Study on binary and ternary systems with cement, hydrated lime and fly ash: thermogravimetric analysis, mechanical analysis and durability behaviour

P. Lorca, L. Soriano✉, M.V. Borrachero, J. Monzó, M.M. Tashima, J. Payá

Institute of Concrete Science and Technology (ICITECH), Universitat Politècnica de València, (Valencia, Spain)
✉: lousomar@upvnet.upv.es

ABSTRACT: The use of high percentages of substitution of Portland cement by pozzolans can provoke the total consumption of portlandite. The present research proposes the study of ternary systems of Portland cement (PC), fly ash (FA), and hydrated lime (CH). After 180 days of curing, the mortar with 50% substitution of PC by FA obtained 65.9 MPa versus the mortars with an addition of 20% of CH and control mortar (100 PC) that obtained 69.9 MPa and 76.7 MPa respectively: this behavior is very positive value considering that tested FA containing mortars had a 50% of Portland cement. Regarding the effect of the amount of extra hydrated lime on durability issues, the evolution against carbonation of PC-FA and PC-CH-FA mortars was studied: the reduction of carbonation velocity was around a 37% for the mortar with CH respect the PC-FA mortar.

KEY WORDS: Hydrated lime; Cement; Fly ash; Thermogravimetry; Portlandite; Mechanical properties; Field emission scanning electron microscopy.

RESUMEN: *Estudio de mezclas binarias y ternarias con cemento, cal hidratada y ceniza volante: análisis termogravimétricos, mecánicos y de durabilidad.* El uso de altos porcentajes de sustitución de cemento Portland por puzolanas puede provocar el consumo total de la portlandita. La investigación propone el uso de un sistema ternario formado por cemento Portland (PC), ceniza volante (FA) y cal hidratada (CH). Después de 180 días de curado, el mortero con un 50% de sustitución de PC por FA obtiene 65.9 MPa de resistencia frente a los morteros con un 20% de CH y control (100 PC) que obtuvieron 69.9 MPa y 76.7 MPa respectivamente; este comportamiento es muy positivo teniendo en cuenta que este mortero tiene un 50% menos de PC. El efecto de añadir la cantidad extra de cal hidratada tiene efectos en la durabilidad; se estudió la evolución de la carbonatación de los morteros con PC-FA y PC-CH-FA. La reducción de la velocidad de carbonatación fue del 37% para los morteros con CH respecto al mortero con PC-FA.

PALABRAS CLAVE: Cal hidratada; Cemento; Ceniza volante; Termogravimetría; Portlandita; Propiedades mecánicas; Microscopía electrónica de emisión de campo.

1. INTRODUCTION

In the late nineteenth century, it was customary in masonry to use lime mortars that could harden over time from the carbonation process and therefore had insufficient short-term strength (1). However, this construction material has lasted until today, although the use of Portland cement has displaced it.

Soon in the early twentieth century, cement was recognized as an essential ingredient in mortars and concretes, improving the mechanical properties of mortars at an early age and their durability performance (2). The construction industry is an activity that uses a significant number of raw materials, and Portland cement manufacturing produces around 7-8 % of anthropogenic CO_2 (3) Reducing these CO_2 levels is paramount to meeting SDG 13 (Sustainable Development Goal). This target calls for a drop in global emissions of this gas by 45%, between 2010 and 2030, and reaches net zero around 2050 (4). It is not easy to achieve this objective, but with the use of less quantity of cement, the emissions of CO_2 may be significantly reduced.

Using pozzolans like fly ash (FA) or metakaolin (MK) to manufacture mortars and concretes is a very common practice, replacing large volumes of cement in the case of FA. Replacing Portland cement (PC) with such material would be a tremendous environmental benefit (5-8) The use of high percentages of substitution of PC by FA has the problem of the low value of mechanical strength at the early age of reaction. Stefanović et al. (8) proposed a method of mechanical activation of PC and FA in a vibrating ring mill to achieve better results; they demonstrated changes in the specific surface area during the grinding process, and consequently, the mixtures had better mechanical values.

The substitution of a large quantity of cement is a problem because of the drastic decrease in the portlandite content and the low alkalinity reservoir of the medium. This point would be critical in the case of reinforced concrete, where the need for an alkaline medium (pH>12) is vital for reinforcement protection against corrosion. Carbonation in pozzolan mixtures is often greater than cement-only mixtures. Justnes et al. (9) compared the carbonation process in a type I cement and a CEM II/B-V cement with 30% fly ash. The authors indicate that the higher carbonation in FA cement is due to three reasons; a lower amount of portlandite, a lower Ca/Si ratio in C-S-H (calcium silicate hydrate) and a greater presence of AF_t and AF_m (hydrated aluminum phases) phases than yield a substantial volume decrease per mole upon carbonation.

Recent studies have proposed using an extra supply of hydrated lime (CH) in the cement-pozzolan blends: this contribution would maintain the mixture's pH and provide more portlandite to react with the pozzolan and achieve better durability (10-14). In Table 1 are shown the main findings of some of these investigations. Lorca et al. (10) proposed the use of an extra addition of CH to have more quantity of calcium hydroxide react with the FA. The authors demonstrated that in the systems with high percentages of cement substitution, adding CH promoted benefits in the mixture. Other authors (11) concluded that adding lime putty improves the compressive strength of the materials containing pozzolans. However, when this lime was added to mixtures with only PC, the strength was lower than that of PC concrete without lime putty. The durability of the blends with pozzolan was improved by adding CH. Anjos et al. (14) studied some pastes with PC-FA and CH by thermogravimetry and XRD (X-Ray diffraction) analysis, and they established that adding CH produced a greater alkalinity reserve and more CSH derived from the pozzolanic reaction. Fonseca et al. (15) demonstrated that adding a 5% of CH in self-compacting concrete (SCC) with a high incorporation of rice husk ash (RHA), limestone and metakaolin (MK), the alkalinity of the system can be restored, and lower carbonation depths can be obtained.

TABLE 1. Summary of the influence of hydrated lime in pastes, mortars and concretes.

Author/year	Quantity of lime	Main findings
Mira et al. 2002 (11)	Addition of 5, 10, 15, 20 and 25% of the cement weight	Improvement of compressive strength at long-term ages, formation of a denser structure
Anjos et al. 2019 (14)	3 and 5% of addition respect cementitious material	Study in pastes with percentages of fly ash of 60%. The greater alkalinity reserve increases the amount of C-S-H derived from the pozzolanic reaction of FA.
Gunasekara et al. 2020 (12)	Mixtures of 35 PC-52FA-13CH and 20PC-62FA-18 CH with incorporation of nanosilica	The incorporation of CH shows a 10% of cost reduction compared to PC concrete
Fonseca et al. 2022 (15)	Addition of 5% respect cementitious material	Replacement of 60% of cement by limestone filler, metakaolin and rice husk ash. The addition of hydrated lime didn´t influence the mechanical strength

To learn how the PC-FA-CH system works, firstly, it is necessary to know how to behave the hydration of selected binary mixtures: PC-FA, CH-FA, and PC-CH. The CH-FA system was less studied in the literature than the PC-FA system (16, 17).

The PC-CH system is most studied in papers related to restoration works and does not focus on aspects of the presence of CH in cement hydration (18-22). Sébaïbi et al. (22) studied the microstructure of cement mortars to which different types of lime were added to the cementing system. The authors suggested that by increasing the percentage of CH, hydration products formed may vary, and then the microstructure of the paste. The substitution of a small percentage does not modify the microstructure, but when high replacement levels are employed, the microstructure changes, producing microcracks.

Fourmentin et al. (23) published an investigation where they proposed the mechanism of reaction when CH was added to the PC. The authors provided specific data from calorimetry, nuclear magnetic resonance, and elastic modulus. They established that the induction period disappears in the presence of lime and that the accelerating effect is due to its high specific surface area that provides an extra surface for the precipitation of CSH in the pores of the cement paste. Other interesting possibility is the use of residual lime in mortars with cement, Sangi-Gonçalves et al. (24) used a lime mud from the Kraft chemical pulping industry. The authors concluded that this residue can be used as a substitute of commercial hydrated lime.

