% and 44.2% resp.), muscovite (10.4% and 24.7% resp.) and quartz (7.3% and 24.1% resp.). Other phases were identified in minor amounts such as kaolinite, rutile, albite and mullite. In the rest of this paper, CC1 and CC2 will be respectively assigned as high-grade and low-grade calcined clays given their amorphous phase content. The impact of this difference in calcined clays composition on the micromechanical properties of cement pastes will be investigated.

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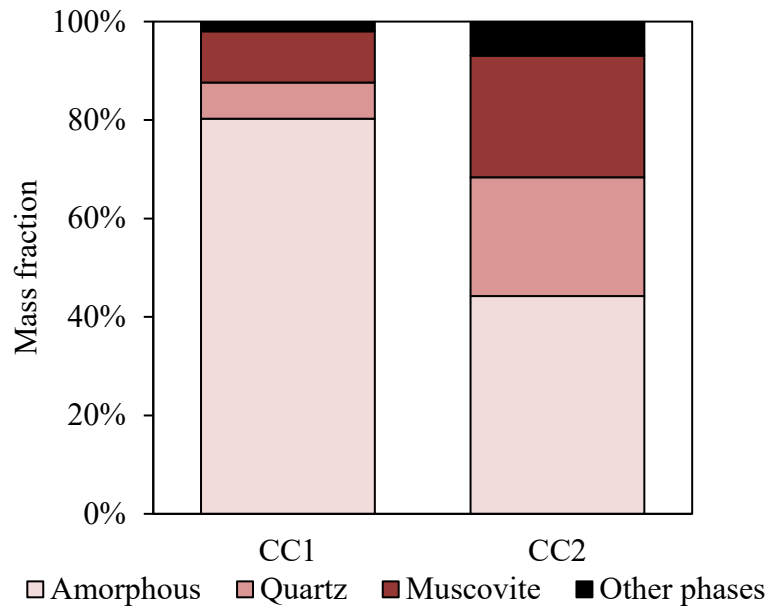
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**Table 1**

Chemical and physical properties of the materials used in this study

		Cement	GBFS	CC1	CC2
Chemical composition (%)	SiO <sub>2</sub>	20.4	37.7	53.95	62.70
	Al <sub>2</sub> O <sub>3</sub>	4.4	10.2	38.48	27.86
	Fe <sub>2</sub> O <sub>3</sub>	2.3	0.6	1.82	2.98
	TiO <sub>2</sub>	-	0.7	1.53	0.35
	CaO	64.0	43.8	0.04	0.10
	MgO	3.9	6.4	0.19	0.39
	SO <sub>3</sub>	2.9	0.1	-	-
	K <sub>2</sub> O	0.66	0.28	1.04	2.50
	Na <sub>2</sub> O	0.15	0.21	0.10	0.14
	P <sub>2</sub> O <sub>5</sub>	0.1	-	0.07	0.08
	Cl <sup>-</sup>	0.02	0.02	-	-
	S <sup>2-</sup>	<0.02	0.7	-	-
	Na <sub>2</sub> O eq.	0.58	0.44	-	-
Physical properties	Specific gravity (g/cm <sup>3</sup> )	3.15	2.9	2.2	2.5
	Specific area (cm <sup>2</sup> /g)	3979	4450	190000	160000

141



**Fig. 1.** Calcined clay compositions as determined using XRD/Rietveld analysis

Using these raw materials, water and superplasticizer (depending on the mix workability), four cement pastes with a constant water-to-binder ratio of 0.3 were manufactured. 30% of cement (by volume) was replaced by mineral additions in the binary and ternary binders. The binder proportions are detailed in Table 2.

**Table 2**

Cement paste binder compositions (volume proportions)

Paste reference	Cement (%)	GBFS (%)	CC1 (%)	CC2 (%)
P <sub>0</sub>	100	-	-	-
PCC1 <sub>30</sub>	70	-	30	-
PCC2 <sub>30</sub>	70	-	-	30
PCC2 <sub>15</sub> S <sub>15</sub>	70	15	-	15

The  $4 \times 4 \times 16 \text{ cm}^3$  cement paste prisms were manufactured, standard cured, demolded at 24 h and kept in lime-saturated water at 20°C until reaching testing age. Then, 1-2 cm cubes were sawn at the testing age, placed in 99.8% isopropanol for 4 days to stop hydration, and dried at 40°C for 4 other days [51]. As explained in [52], all hydration stoppage procedures were proven to cause microscopic modifications to the sample, although isopropanol is weaker and causes less damage.

For the nanoindentation and SEM tests, the cubes were impregnated in cold mounting epoxy resin. Special care was paid to the sample polishing step in order to achieve smooth surfaces: coarse

polishing was performed using SiC abrasive papers of decreasing grain sizes from 120 to 4000 grit (corresponding resp. to 68  $\mu\text{m}$  - 5.3  $\mu\text{m}$ ), then fine polishing using diamond pastes on woven natural silk discs of 3  $\mu\text{m}$  and 1  $\mu\text{m}$  grain sizes. Ethanol was used as a polishing lubricant to prevent further hydration. After each polishing step, the samples were cleaned in an ethanol ultrasonic bath for a few minutes to remove all suspensions and debris on the surface. Surface quality was assessed by means of the Scanning Probe Microscopy (SPM) mode of the nanoindenter, with the Root Mean Square (RMS) roughness being calculated on  $50 \times 50 \mu\text{m}^2$  surfaces.

## 2.2 Methods

### 2.2.1 Macromechanical testing

The compressive strength was measured on  $4 \times 4 \times 16 \text{ cm}^3$  prisms previously split into two, on at least four samples at 2 and 28 days according to NF EN 196-1 standard.

### 2.2.2 Thermogravimetric analysis

Portlandite content in the mixes was determined using TGA in order to assess the binders' pozzolanic activity, according to ASTM C1872-18 standard. For this purpose, a NETZSCH microbalance was used with  $\text{N}_2$  purging gas and a rate of 60 mL/min.  $50 \pm 5 \text{ mg}$  of crushed powder were placed in alumina crucibles and subjected to raising temperatures from  $20^\circ\text{C}$  to  $1000^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ . The weight loss  $WL_{CH}$  (%) of portlandite due to the evaporation of water was determined using the tangential method of Marsh [53] between  $400^\circ\text{C}$  and  $550^\circ\text{C}$ , and the measured mass proportion  $mm_{CH}$  (%) of portlandite as well as its actual mass proportion in the sample  $m_{CH}$  (%) are deduced using respectively the equations below:

$$mm_{CH}(\%) = WL_{CH} \times \frac{M_{CH}}{M_{H_2O}} \quad (1)$$

$$m_{CH}(\%) = \frac{mm_{CH}(\%)}{m_{600^\circ\text{C}} \times \left(1 + \frac{w}{b}\right)} \quad (2)$$

where  $M_{CH}=74 \text{ g/mol}$  is the molar mass of portlandite,  $M_{H_2O}=18 \text{ g/mol}$  is the molar mass of water,  $m_{600^\circ\text{C}}$  is the sample mass at  $600^\circ\text{C}$  and  $w/b=0.3$  is the water-to-binder ratio of all cement pastes.

### 2.2.3 Mercury intrusion porosity

The pore structure of the various cement pastes was investigated using a Micromeritics AutoPore IV mercury porosimeter according to ISO 15901-1:2016 standard. The mercury pressure gauge was used at a maximum pressure of 400 MPa, which corresponds to a minimum pore radius of 1.5 nm. Each cement paste mix was tested at 2 and 28 days.

#### 2.2.4 Scanning electron microscopy - Energy dispersive spectroscopy (SEM/EDS)

Scanning electron microscopy equipped with X-ray energy dispersive spectroscopy (SEM/EDS) was conducted to characterize the blended cement pastes microstructures. Backscattered electron (BSE) images were captured using an accelerating voltage of 15 kV, at working distance of 17 mm and a magnification of 300×. A surface scan of the chemical composition with an EDS detector was needed to roughly detect the nature of certain observed phases on BSE micrographs through the resulting elemental maps.

#### 2.2.5 Nanoindentation

Nanoindentation experiments were performed using a Bruker TS 77 Berkovich nanoindenter, in order to study the micromechanical properties of individual phases of the cement pastes. While in SPM mode, the smoothest parts of the samples ( $RMS < 50$  nm) were targeted in order to carry out nanoindentation tests. Three grids of  $20 \times 20$  indents, equally spaced at 5  $\mu m$ , were executed using a load-controlled function, with a trapezoidal loading composed of a loading phase in 5 s, a holding phase of 60 s at maximum load  $P_{max}$  of 2 mN and an unloading phase of 5 s. Continuous measurements of penetration depth with these applied loads were recorded at a frequency of 200 Hz; consequently, the slope of the unloading curve at maximum load  $S$  could be determined.

The reduced elastic modulus  $E_r$ , elastic modulus  $E$  and hardness  $H$  were all then calculated as per the Oliver and Pharr method [54]:

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A_c}} S \quad (3)$$

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_{ind}^2}{E_{ind}} \quad (4)$$

$$H = \frac{P_{max}}{A_c} \quad (5)$$

where  $\nu$  is the material Poisson's ratio, which equals 0.24 for cement paste [55];  $\nu_{ind} = 0.07$  and  $E_{ind} = 1,141$  GPa are respectively the diamond indenter Poisson's ratio and its elastic modulus.  $A_c$  denotes the projected contact area between the indenter tip and the indented surface, as obtained by the tip-area function calibration on a fused silica standard sample with incremental loads ranging from 100  $\mu N$  to 10,000  $\mu N$  by 100  $\mu N$  increments.

213 In order to calculate viscoelastic properties from the nanoindentation tests, the variation in penetration  
 214 depth  $\Delta h(t) = h(t) - h_0$ , where  $h_0$  represents the initial penetration depth, is logarithmically fitted  
 215 as:

$$216 \quad \Delta h(t) = x_1 \ln(1 + x_2 t) \quad (6)$$

217 where  $x_1$  and  $x_2$  are the parameters to fit; they are related to the creep modulus and characteristic time  
 218 respectively by the following expressions:

$$219 \quad C = \frac{P_{max}}{2a_U x_1} \quad (7)$$

$$220 \quad \tau = \frac{1}{x_2} \quad (8)$$

221 where  $a_U = \sqrt{A_c/\pi}$  is the contact radius.

