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Gildas Medjigbodo, Emmanuel Rozière, Kevin Charrier, Laurent Izoret, Ahmed Loukili. Hydration, shrinkage, and durability of ternary binders containing Portland cement, limestone filler and metakaolin. *Construction and Building Materials*, 2018, 183, pp.114-126. <10.1016/j.conbuildmat.2018.06.138>. <hal-04331765>

HAL Id: hal-04331765

<https://hal.science/hal-04331765v1>

Submitted on 29 Dec 2025

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Hydration, shrinkage, and durability of ternary binders containing Portland cement, limestone filler and metakaolin

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A partial replacement of the clinker by latent hydraulic or pozzolanic materials is encouraged due to environmental and specific technical requirements. Such substitution remains limited to a relatively low level (less than 30% by mass of cementitious materials). An experimental research work was carried out on mortars made with binary and ternary binders (Portland cement; metakaolin; limestone filler) to reach 45% total replacement. In order to investigate the activating effect of reduced water to cement ratio, two series of mixtures were designed with W/C_0 of 0.42 and 0.5. Their heat of hydration, portlandite content, shrinkage, porosity, and carbonation were monitored. The tests were performed to understand the evolution of their relative strength (activity index) and durability parameters. The strength development of mortars with ternary binders was found to depend on metakaolin properties, including manufacturing process and particle size distribution. Reducing W/C_0 ratio accelerated pozzolanic reaction and allowed improving early age strength and durability parameters.

1. Introduction

The use of alternative materials as a substitution to clinker is now a major issue to reduce CO_2 emissions from cement production [1-4]. In addition to conventional supplementary cementitious materials (SCMs) such as silica fume, blast furnace slag, fly ash, etc. [5,92], the use of metakaolin (MK) appears today as a promising alternative to produce "eco materials". Raw material, mainly kaolin rich soil, is locally abundant, and the manufacturing process based on calcination at less than 1000 °C consists in dehydroxylation without CO_2 emission, thus metakaolin presents a lower carbon footprint than Portland cement [6]. The replacement of MK and LF does not systematically reduce the emission of CO_2

and improve the durability of the related cement based materials. The production of MK itself leads to lower CO_2 emissions than cement production; one ton of MK represents 175 kg of CO_2 released [7]. It also requires less thermal energy than clinker production. San Nicolas et al. [8] showed that a French installation consumes 2.2 MJ/t of MK, which is 80% less than the energy consumed during cement production. At the level of concrete, the CO_2 emissions and the cost effectiveness of a ternary system [9] depend on the distance between the production plants. The CO_2 emissions should be compared at equivalent durability, thus it is necessary to assess the actual performances of these cement based materials.

Most of existing studies agree on the significant pozzolanic reactivity of metakaolin compared to other mineral additions [10,11]. Metakaolin is actually an artificial pozzolan, i.e. it can react with Portlandite (CH) from the cement hydration and form

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additional C S H or C A S H [8]. This allows metakaolin to improve greatly the mechanical performance and durability of cementitious materials.

Experimental studies of concrete or mortar incorporating meta kaolin show that up to an optimum level of substitution, the compressive strength of these materials increases significantly (even at early age) compared to that of the reference concrete/mortar (without metakaolin) [12-17]. There is no consensus on the value of this optimum rate, probably because of the variability of MK and cement, mixture proportioning of concrete (W/C ratio, cement content, chemical admixtures, etc.). Nevertheless, all the works agree on the fact that this optimum is connected to the microstructure of the material which itself depends on three main factors: the filler effect, the acceleration of cement hydration (at very early age) and the pozzolanic reaction of the metakaolin with CH (significant at long term) [12,15]. It is generally located between 10 and 20% [14,16]. Below this threshold, the incorporation of the MK has been shown to produce finer pores and a segmentation of the capillary porosity [18,19]. The latter is at the origin of gas permeability and water absorption decrease in the concretes incorporating MK [20]. Therefore, these concretes showed better durability and resistance to aggressive agents [21-25].

The use of high MK content as partial replacement of Portland cement in mortar or concrete can lead to a significant drop in materials performances. One of the reasons is the depletion of portlandite produced by cement hydration. The Portland cement substitution rate p necessary to consume all the portlandite (CH) produced can be estimated by the following equation [26]:

$$\alpha \times \frac{\beta}{M_{AS_2}} \frac{p}{1-p} (3-n)(1-p) \times \frac{\%C_3S}{M_{C_3S}} + (2-n)(1-p) \times \frac{\%C_2S}{M_{C_2S}} \quad (1)$$

where $n = C/S$, M is the molar mass (g/mol), β is the amorphous content of MK and α is the ratio between CH produced and AS_2 contained in MK.

Through this equation, a rate of approximately 30% is obtained with $n = 1.75$, $\beta = 0.55$, $\alpha = 3$, $\%C_3S = 65$ and $\%C_2S = 5.5$. The studies carried out on binary mixtures (PC + MK) show that this value is an upper limit of the MK content that can be added in mortar without lowering its performance. Ambroise et al. [27] and Khatib et al. [28] actually showed that the compressive strength was lower than that of the reference mortar, with more than 30% of Portland cement replacement by MK.

Recent work shows that it is possible to go beyond the 30% substitution of OPC, thus to decrease carbon footprint, by combining metakaolin with a moderate amount of limestone filler [29-31]. For instance, Antoni et al. [29] showed that ternary binders (PC + MK + LF) lead to higher performances than binary binders in terms of heat release and mechanical strength. However, these performances depend both on mix design parameters (cement content, water to binder ratio, etc.) and on the physicochemical properties of the materials.

It is important to note that data on the durability and long term shrinkage of ternary binders incorporating limestone filler and metakaolin are very scarce in literature. Drying shrinkage remains a major issue for concrete durability. It has been widely investigated for binary binders, whereas only Barluenga et al. [32] and Brook et al. [21] focused on ternary binders (OPC + MK + Filler). Similarly, very few studies have been carried out on porosity [33], permeability [34] and carbonation [33] of these ternary binders. High substitution of Portland cement by mineral additions generally results in relatively low early age strength, which is of major concern for durability due to hydration drying coupling. The reduction of water to binder ratio allows optimizing the composition of these materials to meet specifications on early age

strength and durability [5,35]. There are a limited number of references on the influence of water to binder ratio on performances of metakaolin based materials [36].

The paper investigates the feasibility of substituting 45% by mass of ordinary Portland cement by mineral additions while keeping or enhancing mechanical performances and durability. Three sets of mineral additions have been studied, namely: meta kaolins, limestone fillers, and siliceous fillers. They were characterized by different chemical compositions, particle size distributions and specific surfaces. They were first used separately as a substitution of Portland cement, and siliceous filler and limestone filler were associated to metakaolin in order to understand the synergistic effect of these materials. Then, the influence of the quality of metakaolin (purity of kaolin and manufacturing process) on the relative strength was studied. Finally, the major originality of this work consists of an experimental study of the drying shrinkage, water porosity and carbonation of ternary binders (OPC + MK + Filler) and an investigation on the effect of water to binder ratio on these parameters.

2. Experimental program

The chemical compositions of metakaolin and limestone filler make it an interesting combination as a substitute for Portland cement. Their SiO_2 and CaO contents are complementary in order to make an effective mixture thereof as a substitute for the cement. The high crystallized silica content of the Siliceous Filler (SF) makes it valuable as an inert substituent, thus highlighting the possible chemical interaction of limestone filler on Portland cement and Metakaolin.

The different stages of the study presented in this paper are summed up in Fig. 1. Metakaolin (MK), limestone filler (LF and μ LF) and siliceous filler (SF1 and SF2) were used as partial replacement of ordinary Portland cement (PC). In the first part, the effects of inert minerals additions and pozzolanic addition (MK) on cement hydration and compressive strength development are quantified by means of isothermal calorimetry, compressive tests and thermogravimetric analyses (TGA). The tests were carried out both on binary and ternary binders' mixtures. The objectives were defined as follows.

The combination (PC + MK) allows highlighting the effects of MK on cement hydration.

The comparison between LF and SF in binary mixture allows demonstrating how the limestone fillers are likely to influence cement hydration.

(PC + MK + LF) and (PC + MK + SF) allow studying the impact of LF on pozzolanic reactions and its interaction with MK.

The comparison between LF/ μ LF and SF1/SF2 in binary and ternary mixtures shows the effect of fineness on the properties of the cementitious matrix.