In the present paper, thermogravimetric analysis was performed to quantify the influence of CH in PC systems (binary and ternary systems), the study in terms of thermogravimetry is exhaustive and aims to clarify issues less treated from this point of view in publications on this matter. Moreover, the compressive strength of mortars for binary and ternary systems was studied, in some cases up to 180 curing days. Finally, a study of durability was performed to test the effectiveness of the addition of an extra amount of CH in the improvement in carbonation process.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

A Spanish Portland cement type CEM I 52.5R that meets the specification of European standards 197-1 (25) was used to prepare pastes and mortars. The cement (PC) was provided by Cemex (Buñol, Spain). Panreac Quimica S.L.U provided the hydrated lime (CH) used in the preparation of pastes. This material had a purity of 92%. A commercial Spanish hydrated lime CL90-S (26) was supplied by Cales Pascual

(Paterna, Spain) and it was used for the preparation of mortars. This lime had a percentage of 86% purity in calcium hydroxide, the values of purity of both calcium hydroxide was performance by thermogravimetric analysis. The selection of two types of limes responds to the fact that for the thermogravimetric study in pastes it was thought to use a hydrated lime with greater purity. In the case of mortars, it was selected the hydrated lime that usually is employed in construction. The remaining percentage corresponds to calcium carbonate as shown in the TG curve provided in Figure 1. As can be seen in the Figure 1, the main loss for the calcium hydroxide with 92% purity is around 500 ºC. While the hydrated lime with an 86% purity has a peak between 700 and 900 ºC that corresponds to the loss of CO_2 from the $CaCO_3$ decomposition. A calcareous filler (F) was used as substitute of FA in ternary CP-CH-F pastes to facilitate the calculation of the percentage of fixed lime in the CP-CH-FA pastes. Superplasticizer Glenium Ace 32 (Master Builders Solution) was used to prepare mortars with CH and PC because the workability of the mortars with CH was poor. Adding 10, 15, and 20% of CH in PC mortars significantly reduced their workability and increased the water demand for a given flowability. Thus, a small percentage of superplasticizer additive was used to achieve acceptable workability to allow appropriate compacting and filling of the molds, from 0.2 to 0.5% by weight with respect to the Portland cement content. A percentage of 0.2% was used in the mortars with 10 and 15% of CH, and a percentage of 0.5 % for the mortar with 20% of CH.

The thermal power plant of Compostilla II (León, Spain) supplied the fly ash (FA). Original FA was milled in a ball mill for 20 minutes. According to the UNE-EN 197-1 standard (25), the type of FA used can be classified as type V. Table 2 shows the chemical composition of PC and FA.

In Figure 2 is represented the granulometric distribution of the CH used in the preparation of mortars,
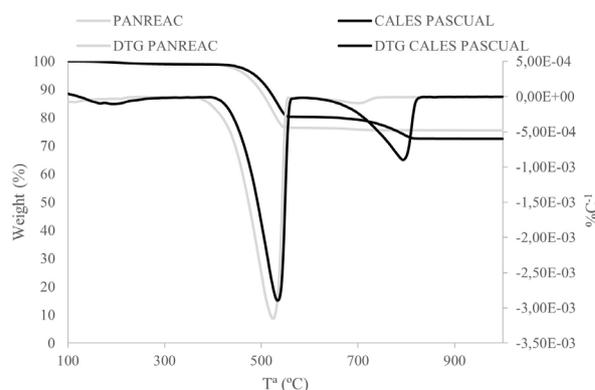

FIGURE 1. TG and DTG curves of Panreac and Cales Pascual hydrated limes.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	K_2O	Na_2O	LOI*
CEM I 52.5 R	19.28	4.58	2.66	62.59	2.64	4.11	0.30	1.04	0.37	2.42
FA	50.93	25.74	7.57	3.54	1.70	0.92	0.97	3.78	n.d	4.85

* Loss of ignition determined at 950ºC for 1 h

PC and milled FA, the mean diameters were 47.96; 17.49 and 11.91 µm respectively. The distribution of the granulometric curve of the CH is bimodal, with particles with diameter higher than 100 µm and particles below 10 µm.
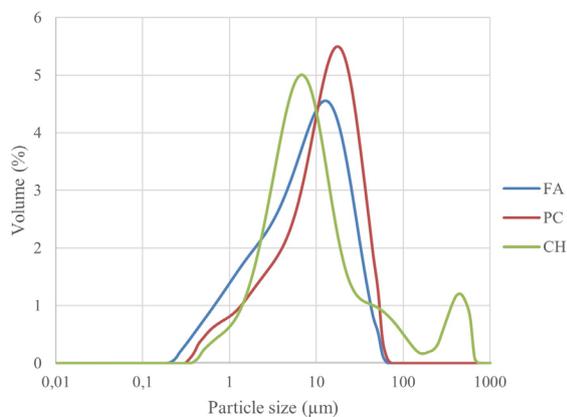

FIGURE 2. Granulometric curve of CH, FA and PC.

The X-ray diffractogram of FA is shown in Figure 3. The image shows that the ash has an important amorphous component, as demonstrated by the deviation of the baseline for 2θ in the range 10-30 °. Main crystalline phases are quartz (Q, SiO_2) as main peak, mullite (M, Al_6Si2O_{13}), magnetite (Fe, Fe_3O_4), calcite (C, $CaCO_3$) and wollastonite (W, $CaSiO_3$).
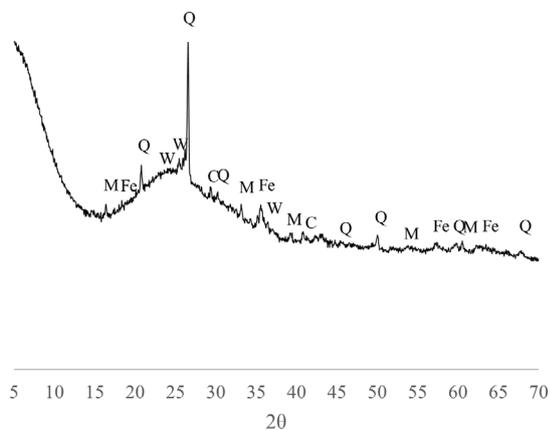

FIGURE 3. X-ray diffractogram of FA.

2.2. Mixing, curing, and sampling procedures for thermogravimetric and microscopy studies

Three types of pastes were made for thermogravimetric analysis. The CH-FA binary paste was prepared by mixing 60% CH and 40% FA using a water/binder ratio of 0.7. This paste was cured at 65 ºC because the reaction of CH and FA is slow, and the high temperature accelerates de pozzolanic reaction. The increase of temperature would favor the reaction degree at a given time would be larger with this temperature increase (27, 28).

The evolution of the reaction of the systems CH-FA was evaluated at 7 and 28 curing days (65 ºC curing temperature). By thermogravimetry, the lime fixation and the hydrated products were studied. Equation [1] was employed (29) for calculating the lime fixation (%), as follows:

$$\%CH_{fixation} = \frac{CH_0 - CH_{FA}}{CH_0} \times 100 \qquad [1]$$

where CH_0 is the initial quantity of CH (60%) and CH_{FA} is the quantity of portlandite in the paste CH-FA at the selected curing age.

The PC-FA binary paste had 50% of PC and 50% of FA (water/binder ratio of 0.5) and was cured at ambient temperature. For the PC-FA pastes the curing ages selected were 7, 28, and 90 days. To calculate the lime fixation, in the case of PC-FA pastes, Equation [2] was used (30). In this case, the percentage of cement substitution by FA was 50%.

$$\%CH_{fixation} = \frac{CH_c \times \%C - CH_{FA}}{CH_c \times \%C} \times 100 \qquad [2]$$

Where CH_C is the quantity of portlandite present in the control paste (only PC) at the selected curing age, %C (equal to 0.5) is the cement proportion in the PC-FA paste, and CH_{FA} is the quantity of portlandite in the PC-FA paste at the selected curing age.

The PC-CH binary pastes were prepared by adding 5, 10, 15, and 20% of CH respect to the PC (water/binder ratio of 0.7) and were cured at ambient temperature. The results presented by other authors such as Mira et al. had percentages of lime addition from 5% to 25% (11). Because the CH was added to the PC-based system, the actual percentage of PC in terms of binder (sum of PC and CH) is given as %PC (See Table 3). For obtaining the percentage of theoretical CH present in these pastes, it is necessary to

consider several factors. Firstly, the water associated with the decomposition of the added hydrated lime (H_{ad}) can be calculated considering the mass of added material, the purity of the hydrated lime, and the total mass of the binder, according to the following Equation [3]:

$$H_{ad} = \frac{m_{CH} \times \%p \times MW_H}{m_t \times MW_{CH}} \qquad [3]$$

Where m_{CH} is the mass of added hydrated lime, $\%p$ is its purity, m_t is the total mass (cement plus hydrated lime), MW_H is the molecular weight of water, and MW_{CH} is the molecular weight of calcium hydroxide.