222 All abnormal load-depth curves [56] were deleted prior to conducting a statistical analysis of the  
 223 results.

#### 224 2.2.6 Deconvolution process

225 The analysis of each indentation curve provides information about the mechanical properties of each  
 226 point  $k$  in the grid, i.e. values of elastic modulus, hardness and contact creep modulus ( $E_k, H_k, C_k$ ).  
 227 In this deconvolution process, the total distribution  $x$  of both elastic modulus and hardness  $x = (E, H)$   
 228 was assumed a mixture of individual phases, where each phase is seen as a two-dimensional Gaussian  
 229 distribution. The statistical deconvolution is then performed to cluster all the data into  $N$  mixture  
 230 components, i.e.  $N$  clusters. The number of clusters was chosen based on the Bayesian Information  
 231 Criterion (BIC). The probability density function of the Gaussian Mixture Model (GMM) is given in  
 232 equation (9), and the one for each phase is given in equation (11):

$$233 \quad p(x) = \sum_{i=1}^N \pi_i N(x|\mu_i, \Sigma_i) \quad (9)$$

$$234 \quad \sum_{i=1}^N \pi_i = 1 \quad (10)$$

$$235 \quad N(x|\mu, \Sigma) = \frac{1}{\sqrt{\det(2\pi\Sigma)}} e^{-\frac{1}{2}(x-\mu)\Sigma^{-1}(x-\mu)} \quad (11)$$

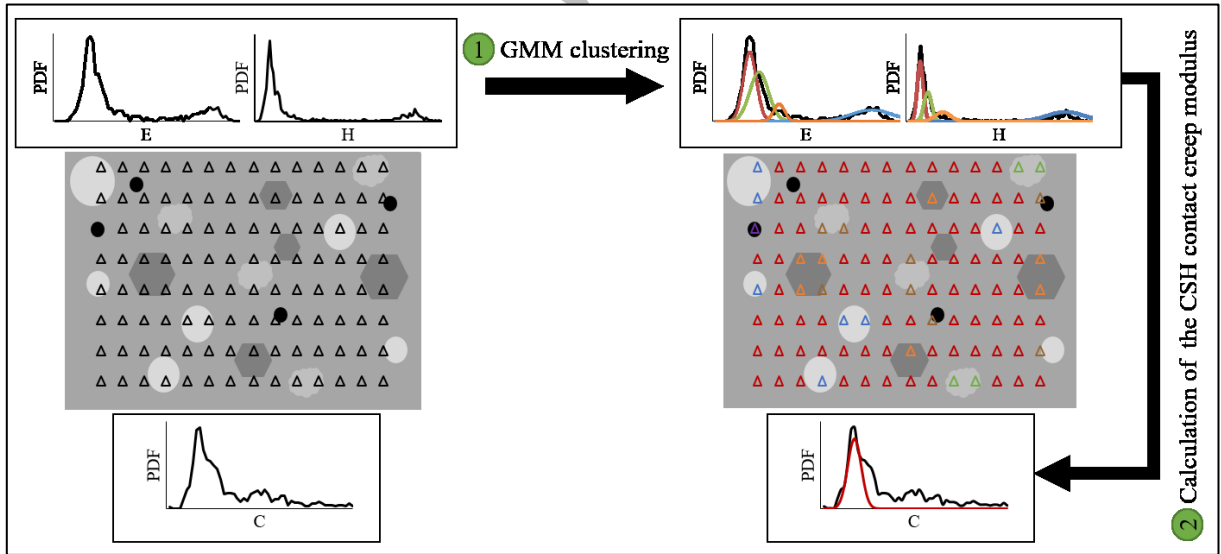
236 where  $\pi_i$ ,  $\mu_i$  and  $\Sigma_i$  are respectively the weighting coefficient, the mean value and the covariance of  
 237 the i-th component.

238 To find the parameters (the weighting coefficient, the mean and the covariance) that maximize the  
 239 joint probability, the following optimization problem is solved using Monte-Carlo search:

$$240 \quad \max(\ln(\prod_{j=1}^M p(x_j))) = \max(\sum_{j=1}^M \ln(\sum_{i=1}^N \pi_i N(x|\mu_i, \Sigma_i))) \quad (12)$$

241 where M is the number of observations, which is the number of indents.

242 To achieve this, Expectation-Maximization (EM) algorithm was used, where data were assigned to  
 243 the closest randomly chosen means, the means recalculated based on the assigned data and so on until  
 244 the calculated means are no more changing. Initial values were given by K-means algorithm in order  
 245 to reduce the calculation time. This first step of calculation was referred to as (1) in Fig. 2 illustrating  
 246 the calculation process. Finally, the mean and standard deviation of contact creep modulus on the  
 247 CSH resulting clusters were calculated for all the samples, which was referred to as (2) in Fig. 2.



249 **Fig. 2.** Calculation process of the clusters micromechanical properties

251 The clusters determined by this deconvolution process do not necessarily correspond to pure phases,  
 252 but the predominant ones can be determined depending on the mean and standard deviation values of  
 253 E and H. In literature, the properties of the known main phases in Portland cement pastes (LD and  
 254 HD CSH, portlandite, unhydrated cement) were widely reported. In addition to these known phases,

the values of elastic properties of some others, contained in our pastes and brought by the mineral additions, are given in Table 3 with the references from the literature. The assignment of predominant phases in each cluster starts by looking at the standard deviation: if it is high with respect to the mean value, then the cluster contains more than a predominant phase; if it is low, then the cluster is mono-phase. Then, the cluster's mean property is compared to values reported in the literature to assign suitable phase(s) to each cluster.

**Table 3**

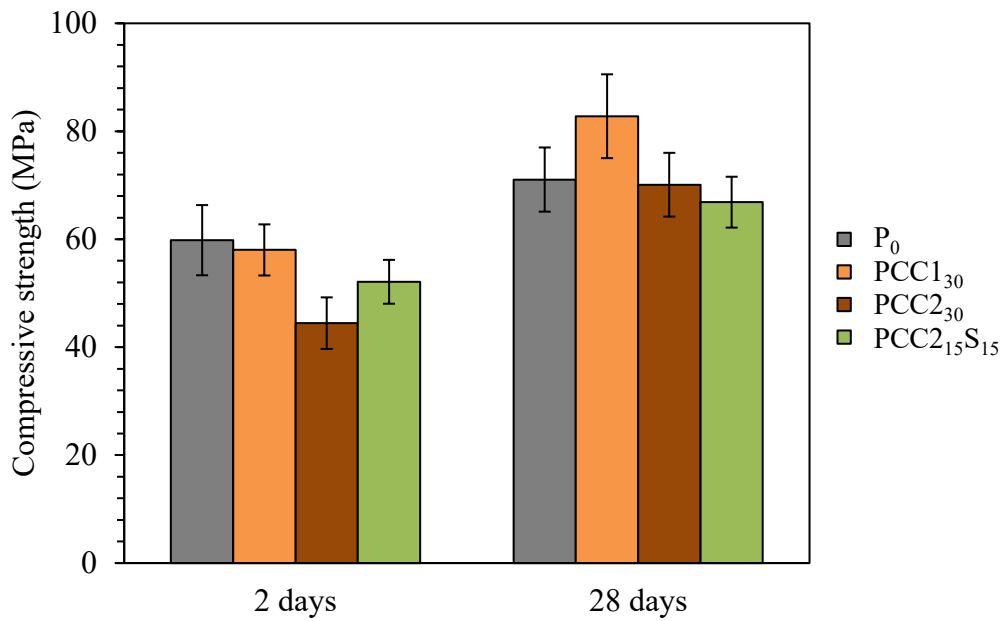
Elastic properties of some phases in the literature (mean or mean  $\pm$  standard deviation)

Phase	E (GPa)	H (GPa)	Reference
Unhydrated slag	72.4 $\pm$ 8.7	5.06 $\pm$ 1.18	[40]
Quartz	77.4	10.2	[57]
Muscovite	55.6	2.7	[57]

### 3. Results

#### 3.1 Macroscopic compressive strength

Fig. 3 compares the compressive strength of the four cementitious systems at 2 and 28 days. First, we can notice a strength-gain from 2 to 28 days in all the mixes, which is higher for the blended cement pastes compared to the reference mix, and the highest in PCC2<sub>30</sub> with 57.7% gain. At 2 days, the average compressive strength of the reference mix and PCC1<sub>30</sub> are maximum, reaching nearly 60 MPa. Incorporating CC2 into the system causes a drop in compressive strength of 25.7% relative to the reference mix. This finding indicates a better mechanical performance for PCC1<sub>30</sub> at an early age. Incorporating slag with CC2 increased by 17.2% the compressive strength with respect to PCC2<sub>30</sub>, which suggests a synergistic effect between the two additions. At 28 days, PCC1<sub>30</sub> developed the highest compressive strength among all cement blends. Interestingly, PCC2<sub>30</sub> developed an equivalent compressive strength to the reference mix, therefore proving the benefit of using low-grade calcined clay. It is also worth noting that small differences in strength were obtained between the ternary binder and the reference mix.