This analysis leads, in the second part, to the choice of the best combination (PC; MK; X = {LF, μ LF, SF1, SF2}), which can be used for the study of the influence of metakaolin quality on hydration and compressive strength. Finally, the metakaolin MK3 which exhibited the best mechanical performance was used to highlight the effect of water to binder ratio (noted W/C₀) on durability properties of binary and ternary mixtures including MK.

2.1. Materials

The chemical compositions and physical properties of the ordinary Portland cement (PC), metakaolins (MK), limestone fillers (LF) and siliceous fillers (SF) are given in Table 1. Three metakaolins

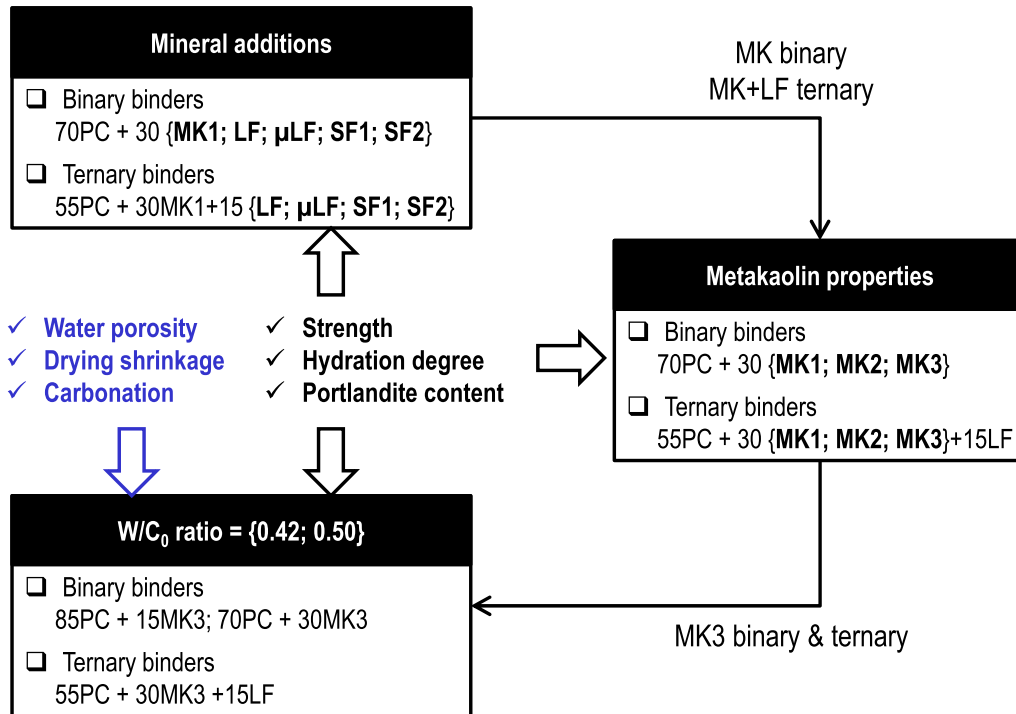


Fig. 1. Experimental program.

Table 1
Chemical composition and properties of Portland cement and additions used in this study.

	PC	Metakaolin			Limestone Filler		Siliceous Filler	
		MK1	MK2	MK3	LF	μ LF	SF1	SF2
<i>Chemical composition (%)</i>								
SiO ₂	20.6	93.16	55	55	0.0005	0.3	99.1	99
Al ₂ O ₃	5.3	–	40	39	–	–	0.0048	0.0052
Fe ₂ O ₃	2.11	–	1.4	1.8	–	–	0.0003	0.0003
CaO	66.3	0.36	0.3	0.6	98.76	99.6	0.0003	0.0003
MgO	1.09	0.04	–	–	–	–	–	–
K ₂ O	0.28	–	0.8	1	–	–	0.0037	0.0042
Na ₂ O	0.18	–	–	–	0.0046	–	–	–
SO ₃	3.3	–	–	–	–	–	–	–
TiO ₂	0.19	–	1.5	1.5	–	–	0.0002	0.0002
<i>Physical properties</i>								
Specific gravity (g/cm ³)	3.12	2.5	2.4	2.2	2.71	2.7	2.65	2.65
Specific area BET (m ² /g)	0.34	16	17	19	0.88	2.2	0.29	0.47
Water demand (g/kg)	0.34	0.56	0.90	1.65	0.31	0.10	0.29	0.52
Pozzolanic index (mg Ca(OH) ₂ /g)	–	754	1000	1400	–	–	–	–
Loss on ignition (%) – 1050 °C	1.2	1.63	1	1	–	–	0.2	0.2
<i>Particle size distribution (μm)</i>								
d ₁₀	–	15	–	–	2	1	5	3
d ₅₀	–	31	15	1.5	8.5	3.7	34	17
d ₉₀	–	85	60	6	50	15	100	47

from two extraction areas, calcined according to two different processes were studied. MK1 was obtained by “flash” calcination [8] of kaolinic clay from Fumel (France). Its 53% reactive product content was given by the provider for the used sample. It was deduced from the determination on amorphous content from XRD analyses. MK2 and MK3 were obtained by calcining and micronizing kaolinic clay from the Charentes basin (France). XRD patterns of used metakaolins can be found in Ref. [37].

Two limestone fillers were used: LF from Orgon, France and μ LF from Arboç, Spain. The last one is much thinner. Similarly, two siliceous fillers were used in this study. The main difference between the two siliceous fillers (SF1 and SF2) is their particle size

distribution: the proportion of particles passing 40 μ m was 86% for SF2 compared to 65% for SF1.

2.2. Mixtures proportions and samples

Twenty three mortars were prepared. Table 2 gives the compositions of the first twenty mortars. All mixtures were designed with the same paste volume (530 L/m³) and the same sand content (1241 kg/m³).

PC was considered as the reference mixture made with only OPC. Mixtures CX_L were made with L% of X, where X = {MK1; MK2; MK3; LF; μ LF; SF1; SF2}. Mixtures CX_MY_N were made with M

Table 2
Mortar mix designs (binary or ternary binders).

Reference	Constituent materials, kg/m ³						
	W/ C ₀	Binders content	Percentage		Sand 0/2	Water	SP,% by weight of cement
			X	Y			
PC	0.5	600	-	-	1241	300	-
CX ₁₅			MK3	-			-
CX ₃₀			MK1	-			-
			MK2	-			1
			MK3	-			1
			LF	-			-
			μLF	-			-
			SF1	-			-
			SF2	-			-
CX ₃₀ Y ₁₅			MK1	LF			-
			MK1	μLF			-
			MK1	SF1			-
			MK1	SF2			-
			MK2	LF			1
			MK3	LF			1.5
PC	0.42	662	-	-	1241	278	-
CX ₁₅			MK3	-			0.55
CX ₃₀			MK3	-			1.20
CX ₃₀ Y ₁₅			MK3	LF			1
PC	0.35	731	-	-	1241	256	0.2

Table 3
Mortars mixes based on gypsum.

Designation	PC (%)	MK1 (%)	LF (%)	Gypsum (%)	W/C ₀
GYP1.5	54.18	29.55	14.78	1.5	0.5
GYP3.27	53.2	29.02	14.51	3.27	
GYP7.12	51.08	27.86	13.93	7.12	

% of X and N% of Y, where $Y = \{LF; \mu LF; SF1; SF2\}$. L, M and N were expressed as the mass fraction of the mineral additions in the binders. The replacement ratios vary between 15% and 45%. The workability was measured using 15 cm high mini cone. It was adjusted when necessary using *TEMPO11* superplasticizer to reach slump of approximately 5 cm and ensure good compaction of samples. Adding limestone filler to metakaolin cement mixtures improved their workability as its water demand was lower (Table 1) and the needed superplasticizer content was lower (Table 2). Recent studies have shown that this difficulty can be overcome by modifying the mixing process [33] or using chemical and mineral admixtures [36].

In order to study the gypsum effect on the activity index of ternary binders, three other mortars were designed. These samples were obtained by modifying the mortars mixtures with ternary binders CMK1₃₀LF₁₅. Gypsum was added to this composition, substituting 1.5 3.27 7.12% of the binders (Table 3).

2.3. Testing procedures

2.3.1. Isothermal calorimetry and TGA

Isothermal tests were conducted on mortar samples at 20 °C as described in Lenormand et al. [38,39]. It allows continuous measurement of hydration heat and evaluation of the degree of hydration. The degree of hydration is assumed proportional to the heat flow q , generated from the cement hydration reaction. Thus, the time evolution of the hydration degree $\alpha(t)$ can be approximated by Eq. (2) [40].

$$\alpha(t) \approx \frac{Q(t)}{Q_{tot}} = \frac{\int_0^t q(\tau) d\tau}{Q_{tot}} \quad (2)$$

where $Q(t)$ is the cumulated heat (J/g cement) at a given time t and Q_{tot} is the ultimate cumulated heat.