Secondly, the percentage of theoretical CH expressed as the released water (H_T) due to calcium hydroxide decomposition for the PC-CH mixture (Equation [4]). To do this, we consider the percentage of water loss associated with the portlandite developed by the control sample (H_C). To calculate it in the PC-CH mixture, we multiply the value of CH_c by the actual percentage of cement regarding the total binder (% PC, see Table 3). H_T is calculated as the sum of the above product, and the value of water associated with CH added H_{ad}.

$$H_T = H_c \times \%PC + H_{ad} \qquad [4]$$

The percentage of theoretical CH present ($\%CH_{theor}$) is calculated according to the following Equation [5].

$$\%CH_{theor} = H_T \times \frac{MW_{CH}}{MW_H} \qquad [5]$$

From the obtained thermograms, the amount of water (H_{exp}) associated with the dehydroxilation of calcium hydroxide in the 520-600 ºC range can be measured. From this, the experimental percentage of CH present in the hydrated paste can be calculated from the following Equation [6]:

$$\%CH_{exp} = H_{exp} \times \frac{MW_{CH}}{MW_H} \qquad [6]$$

Finally, the PC-CH-FA ternary paste was a mixture of 50% PC and 50% FA with 20% CH addition, using a water/binder ratio of 0.5, and was cured at ambient temperature, similar procedure performed by Anjos et al. (14). The calculation of fixed lime for these systems was performed using an inert material (filler-F) replacing FA as a reference sample. The lime fixation was calculated using Equation [7], as follows:

$$\%CH_{fixation} = \frac{CH_f - CH_{FA}}{CH_f} \times 100 \qquad [7]$$

Where CH_f is the hydrated lime presented in the cement paste with filler and hydrated lime (reference sample), and CH_{FA} is the hydrated lime presented in the paste with FA.

The pastes were mixed manually for five minutes and placed in sealed plastic containers to avoid carbonation of the sample. Pastes were maintained in a plastic container until testing age. At the designated period, the hydration was stopped: the paste was ground in an agate mortar with acetone and filtered. Subsequently, the solid was dried at 60 ºC for 30 minutes to complete the evaporation of acetone.

The samples for scanning electron microscopy studies were pieced and maintained in acetone for 30 minutes. Subsequently, they were dried at 60 ºC to complete the evaporation of acetone. The samples were stored in a desiccator until the test period to avoid carbonation.

Thermogravimetric analysis was carried out using a TGA 850 Mettler-Toledo module, under a N_2 atmosphere (75 mL.min⁻¹ gas flow) at a heating rate of 10 ºC/min, in a heating range of 35 ºC to 600 ºC. A 100 µL aluminum crucible was used, and this crucible had a sealable lid with a microhole. The present calcium hydroxide percentage in pastes was determined by the mass loss in the range between 520-600 ºC (dehydroxylation process of calcium hydroxide).

Field emission scanning electron microscopy (FESEM) was carried out using Zeiss ULTRA 55 equipment. The pastes were carbon coated, and the images were taken at 2kV.

2.3. Mortars for mechanical strengths (flexural and compressive) measurements

The influence of the CH in the strength of the PC-CH system was studied: mortar specimens of 4x4x16 cm³ were made using a Portland cement:sand:water ratio

TABLE 3. PC-CH mixture proportions (in g).

	PC	PC+CH5%	PC+CH10%	PC+CH15%	PC+CH20%
PC	100	100	100	100	100
CH	0	5	10	15	20
Water	50	50	50	50	50
%PC	100	0.95	0.91	0.87	0.83

of 1:3:0.5, and other three mixtures were prepared by addition of CH in 10, 15, and 20% by weight of PC. The flexural and compressive strengths were measured at 7 and 28 curing days.

For studying the influence of CH in the ternary system, the compressive strength was assessed in mortar specimens of 4x4x16 cm³ using mixtures of 50% PC and 50% FA and adding CH in the range of 0-20%. These mortars were cured at 28, 90, and 180 days to corroborate the effect of FA at medium-long curing age. The batch of cement used for PC-CH mortars differed from that used in the PC-FA-CH system.

Mortars were stored in the mould during the first 24 hours. Then, the specimens were stored in a water vapor-saturated atmosphere at 23 ºC. At the required curing age, the specimens were taken from their storage, broken in flexure (three values), and each half was tested for strength in compression (six values).

2.4. Carbonation test

Mortar specimens of PC-FA, PC-FA-CH5%, PC-FA-CH10%, PC-FA-CH15% and PC-FA-CH20% were prepared to carbonation tests, the mortars were cured for 90 days. The carbonation test been carried out in the so-called carbonation chamber which consists of an airtight container (a desiccator) to which a CO_2 bullet has been connected (> 99.9% dry richness). The CO_2 flux that has been used has been discontinuous (two daily discharges) and with an approximate flow of 10 l/min. The temperature of the carbonation chamber has been maintained between 18 and 20 ºC, and the relative humidity of the same has been controlled so that it was in a range between 60 and 70%. For this, a glycerin solution has been introduced that has maintained humidity around 65% throughout the process.

After the carbonatation process, a cut is made to the specimen and by means of a colorimetric test of phenolphthalein (spraying of the specimens with indicator solution) the carbonation fronts were revealed. This method to measure the carbonation front is used by other authors in mixtures with FA (31, 32).

3. RESULTS

3.1. Thermogravimetric studies

The present section is divided into four parts to study the CH-FA, PC-CH, and PC-FA binary systems and the PC-CH-FA ternary system.

3.1.1. CH-FA system

Using the equation [1] explained in the experimental procedure was calculated the percentages of lime fixation, these values are summarized in Table 4. In the same table is expressed the percentage of water associated (%H_{comb}) with the hydrated products formed during the pozzolanic reaction between the CH and FA.

The percentages of lime fixation were higher than 70% at both curing ages. The difference between the lime fixation was slight because of the rapid reaction at 65 ºC. There is a significant lime fixation, above 80%, after 28 days of curing. This high lime fixation means that for every 100 grams of CH-FA mixture, 48 g of the initial 60 g of CH were chemically combined with the reactive phases (amorphous phases) of FA. The amount of CH combined with FA is approximately 1.2 gCH/gFA. This value is very high, so FA is a very reactive pozzolan in high temperature curing conditions.

TABLE 4. Percentages of lime fixation and combined water in the CH-FA paste after 7 and 28 curing days.

	7d	28d
%$CH_{fixation}$	72.1	81.7
%H_{comb}	12.9	14.4

After 7 days of curing, the FA fixed a large amount of CH in the mixture. The pozzolanic reaction continued to evolve, as seen in the increased percentage of combined water. This value rose from 12.9% at 7 days to 14.4% at 28 days of curing.

Figure 4 represents the first derivative thermogravimetric (DTG) curve at 28 days. Three principal peaks correspond to the loss of water from pozzolanic products, and one peak is related to the hydrated lime. The peak assignment is (29): peak 1 corresponds to the water loss associated with CSH (100-180 ºC); peaks 2 and 3 correspond to the water loss associated with CASH and CAH (180-240 ºC and 240-300 ºC). The mass loss in the 520-600 ºC corresponds to the dehydroxylation of hydrated lime (peak 4).
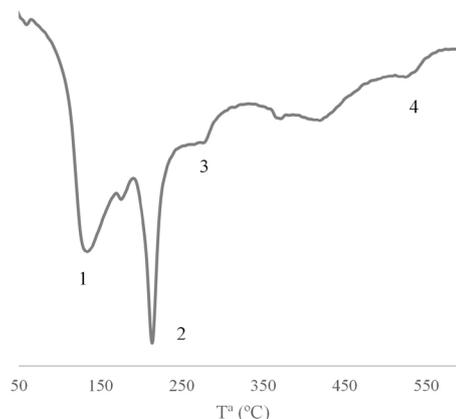

FIGURE 4. DTG curve of CH-FA paste at 28 curing days.

3.1.2. PC-FA system

In the system PC-FA the curing temperature was 23 ºC, for this reason the values of lime fixation were calculate until 90 days. Table 5 shows the percentages of lime fixation and combined water in the hydrates.

TABLE 5. Percentages of lime fixation and combined water for the PC-FA paste at 7, 28, and 90 curing days.

	7d	28d	90d
%CH$_{fixation}$	-24.4	20.4	50.9
%H$_{comb}$	10.7	11.5	13.3

Negative values are observed in the lime fixation for the 7 days cured PC-FA paste. The negative values in the lime fixation are due to a physical effect of the FA. FA particles act as nucleation sites. This role favors the hydration of the PC and therefore releases the latter higher amount of portlandite. In addition, the water/binder ratio was 0.5 for both pastes (PC and PC-FA). Consequently, the amount of available water for cement hydration at an early age is higher in FA paste than in control paste (in control paste, the water/PC ratio is 0.5, while in PC-FA, the ratio is 1). The pozzolanic reaction of FA is relatively slow, proven by the significant increase in lime fixation from 28 to 90 days. The percentages of combined water also increased as the curing age did (from 10.7% at 7 days to 13.3 % at 90 days).