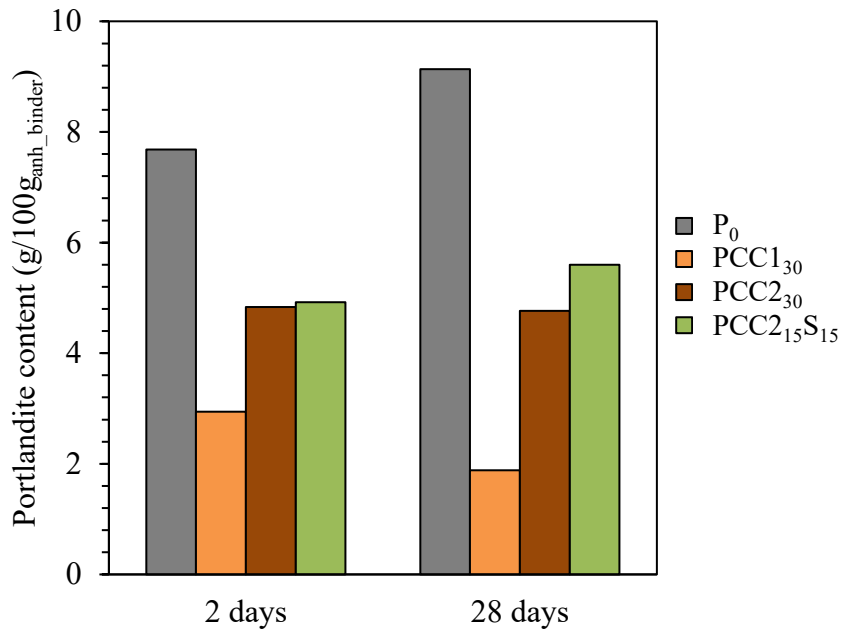


**Fig. 3.** Compressive strength of the cement paste mix designs at 2 and 28 days

### 3.2 Microstructure investigation

#### 3.2.1 Pozzolanic activity

Portlandite content was accurately quantified by means of thermogravimetric analysis as shown in Fig. 4. First of all, it can be noticed that the P<sub>0</sub> mixture showed the highest portlandite content at early and mature ages, whereas it was lower in PCC1<sub>30</sub>, PCC2<sub>30</sub> and PCC2<sub>15</sub>S<sub>15</sub> due to clinker dilution effect and secondary hydration reactions. When comparing both binary binders, PCC1<sub>30</sub> had a lower portlandite content which suggests that CC1 has a higher pozzolanic potential than CC2 leading to more portlandite consumption. The low portlandite content for PCC1<sub>30</sub> at 2 days suggests that portlandite started being consumed at least at this point of hydration and thus that CC1 did already start reacting. The portlandite content continues to decrease until 28 days of hydration with CC1 use. Portlandite content do not seem to decrease in PCC2<sub>30</sub> at 28 days, which can be a result of the filler effect of CC2 high quartz content, promoting further portlandite formation and compensating its consumption by pozzolanic reactivity. The ternary binder shows lower pozzolanicity compared to binary binders, suggesting the hydration of slag and more portlandite formation especially at 28 days.

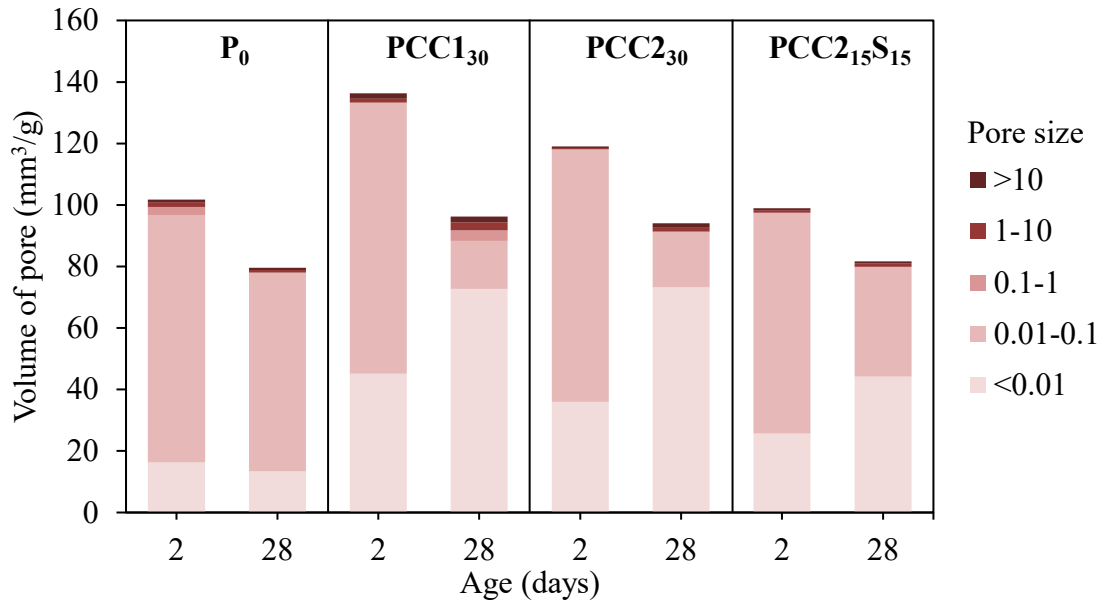


**Fig. 4.** Portlandite content (per g of anhydrous binder) of the cement paste mix designs at 2 and 28 days as determined by TGA

### 3.2.2 Pore structure

Fig. 5 displays the pore diameter distribution of each cement paste at both 2 and 28 days. It can be noticed that total porosity decreases from 2 to 28 days across all mixes, which is to be expected as hydration fills the pores. In addition, the pore structure changes significantly from 2 to 28 days in the cement blends, given the domination of pores with a diameter smaller than  $0.01 \mu\text{m}$  at 28 days, as opposed to a diameter of between  $0.01$  and  $0.1 \mu\text{m}$  at 2 days. This result was reported in [58] for metakaolin-incorporated pastes, and was explained by its pozzolanic reaction that results in higher amounts of CSH phase.

It can also be noticed that the total porosity of binary blends is higher than that of the reference mix, especially at early age. However, the quantity of pores with a diameter of between  $0.01$  and  $0.1 \mu\text{m}$  is considerably reduced in the binary mixes, especially at 28 days. Moreover, the similar pore structure of these binders is refined, potentially enhancing durability properties. It is interesting to note that the low-grade calcined clay blend is less porous than PCC1<sub>30</sub>, especially at early age, most likely due to the presence of quartz, which has a crystalline phase of minor porosity. As for the ternary blend, it can be noticed that the amount of total porosity is comparable to that of the reference mix at 2 and 28 days, yet the quantity of capillary pores is significantly reduced, especially at 28 days in the ternary binder, which could lead to enhanced durability properties, proving a good synergy between GBFS and CC2.



**Fig. 5.** Pore structure development for the cement pastes between 2 and 28 days (the pore size described is the pore diameter in  $\mu\text{m}$  and was limited to 100  $\mu\text{m}$ )

### 3.2.3 Microstructural analysis

The BSE micrographs of binary and ternary calcined clay systems at 2 and 28 days are shown in Fig. 6, as a means of comparing their microstructures. The main phases were annotated in the last image to indicate the greyscale level of each phase and make the BSE images easier to read. For all mixes, it is clear that the amount of unhydrated particles decreases from 2 to 28 days due to the hydration process.

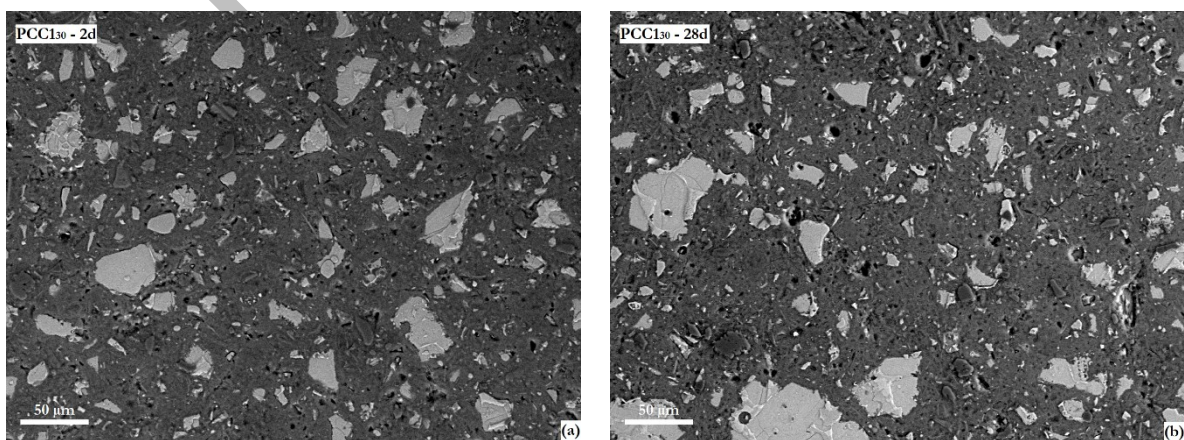
Figs. 6a and 6b show SEM images of CC1-binary binder respectively at 2 and 28 days, where few visible calcined clay particles are observed (some small darker particles); which suggests its good reactivity, especially at 28 days. No apparent microcrack-type defects are observed, explaining the high compressive strength measured on this paste.

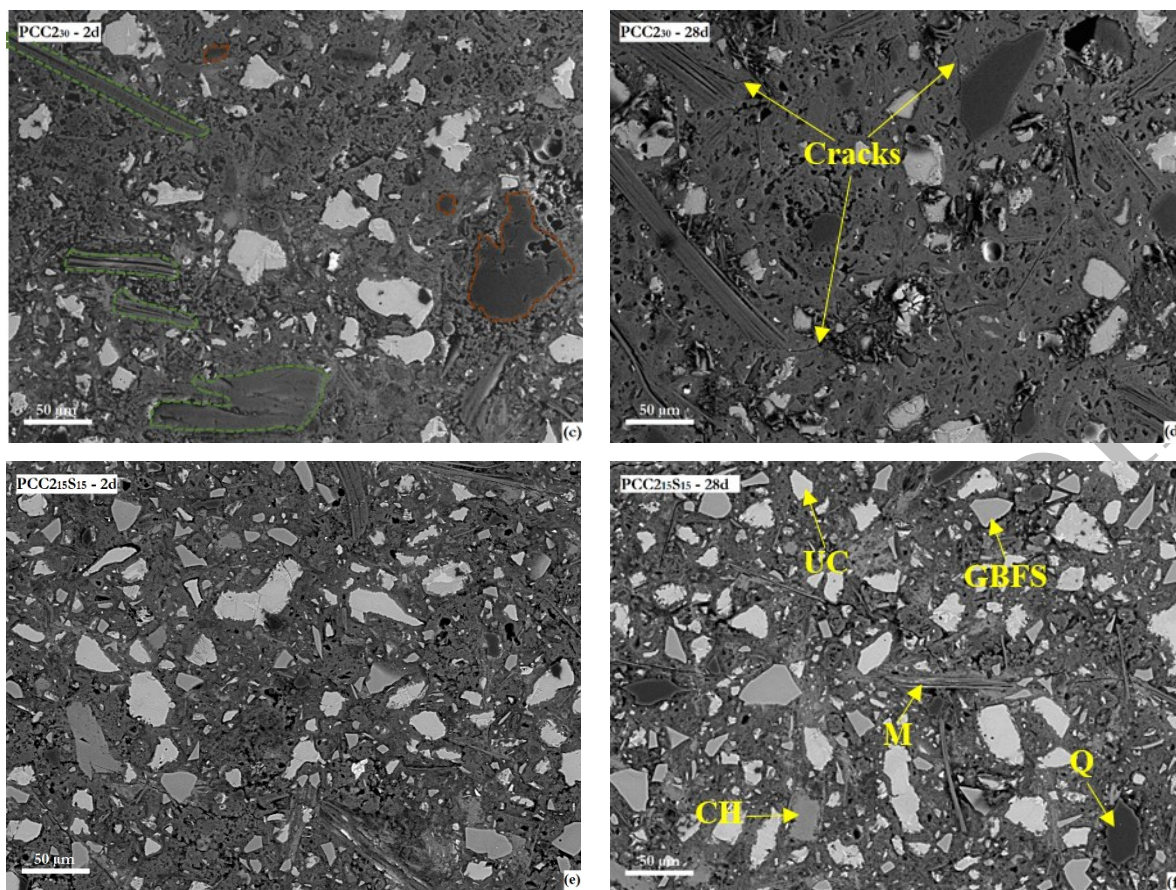
In comparison of PCC<sub>130</sub>, PCC<sub>230</sub> shows smaller amounts of unhydrated cement particles at 2 and 28 days. Knowing that both binary pastes have the same amount of cement, we can conclude that PCC<sub>230</sub> has a higher degree of reaction of clinker at both ages. PCC<sub>230</sub> has also higher amounts of the dark particles, in addition to some needle-shaped ones, circled respectively in brown and green dashed lines in Fig. 6c, which are probably calcined clay particles, suggesting the lower reactivity of CC2 compared to CC1. In addition, some microcracks pointed in Fig. 6d appear at the edges of these particles, which suggests a poor interface and weakening of the paste by these particles of impure calcined clay.