A graphical method was used for the estimation of ultimate cumulated heat Q_{tot} . The cumulated heat was plotted as a function of $1/\sqrt{t}$. A linear evolution is obtained for small values of $1/\sqrt{t}$. The intersection of this linear function with the y axis gives an estimation of Q_{tot} .

Thermogravimetric analyses (TGA) were performed using a Netzsch STA 449 F3 Perseus device. The studied materials were dried at 80 °C then crushed to obtain 200 mg samples. They were heated at 10 °C/min from 25 °C to 1200 °C. Portlandite content was determined from mass curves according to the tangent Method [41].

2.3.2. Compressive strength and activity index

Compressive test was performed on $4 \times 4 \times 8$ cm³ specimens at 1, 2, 7 and 28 days. The tests were carried out on three specimens and the average values were retained. Activity index of binary and ternary mixtures is the ratio between compressive strength of mortar with mineral addition (f_p) and compressive strength of reference mortar (f_0), as expressed in Eq. (3).

$$i = \frac{f_p}{f_0} \quad (3)$$

where p is the mass percentage of mineral addition.

2.3.3. Porosity

According to the vacuum saturation method [42,43], the water porosity was measured on cylindrical samples of 110 mm of diameter and 50 mm of thickness. They were taken from samples stored in water at 20 °C. The Eq. (4) was used to assess the porosity [44] at 28 days:

$$P = \frac{M_{sat} - M_{dry}}{M_{sat} - M_{wat}} \times 100 \quad (4)$$

where M_{sat} is the mass in air of saturated sample (g), M_{dry} is the mass of oven dried sample and M_{wat} is the mass in water of saturated sample. The specimens were dried at 105 °C until constant mass (mass variation lower than 0.1% within 24 h).

2.3.4. Shrinkage

The total shrinkage was measured with LVDT sensors on prismatic samples ($20 \times 20 \times 160$ mm³). These specimens were demolded after 1 day sealed curing and stored in climatic chamber under controlled conditions (20 ± 1 °C and $50 \pm 5\%$ of RH).

The total shrinkage magnitude after a given drying time cannot be considered as an intrinsic concrete characteristic as it depends on time and specimen size [45,46]. Extrapolation models can be used to determine two parameters: characteristic time and ultimate shrinkage. One of the most commonly used model is the hyperbolic form given by Eq. (5) [47 50].

$$\varepsilon_{dry} = \frac{(t - t_0)}{(t - t_0) + N_s} \varepsilon_{\infty} \quad (5)$$

where ε_{∞} is the ultimate shrinkage ($\mu\text{m/m}$) and N_s the shrinkage half time (days), determined from the experimental data by minimizing the mean square error. Many models exist in literature, but the hyperbolic form introduced by Hansen & Mattock [49] and presented in Eq. (5) provides reliable results in a shorter time, as shown by Samouh et al. [46]. For this model, the characteristic time is also called the shrinkage half time as it corresponds to the time when the strain reaches half of the ultimate shrinkage.

2.3.5. Carbonation

The carbonation progress was measured on prismatic samples ($40 \times 40 \times 160 \text{ mm}^3$). After their preparation the specimens were sealed cured for one day then directly exposed to ambient CO_2 concentration (0,04%) in climatic chamber under controlled conditions ($20 \pm 1 \text{ }^\circ\text{C}$ and $50 \pm 5\%$ of RH). Phenolphthalein is used as an indicator in acid base titrations to assess the carbonated depth [51,35]. The phenolphthalein solution is sprayed on cross sections and turns pink in basic area which represents the non carbonated mortar.

3. Results and discussions

3.1. Influence of mineral additions

3.1.1. Effect of mineral addition ($W/C_0 = 0.5$)

Activity index of mortars with 30% replacement of metakaolin MK1 and four different fillers are given in Fig. 2 for 7 and 28 days. It can be observed that the replacement of Portland cement (PC) by any mineral addition of the study lead to a reduction of compressive strength compared to reference mortar (with PC only) both at 7 and 28 days. However, for the four fillers used, the relative compressive strengths were higher at 7 days than at 28 days. This can be explained by the nucleation process as it contributes to the increase and acceleration of cement hydration [52]. As illustrated in Fig. 4a which depicts heat flow versus time of binary blends, the hydration heat closely depends on cement content. Compared to reference mortar, the heat flow at the first peak actually increased with the incorporation of fillers. According to other studies [52–54], this increase due to nucleation process is a “physical effect” of filler on short term hydration. As reported in Kadri et al. [54], the accelerating effect of fine particles disappears at advanced stages of hydration. Thus, at long term only the degree of hydration of Portland cement becomes preponderant. At 28 days, neither the nature of the filler nor its fineness had any significant influence on the compressive strength of mortars (Fig. 2). The same conclusions are reported in Refs. [55,56] where the authors showed that the decrease in relative compressive strength at 28 days is mainly due to a dilution effect of the cement.

The mortar with 30% replacement of MK1 had a better relative compressive strength at 28 days compared to the other binary mixtures (Fig. 2). This is due to the high chemical reactivity of metakaolin compared to the fillers. In the presence of Portlandite (CH) and water, metakaolin reacts to produce neoformed hydrated phases, CSH gel and alumina phases (C_2ASH_8 , C_4AH_{13} and C_3AH_6) [57,58] resulting in higher strength of mortar. However, in contrary

to studies carried out by Khatib et al. [28] and Antoni et al. [29] where the mortar incorporating 30% of metakaolin had 120–130% of the reference mortar 28 day compressive strength, in this study the mortar reached only 74% of PC strength. Several reasons could explain this trend:

The properties of the cement [59,60]: the cement used here was CEM I 52.5, which resulted in relatively high strength of the reference. The strength class of the cement used in Antoni et al. [29] is not known. It contained 77.3% of ($\text{C}_3\text{S} + \text{C}_2\text{S}$) against 69.8% in the cement used in this study. This means that in MK1 blend cement mortar, there is probably less Portlandite produced and additional metakaolin would be present as inert phase in cementitious matrix.

The chemical composition of the metakaolin: MK1 contents 93.16% of ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) against 97.53% in the study of Antoni et al. [29] for example.

The purity of metakaolin, which is directly related to the quality of the kaolin used: despite the use of the same manufacturing process (flash calcination), Antoni et al. [29] used a very high purity metakaolin whereas MK1 contains only 53% of reactive products. This suggests that there is a significant amount of crystalline silica which is likely to improve packing density but not chemical reactivity. Avet et al. [61] actually showed that compressive strength is a linear function of calcined kaolinite content. In their study 28 day strength decreased by nearly 30% as calcined kaolinite content was reduced by 50%.

Using pure metakaolin is generally not a cost effective solution today. Moreover the replacement of cement is not necessarily the optimal use of such high quality raw material. Its use in previous studies was mainly for research purposes. In this experimental study the authors chose three different metakaolins with different production process and kaolinite content. The $\text{Al}_2\text{O}_3(\text{SiO}_2)_2$ content of MK1 was only 53% and it was obtained from flash calcination thus with lower energy consumption than fluidized bed. 28 day results in Fig. 2 shows that the synergistic effect of the ternary system can be observed even at intermediate kaolinite content. Recent studies also showed the potential reactivity of other clays such as calcined material with approximately 40% kaolinite and 40% of other clay minerals [62], calcined smectitic clays [63], flash calcined smectite and illite [36].