Figure 5 represents the DTG curves of PC and PC-FA pastes at 28 curing days. The peaks represented are the same as in Figure 4, but in this case, peak 1 is the most intense. This peak was attributed to the water loss mass of the CSH gel.
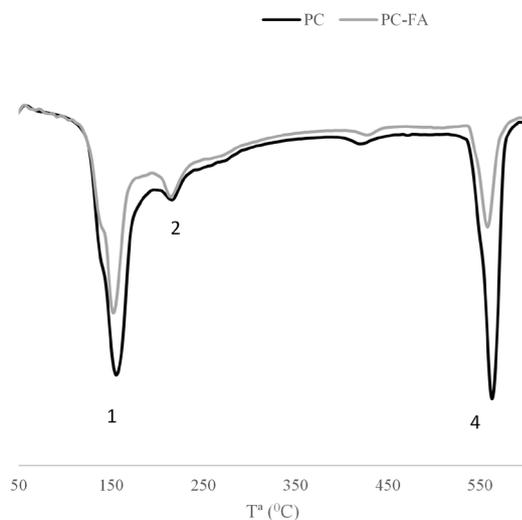

FIGURE 5. DTG curves of PC and PC-FA pastes at 28 curing days.

3.1.3. PC-CH system

According to Table 3, several pastes were prepared for thermogravimetric analysis and for assessing the development of hydrates and calcium hydroxide.

Table 6 summarizes the experimental CH (%CH$_{exp}$) present obtained by thermogravimetry and the corresponding theoretical values (%CH$_{theor}$) at different curing ages. In all cases, it can be noted that for the PC-CH mixtures, the experimental and theoretical values were mismatched. Thus, the experimental values were always less than the theoretical ones. A ratio (β) between experimental and theoretical values for calcium hydroxide was calculated (see Table 6). For the mixture C+CH20%, at 28 curing days, 6.5% of portlandite less than the theoretical percentage of CH was observed, which corresponds to a value of β = 0.76. In general, β values obtained were in the 0.71-0.88 range, meaning that for all CH-added pastes and for all curing times tested, there is a strong influence of the presence of added CH. This result demonstrates that the amount of portlandite generated in the hydration of the cement is lower than that corresponding to the amount of cement present in the sample if this cement is hydrated in the same way as the control paste (only PC). Therefore, it can be established that adding CH reduces the production of portlandite, probably due to Le Chaterlier´s principle and kinetics of reaction. In this sense, it can be established that the nature of the hydration products of cement could be slightly different. However, the DTG curves (see Figure 6) demonstrate no significant differences in the water losses of the hydrates formed. Figure 6 shows the DTG curves for the control (PC) and C+CHα% pastes for 28 days. As can be seen, the dehydroxylation range (520-600 ºC) shows a single peak for all samples. This behavior means that it is impossible, using this technique, to differentiate the calcium hydroxide added from that generated in the hydration of the cement. Moreover, no significant differences in the temperature of the dehydration processes of the developed cementitious products were observed. An intense peak in the 100-160 ºC range corresponds to the dehydration of CSH gel and ettringite (both had overlapped decomposition processes). Likewise, a peak in the 180-240 ºC range is observed, which corresponds to dehydration of the calcium aluminates and silicoaluminates hydrates (CAH, CASH). Since there are no differences, it can be stated that the products formed in the hydration of the cement are not significantly different in the presence of added hydrated lime.

Although CH affects the formation of portlandite, PC-CH pastes contain a similar percentage of hydrates than that found in PC paste (see Table 7). The percentage of water associated with the Portland cement hydrates (different from CH) at 28 days was 15.88%. This value is obtained by subtracting the total mass loss less
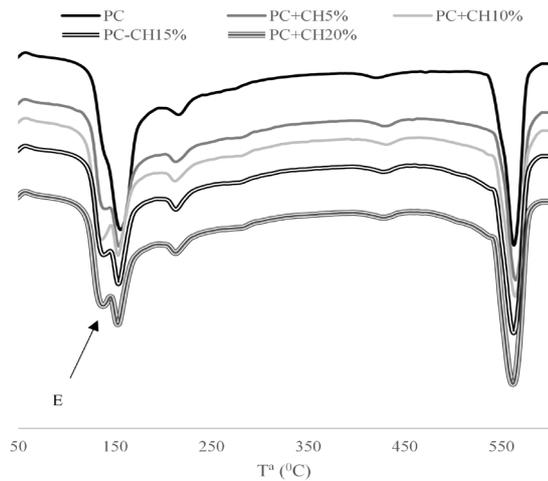
Figure 6. DTG Curves samples control PC and PC+CHα%: paste prepared with PC and 5%,10%,15%, 20% of CH at 28 days.

Table 6. Experimental and theoretical CH percentages in the studied PC-CH pastes.

	PC-CH	H_{ad}	PC (%)	% CH_{exp}	% CH_{theor}	β
1 day	PC	0	1.00	10.24	10.24	1.00
	PC+CH5%	1.08	0.95	11.92	14.18	0.84
	PC+CH10%	2.06	0.91	14.27	17.76	0.80
	PC+CH15%	2.95	0.87	15.75	21.03	0.75
	PC+CH20%	3.77	0.83	18.24	24.03	0.76
3 days	PC	0	1.00	12.23	12.23	1.00
	PC+CH5%	1.08	0.95	13.78	16.07	0.86
	PC+CH10%	2.06	0.91	15.33	19.57	0.78
	PC+CH15%	2.95	0.87	15.72	22.76	0.69
	PC+CH20%	3.77	0.83	18.65	25.69	0.73
7 days	PC	0	1.00	13.39	13.39	1.00
	PC+CH5%	1.08	0.95	14.91	17.18	0.87
	PC+CH10%	2.06	0.91	15.91	20.63	0.77
	PC+CH15%	2.95	0.87	18.10	23.77	0.76
	PC+CH20%	3.77	0.83	18.87	26.66	0.71
14 days	PC	0	1.00	12.38	12.38	1.00
	PC+CH5%	1.08	0.95	14.33	16.22	0.88
	PC+CH10%	2.06	0.91	16.59	19.71	0.84
	PC+CH15%	2.95	0.87	16.93	22.90	0.74
	PC+CH20%	3.77	0.83	19.16	25.82	0.74
28 days	PC	0	1.00	13.85	13.85	1.00
	PC+CH5%	1.08	0.95	15.99	17.62	0.91
	PC+CH10%	2.06	0.91	17.27	21.05	0.82
	PC+CH15%	2.95	0.87	19.04	24.18	0.79
	PC+CH20%	3.77	0.83	20.54	27.04	0.76

the mass loss from the calcium hydroxide decomposition. Adding CH to PC represents only a slight increase of this value, between 16.03-16.89%. Since in the PC-CH mixtures, the amount of cement is relatively lower than for the control, it can be established that the formed hydrates differ in water content. Zhang et al. (33) studied by thermogravimetry the influence of adding CH in percentages of 5 and 7% in cement pastes. The authors observed that the mass losses of combined water in the mass loss zone of C-S-H gels, AFm and ettringite were lower than the mass loss of control paste. This indicates that the additional CH suppressed partially the cement hydration.

Table 7. Percentages of water loss associated with hydrates (C-S-H, Ettringite, C-A-H, C-A-S-H) after 28 days of curing.

Paste	% Water in hydrates
PC	15.88
PC+CH5%	16.75
PC+CH10%	16.89
PC+CH15%	16.03
PC+CH20%	16.06

3.1.4. PC-CH-FA ternary system

The previous section shows that the presence of additional hydrated lime affects the hydration of Portland cement and, more specifically, the portlandite released by its hydration. For this reason, it was proposed to add a filler material (F).

The values of lime fixation (%$CH_{fixation}$) in the paste with FA are shown in Table 8. This table summarizes the total combined water H_T (measured between 35 and 600 °C), the combined water released between 100 and 180 °C (H_1), and the combined water released between 180 and 240 °C (H_2), data taken from TG curves for 7, 28 and 90 curing days. The pozzolanic reaction is favored by the large amount of CH in these mixtures, so it also influences the quantity of hydrates (H_1 and H_2) in the paste with FA, which was higher than those from the paste with filler.

3.2. FESEM studies

The reaction products were observed by FESEM in the PC, PC-FA, PC+CH20%, and PC-CH-FA pastes cured during 28 days at ambient temperature (Figure 7). In ternary paste, the percentage of hydrated lime employed was 20% of addition with respect to the mass of the PC-FA mixture.

