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Effect of pozzolans on the hydration process of Portland cement cured at low temperatures

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ABSTRACT

The aim of this paper is to study hydration processes in cement pastes and mortars, blended with either metakaolin (MK) or a catalyst used in catalytic cracking (FCC), and cured at low temperature. The amounts of hydrates and portlandite in pastes have been determined for 3–28 days curing at 5–20 °C. Microstructural study, using thermogravimetric analysis of the pastes, has shown that FCC acts mainly as a pozzolan at low temperatures (5–10 °C), whereas MK also accelerates Portland cement hydration. Mechanical strengths of a control mortar, and mortars made with 15% replacement of cement by these two pozzolans, have been measured. Both mortars containing pozzolans exhibited a relative increase in compressive strength when cured at 5 °C. A limestone filler (LF) has been used to compare the effects of adding inert or pozzolanic materials. Finally, mortars were prepared by partially replacing aggregates with either MK, FCC or LF. The MK and FCC are effective materials even for low curing temperatures, especially when they are used to replace a fraction of the aggregates in mortars.

1. Introduction

The influence of curing temperature on the properties of concrete is of great importance. According to the manual of cold weather concreting practices recommended by the American Concrete Institute – ACI [1] cold weather exists when the air temperature is expected to fall below 4 °C and when peak temperatures above 10 °C occur during no more than half of any 24-h period for 3 consecutive days.

The Spanish standard EHE-08 [2] indicates the temperature of 5 °C as a critical condition for mixing in cold weather, since at lower temperatures Portland cement hydration is delayed. Furthermore, freezing damage may take place when the concrete temperature falls below 0 °C.

Several studies related to the influence of temperature and curing time on concrete and mortar have been reported in the literature [3–11]. In general, a reduction in the curing temperature (from 20 °C to values below), causes a decrease in the early age mechanical strength and, this value increases slowly for longer curing periods.

The low curing temperature affects the hydration of Portland cement directly and, consequently, the pozzolanic reaction that occurs in blended Portland cements.

The delay in the process of Portland cement hydration at low temperatures affects the production of portlandite directly and, consequently, the pozzolanic reaction may be modified in these severe curing conditions. Some research on the low temperature curing of blended Portland cement [12–14] has concluded that, depending on the type of pozzolan, the curing behavior at low temperature may vary. Escalante-García and Sharp [12,13] reported the behavior of mortars with three different mineral additions: PFA (Pulverized fuel ash), VA (volcanic ash) and GGBFS (ground granulated blast furnace slag), cured at 10, 20, 30, 40 and 60 °C. In general terms it has been observed that, for all mixtures containing any type pozzolanic material, the compressive strengths are higher with increasing curing temperature. For mortars with PFA, the pozzolanic reaction was slower for the temperature of 10 °C when compared with higher curing temperatures.

In the case of VA addition, mechanical strength of mortars has been improved when samples were cured at 40–60 °C, but not when these were cured at low temperature. Finally, the addition of GGBFS showed that at 10 °C, the contribution of such addition to the compressive strength gain was very low even at 28 days of curing.

A study related to the influence of silica fume in mortars with different cements cured at 0, 27 and 60 °C was made by Chakraborty et al. [14], where strength values were higher than their respective controls for all curing temperatures. These authors concluded that the rate of hydration of C_3S is heavily influenced by lower curing temperature, thus greatly affecting the mechanical strength for early curing age. The strength loss is compensated

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by the replacement of cement by silica fume in a proportion between 8% and 12%.

The aim of this paper is to study two pozzolans in order to observe their evolution in pastes and mortars cured at different temperatures, by using thermogravimetric analysis technique (TGA) and compressive strength testing. For this research, the pozzolans selected are metakaolin (MK) and spent catalyst from fluidized bed catalytic cracking process (FCC). MK is a synthetic product, which is obtained by kaolin calcination; it is a very fine material with high pozzolanic activity, which improves both mechanical strength and durability of blended mortar and concrete [15–18]. For this product, the pozzolanic reaction has been studied in depth. So, Cabrera et al. [19] studied the reaction kinetics of a mixture of metakaolin and lime (calcium hydroxide) in water at 60 °C by using thermal analysis. The numerical results have been used to determine the nature of the reaction. It is shown that, on the whole, this pozzolanic reaction is diffusion controlled and can be represented by the Jander diffusion equation [19]. The mechanism of hydration of MK in the lime–water system and other temperatures [20] and the properties of MK as well as addition to cement has also been reported [16]. On the other hand, some references about the use of metakaolin produced by calcinations of sludge paper are also reported [21,22]. Recently, metakaolin has also been used in the preparation of self-compacting concrete and its effect on the durability is assessed [23,24].