Due to several phenomena, the optimal replacement rate of PC by metakaolin which helps to keep or improve the mechanical properties of mortar is very variable [14,16]. As shown in Fig. 3a, the relative compressive strength of mortar with 30% of MK1

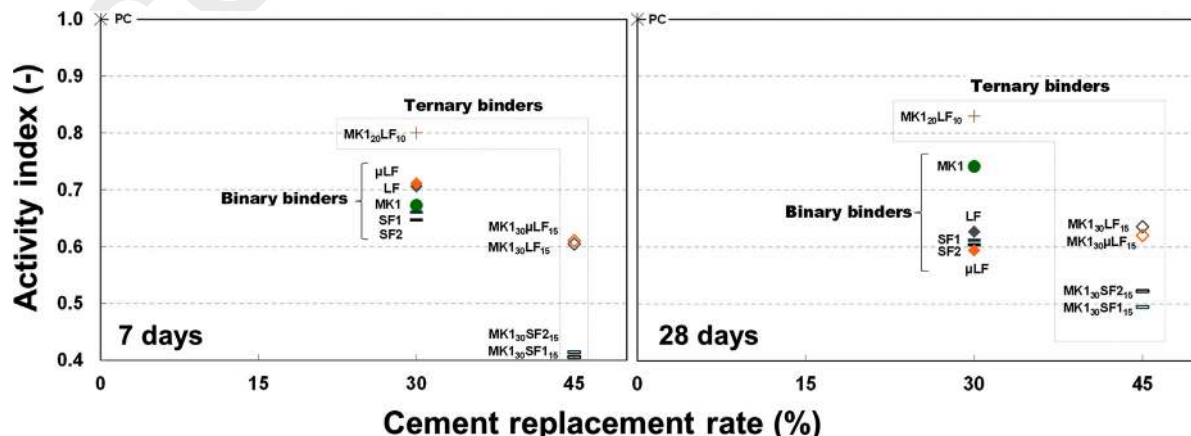


Fig. 2. Activity index of binary and ternary binders mixes at 28 days ($W/C_0 = 0.5$).

increased with time. The main reason is the progressive activation of the pozzolanic reaction of amorphous silica and alumina contained in the metakaolin [8,15,16,64].

The presence of metakaolin also increased significantly the first peak of heat flow (Fig. 4a). Moreover, the time corresponding to the appearance of the first peak was getting shorter compared to filler blended cement mortar. This trend confirms that MK contributes to the increase of hydration rate at very early age. This behavior can be attributed to the combination of two effects: creation of nucleation sites which is much more pronounced with metakaolins due to high specific surface (Table 1), and chemical effect which consists to the stimulation of anhydrous particles of cement [65]. The effect of the presence of MK in cementitious matrix is clearly illustrated by the intensity and position of the second peak. This peak has been interpreted by Lerch [66] as the “sulfate depletion peak”, as it is clearly influenced by calcium sulfate content. Hesse et al. [67] actually showed that this heat flow maximum can be attributed to an acceleration of the aluminate reaction with the enhanced dissolution of C_3A and the final formation of ettringite. This acceleration occurs as soon as the calcium sulfate phase is exhausted. After this hydration stage the sulfate concentration of the pore solution of the cement paste decreases and less C_3A is present in the cement paste thus a conversion of ettringite to mono sulfate should start [68]. The same observations were made by Lagier et al. [59]. They reported an increase of the height of the second peak with the specific surface area of metakaolin and the alkali content of cement. Both factors are likely to accelerate the dissolution of metakaolin and the increase in solubilized aluminum. Thus, an increase in metakaolin dissolution rate would promote the hydration of C_3A , and the metakaolin reaction itself could contribute to the magnitude of the peak.

This second peak was also present to a larger extent in the ternary mixtures (Fig. 4b), and appeared almost at the same time. However, in ternary mixtures (PC + MK1 + Filler), both nucleation and chemical effects could not offset the dilution effect due to the high replacement rates of cement (45% by weight). Consequently, ternary binder mixtures just reached 65% of the reference mortar compressive strength (Figs. 2 and 3b). This compressive strength reduction was even more pronounced in ternary binders containing siliceous fillers than those containing limestone filler (Fig. 3b). The synergistic effect of metakaolin and limestone filler can clearly be seen on this graph, as the difference between activity indices of SF based mixtures and LF based mixtures kept increasing from 1 day to 7 days and allowed reaching higher strengths at 28 days. In spite of significant increase of specific area (Table 1), the replacement of limestone filler LF by μ LF did not result in an acceleration of hydration. However, for a given hydration degree, μ LF mixtures generally showed higher activity index, especially for binary binders and early age values (Fig. 4a). This suggests that smaller μ LF particles (Table 1) improved the packing density of

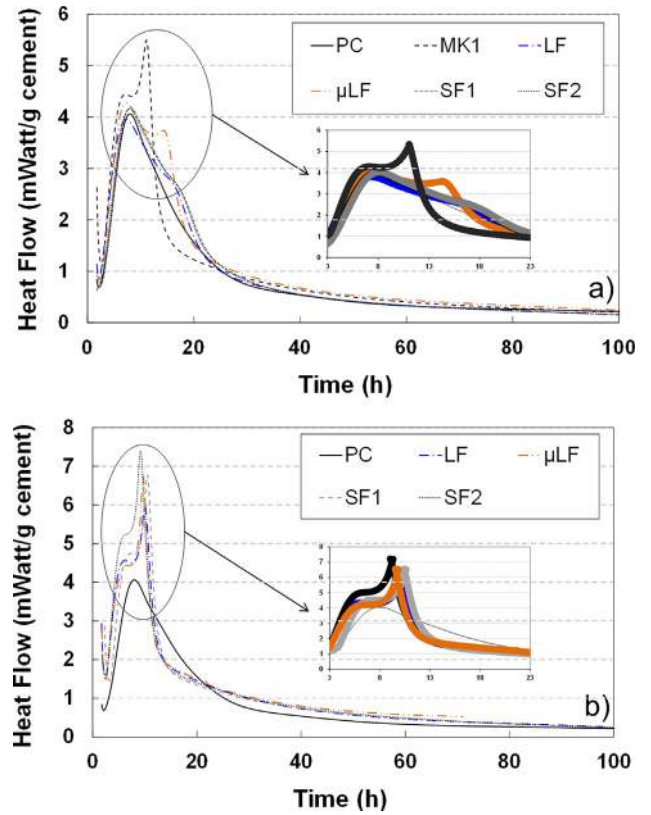


Fig. 4. Hydration heat ($W/C_0 = 0.5$): (a) binary binders, (b) ternary binders.

cement paste, which is an interesting behavior to optimize early age strength.

In order to understand the evolution of binary and ternary binders hydration, the variation in portlandite content $\Delta Ca(OH)_2$ was calculated as expressed in Eq. (6). $\Delta Ca(OH)_2$ has been assessed to distinguish the pozzolanic or nucleation reactions effect from the dilution effect. When cement is replaced by metakaolin, the portlandite content actually varies due to lower cement content (dilution effect), and other hydration reactions which consume portlandite (pozzolanic effect) or enhance portlandite formation (nucleation effect). In Eq. (6), the second term represents the dilution. If $\Delta Ca(OH)_2$ is negative, this means that only taking into account the dilution effect would lead to higher Portlandite content than that actually measured, thus pozzolanic reaction occurred (see $CMK1_{30}$ in Table 4). If $\Delta Ca(OH)_2$ is positive, this means that only taking into account the dilution effect would lead to an underestimation of Portlandite content, thus nucleation has

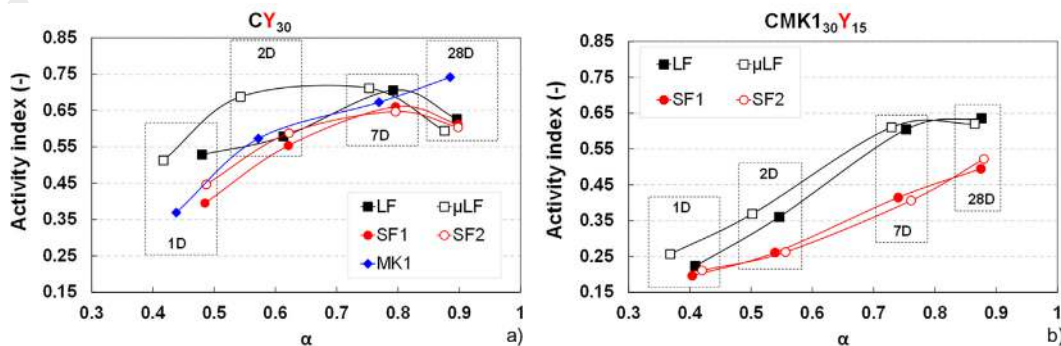


Fig. 3. Activity index vs. hydration degree ($W/C_0 = 0.5$). (a) Binary binders, (b) ternary binders.

Table 4
Variation in portlandite content after 28 days ($W/C_0 = 0.5$).