According to Gleize et al. (34), in Portland cement pastes, there is the coexistence of CSH type I ("acicular"), type II ("honeycomb"), type III ("compact") and large hexagonal calcium hydroxide crystals. In

TABLE 8. Percentages of lime fixation and percentages of water loss associated with hydrates.

		%CHfixation	%HT (35-600 ºC)	%H1 (100-180 ºC)	%H2 (180-240 ºC)
7 days	PC-F-CH	-	11.49	2.80	2.01
	PC-FA-CH	32.36	11.25	3.50	2.12
28 days	PC-F-CH	-	14.83	3.92	2.42
	PC-FA-CH	35.93	15.59	5.20	2.84
90 days	PC-F-CH	-	13.08	2.41	2.15
	PC-FA-CH	55.35	14.26	3.57	3.19
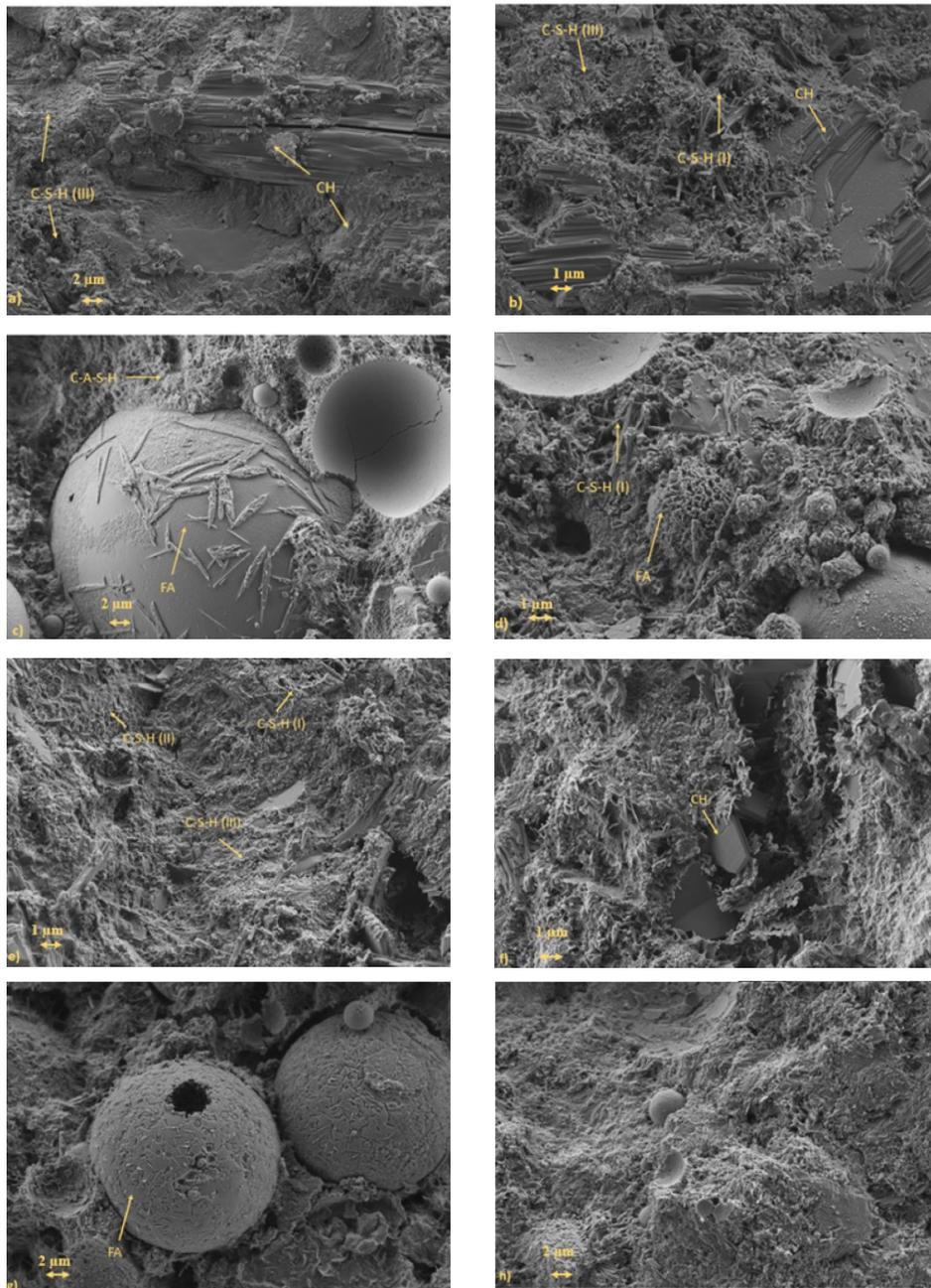
FIGURE 7. FESEM micrographs at 28 curing days: a) PC paste (x2000 magnification); b) PC paste (4000 magnification); c) PC-FA paste (x2000 magnification); d) PC-FA paste (x5000 magnification); e) PC+CH 20% (x4000 magnification); f) PC+CH 20% (x5000 magnification); g) PC-CH-FA paste (x3000 magnification) and h) PC-CH-FA paste (x2000 magnification).

micrographs 7a and 7b, the presence of the CSH type I and type III in the pastes with only PC and the existence of calcium hydroxide as stacked crystals can be observed. In the PC-FA paste (micrographs 7c and 7d), partially reacted fly ash particles and CASH and CSH gel types were observed. In the pastes with an extra hydrated lime percentage, PC-CH20%, it can be observed CSH type II, together with the formation of the other types of CSH (I and III) and hexagonal calcium hydroxide crystals (micrographs 7e and 7f). Finally, in the ternary paste, it can be observed that the FA particles are more reacted than in the case of binary cement pastes with fly ash (micrograph 7g). The extra amount of hydrated lime can make higher progress in the pozzolanic reaction.

The analysis by EDS of the reaction products of PC pastes showed that there were three types of C-S-H gels with CaO/SiO$_2$ ratio between 1.61-1.98, 2.31-2.51, and 3.41-3.83. Gleize et al. (34) reported a ratio between 2.2-2.5 for CSH type III and around 3.6 for CSH type I.

Manzano et al. (35) studied 22 crystalline types of CSH, their structure, and their properties. The CaO/SiO$_2$ ratio had values between 0.5-3.5, which are values like those found in the PC paste studied. Izadifar et al. (36) reported values between 0.67 and 3 for the tobermorite 14Å (Ca$_8$Si$_{12}$O$_{47}$H$_{28}$) and jaffeite (Ca$_6$Si$_2$O$_{13}$H$_6$), respectively.

In PC-CH20% paste, the CaO/SiO$_2$ ratio intervals were 2.26-2.86, 3.12-3.71, and 4.26-5.51. It is corroborated that these ratios are higher than in the PC pastes. More proportion of calcium is incorporated in the C-S-H gels.

In the case of the pastes with FA (PC-FA and PC-CH-FA), the CaO/SiO$_2$ ratios were lower because the aluminum present in the FA is incorporated into the gel structure. The CASH gel is the main product formed.

Figure 8 represents the PC-FA, and PC-CH-FA pastes at 90 curing ages: for this longer curing time, it was corroborated the most reactive surface of the FA in the pastes with the presence of hydrated lime addition.

3.3. Mechanical studies

3.3.1. PC-CH binary system

Figure 9 represents the flexural and compressive strengths of the mortars cured at 7 and 28 days. Regardless of the percentage of added CH, similar mechanical strengths were yielded. At 7 curing days, a slight influence on compressive strength was observed when CH was added. This fact may be because there was some influence on Portland cement hydration.