338 To precisely assess the nature of the dark and needle-shaped particles, further EDS analyses were  
339 carried out at the location of the same marked image (Fig. 6c) in order to obtain the aluminum,  
340 calcium, silicon and potassium maps, as depicted respectively in the images of Fig. 7. All these  
341 particles show no calcium traces, which confirms they are calcined clay phases. The elemental maps  
342 show a strong correlation between Al and K locations, with small amounts of Si, which match with  
343 the needle-shaped particles; this indicates that these are muscovite particles. The darkest particles  
344 (e.g. the one marked in brown) belong to quartz, given that only Si can be detected in their location  
345 using EDS. The existence of these calcined clay impurities prevents cement grains from being  
346 uniformly dispersed in the cement matrix, thus causing reduced resistance, yet accompanied by  
347 improved porosity, as explained above. Compared to PCC1<sub>30</sub>, CC2-binary binder shows higher  
348 amounts of calcined clays impurities (mainly quartz and muscovite) which is consistent with the XRD  
349 quantification of both calcined clays. Besides, more portlandite is noticeable in the SEM images of  
350 PCC2<sub>30</sub>, which is consistent with TGA results.

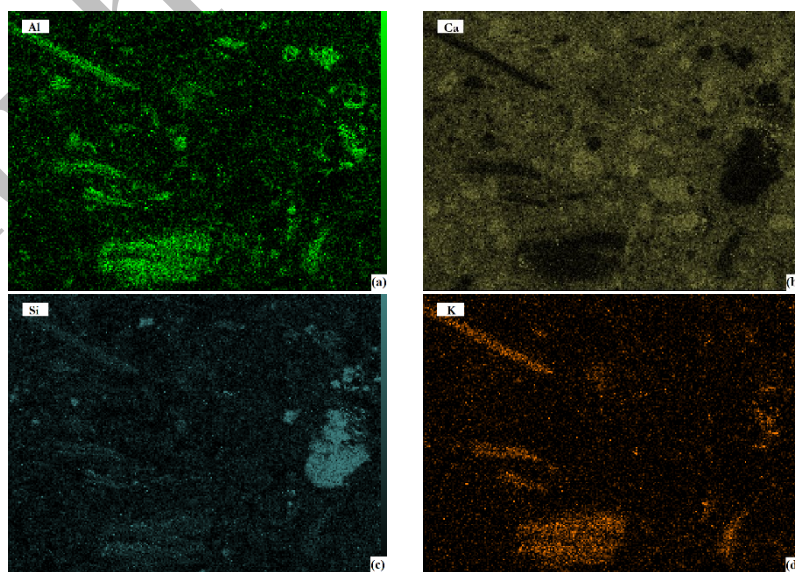
351 Micrographs from the ternary mix (Figs. 6e and 6f) reveal a more heterogeneous cement paste with  
352 the presence of both slag and CC2. Slag particles have sharper angles and are less lightly colored than  
353 the unhydrated cement grains as annotated in the Fig. 6f. Compared to binary cement pastes, this  
354 formulation shows a clear decrease in porosity. Compared to PCC2<sub>30</sub>, the amount of residual  
355 unhydrated particles at both ages is greater, but with higher portlandite amount that can be observed  
356 on the SEM images and quantified by TGA. This suggests a probable hydration of some slag grains  
357 promoted by CC2 filler effect (synergistic effect of both additions). In addition, the different  
358 unhydrated cement and slag particles are well distributed in the cement paste, without apparent  
359 decohesion or visible cracks, which may explain the paste's good macromechanical property.

360





**Fig. 6.** SEM images of blended cement pastes: (a) PCC1<sub>30</sub> at 2 days, (b) PCC1<sub>30</sub> at 28 days, (c) PCC2<sub>30</sub> at 2 days, (d) PCC2<sub>30</sub> at 28 days, (e) PCC2<sub>15</sub>S<sub>15</sub> at 2 days and (f) PCC2<sub>15</sub>S<sub>15</sub> at 28 days. Brown dashed lines show quartz particles, and green ones show muscovite

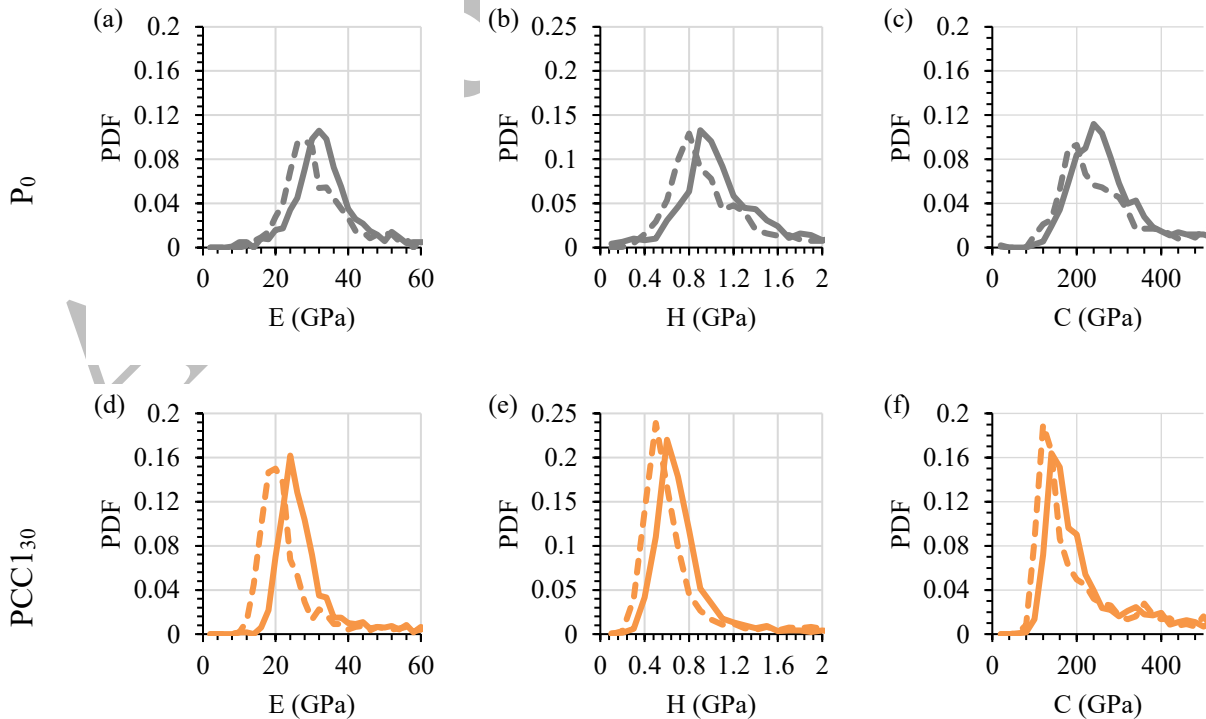


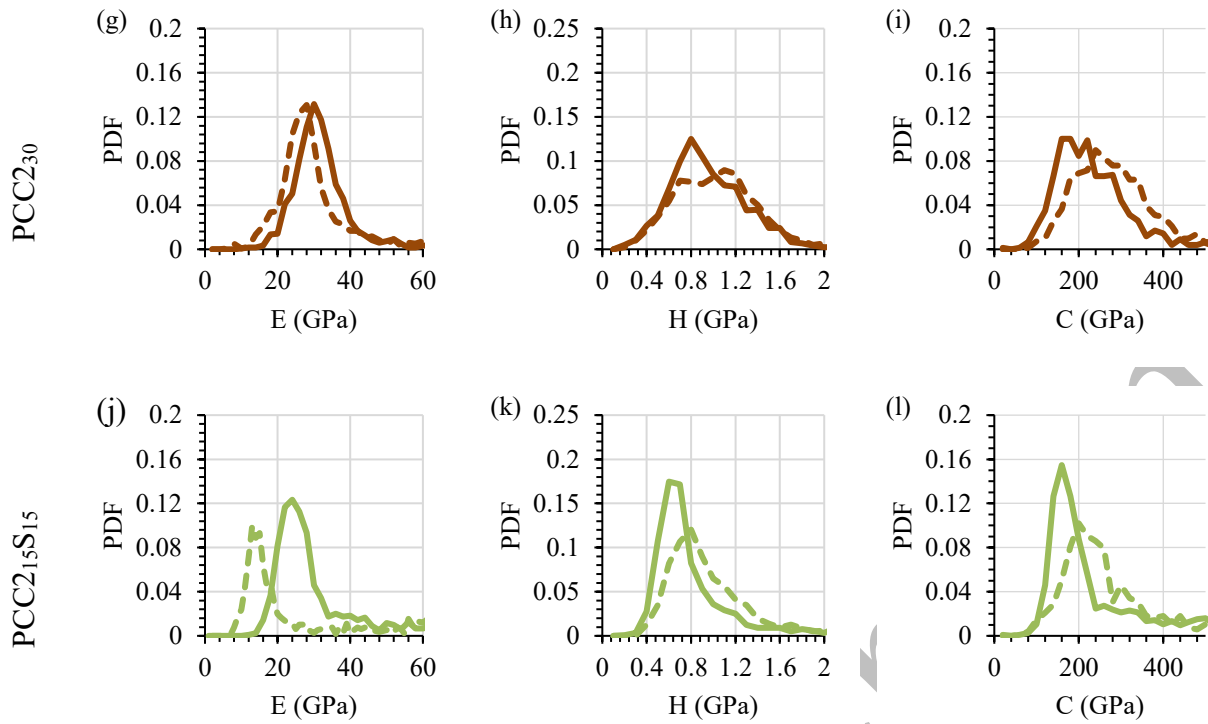
**Fig. 7.** SEM/EDS elemental maps of PCC2<sub>30</sub> at 2 days (Fig. 6c) for (a) aluminium, (b) calcium, (c) silicon and (d) potassium