	Ca(OH) ₂ content (%)	ΔCa(OH) ₂ (%)
PC	13.71	
CMK1 ₃₀	6.03	-3.57
CSF1 ₃₀	10.20	0.60
CSF2 ₃₀	12.31	2.71
CLF ₃₀	7.48	-2.12
C _μ LF ₃₀	7.67	-1.93
CMK1 ₃₀ SF1 ₁₅	4.38	-3.16
CMK1 ₃₀ SF2 ₁₅	6.12	-1.42
CMK1 ₃₀ LF ₁₅	2.17	-5.38
CMK1 ₃₀ μLF ₁₅	1.23	-6.32

avored its formation (see CSF1₃₀ and CSF2₃₀). Table 4 reports the results obtained for binary and ternary binders mixtures at 28 days.

$$\Delta Ca(OH)_2 = \%Ca(OH)_2(MA(p)) - \%Ca(OH)_2(PC) \times (100\% - p\%) \quad (6)$$

where p is the mass percentage of mineral addition.

Ternary binder mixtures showed a higher reduction in the amount of CH than binary binder mixtures, which was not only due to dilution effect. This shows that the combination (MK + Filler) has a positive impact on reactivity of MK. The combination (MK + LF/μLF) exhibited a better consumption of Portlandite than siliceous filler combination. This can explain the lower reduction of compressive strength in systems (PC + MK1 + LF/μLF), assuming that the consumption of CH leads to the formation of new hydration products which densify the cementitious matrix, as confirmed by Fig. 4b.

The XRD patterns performed by Antoni et al. [29] on ternary binders incorporating 30% of MK and 15% of limestone filler actually showed a modification of the products formed. Their observation helps to confirm the positive effect of limestone on the development of mortar strength. A significant and increasing presence of ettringite (Aft) and hemicarboaluminate (Hc) as a function of age was actually noted. This significant quantity of hemicarboaluminate is explained by the chemical reaction between the calcium carbonate (from limestone filler) and the aluminate supplied by cement and metakaolin. This reaction requires the presence of portlandite [30,69,70], that is why CH consumption was higher in the ternary mixture (Table 4). The strength increases of the (PC + MK + LF/μLF) mixtures was much lower after 28 days. This trend was also observed by Antoni et al. [29] and Vance et al. [30]. It can be explained by nearly total depletion of portlandite at this age in these mortar mixtures (Table 4).

Fig. 2 also shows that with equal replacement ratio, mortar containing 20% of MK1 and 10% of LF (replacement of 30% of Portland cement) developed better compressive strength than mortar containing 30% of MK1. Limestone filler is known to accelerate the hydration of C₃S and thereby increase the early compressive strength of the mortar [71–73]. When limestone filler is combined with metakaolin, this effect is less clear, as showed by heat flow (Fig. 4) and activity index (Fig. 3) values. The higher specific area of MK seems to have a prevailing effect on cement hydration at early age. In addition to this phenomenon, some unreacted CaCO₃ can also improve the packing density of the mortar by filler effect. However, it is important to note that in spite of the same ratio CaCO₃/AS₂ in mixtures CMK1₃₀LF₁₅ and CMK1₂₀LF₁₀, this latter developed a greater activity index. This confirms that these mixtures are also influenced by dilution effect of the cement.

The use of siliceous filler in ternary binders also induced highly exothermic reactions at very early age (Fig. 4) without enhancing mortar strength. Finally, (PC + MK1 + LF) system offered the best

compromise in terms of reduction of CO₂ emission, relative strength, and heat flow. Despite the reduction of heat flow at the first peak in the system (PC + MK1 + LF), the results showed a higher peak intensity compared to that of reference mortar (Fig. 4). Similarly, despite the apparent acceleration of hydration, compressive strength of ternary binder mixtures remained very low at early age (Fig. 3). Knowing that the ternary mixtures contain less Portland cement, one of the factors that can explain this peak is the influence of C₃A on hydration due to insufficient gypsum. Thus, it appeared useful to investigate the influence of adding extra gypsum on strength development of heat flow of system (PC + MK1 + LF).

3.1.2. Effect of gypsum

It is generally agreed that the effect of gypsum is to control the rapid reaction normally shown by the calcium aluminates. However, the mechanisms that govern the reaction between calcium sulfate and C₃A are not well known. Some authors suggest there is a formation of protective and waterproof barrier around C₃A which limit water and ions diffusion necessary for C₃A precipitation [74,75]. According to Feldman et al. [76], the slowdown of C₃A hydration in the presence of gypsum would be due to the adsorption of sulfate ions on the surface of these particles. Fig. 5 illustrates the evolution of heat flow, registered as a function of time with different amounts of gypsum (0, 1.5, 3.27 and 7.12% by weight of binders). Note that these percentages do not include the initial amount of gypsum contained in Portland cement.

The heat evolution rate curves show a slight increase of the first exothermic peak when the amount of gypsum increases. Nevertheless, for all mixtures tested, the differences in the intensity of the first peak were not significant. Similarly, this peak seems to appear at the same time. As shown in Fig. 5, fundamental effect of adding extra gypsum was seen at the second peak. Without adding extra gypsum to the ternary mixture, the second exothermic peak appeared earlier (11 h). As gypsum content increased, the intensity of the second peak decreased and it appeared later. Minard et al. [77] have highlighted that between the two peaks, the main reaction is governed by the dissolution of C₃A and precipitation of ettringite. They also showed that the occurring of the second peak is due to depletion of gypsum.

Fig. 6 illustrates the influence of extra gypsum on relative compressive strength at 1, 2, 7 and 28 days. At early age, with increasing of gypsum amount up to 1.5%, the compressive strength was improved between 5 and 20% compared to ternary binder without addition. This is consistent with the evolution of the cumulated heat of hydration over time.

For large amounts of gypsum, the strength decreased compared to a mortar without additional gypsum addition. This can be partly

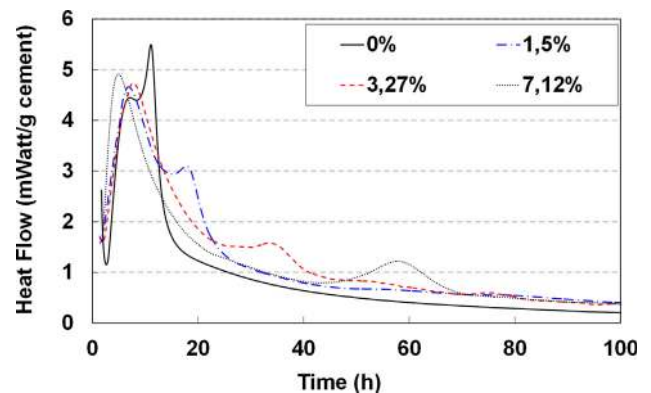


Fig. 5. Effect of gypsum ratio on the hydration heat ($W/C_0 = 0.5$).

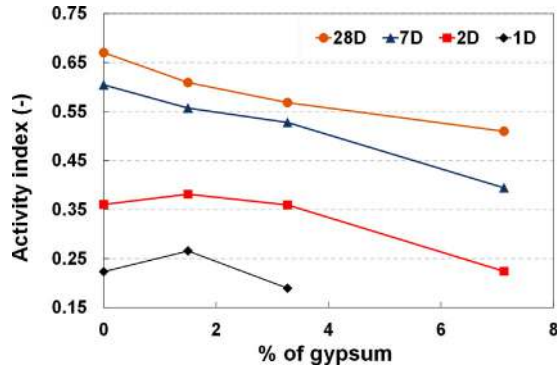


Fig. 6. Activity index for different gypsum ratios ($W/C_0 = 0.5$).

explained by the dilution effect of gypsum [78]. As the mixtures were designed at constant binder content, the increase of gypsum content implies a decrease of C_3S content thus less CSH formed in hydrated cement paste. The filling of the porosity by the hydration products is reduced, which affects the long term compressive strength of mortars. Up to 1.5% of gypsum substitution, results presented in Figs. 5 and 6 show an enhancement of early compressive strength of ternary mixture system. However, when considering the mortar behavior at 7 and 28 days, it is observed that adding extra gypsum leads to significantly lower compressive strength.

3.2. Influence of metakaolin properties

In Fig. 7, the activity index of metakaolin mixtures is plotted at different ages: 1, 2, 7 and 28 days. The three metakaolins have different origins, composition and microstructure (Table 1). It can be observed that depending on the type of metakaolin, the relative compressive strength significantly varied.

For both series of mixtures (with binary and ternary binders), mortars containing MK3 developed higher compressive strength than mortars containing MK1, whatever their age. Similar results were reported by Cassagnabère et al. [79] for MK blended cements. This difference was attributed to the purity of metakaolin, which depends on the nature of the kaolin used. MK1 contained only 53% of reactive metakaolin for about 68% for MK3 [37]. The reactive products content was deduced from the determination on amorphous content from XRD analyses.