The spent catalyst from Fluidized-bed Catalytic Cracking process (FCC) is a silicoaluminous zeolite, which is generated as waste in the process of catalytic cracking for obtaining naphtha. This residue has proved to behave as an excellent pozzolan for early curing age, improving both durability and mechanical behavior of the cementitious matrices that contain it [25–31]. Recently, its use as a substitute of bauxite in the preparation of cement clinker Portland [32] has been investigated. FCC has been evaluated for use in road construction as a whole replacement for crushed aggregates in the sub-base and base layers and as a partial replacement for Portland cement in masonry blocks manufacturing [33].

For this paper, these two pozzolans (MK and FCC) have been chosen due to their high reactive properties in early curing age [16,25,26], so their effect at low temperatures, where the processes of Portland cement hydration and pozzolanic activity are reduced, should be detected. The use of other pozzolans, such as fly ash or natural pozzolans, whose pozzolanic reactivity at room temperature occurs at long curing times [34,35] would not be interesting for studies at low curing temperatures.

Thus, the main objective is to assess the behavior of the pastes and mortars of Portland cement partially replaced by MK and FCC – at different temperatures and curing times to evaluate their behavior under such severe conditions. Furthermore, a limestone filler (LF) was used as an inert material in order to compare the effect of a pozzolanic material and an inert material.

2. Experimental section

2.1. Materials, equipment and methodology

The materials used were Spanish Portland cement type CEM I 52.5 R, supplied by Cemex S.A (Buñol, Valencia), spent catalytic cracking catalyst from BP Oil, S.L refinery from Castellón (Spain) and finally, commercial metakaolin supplied by ECC International company, under the name Metastar. The chemical composition, determined by means of X-ray fluorescence, of these materials is shown in Table 1. The limestone filler (97% of $CaCO_3$) used in this study was named "LF" and this material was also supplied by Cemex S.A. Siliceous sand with a specific gravity of 2.68 and fineness modulus of 4.1 (UNE-EN 196-1) was used to prepare mortar samples.

FCC residue undergoes a milling process in order to improve its reactivity, as previous studies have shown that pozzolanic behavior increases with the decrease in the particle size. The grinding time determined as optimal by Payá et al. [25] was 20 min, since longer grinding time did not improve the reactivity of the material. Fig. 1 shows the particle size distribution, determined by laser granulometry, of the Portland cement, FCC and MK pozzolans, and limestone filler (LF).

The mean particle diameter of Portland cement is 19.2 μm; ground FCC residue is 19.73 μm, 22.03 μm in the case of LF and, finally, 5.84 μm for MK.

The thermogravimetric equipment used is a 850 TGA Mettler-Toledo module. The heating range was 35–600 °C, using a continuous 75 mL/min flow of N_2 and a heating rate of 10 °C/min. Aluminum crucibles with a pinhole lid were used and then sealed with the aim of achieving a water vapor self-generated atmosphere.

For thermogravimetric analysis studies, paste samples were prepared with water/binder ratio of 0.5, and the percentage replacement of cement by mineral addition was fixed in 15%. The selected curing temperatures were 5, 10, 15 and 20 °C, by means of storing samples in a water bath with controlled temperature. Paste samples were analyzed for 3, 7, 14 and 28 curing days.

For each selected curing time, part of the paste sample was extracted and the hydration process was stopped by the addition of acetone. Subsequently, the mixture was filtered and dried in a furnace at 60 °C during 30 min.

To assess mechanical strength behavior, two types of mortars were produced. Firstly, mortars were prepared with the replacement of a part of cement. These mortar samples were prepared by using the mixing method proposed in UNE-EN 196-1 [36], with an aggregate/cement ratio of 3:1 and water/binder ratio of 0.5. The replacement percentage of cement by pozzolan was maintained in 15%, the same one used in the preparation of cement pastes. The curing temperatures tested were 5 and 20 °C and mechanical strengths were measured for 1, 2, 7 and 28 days of curing. In a second phase, mortars were produced by the addition of mineral admixture by replacing a part of the aggregate with pozzolan (10% replacement), thus maintaining the water/cement ratio constant (0.5) and decreasing the water/binder ratio (0.38). For these mortars, it was necessary the addition of a superplasticizer. The curing temperatures and times were the same ones used in the previous phase (5 and 20 °C).