### 370 3.2.4 Micromechanical properties of the cement blends

371 Elastic properties were investigated at the microscale by means of nanoindentation. Figs. 8a-d-g-j  
 372 show the probability density function in the elastic modulus for the four cement pastes at both 2 and  
 373 28 days. Only the elastic moduli less than 60 GPa were depicted for analyzing hydration products'  
 374 properties. From the outset, a shift can be observed towards higher values of elastic modulus from 2  
 375 to 28 days across all mixes since the matrix stiffens with time of hydration. This shift equals 84.6%  
 376 of the value at 2 days for the ternary binder and is much higher compared to the other cement pastes,  
 377 reaching 14.3%, 20% and 7.1% respectively for  $P_0$ , PCC1<sub>30</sub> and PCC2<sub>30</sub>. To explain this rate of  
 378 microstructural development, the results of statistical deconvolution will be further presented and  
 379 analyzed. The main peaks of hydration products at 2 and 28 days seem higher and narrower in PCC1<sub>30</sub>  
 380 which suggests a mono-phase predominance of a hydration product (CSH), and which is consistent  
 381 with the small amount of portlandite found in PCC1<sub>30</sub> determined by TGA. The larger distributions  
 382 in the other cement pastes indicate the presence of multiple hydration products with a higher content  
 383 of the phase with properties towards the peak.

384 Likewise, the probability density functions of the hydrates' hardness are shown in Figs. 8b-e-h-k.  
 385 Unlike elastic modulus, there is a shift towards decreasing hardness from 2 to 28 days in CC2 blended  
 386 cement pastes (i.e. PCC2<sub>30</sub> and PCC2<sub>15</sub>S<sub>15</sub>).





**Fig. 8.** Probability density functions from statistical nanoindentation of (a-d-g-j) elastic modulus (bin size = 2 GPa), (b-e-h-k) hardness (bin size = 0.1 GPa) and (c-f-i-l) contact creep modulus (bin size = 20 GPa), for the different formulations at 2 and 28 days. Dashed and continuous lines are respectively for 2 and 28 days analysis

Fig. 9 shows the volumetric composition of each cement paste, and the details of deconvolution are summarized in Appendix A (tables A1 and A2 present the micromechanical properties of the clusters issued from statistical deconvolution for 1200 indents probed in the four cement pastes at 2 and 28 days, and Fig A1 allows the visualization of the indents repartition in the two dimensions space composed of elastic modulus and hardness). For  $P_0$ , four pure clusters could be detected and attributed as HD CSH, portlandite, interfaces between hydrates and unhydrated particles and finally unhydrated cement grains. The properties from the indents on interfaces can change depending on the amount of different phases in contact with the tip, and thus the standard deviations of these properties are high. Only HD CSH could be detected as the paste's w/b ratio is low, and its amount is higher from 2 to 28 days, while it decreases for the unhydrated cement grains as shown in Fig. 9. It is worth noting that CSH can exist in two forms: low-density LD and high-density HD depending on the initial mix proportions of the pastes (mainly water-to-cement ratio, existence of chemical admixtures, mineral additions incorporations). Thus, these two forms have different micromechanical properties, lower for LD CSH, as widely proved in the literature [36].

406 In the cement blends, this same figure (Fig. 9) shows that the amount of unhydrated cement grains is  
407 reduced due to the replacement of Portland cement with mineral additions, and different clusters with  
408 more or less pure phases could be detected.

409 According to Fig. 9, the incorporation of 30% of CC1 resulted in 79% of CSH, higher than the  
410 reference mix, with a high amount of LD CSH at 2 days and smaller one for HD CSH. The third  
411 cluster was found to belong to both portlandite and interfaces as the amount of portlandite in this  
412 paste is low. Then a last cluster that seems to be mainly for unhydrated cement grains but mixed with  
413 some quartz particles brought by CC1, due to the slightly decreased mean properties along with higher  
414 standard deviation of the properties compared to unhydrated particles properties from P<sub>0</sub>. At 28 days,  
415 more intermixed phases are detected as clusters, where it seems that there is a higher amount of HD  
416 CSH compared to 2 days, probably due to the pozzolanic reaction of CC1.

417 Besides HD CSH, new clusters appeared in PCC2<sub>30</sub> at 2 days composed of CC2 most important  
418 impurities, namely muscovite and quartz, which could be clearly identified in SEM images of PCC2<sub>30</sub>  
419 shown in Fig. 6. The second cluster was attributed to mixed portlandite and muscovite due to slightly  
420 higher mean properties and standard deviation compared to portlandite in P<sub>0</sub>. The average properties  
421 of the third cluster seem to correspond to only quartz as the standard deviation of the properties is not  
422 high, and the fourth one seems to belong to unhydrated cement grains but also to some interfaces  
423 because the values of the properties are lower and more dispersed. At 28 days, only three clusters  
424 could be detected among which there is HD CSH with higher amount than at 2 days. The higher  
425 proportion of CSH observed in both binary binders in comparison with the reference mix is in  
426 accordance with the higher fraction of gel pores observed using mercury porosity.

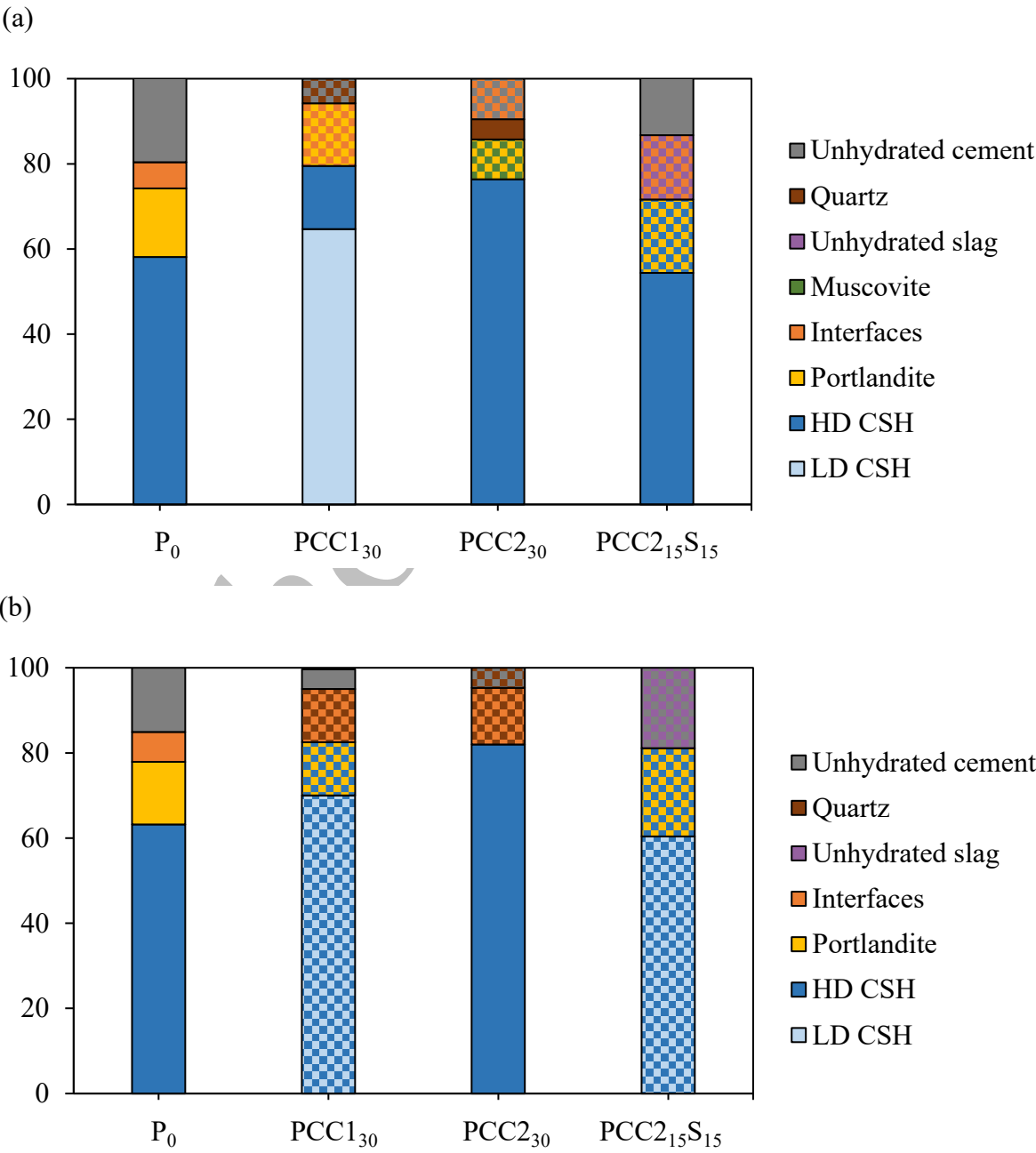
427 Finally, the ternary binder had clearly a slower reaction at 2 days with still a relatively high amount  
428 of unhydrated cement particles (14.3%) and detected unhydrated slag grains. This agrees with the  
429 images of PCC2<sub>15</sub>S<sub>15</sub> microstructure shown in Figs. 5e and 5f where it visually appears that the paste  
430 has higher amounts of unhydrated particles compared to the binary binders. Some portlandite was  
431 also found to be mixed with HD CSH. At 28 days, it was hard to differentiate clusters with pure  
432 phases due to the high heterogeneity of the cement paste, but it was naturally found to be a mixture  
433 of LD and HD CSH, portlandite and unhydrated cement and slag particles.