At early age, compressive strength of the mixtures increased with the fineness of MK. With approximately the same chemical composition of both metakaolins, the compressive strength of MK3 was higher than that of MK2 blended cement mortar. These results suggest that during the first stages of hydration, pozzolanic reactivity has a weak influence on compressive strength. According to Wild et al. [15] and Kiattikimol et al. [80], who studied metakaolin and fly ash respectively, the increase of compressive strength at these stages is attributable to the filler effect. This filler effect consists in filling the space between cement particles and so leading to a better packing. Moreover, the smaller the particle size, the more they act as nucleation sites where the first hydration products can precipitate [81]. At 7 days, the finer MK3 metakaolin showed a greater strength enhancing effect than MK2. In binary mixtures, the 7 day activity index increased from 0.62 for MK2 to 0.87 for MK3, i.e. an increase in compressive strength of 40%. In ternary mixtures, the activity index increased from 0.49 for MK2 to 0.85 for MK3, i.e. an increase in compressive strength of 73%. This can be attributed to the acceleration of pozzolanic reactivity as MK fineness increases. These results are in agreement with other studies on mineral additions [55].

At 28 days, the activity index strongly increased for MK2 and MK3 blended cement mortars. At this stage, their compressive

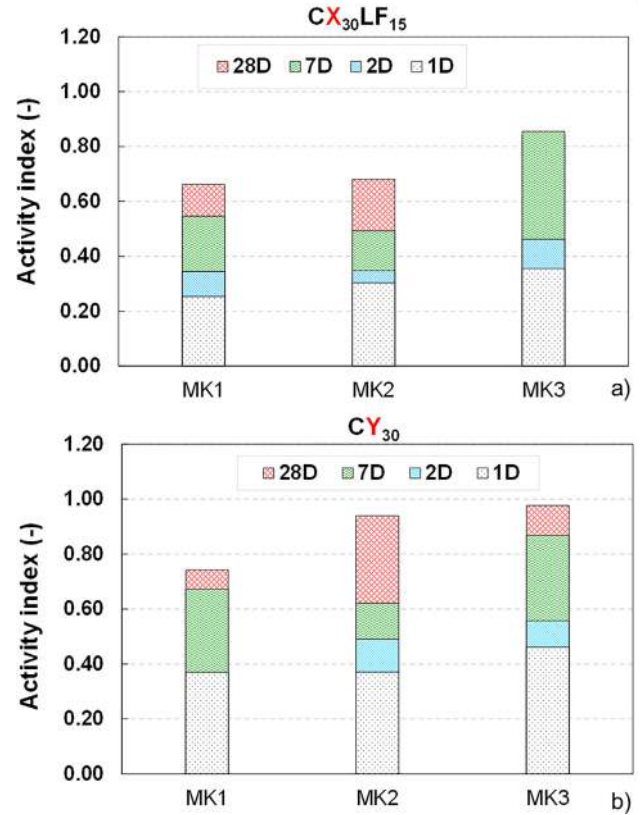


Fig. 7. Effect of metakaolin type on the activity index ($W/C_0 = 0.5$): (a) binary binders; (b) ternary binders.

strength was close to reference mortar, confirming that with better quality of MK, a replacement ratio of 30% can allow to achieve the same compressive strength as reference mortar. Contribution of pozzolanic reactivity in the development of this high strength is illustrated in Table 5 where the variation in portlandite content is reported. Compared to MK1 blended cement mortars, the two systems (PC + MK3) and (PC + MK3 + LF) showed significant reduction in CH content at 28 days. This is consistent with variations of MK pozzolanic indexes given in Table 1. It should also be noted that between 7 and 28 days, there was no sign of strength development in system (PC + MK3 + LF). The degree of hydration in this system only changed from 0.83 to 0.84. This indicates a very high acceleration of the pozzolanic reactivity between 2 and 7 days due to the fineness of the MK3. The hydration of this ternary binder seems to be limited by the depletion of portlandite, as shown by portlandite content at 28 days given in Table 5.

3.3. Influence of W/C_0 ratio and durability

3.3.1. Mechanical properties

It is known that concrete strength is affected by the water to binder ratio (W/C_0) and cement content. The lower the W/C_0 ratio,

Table 5
Effect of metakaolin on portlandite content at 28 days ($w/c_0 = 0.5$).

		Ca(OH) ₂ content (%)	Δ Ca(OH) ₂ (%)
CX ₃₀	MK1	6.03	-3.57
	MK3	4.44	-6.91
CX ₃₀ LF ₁₅	MK1	2.17	-5.38
	MK3	0	-8.24

the higher the strength is. These results are well known [82] and models such as Feret's or Bolomey's equation can be used to optimize mix design of cement based materials as mineral additions show relatively low coefficient of activity at early age [5]. In the case of concretes or mortars containing pozzolanic addition such as metakaolin, very few studies have been carried out on the influence of W/C_0 on compressive strength. In this study, the effect of two initial W/C_0 (0.42 and 0.5) on the compressive strength of mortars including binary (70PC + 30MK3) and ternary (55PC + 30MK3 + 15LF) binders is discussed. Fig. 8 represents the activity index versus degree of hydration of these four mixtures.

At 1 day, as expected, an increase in the activity index with lower W/C_0 was observed, for both binary and ternary binders. This means that the development of the compressive strength of these mortars evolved in the same direction and approximately the same magnitude as the reference mortar. These results are consistent with previous studies on the influence of the water to binder ratio. This trend can be explained by better hydration of the cement (α increased) and a reduction of the capillary porosity as W/C_0 decreased. Moreover, theoretical hydration models [82–84] show that a water to cement ratio of 0.42 is high enough for a complete hydration of Portland cement. The difference of activity index expressed by Eq. (7) was higher for binary binders (10%) than for ternary binders (4%). This variation can be attributed to the dilution effect due to a high substitution of the cement in the mortar incorporating ternary binders. Nevertheless, at this age, the quantity of CH consumed (Fig. 9) indicates that in mixture with $w/c = 0.42$, the pozzolanic activity has already begun whereas in $W/C_0 = 0.5$ mixture, the chemical effect of metakaolin was less significant yet.

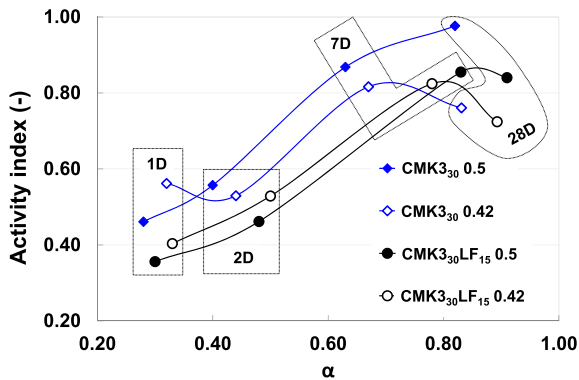


Fig. 8. Activity index vs. hydration degree for different W/C_0 ($X = MK3$).

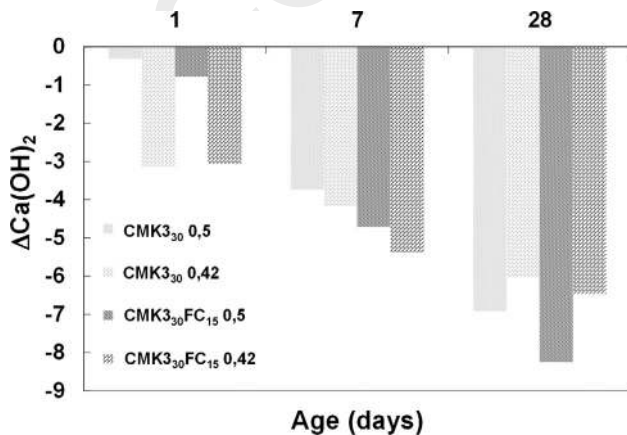


Fig. 9. Evolution of the CH consumed normalized to PC content in the paste.

$$\Delta_i(p, t) = i\left(p, t, \frac{W}{C} = 0.42\right) - i\left(p, t, \frac{W}{C} = 0.5\right) \quad (7)$$

From 2 days $\Delta_i(p, t)$ decreased until becoming negative. This inversion of $\Delta_i(p, t)$ evolution appeared at 2 days for binary binders and from 7 days for ternary binders. At 28 days, despite a similar degree of hydration for both W/C_0 ratios, the activity index significantly decreased for $W/C_0 = 0.42$. Several phenomena could explain these variations. Lower W/C_0 resulted in activation of MK at early age but for longer hydration time, there was not enough free water to allow pozzolanic reaction with CH. Consequently, the slowdown of CH consumption limited later strength development. In contrast, for $W/C_0 = 0.5$ mixtures, the pozzolanic activity was very slow (Fig. 9) at early age, whereas a higher CH consumption at 28 days illustrates a higher pozzolanic activity. This was made possible due to the availability of water in the cementitious matrix.