It is important to state that in all experiments, the materials used for mixing were maintained at the required curing temperature for 24 h before their use.

3. Results and discussion

3.1. Thermogravimetric analysis studies (TGA)

The reaction of Portland cement with water results in the formation of different hydration products. The released Portlandite is required for pozzolanic reaction. This portlandite, in the presence of active pozzolanic materials, may lead to the formation of new hydration products similar to those formed in the hydration of cement. In order to study the formation of hydration products cement/pozzolan pastes were prepared as described in Section 2. These pastes were analyzed by the thermogravimetric analysis technique, where the change in mass of a sample placed in a controlled atmosphere is continuously recorded [37]. Thus, during the heating of hydrated cement pastes, decomposition processes took place and water loss concerning to hydrated compounds formed

Table 1
Chemical composition of cement, FCC and MK (%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	$Na_2O + K_2O$	P_2O_5	TiO_2	LOI[a]	IR[b]
CEM	19.29	5.22	3.51	61.75	2.07	3.55	1.23	0.26	0.27	1.96	0.89
FCC	47.76	49.25	0.60	0.11	0.17	0.03	0.33	0.02	1.22	0.51	n.d
MK	51.97	41.61	4.67	0.09	0.16	0.01	0.89	n.d.	n.d.	0.6	n.d

n.d. not determined.
[a] LOI: Loss on ignition.
[b] Insoluble residue.

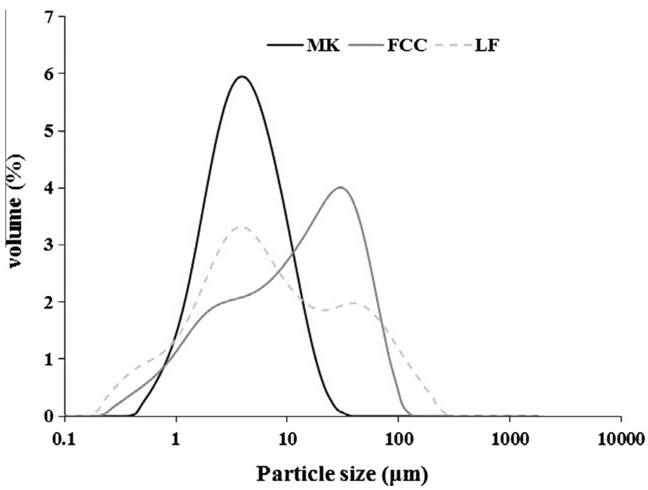

Fig. 1. Granulometric density curves of FCC, MK and LF.

in the reaction of Portland cement hydration and the pozzolanic reaction, are observed and quantified [38].

The temperature range 35–600 °C was chosen because the processes of dehydration of products formed and the dehydroxilation of portlandite are achieved within this temperature range.

In the thermogravimetric curve (TG) for hydrated cement paste, it is observed a continuous weight loss in the range 80–250 °C. The derivative curve (DTG) of the TG curve allows us to identify different decomposition processes as observed in Fig. 2a. Additionally, weight loss associated to the combined water of calcium silicates hydrates (peak 1), ettringite (peak 2) calcium aluminate hydrates (C_4AH_{13}) and calcium aluminosilicate hydrates (C_2ASH_8) (peak 3) are identified. The weight loss that occurs in the temperature range 520–600 °C (peak 4) is related to the dehydroxilation of portlandite. Fig. 2a depicts the DTG curves for control, MK and FCC pastes cured at 5 °C for 7 days. Fig. 2b depicts the DTG curves of FCC pastes cured for 3 days at different curing temperatures (5–20 °C).