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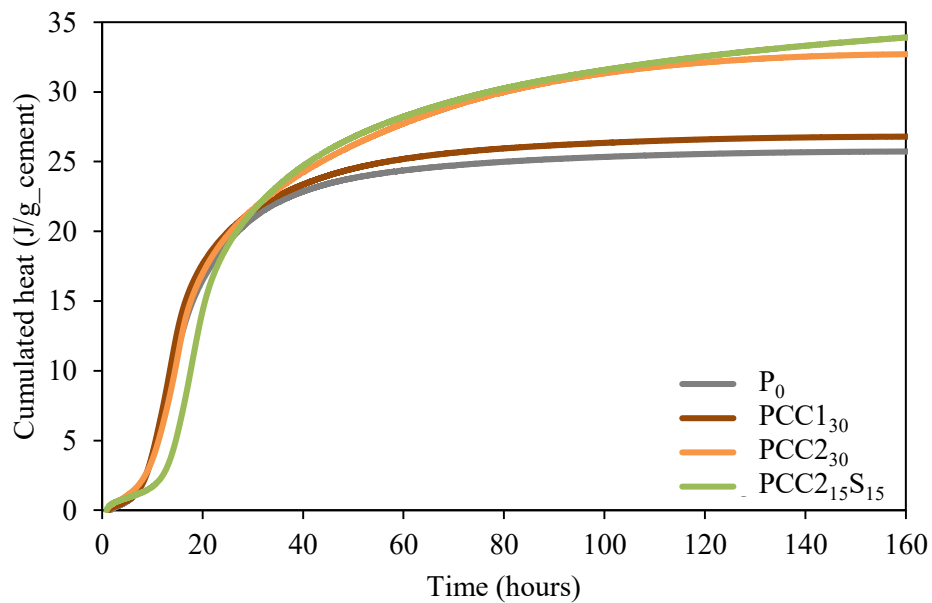
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**Fig. 9.** Cement pastes compositions according to nanoindentation deconvolution results at (a) 2 days and (b) 28 days. Two-tone clusters (with two colours) indicate the existence of two phases in the same cluster according to the legend

In order to understand the cause of low-density phase dominance in PCC1<sub>30</sub> compared to the other mixes, calorimetric tests were run according to ASTM C1679-08 standard, and the results are depicted in Fig. 10. It can be seen that PCC1<sub>30</sub> exhibits much higher cumulative heat by gram of cement compared to P<sub>0</sub> after 30 hours of hydration. Based on this observation plus the fact that a higher degree of reaction of clinker was observed by SEM in PCC2<sub>30</sub>, as compared to PCC1<sub>30</sub>, it can be concluded that CC1 is much more reactive than CC2 and moreover that the observed heat difference stems from the CC1 reaction; which is consistent with TGA results and is probably due to its higher amorphous content. Also, a greater amount of cement is hydrated in PCC2<sub>30</sub>, a probable consequence of the filler effect. This suggests that the hydration of calcined clay is the main cause of low-density CSH formation inside the cement paste.



**Fig. 10.** Normalized cumulative heat (per gram of cement) as obtained by calorimetry

### 3.2.5 Viscoelastic properties

#### 3.2.5.1 General distribution of creep in the cement pastes

Figs. 8c-f-i-l show the probability density plots of the contact creep modulus for all four mix designs at both early (2 days) and advanced ages (28 days). These plots were limited to 500 GPa so as to compare the hydrates since they account for the predominant creep behavior in cementitious materials. The 2- to 28-day trend changes from one mix design to the next.

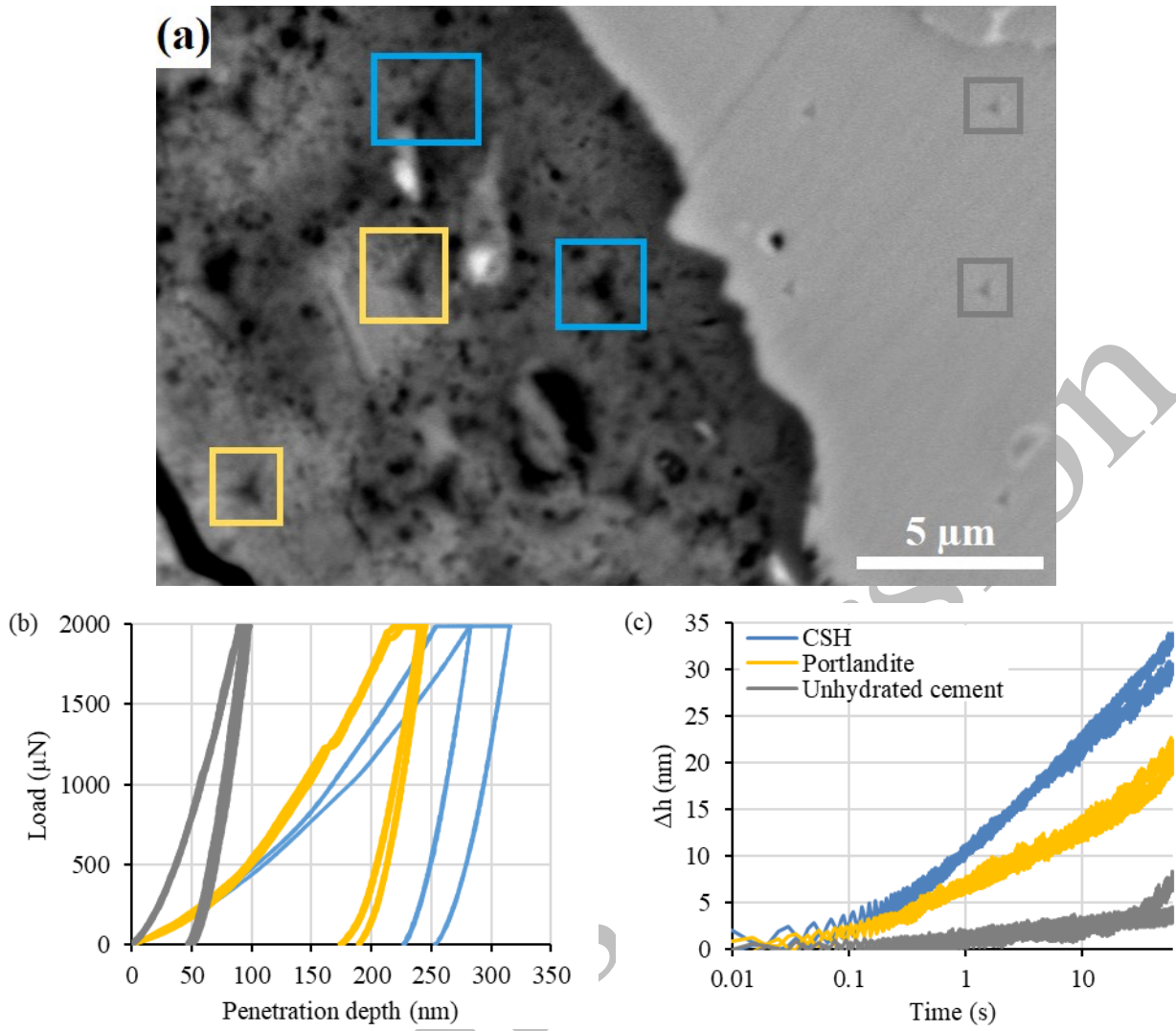
For CC2-based pastes, the mean contact creep modulus equals 200 GPa and 240 GPa for PCC2<sub>15</sub>S<sub>15</sub> and PCC2<sub>30</sub> at 2 days, which proves to be respectively equivalent and 20% higher than the reference mix. These mean values are consistent with HD CSH creep moduli according to [49]. Interestingly, these two binders can be used for their strong creep resistance at an early age, with similar or even better properties than CEM I paste albeit a smaller carbon footprint [1,59]. Then, a shift towards a lower contact creep modulus can be observed from 2 to 28 days, which means that these pastes develop good creep resistance at an early age, in decreasing with hydration, a finding that can be explained by the formation of porous hydrates with limited creep properties, which was noticed in mercury porosity results (i.e. the total porosity of these pastes remains relatively unchanged, despite being much finer and containing a larger amount of gel pores).

As for P<sub>0</sub> and PCC1<sub>30</sub>, an increase in the contact creep modulus can be noticed from 2 to 28 days. The contact creep modulus of PCC1<sub>30</sub> at the peak was 40% and 38.5% lower than P<sub>0</sub> resp. at 2 and 28 days. This indicates a predominance of LD CSH in PCC1<sub>30</sub>, with the formation of some HD CSH at 28 days. These observations are in accordance with calculated proportions of individual phases (shown in Fig. 9) and mercury porosity results, and can be explained by combined calorimetry and SEM results where CC1 was found to be with a high reactivity with lower clinker hydration rate.

#### 3.2.5.2 Creep of individual phases

Fig. 11a shows a portion of indented area (a grid of 5 by 3 indents) in P<sub>0</sub> at 28 days where the imprints of the 2 mN – indents are visible. Two indents from each phase were selected and their load-penetration depth curves and logarithmic penetration depth change with time are shown in Figs. 11b and 11c respectively. The selected indents were boxed in blue, gold and grey to refer to CSH, portlandite and unhydrated cement respectively, identified on the basis of greyscale analysis of the image. It can be noticed visually on the image that the size of imprints in the hydration products is higher than that in unhydrated cement. This difference of size is less visible among indents in CSH and portlandite. This observation is translated in the load-penetration depth curves with smaller maximum penetration depth of indents in unhydrated cement, then in portlandite and CSH.