At 28 days of curing age, in which the compressive strength was satisfactorily developed, adding CH affects the flexural strength behaviour. With
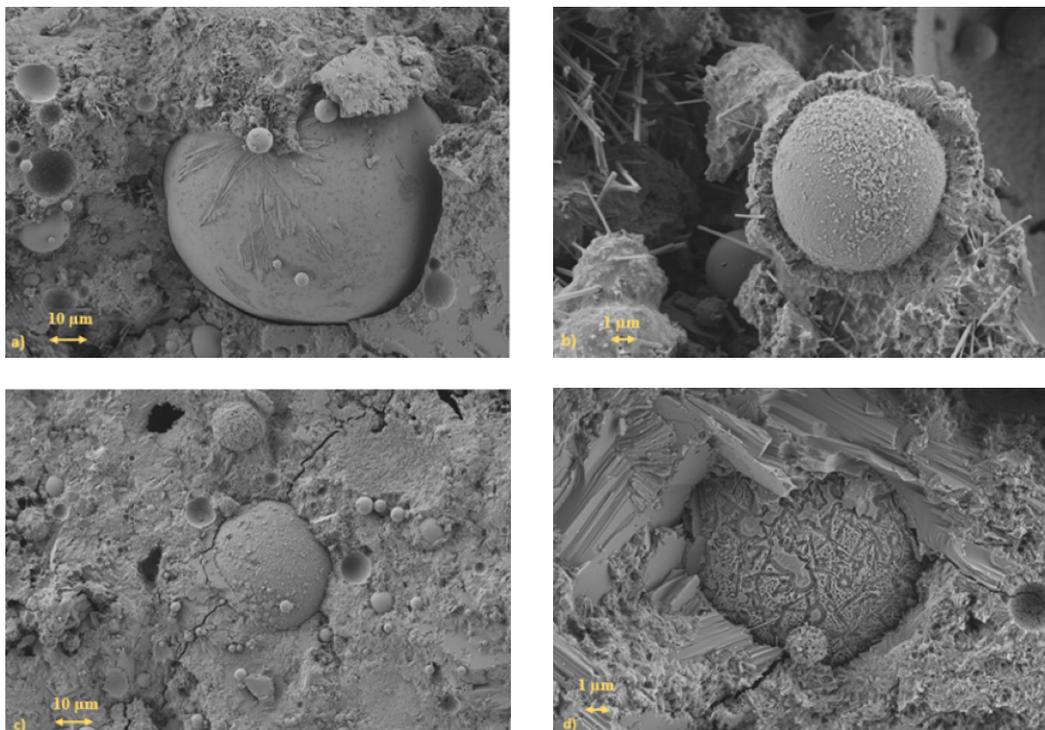

FIGURE 8. FESEM micrographs at 90 curing days: a) PC-FA paste (x1000 magnification); b) PC-FA paste (x4000 magnification); c) PC-CH-FA paste (x1000 magnification) and d) PC-CH-FA paste (x5500 magnification).

an increasing percentage of added CH, the flexural strength decreased. This behaviour could be attributed to the agglomeration of CH particles, which were not well dispersed in the mixture, creating zones of soft material that weaken the matrix (See Figure 10). This effect is more evident for higher percentages of CH addition, which causes a slight loss of strength.

Based on the results for mortar with 10% added CH, it was reported that an increase of 1% of hydrated lime in the binder by volume led to a 1.4% loss in compressive strength (37). In the present study, those mechanical losses so pronounced in strength are not observed.

FIGURE 10. Image of PC-CH mortar in which minor white points are attributed to bad-dispersed hydrated lime powder in the cementing matrix.
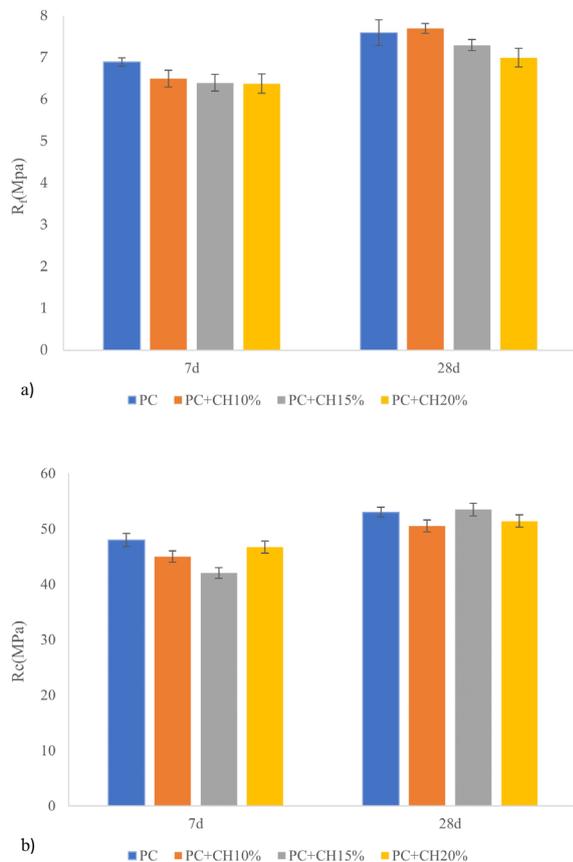

FIGURE 9. Flexural and compressive strengths of PC-CH binary system at 7 and 28 curing days.

3.3.2. PC-FA and PC-CH-FA ternary

The evolution of the pozzolanic reaction for the ternary system was studied for 180 days because the FA is a pozzolan of reactivity at medium-large curing days. Figure 11 depicts the flexural and compressive strength ratios (R_i/R_{PC}; R_i the strength for the PC-FA binary or PC-CH-FA ternary system, and R_{PC} the strength for control mortar).

Both flexural and compressive strengths, compared to those obtained by the mortar with only Port-
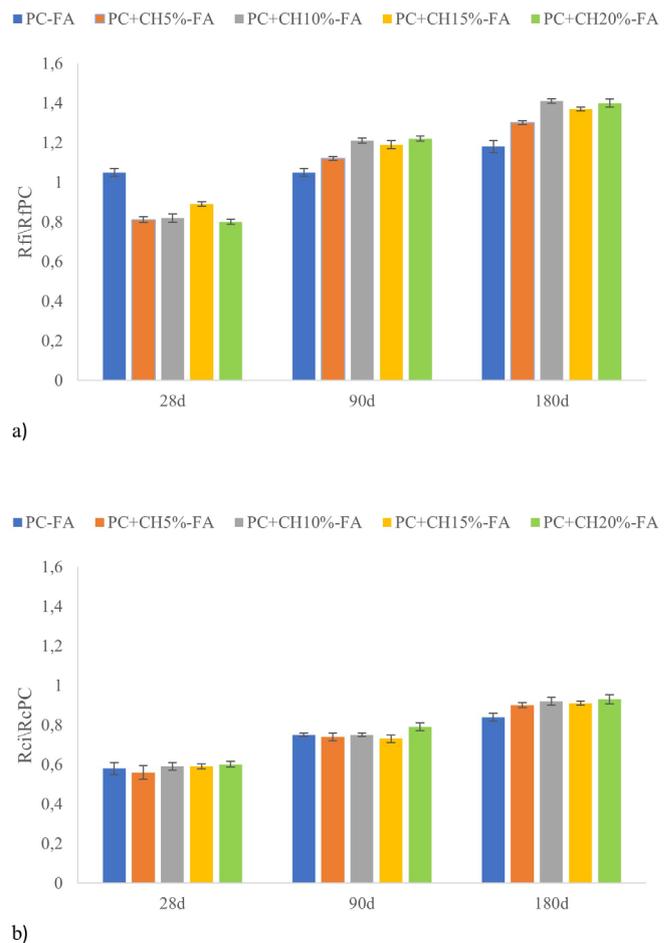

FIGURE 11. Flexural (a) and compressive (b) strength ratios for PC-FA binary system and PC-CH-FA ternary system respect the mortars with only PC at 28, 90, and 180 curing days.

land cement, improved as the curing age increased. This behavior corroborates that fly ash is a pozzolan of high reactivity at medium and long curing times. The improvements are more effective in flexural strength, standing at values higher than 0.8 for the 28 days of curing and consistently higher than 1.0 for 90 and 180 days of curing. The values for compressive strength are around 0.6 for all mortars at 28 days of curing, a very positive value if we consider that FA replaced 50% of cement. At 90 days, the ratio is between 0.72 and 0.76, and values between 0.86 and 0.90 for the 180 days, with the highest value obtained by the PC-CH20%-FA ternary system.

These results align with some reported data from other authors: Adesina and Olutoge (38) studied concretes with cement, rice husk ash (RHA), and hydrated lime. The authors concluded that increased strength was brought about by including hydrated lime in RHA cement concrete, and this enhancement became more significant as the replacement level increased.

Acharya and Patro (39) studied the influence of cement replacement by ferrochrome ash and lime, fixing the percentage of lime at 7%, and the ash varied between 10 and 40%. The maximum increase in strength was obtained for the concrete mix with 10% pozzolan, but the concrete containing 40% ash was relatively close to the control concrete.

The addition of hydrated lime, therefore, generates benefits at long curing ages providing an extra CH for the pozzolanic reaction. The formation of increased hydrated products promotes the densification of matrix, fact that could imply in enhanced durability performance.

3.4. Carbonation test

The carbonation test has been carried out for 16 days, in the control sample the carbonate front barely advances and has not been placed in the photographs of the specimens at the different ages of curing. Figure 12 shows the photos of the binary sample PC-FA and the ternary mixtures PC-FA-CH with the different percentages of lime for the 7,11, 14 and 16 days of carbonation.