3.3.2. Shrinkage

As shrinkage magnitude at a given time can be misleading to compare materials performances [45], the drying shrinkage results were analyzed through the hyperbolic shrinkage model (Eq. (5)). The analysis of experimental data provides two parameters. The obtained ultimate drying shrinkage and the shrinkage half time are presented in Table 6.

For a given proportion of mineral addition, the higher the W/C_0 ratio, the higher the ultimate shrinkage was. This trend has been observed in previous studies [85,86]. It is due to opposite effects of different properties such as pore size distribution, total porosity, modulus of elasticity, creep, and water diffusion. Higher W/C_0 ratio results in coarser porosity, which theoretically induces lower capillary stresses according to Young Laplace Equation (Eq. (8)). However the modulus of elasticity decreases and creep increases, which tends to induce higher shrinkage strain. Higher W/C_0 generally results in faster water diffusion thus higher evaporation and shrinkage rates, which was not observed here for PC and CMK3₁₅ mortars (N_s was higher for $W/C_0 = 0.5$) (Table 6). This could be due to couplings between self desiccation and drying. The reduction of W/C_0 ratio has actually been shown to accelerate hydration reactions during the first days (Figs. 8 and 9). The shrinkage half times were actually close to the characteristic times of self desiccation, thus shrinkage rates could have been influenced by this phenomenon. The free water available to drying is lower and it decreases with the hydration evolution especially when the water to cement ratio is low [87]. Thus, a high proportion of the evaporable water evaporates at early stages and then the water becomes less and less available for drying. This variation of drying rate is likely to influence the rate of the drying shrinkage.

For both studied water to binder ratios, the substitution of cement by additions provided in all studied cases a lower ultimate shrinkage. According to the Young Laplace Eq. (8), this result can

Table 6

Long term drying shrinkage, N_s , slope of total shrinkage vs. weight loss curve and porosity of blended cement mortar with different ratio of MK and/or LF.

		PC	CMK3 ₁₅	CMK3 ₃₀	CMK3 ₃₀ LF ₁₅
0.5	Long term drying shrinkage ($\mu\text{m/m}$)	978	833	558	890
	N_s (days)	3.2	3.1	1.3	1.0
	K	270	237	140	189
	Porosity (%)	22	24.5	25.2	26.6
0.42	Long term drying shrinkage ($\mu\text{m/m}$)	773	572	522	488
	N_s (days)	2.8	1.8	1.7	1.5
	K	276	199	-	132
	Porosity (%)	19.9	23	23.3	25

be explained by the higher internal pressure due to the lowest and finest porosity when only Portland cement is used (Table 6) [88].

$$\sigma_{cap} = \frac{2\sigma}{r} \cos \alpha_m \quad (8)$$

where σ is surface tension of gas liquid interface ($\sigma = 72.75 \cdot 10^{-3} \text{ N} \cdot \text{m}^{-1}$ for water), r is pore radius (m), and α_m is wetting angle (rad).

In order to confirm this assumption, the drying shrinkage was plotted against mass loss in Fig. 10. Two stages can be observed. The second stage seems to indicate a linear relationship between drying shrinkage and mass loss [89]. The slope of this linear phase K can also be used to model long term shrinkage of concrete structures. PC mortar showed the highest values (Table 6). The porous network of mortar containing only PC was finer than that of mixtures with binary or ternary binder. This induced higher ultimate shrinkage due to higher capillary stresses, and slower drying shrinkage rate, as shown by N_s values.

Concerning the water to binder ratio of 0.42, the ultimate drying shrinkage decreased with the mineral addition proportion. For the water to binder of 0.5, the same tendency was observed excepted for 45% substitution of cement. In this last case with a ternary binder, an increase in the ultimate shrinkage was observed compared to the CMK₃₀ mixture with binary binder and the same MK content. The CMK₃₀LF₁₅ mixture actually had the highest water to cement ratio. Even if all the mixtures had the same W/C_0 ratio, the actual water to cement ratio is a major parameter when specimens are exposed to drying at one day. At this early age, the cement hydration can be slowed down or stopped by exposure to drying [39]. For the mixture with ternary binder and water to binder ratio of 0.5, the highest cement substitution and the highest water content generate a faster water loss whereas the elastic modulus was lower due to the higher porosity (Table 6). Thus, the generated strain was also higher. According to the Table 6 this mixture had the lowest shrinkage halftime, which means the fastest drying (1 day to develop 50% of the ultimate shrinkage).

The shrinkage half time decreased with the cement substitution proportion for both studied water binder ratios. This result can be explained by the lower proportion of hydration products and the higher porosity for the mixtures with the lower cement content. The moisture diffusion coefficient theoretically decreases with the cement content and likewise for the drying rate which is behind the drying shrinkage rate. For the mixtures with proportions of mineral addition equal or higher than 30%, the faster drying can be explained by the highest free water content and highest initial porosity. This is confirmed by the experimental values of K . This coefficient generally decreased with mineral addition content, which corresponds to a coarser porosity. This is consistent with a decrease in shrinkage halftime.

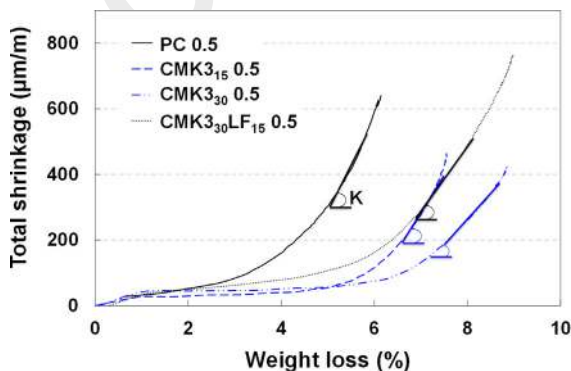


Fig. 10. Drying shrinkage vs. weight loss of binary and ternary binders with $W/C_0 = 0.5$.

3.3.3. Durability indicators

Water porosity is one of main indicators used to characterize the durability of cementitious materials. In the range of water to binder ratios studied in this work ($W/C_0 > 0.3$), global porosity increases with W/C_0 . All the other parameters being equal, it can be assumed that the porosity of the concrete is conditioned by that of the cementitious matrix. In this matrix, the gel pores associated to the hydration products are generally distinguished from the capillary pores. Furthermore, Powers et al. [84] assumed that the gel pores would be conditioned by the advancement of the degree of hydration whereas capillary pores would be attributed to evaporation of free water. On the one hand, water porosity is correlated to mechanical properties such as compressive strength. It is well known that an increase in the porosity of cementitious materials generally cause a decrease in their compressive strength [90,91]. On the other hand, porosity can be used as a durability indicator in performance based specifications [92] and its value is often needed for modelling purposes [93].

Results presented in Table 6 show an increase in water porosity with W/C_0 ratio, independently of the substitution rate. For a given W/C_0 ratio, the water porosity increased by 11–16% for binary mixtures and up to 26% for ternary mixtures, considering the PC mixture as a reference. The same trends have been obtained by Bredy et al. [94] on metakaolin blended cement paste. This increase was explained by the agglomeration of unreacted metakaolin. For lower substitution rate of Portland cement, other authors have made the same observation [18,19]. However, inverse phenomena are observed in other studies. Ambroise et al. [23], Poon et al. [95] reported a decrease in total porosity for cement pastes incorporating metakaolin. These tests were carried out with a lower water to cement ratio (< 0.3). According to these studies, the main observations are that other physicochemical properties of addition, mix design parameters such as cement and water contents, and w/c ratio have a strong effect on packing density and hydration process and consequently on the microstructure of the mortar.