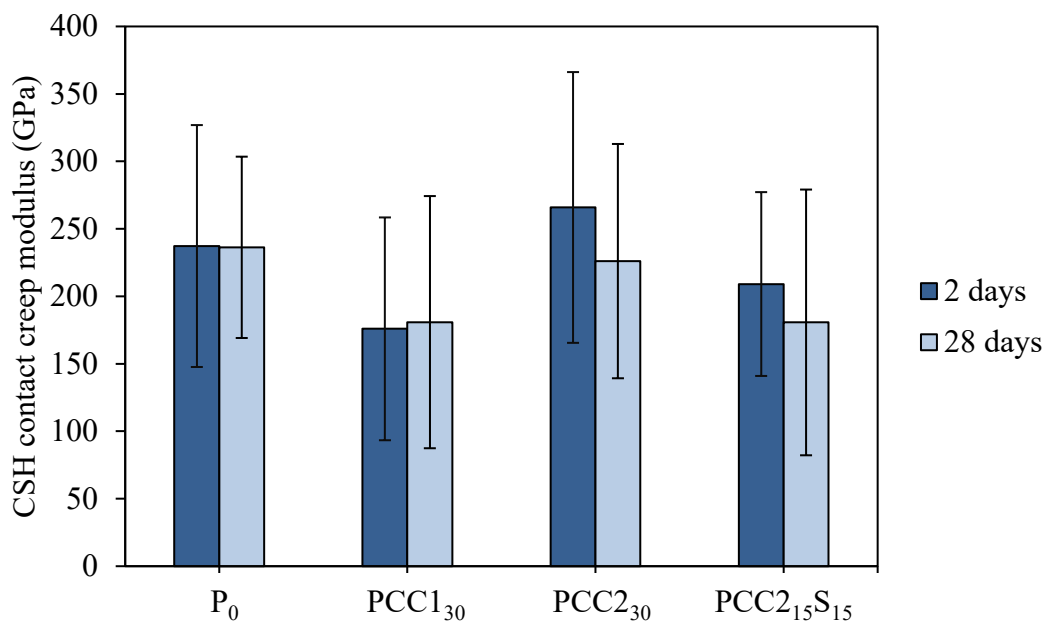
As for creep properties, it can be noticed that CSH has the highest deformation with a recorded depth change of  $31.8 \pm 2.6$  nm in 60 s creep. Meanwhile, the recorded depth change in portlandite on the two indents is of  $20.6 \pm 1.0$  nm, which represents 65% of that of CSH, commonly considered to be responsible of concrete creep. This means that amount of portlandite in the hydration products and its creep should be taken into account when analyzing the concrete behavior when subjected to creep.



**Fig. 11.** (a) SEM image of indented area on  $P_0$  at 28 days. Example of (b) load-penetration depth curves and (c) logarithmic penetration depth change vs. time of CSH, portlandite and unhydrated cement of the boxed indents

As explained in paragraph 2.2.6, contact creep modulus for CSH phase was calculated for all the mixes at 2 and 28 days. A mean value was taken into account when two types of CSH were found for one mix, and results are shown in Fig. 12. It can be noticed that all the calculated creep properties are within a range of 175 to 266 GPa which corresponds to the values reported in the literature for CSH phases. Some standard deviation values are high; this can be due to existence of some indents of portlandite in CSH-considered cluster, which are of higher contact creep modulus. It can also be noticed that PCC1<sub>30</sub> creeps more than other formulations at 2 and 28 days, and this is because of the high amount of LD CSH detected in this mix design. As already noticed on the PDFs, the contact creep modulus tends to decrease in CC2-incorporated pastes, but in general, this property does not

511 vary significantly between 2 and 28 days. This means that the commonly observed trend of increased  
 512 creep with hydration time is mostly due to the higher fraction of CSH.



513  
 514 **Fig. 12.** CSH contact creep modulus for the four formulations at 2 and 28 days

515  
 516 **4. Discussion**

517 *4.1 Impact of calcined clay composition on the cement paste properties*

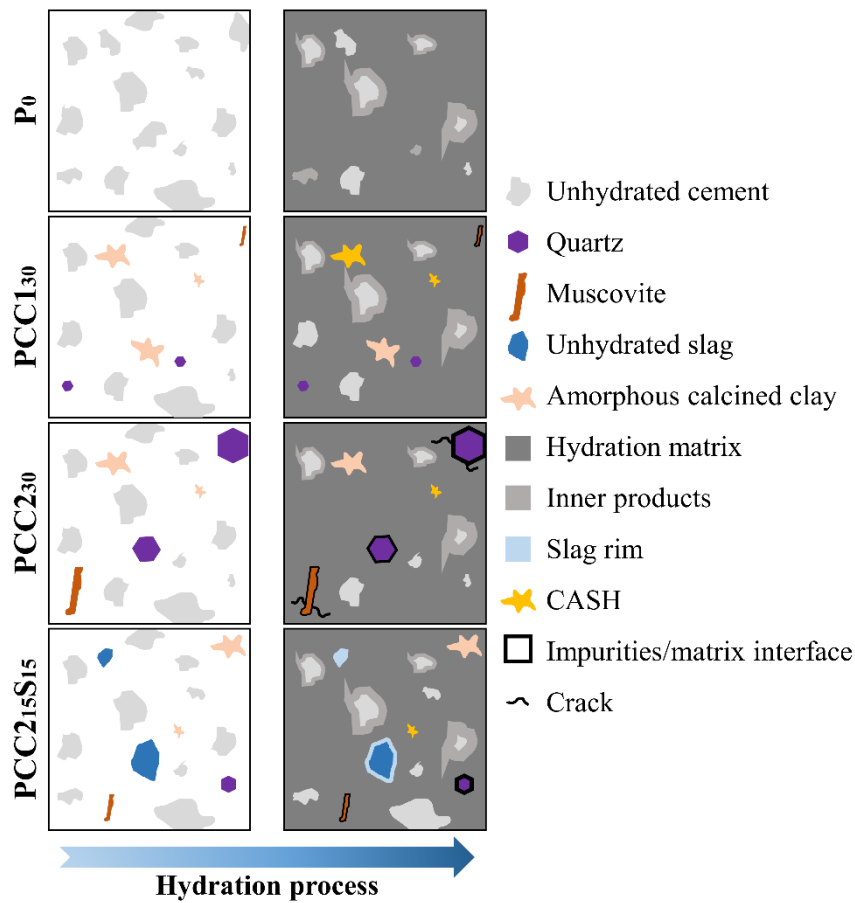
518 At the microscale, cement paste can be seen as a heterogeneous material of hard inclusions, which  
 519 are mainly the unhydrated cement grains, muscovite and quartz contributed by calcined clays and  
 520 embedded in a porous binding cement matrix constituted of softer hydrated phases, as shown in Fig.  
 521 13. Besides promoting the hydration capability of the unhydrated binder, the distribution of hard  
 522 particles in the hydrate matrix can influence the behavior of cement paste specimens regarding  
 523 compressive strength. Cementitious materials failure starts with the propagation of microcracks and  
 524 extends to the formation of major cracks; the existence of tough inclusions in cement pastes results  
 525 in greater toughness and crack inhibition [60].

526 At an age of 2 days, the microstructural investigation has shown that PCC1<sub>30</sub> most important  
 527 hydration product is LD CSH which resulted in a higher porosity of the blend. Despite its high  
 528 reactivity at early age proved by combined TGA, SEM and calorimetry, high-grade calcined clay  
 529 resulted in low-density hydration products, which caused a deterioration of micromechanical  
 530 properties. However, PCC1<sub>30</sub> does develop a higher compressive strength than PCC2<sub>30</sub>. This outcome  
 531 can be explained by the nature of the interface between the hydrate matrix and the hard inclusions: a

smooth transmission of some microcracks to hard particles can prevent their transformation into macrocracks. Indeed, the system of hard inclusions in PCC1<sub>30</sub> is mainly composed of pure constituents of Portland cement clinker, while PCC2<sub>30</sub> also contains a sizable amount of quartz and muscovite contributed by CC2, which appear to cause some microcracks on the SEM images. The nature of connection between these two distinct types of hard particles and cement matrices differs, since quartz and muscovite do not participate in the hydration process, while the latter starts from unhydrated cement particles and proceeds as a continuous process over time, which is illustrated in Fig. 13. This finding is consistent with the results presented in [61], wherein the authors observed a high compressive strength even at a 60% replacement rate of natural pozzolan (NP, slowly reactive), which was explained by the optimal distribution of NP and cement grains from an incomplete reaction in the mix.

At 28 days, this same behavior is still observed, although it is slightly reduced at the microstructural scale as the hydration process continues over time. It becomes more effective in PCC1<sub>30</sub> since CC1 has greater amorphous content, as proven by a higher cumulative heat observed at 7 days, with a stable outlook over the subsequent days of hydration. This explanation is also supported by the SEM images of the microstructure, where it is shown that PCC1<sub>30</sub> has a uniform distribution of unhydrated cement particles, with no visible microcracks, compared to PCC2<sub>30</sub>, exhibiting fewer cement inclusions and highly distinct quartz and muscovite particles.

The viscoelastic properties of calcined clay-based mixes tend to differ considerably at early age. PCC1<sub>30</sub> tends to display a LD CSH-predominant microstructure with a small overlapping peak of HD CSH, while PCC2<sub>30</sub> has a wide distribution that seems to cover the ranges of LD CSH and more of HD CSH. In practice, creep can be both beneficial and harmful depending on the main goal of the material used. A high creep resistance at early age can be beneficial for the prefabrication of large structural elements subjected to their own weight that were unable to gain a sufficient level of resistance. On the other hand, lower creep resistance enables a relaxation of stresses inside the concrete matrix, as caused by temperature variation and shrinkage [62], thus lowering the risk of cracking especially at an early age.



**Fig. 13.** Schematic representation of the cement pastes microstructures

#### 4.2 Synergistic effect of low-grade calcined clay and slag

An interesting synergistic effect between low-grade calcined clay and slag was observed at multiple scales. At the engineering scale, the compressive strength of PCC2<sub>15</sub>S<sub>15</sub> is higher, relative to PCC2<sub>30</sub> at early age. At 28 days, the values remained quite similar regarding the overlapping error bars. This result is consistent with those of Khatib and Hibbert [63], or also Li *et al.* [19], who observed an increase in compressive strength with both additions, as compared to a replacement with respectively only slag or only metakaolin. Compared to a replacement with only low-grade calcined clay as measured for PCC2<sub>30</sub>, or with only slag as studied by Gruyaert *et al.* [64], who show lower cumulative heat for a paste with 30% replacement of slag with respect to ordinary Portland cement (w/b=0.5), a higher heat release was shown at 7 days for the ternary binder, compared to both PCC2<sub>30</sub> and P<sub>0</sub>, which tends to be higher at advanced ages, thereby confirming the underlying synergy.