For the mortars tested, the advance of the carbonation front is measured by the two carbonated faces and the surface that remains uncarbonated is calculated, the other two faces were painted with epoxy paint and al-
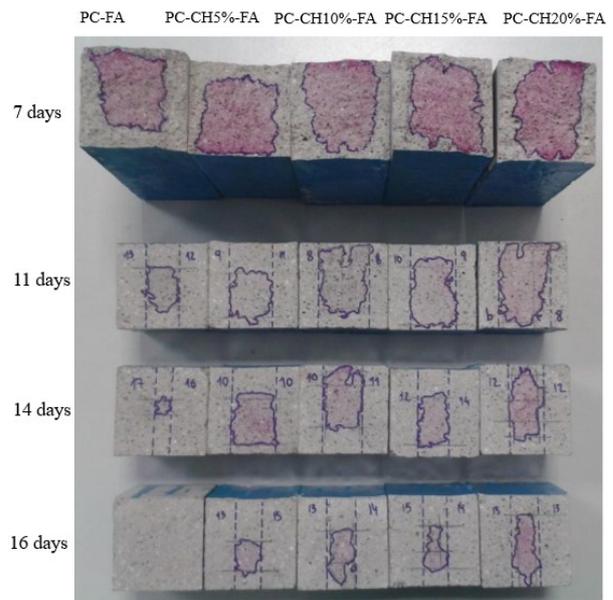

FIGURE 12. Surface area of carbonate simples at 7, 11, 14 and 16 days.

though it has not prevented the front from advancing, it is more irregular and are not taken to perform the calculations. The values of the surface without carbonation at the different ages tested are shown in Table 9.

At 14 days it is observed that the PC-FA sample has a much smaller non-carbonated surface than those that contain CH, due to the lower lime content of these samples. This small alkaline reserve is depleted after 16 days of accelerated testing. It can also observe that regardless of the addition of CH, at all ages there is a similar reserve between them, as well as their carbonate front. However, if we look at the non-carbonated surface, it is clear from Figure 12 that the greater the addition of CH, the greater the surface area colored by phenolphthalein and, therefore, the greater its alkaline reserve.

The carbonation front (x) is related to the exposure time, according to a simple simplification of Fick's second law (Equation [8]) (40).

$$k = \frac{x}{\sqrt{t}} \qquad [8]$$

Where x is the front measured in mm, t is the time measured in years and k is the velocity constant measured in mm/year$^{0.5}$.

TABLE 9. Data of the non-carbonated surface (mm^2).

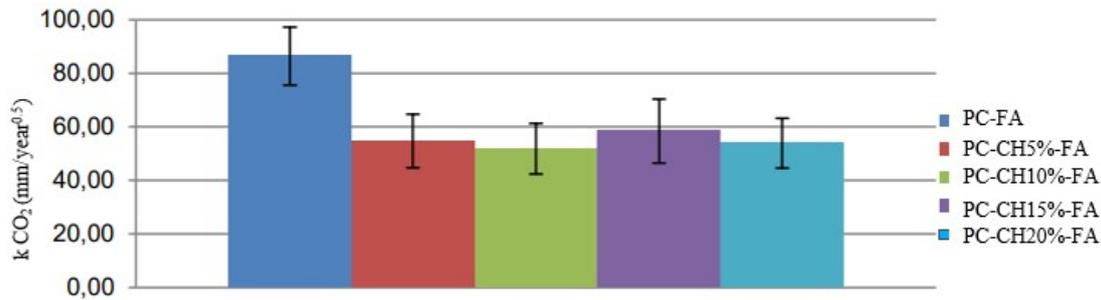|	PC-FA	PC-CH5%-FA	PC-CH10%-FA	PC-CH15%-FA	PC-CH20%-FA
7 days	784	868	918	896	900
11 days	238	380	511	530	682
14 days	50	400	375	295	345
16 days	0	144	188	138	233

FIGURE 13. Values of carbonation velocity for binary and ternary systems.

From the fronts obtained at different ages of carbonation and by means of the equation presented it can be obtained the constant of velocity k (carbonation velocity). Figure 13 shows that the variation in the percentage of addition of CH in mortars does not imply a drastic decrease in their carbonation constant, but it does clearly differ from the binary system with PC-FA.

CONCLUSIONS

From the results obtained in the experimental procedure, it can be concluded:
- The addition of calcium hydroxide affects cement hydration. Adding calcium hydroxide to the cement matrix reduces the portlandite generation from the hydration of PC. The larger the addition of CH, the lower the portlandite generated from the cement.
- The presence of extra quantities of CH affected the Portland cement strength, mainly at short curing ages, and significantly influenced flexural strength.
- The ternary system PC-CH-FA is an excellent alternative to enhance the reactivity of FA at longer curing ages. The pozzolanic reaction is favored by having an additional contribution of hydrated lime, and the ashes appear more reacted than in the PC-FA binary system. At long curing ages (180 days) PC-CH-FA ternary mortar increases the compressive strength about 6.1% compared to PC-FA mortar.
- An extra quantity of hydrated lime in ternary systems allows for obtaining, after hydration, a certain amount of alkaline reservoir. This fact is crucial for reinforced concrete.
- It has been observed that the addition of hydrated lime reduces carbonation progress due to the extra alkaline reserve provided by the addition of this material. The reduction of carbonation velocity was around a 37% for the mortars with CH respect the mortar with PC-FA.

AUTHOR CONTRIBUTIONS:

Conceptualization: J. Payá, M.V. Borrachero. Data curation: P. Lorca. Investigation: P. Lorca, L. Soriano. Supervision: J. Monzó, M.V. Borrachero, J. Payá. Writing, original draft: M.M. Tashima, L. Soriano. Writing, review & editing: J. Payá, M.V. Borrachero, J. Payá, M.M. Tashima, L. Soriano.

REFERENCES

1. Ayasgil, D.; Ince, C.; Derogar, S.; Ball, R.J. (2022) The long-term engineering properties and sustainability indices of dewatering hydrated lime mortars through Jacaranda seed pods. *Sustain. Mater. Techno.* 32, e00435. https://doi.org/10.1016/j.susmat.2022.e00435.
2. Elsen, J.; Mertens, G.; Snellings, R. (2011) Portland cement and other calcareous hydraulic binders: History, production and mineralogy. *Eur. Mineral. Union Notes Mineral.* 9 [1], 441-479. https://doi.org/10.1180/EMU-notes.9.11.
3. Andrew, R.M. (2019) Global CO_2 emissions from cement production, 1928-2018. *Earth Sys. Sci. Data.* 11 [4], 1675-1710. https://doi.org/10.5194/essd-11-1675-2019.
4. Sustainable development goals. United Nations Development Programme. Accessed January 9, 2023. Retrieved from https://www.undp.org/sustainable-development-goals.
5. Wongkeo, W.; Thongsanitgarn, P.; Chaipanich, A. (2012) Compressive strength and drying shrinkage of fly ash-bottom ash-silica fume multi-blended cement mortars. *Mater. Des.* 36, 655-662. https://doi.org/10.1016/j.matdes.2011.11.043.
6. Teara, A.; Shu Ing, D. (2020). Mechanical properties of high strength concrete that replace cement partly by using fly ash and eggshell powder. *Phys. Chem. Earth.* 120, 102942. https://doi.org/10.1016/j.pce.2020.102942.
7. Sun, X.; Zhao, Y.; Tian Y.; Wu, P.; Guo, Z.; Qiu, J.; Xing, J.; Xiaowei, G. (2021) Modification of high-volume fly ash cement with metakaolin for its utilization in cemented paste backfill: The effects of metakaolin content and particle size. *Powder Technol.* 393, 539-549. https://doi.org/10.1016/j.powtec.2021.07.067.
8. Stefanović, G.; Ćojbašć, L.; Sekulić, Ž.; Matijašević, S. (2007) Hydration study of mechanically activated mixtures

of Portland cement and fly ash. *J. Serb. Chem. Soc.* 72 [6], 591-604. https://doi.org/10.2298/JSC0706591S.

9. Justnes, H.; Skocek, J.; Østnor, T.A.; Engelsen, C.J.; Skjølsvold, O. (2020) Microstructural changes of hydrated cement blended with fly ash upon carbonation. *Cem. Concr. Res.* 137, 106192. https://doi.org/10.1016/j.cemconres.2020.106192.

10. Lorca, P.; Calabuig, R.; Benlloch, J.; Soriano, L.; Payá, J. (2014) Microconcrete with partial replacement of Portland cement by fly ash and hydrated lime addition. *Mater. Des.* 64, 535-541. http://doi.org/10.1016/j.matdes.2014.08.022.