The increase in water porosity with the cement replacement rate led to an increase in the natural carbonation depth of studied mixtures (Fig. 11). Carbon dioxide actually penetrates into cementitious materials through its open porosity then reacts with CH and CSH, which causes a drop in pH. The lower the porosity and the smaller the pore size, the slower the diffusion and CO_2 ingress and the lower the carbonation depth is at a given exposure time. Both factors (porosity and CH content) explain why ternary mixtures carbonate more compared to the reference mortar [16,96–98]. However, it can be noted that lower W/C_0 ratio reduce the carbonation depth, confirming that this mix design parameter can be used to mitigate the carbonation of concretes incorporating metakaolin. The dilution effect is also an important parameter in the

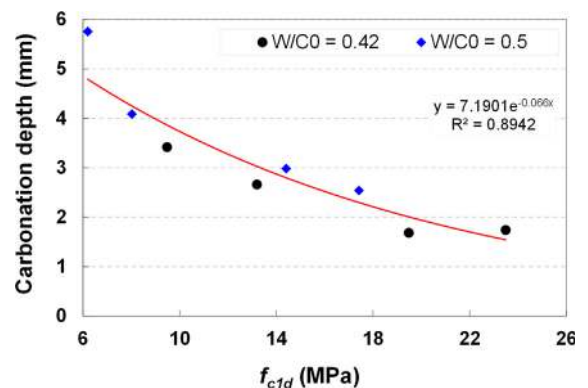


Fig. 11. Correlation between carbonation depth at 28 days and 1-day compressive strength.

carbonation phenomenon. For mortars including up to 15% of metakaolin in substitution of Portland cement, Mota et al. [99] observed an increase in the carbonation depth despite an improvement in the mechanical performance of these mortars. However, the same tests carried out by adding metakaolin (instead of replacing it with cement) showed an improvement in both mechanical performance and resistance to carbonation. This fundamental difference is due to the lack of CH (consumed by the pozzolanic reaction with MK) to control the pH and avoid the acidification of mortars.

Carbonation depth at 28 days was found to correlate with 1 day compressive strength (Fig. 11). The mortar specimens were exposed to drying and carbonation at 1 day. At this age cementitious materials are mainly unreacted as hydration of cement as well as pozzolanic reactions require water. As drying starts, free water, which was meant to react with cementitious materials at later ages, evaporates and coarser capillary porosity is produced. Reducing the W/C₀ ratio allowed increasing the 1 day hydration degree (Figs. 8 and 9), thus mitigating carbonation. Pozzolanic reaction is actually known to induce finer porosity [38] thus lower CO₂ diffusion coefficient.

In order to better understand the processes leading to concrete carbonation, mathematical model was developed by Papadakis et al. [97] for one dimensional geometry, the carbonation depth x_c (m) is given by the following analytic expression:

$$x_c = \sqrt{\frac{2D_{e,CO_2}[CO_2]_0 t}{[CaO]_0}} \quad (9)$$

where $[CO_2]_0$ is the molar concentration of CO₂ per unit volume of the gas phase, $[CaO]_0$ is the total molar concentration of CaO and D_{e,CO_2} is the effective diffusivity of CO₂ in carbonated concrete (m²/s) which is expressed by [96]:

$$D_{e,CO_2} = 10^{-7} \times 10^{0.025f_c} \quad (10)$$

where f_c is the compressive strength of the concrete (MPa).

Results are presented in Table 7 for mortar with binary or ternary binder. Predicting values are in good agreement with the corresponding experimental data when effective diffusivity is calculated with f_{c7d} (compressive strength at 7 days).

For a given W/C₀ ratio, the effective diffusion of CO₂ was significantly higher for mortars with more than 30% of PC replacement, confirming that the porous network of these mortars was coarser. The reduction of W/C₀ ratio from 0.50 to 0.42 allowed reaching the 7 day strength of reference mortar with W/C₀ = 0.50 thus reducing the CO₂ diffusion coefficient (Table 7). Despite equivalent D_{e,CO_2} , CMK₃₀ 0.42 and CMK₃₀LF₁₅ 0.42 mixtures showed higher carbonated depth than reference mortar mixture due to lower CaO content. The carbonated depth of CMK₃₀ 0.50 and CMK₃₀LF₁₅ 0.50 mixtures was slightly underestimated. If CaO content is assumed to be well known, this could come from an underestimation of

CO₂ diffusion coefficient. These two mixtures were actually found very sensitive to hydration drying coupling as shown on Fig. 10. They actually showed significant water loss without shrinkage. This first stage can be observed when cement based materials are exposed to drying at early age. This is due to the formation of drying depth [42] where permeability is higher due to microcracking, wall effect, and coarser porosity as hydration has been nearly stopped by early drying. As 7 day compressive strength has been used to assess CO₂ diffusion coefficient, the obtained values do not take into account this strong early drying effect for mixtures with relatively high w/c ratio.

4. Conclusions

The objective of this study was to investigate the behavior of ternary binders based on metakaolin and limestone filler. The experimental study showed that the combination of both mineral additions and Portland cement is a promising alternative to current plain and blended Portland cements, not only in terms of strength but also for the potential durability. Experimental results on hydration obtained by using TGA and isothermal calorimetry are presented in this paper and correlated with compressive strength data. Shrinkage and durability parameters of binary and ternary binders mixtures are also analyzed. The following conclusions can be drawn:

- Equivalent strength of metakaolin based binary mixtures can be ensured provided that the replacement of Portland cement by metakaolin does not exceed 30% and that highly reactive metakaolin is used. However, there is evidence that higher substitution of Portland cement is possible by combining metakaolin with limestone filler. The presence of both additions in cementitious systems fosters primary and secondary hydration reactions and improves the packing density of cement paste. The extent of the pozzolanic reaction with metakaolin is enhanced. The performance of metakaolin based binary or ternary mixtures was found to depend on metakaolin properties. These include the proportion of reactive phase as well as manufacturing process, specific area, and particle size distribution.
- The presence of metakaolin influences cement hydration from very early age, as highly exothermic reactions were observed in binary and ternary binders, then a drop of heat flow. The results show that incorporation of additional gypsum in the binder allows a better control of aluminates related reactions. Consequently, heat flow and second peak of hydration are reduced. However, whatever the gypsum content, this beneficial effect is accompanied by a drop in mechanical performance at later ages. Thus, it is recommended to keep only the gypsum initially present in the Portland cement.

Table 7
Experimental results and model predictions of carbonation depth of mortars.

W/C ₀	Input data		Model prediction		Experimental results x_c (mm)	D_{e,CO_2} estimated from experimental results (m ² /s)
	f_{c7} (MPa)	[CaO] ₀ (mol/m ³)	D_{e,CO_2} (m ² /s)	x_c (mm)		
0.5	PC	43.0	7071	8.41E-09	2.54	8.64E-09
	CMK ₃₀ 15	41.5	5634	9.16E-09	2.93	9.50E-09
	CMK ₃₀ 30	37.3	4373	1.17E-08	3.75	1.38E-08
	CMK ₃₀ LF ₁₅	36.8	3394	1.20E-08	4.33	2.13E-08
0.42	PC	53.9	7802	4.50E-09	1.74	4.47E-09
	CMK ₃₀ 15	41.4	6235	9.22E-09	2.79	3.35E-09
	CMK ₃₀ 30	44.0	4856	7.96E-09	2.94	6.52E-09
	CMK ₃₀ LF ₁₅	44.4	3736	7.76E-09	3.31	8.27E-09

- (c) A decrease in W/C_0 ratio resulted in an increase in the activity index of blended cement mortars at early age. This was due to an accelerated pozzolanic reaction. At longer term, at lower W/C_0 ratio, the relative compressive strength decreased. A possible explanation is a slowdown of the pozzolanic reaction caused by rapid depletion of available water.
- (d) All the metakaolin based mixtures showed lower ultimate shrinkage than reference mortar with plain Portland cement, but higher shrinkage rate. The analysis of shrinkage versus mass loss curves actually showed that the replacement of cement by metakaolin and/or limestone filler produced coarser porosity. At $W/C_0 = 0.50$, the binary and ternary mixtures with 30% metakaolin proportions were highly sensitive to early drying, as confirmed by carbonation data.
- (e) For a given W/C_0 ratio, the cement replacement by metakaolin or metakaolin + limestone filler led to an increase in total water porosity, coarser porosity, and an increase in the natural carbonation depth. This trend can be explained by two compounded effects. Faster CO_2 diffusion in the mortars and limited content of carbonatable materials in blended cement mortar accelerated carbonation. Moreover, it can be noted that for a given replacement rate, lower W/C_0 ratio allowed reducing the carbonation depth, confirming that this mix design parameter can be used to mitigate the carbonation of concretes incorporating metakaolin.

Conflict of interest

There are no known conflicts of interest.

Acknowledgement

This study has been supported by l'ATILH (**Association Technique de l'Industrie des Liants Hydrauliques** In French). The assistance of the Project partners is gratefully acknowledged. Ecole Centrale de Nantes provided technical and material supports for this work.

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