At the microscale, a finer pore structure was observed with both additions, as well as a lower total porosity at 2 and 28 days. This finding is in agreement with the results reported in [65], wherein a reduced porosity was noticed for a mix replaced jointly by slag and metakaolin using MIP and

SEM - BSE in ultra-high performance concretes. Also, the ternary binder displayed faster stiffening capability of the mix from 2 to 28 days, with respect to the other mixes.

## Conclusion and perspectives

In this study, the utility of low-grade calcined clay in binary and ternary binders was highlighted through a micromechanical study of cement pastes with 30% cement replacement at early (2 days) and advanced (28 days) ages of hydration, supported by microstructural investigation in order to explain macroscopic compressive strength. The main findings of this study can be summarized as follows:

- Binary binder with low-grade calcined clay has 28 days-compressive strength equivalent to ordinary Portland cement paste, results in finer pore structure with equivalent total porosity with respect to ordinary Portland cement paste, all with lower hydration heat compared to high-grade calcined clay
- High-grade calcined clay reacts faster and has higher pozzolanic activity compared to low-grade one
- The fast reaction of high-grade calcined clay results in a higher gel porosity associated with the formation of a low-density phase detected by nanoindentation especially at early age. Therefore, low-grade calcined clay binary cement paste has better micromechanical properties
- The mix proportions do not seem to influence the contact creep modulus of the pastes' CSH
- The calcined clay impurities (mainly quartz and muscovite) prevent good distribution of the unhydrated cement particles and cause some microcracks, which influences the macroscale compressive strength
- Ternary mix with both low-grade calcined clay and slag shows higher 2 days-compressive strength compared to the substitution with only low-grade calcined clay, and has equivalent 28 days-compressive strength to Portland cement mix, with finer pore structure and slightly lower total porosity

These results highlight the interest of mixing low-grade calcined clay with slag to enhance the properties of binary mixes incorporating low-grade calcined clays. Similar performance could be obtained with the same low-grade calcined clay, having a relatively high proportion of crystalline phases, such as quartz, which has a filler effect during hydration, but whose large particles are prone to create weaknesses favoring cracking.

607 Further tests on the nature of interfaces between hard inclusions and the hydrate matrix can be useful  
608 in correlating micromechanical observations with the macroscale ones. In addition, classical  
609 deconvolution processes should be combined to other techniques to better define clusters of single  
610 pure phases.

## 611 **Acknowledgements**

612 The authors would like to acknowledge the raw materials examinations and tests performed by Vicat.

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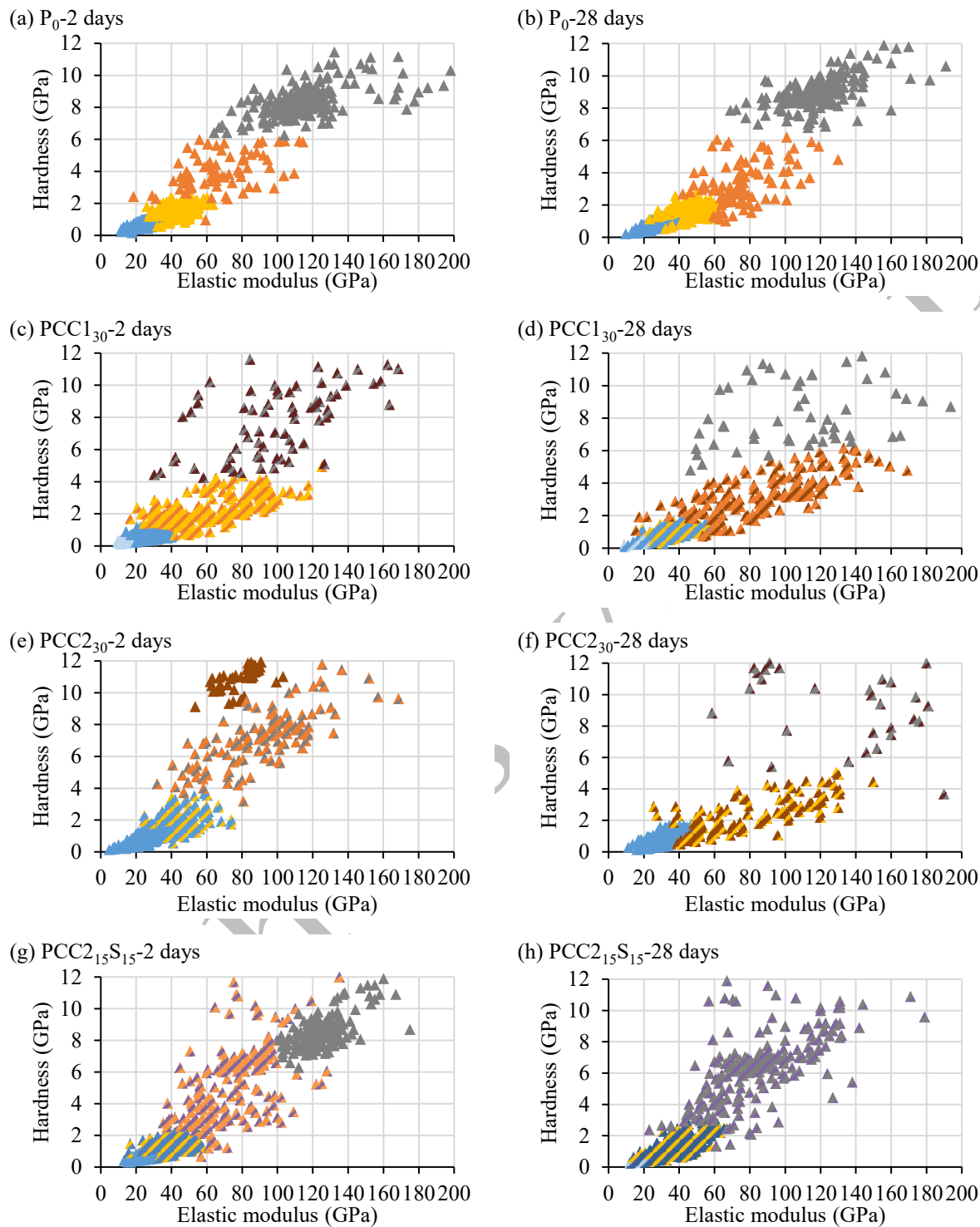
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**Fig. A1.** Results of mechanical clustering using hardness vs. elastic modulus (light blue: LD CSH, dark blue: HD CSH, yellow: portlandite, orange: interfaces, green: muscovite, purple: unhydrated slag, brown: quartz and grey: unhydrated cement)

632 **Table A1**

633 Mean properties  $\pm$  standard deviation of the clusters resulting from the deconvolution of the four  
 634 cement pastes and identification of the predominant phase(s) at 2 days.

Paste reference		1	2	3	4
<b>P<sub>0</sub></b>	E (GPa)	26.63 $\pm$ 5.17	41.33 $\pm$ 7.92	67.69 $\pm$ 20.06	117.06 $\pm$ 20.86
	H (GPa)	0.79 $\pm$ 0.21	1.51 $\pm$ 0.38	4.02 $\pm$ 1.14	8.44 $\pm$ 0.89
	Predominant phase	HD CSH	Portlandite	Interfaces	Unhydrated cement
<b>PCC1<sub>30</sub></b>	E (GPa)	18.30 $\pm$ 3.13	27.72 $\pm$ 5.24	64.12 $\pm$ 23.14	99.22 $\pm$ 31.91
	H (GPa)	0.47 $\pm$ 0.12	0.76 $\pm$ 0.25	2.38 $\pm$ 0.92	7.74 $\pm$ 2.09
	Predominant phase	LD CSH	HD CSH	Portlandite + interfaces	Unhydrated cement + Quartz
<b>PCC2<sub>30</sub></b>	E (GPa)	26.09 $\pm$ 5.73	45.72 $\pm$ 9.11	79.55 $\pm$ 9.84	90.42 $\pm$ 26.34
	H (GPa)	0.98 $\pm$ 0.34	2.00 $\pm$ 0.68	9.84 $\pm$ 0.74	7.10 $\pm$ 1.78
	Predominant phase	HD CSH	Portlandite + muscovite	Quartz	Unhydrated cement + Interfaces
<b>PCC2<sub>15</sub>S<sub>15</sub></b>	E (GPa)	26.44 $\pm$ 4.77	37.62 $\pm$ 7.28	72.72 $\pm$ 17.60	118.50 $\pm$ 11.25
	H (GPa)	0.74 $\pm$ 0.18	1.33 $\pm$ 0.30	4.95 $\pm$ 2.11	7.72 $\pm$ 0.93
	Predominant phase	HD CSH	HD CSH + Portlandite	Interfaces + Unhydrated slag	Unhydrated cement

642 **Table A2**

643 Mean properties ± standard deviation of the clusters resulting from the deconvolution of the four  
644 cement pastes and identification of the predominant phase(s) at 28 days.

Paste		1	2	3	4
reference					
<b>P<sub>0</sub></b>	E (GPa)	29.73 ± 6.02	41.59 ± 7.39	72.18 ± 16.09	111.63 ± 20.29
	H (GPa)	0.90 ± 0.26	1.54 ± 0.39	2.89 ± 1.08	7.98 ± 1.15
	Predominant phase	HD CSH	Portlandite	Interfaces	Unhydrated cement
<b>PCC1<sub>30</sub></b>	E (GPa)	23.90 ± 3.72	37.47 ± 7.50	87.77 ± 30.85	109.84 ± 38.88
	H (GPa)	0.60 ± 0.14	0.99 ± 0.32	3.34 ± 1.19	8.14 ± 1.92
	Predominant phase	LD CSH + HD CSH	HD CSH + Portlandite	Interfaces + Quartz	Unhydrated cement
<b>PCC2<sub>30</sub></b>	E (GPa)	29.50 ± 5.60	78.03 ± 29.82	120.16 ± 40.23	
	H (GPa)	0.88 ± 0.30	2.36 ± 1.11	9.15 ± 2.23	
	Predominant phase	HD CSH	Interfaces + Quartz	Unhydrated particles + Quartz	
<b>PCC2<sub>15</sub>S<sub>15</sub></b>	E (GPa)	22.93 ± 3.63	37.85 ± 9.24	82.86 ± 22.81	
	H (GPa)	0.60 ± 0.14	1.36 ± 0.58	6.49 ± 2.50	
	Predominant phase	LD CSH + HD CSH	HD CSH + Portlandite	Interfaces + Quartz + Unhydrated slag and cement	

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