11. Mira, P.; Papadakis, V.G.; Tsimas, S. (2002) Effect of lime putty addition on structural and durability properties of concrete. *Cem. Concr. Res*. 32 [5], 683-689. https://doi.org/10.1016/S0008-8846(01)00744-X.

12. Gunasekara, C.; Sandanayake, M.; Zhou, Z.; Law, D.W.; Setunge S. (2020) Effect of nano-silica addition into high volume fly ash–hydrated lime blended concrete. *Constr. Build. Mater.* 253, 119205. https://doi.org/10.1016/j.conbuildmat.2020.119205.

13. Filho, J.H.; Medeiros, M.H.F.; Pereira, E.; Helene, P.; Asce, M.; Isaia, G.C. (2013) High-volume fly ash concrete with and without hydrated lime: chloride diffusion coefficient from accelerated test. *J. Mater. Civ. Eng.* 25 [3], 411-418. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000596.

14. Anjos, M.A.S.; Reis, R.; Camões, A.; Duarte, F.; Jesus, C. (2019) Evaluation of hydration of cement pastes containing high volume of mineral additions. *Eur. J. Environ.* 23 [8], 987-1002. https://doi.org/10.1080/19648189.2017.1327892.

15. Fonseca, T.V.; dos Anjos, M.A.S.; Ferreira, R.L.S.; Branco, F.G.; Pereira, L. (2022) Evaluation of self-compacting concretes produced with ternary and quaternary blends of different SCM and hydrated-lime. *Constr. Build. Mater.* 320, 126235. https://doi.org/10.1016/j.conbuildmat.2021.126235.

16. Luxán, M.P.; Sánchez de Rojas, M.I.; Frías, M. (1989) Investigations on the fly ash-calcium hydroxide reactions. *Cem. Concr. Res.* 19 [1], 69-80. https://doi.org/10.1016/0008-8846(89)90067-7.

17. Vigil de la Villa, R.V.; De Soto, I.S.; García-Giménez, R.; Frías M. (2017) Thermodynamic evaluation of pozzolanic reactions between activated pozzolan mix of clay waste/ fly ash and calcium hydroxide. *J. Mater. Civ. Eng.* 29 [8], 04017065. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001940.

18. Arandigoyen, M.; Bicer-Simsir, B.; Alvarez, J.I.; Lange, D.A. (2006) Variation of microstructure with carbonation in lime and blended pastes. *Appl. Surf. Sci.* 252 [20], 7562-7571. https://doi.org/10.1016/j.apsusc.2005.09.007.

19. Arandigoyen, M.; Alvarez, J.I. (2007) Pore structure and mechanical properties of cement-lime mortars. *Cem. Concr. Res.* 37 [5], 767-775. https://doi.org/10.1016/j.cemconres.2007.02.023.

20. Pacheco-Torgal, F.; Faria, J.; Jalali, S. (2012) Some considerations about the use of lime-cement mortars for building conservation purposes in Portugal: A reprehensible option or a lesser evil? *Constr. Build. Mater.* 30, 488-494. https://doi.org/10.1016/j.conbuildmat.2011.12.003.

21. Sébaïbi, Y.; Dheilly, R.M.; Quéneudec, M. (2004) A study of the viscosity of lime-cement paste: Influence of the physico-chemical characteristics of lime. *Constr. Build. Mater.* 18 [9], 653-660. https://doi.org/10.1016/j.conbuildmat.2004.04.028.

22. Sébaïbi, Y.; Dheilly, R.M.; Beaudoin, B.; Quéneudec, M (2006) The effect of various slaked limes on the microstructure of a lime-cement-sand mortar. *Cem. Concr. Res.* 36 [5], 971-978. https://doi.org/10.1016/j.cemconres.2005.12.021.

23. Fourmentin, M.; Faure, P.; Gauffinet, S.; Peter, U.; Lesueur, D.; Daviller, D.; Ovarlez, G.; Coussot, P. (2015) Porous structure and mechanical strength of cement-lime pastes during setting. *Cem. Concr. Res.* 77, 1-8. http://doi.org/10.1016/j.cemconres.2015.06.009.

24. Sangi-Gonçalves, H.; Penteado-Dias, D.; Castillo-Lara, R. (2022) Replacement of hydrated lime by lime mud-residue from the cellulose industry in multiple-use mortars

25. AENOR. UNE-EN 197-1. Cement. Part 1: Composition, specifications and conformity criteria for common cements. (2011).

26. AENOR. UNE-EN 459-1. Building lime. Part 1: Definitions, specifications and conformity criteria (2016).

27. Rao, S.M.; Asha, K. (2012) Activation of fly ash–lime reactions: kinetic approach. *J. Mater. Civ. Eng.* 24 [8], 1110-1117. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000482.

28. Payá, J.; Borrachero, M.V.; Monzó, J.; Peris-Mora, E.; Amahjour, F. (2001) Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity. *Cem. Concr. Res.* 31 [1], 41-49. https://doi.org/10.1016/S0008-8846(00)00434-8.

29. Payá, J.; Monzó, J.; Borrachero, M.V.; Velázquez, S.; Bonilla M. (2003) Determination of the pozzolanic activity of fluid catalytic cracking residue. Thermogravimetric analysis studies on FC3R-lime pastes. *Cem. Concr. Res.* 33, 1085-1091. 33 [7], https://doi.org/10.1016/S0008-8846(03)00014-0.

30. Soriano, L.; Monzó, J.; Bonilla, M.; Tashima, M.M; Payá, J.; Borrachero, M.V. (2013) Effect of pozzolans on the hydration process of Portland cement cured at low temperatures. *Cem. Concr. Compos.* 42, 41-48. http://doi.org/10.1016/j.cemconcomp.2013.05.007.

31. Zhang, D.; Wang, Y.; Ma, M.; Guo, X.; Zhao, S.; Zhang, S.; Yang, Q. (2022) Effect of equal volume replacement of fine aggregate with fly ash on carbonation resistance of concrete. *Materials.* 15 [4], 1550. https://doi.org/10.3390/ma15041550.

32. Jia, Y.; Aruhan, B.; Yan, P. (2012) Natural and accelerated carbonation of concrete containing fly ash and GGBS after different initial curing period. *Mag. Concr. Res.* 64 [2], 143-150. https://doi.org/10.1680/macr.10.00134.

33. Zhang, G.; Peng, G.F.; Zuo, X.Y; Niu, X.J.; Ding, H. (2023). Adding hydrated lime for improving microstructure and mechanical properties of mortar for ultra-high-performance concrete. *Cem. Concr. Res.* 167, 107130. https://doi.org/10.1016/j.cemconres.2023.107130.

34. Gleize, P.J.P.; Müller, A.; Roman, H.R. (2003) Microstructural investigation of a silica fume-cement-lime mortar. *Cem. Concr. Compos.* 25 [2], 171-175. https://doi.org/10.1016/S0958-9465(02)00006-9.

35. Manzano, H.; González-Teresa, R.; Dolado, J.S.; Ayuela, A. (2010). X-ray spectra and theoretical elastic properties of crystalline calcium silicate hydrates: comparison with cement hydrated gels. *Mater. Constr.* 60 [299], 7-19. https://doi.org/10.3989/mc.2010.57310.

36. Izadifar, M.; Königer, F.; Gerdes, A.; Wöll, C.; Thissen, P. (2019) Correlation between composition and mechanical properties of calcium silicate hydrates identified by infrared spectroscopy and density functional theory. *J. Phys. Chem. C.* 123, 10868-10873. https://doi.org/10.1021/acs.jpcc.8b11920.

37. Ramesh, M.; Azenha, M.; Lourenço, P.B. (2019) Quantification of impact of lime on mechanical behaviour of lime cement blended mortars for bedding joints in masonry systems. *Constr. Build. Mater.* 229, 116884. https://doi.org/10.1016/j.conbuildmat.2019.116884.

38. Adesina, P.A.; Olutoge, F.A. (2019) Structural properties of sustainable concrete developed using rice husk ash and hydrated lime. *J. Build. Eng.* 25, 100804. https://doi.org/10.1016/j.jobe.2019.100804.

39. Acharya, P.K.; Patro, S.K. (2015) Effect of lime and ferrochrome ash (FA) as partial replacement of cement on strength, ultrasonic pulse velocity and permeability of concrete. *Constr. Build. Mater.* 94, 448-457. https://doi.org/10.1016/j.conbuildmat.2015.07.081.

40. Sisomphon, K.; Franke, L. (2007) Carbonation rates of concretes containing high volume of pozzolanic materials. *Cem. Concr. Res*. 37 [12], 1647-1653. https://doi.org/10.1016/j.cemconres.2007.08.014.

production. *Mater. Constr.* 72 [347], e292. https://doi.org/10.3989/mc.2022.17721.