It is concisely reported [39,40] that the main phases that form during the pozzolanic reaction between MK and hydrated lime at room temperature are C–S–H, C_2ASH_8 and C_4AH_{13}. Various factors can influence the reaction kinetics and the amounts of the hydrated phases produced. Among them, curing temperature is the most important factor because it influences on the stability and the transformation of the hydrates. A significant change occurs in the phase development pattern of MK mixed with $Ca(OH)_2$ with curing temperature (20 and 55 °C) after 3 days of hydration. C_2ASH_8 and C_4AH_{13} phases are not stable and normally turn into hydrogarnet at elevated temperature [19]. It was reported that C_2ASH_8 and C_4AH_{13} were stable under the conditions of the study, and there was no evidence of a possible conversion reaction from these phases to hydrogarnet [19,20].

The following features can be noted:

- From DTG curves of the control, FCC and MK pastes cured for 7 days at 5 °C, it is observed the presence of calcium silicate hydrates (CSH) and ettringite (peaks 1 and 2) in all of them.

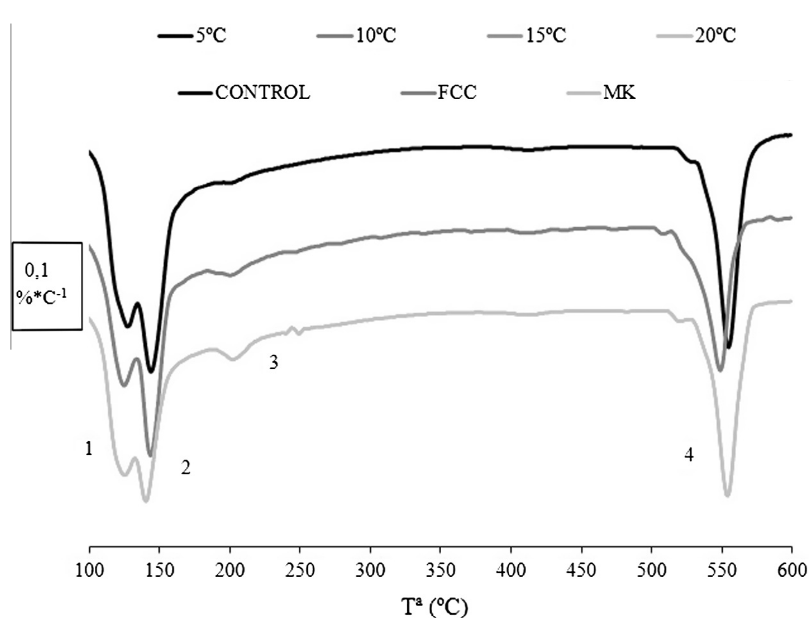

Fig. 2. DTG curves for control, MK and FCC pastes: (a) Pastes cured at 5 °C and 7 days curing time. (b) DTG curves for FCC pastes cured at different temperatures, for 3 days curing time.

The peak corresponding to the calcium aluminate hydrates (C_4AH_{13}) and hydrated gehlenite (C_2ASH_8) (peak 3) is clearly observed in the FCC and MK pastes [40]. This behaviour confirms that in the development of the pozzolanic reaction these silicoaluminous products are typical: a greater amount of these hydration products in pozzolan pastes respect to the control paste is observed.

- For the FCC pastes cured for 3 days at different curing temperatures, it is observed that a greater amount of hydration products is formed when increasing curing temperature. As shown in Fig. 2b, the peak corresponding to C_4AH_{13} and C_2ASH_8 is observed for pastes cured at 15 and 20 °C [19,20]. In any case, according to the literature the transformation of these metastable hydrated phases in hydrogarnet (C_3ASH_6) was not shown [39].

An integration procedure suggested by Taylor and Turner [41] was used to evaluate the weight loss related to the portlandite decomposition, because the baseline does not remain horizontal during the heating process. Straight tangential lines to the weight loss curve at the beginning, the stationary point and the end of the dehydration of portlandite, are drawn. The two intersection points of the tangents define the initial and final temperatures of the process to calculate the weight loss involved. In the case of a paste with a pozzolanic material, this peak represents the unreacted portlandite content. From these data, it can be determined the amount of reacted portlandite by the pozzolan in the paste [42].

The dehydroxilation of portlandite (CH) is related to the reaction:

$$Ca(OH)_2 \rightarrow CaO + H_2O \uparrow \quad \text{(E1)}$$

To calculate the percentage of fixed lime (%CH), the following equation is used [42]:

$$\%CH = \frac{(CH_C * C_{\%}) - CH_P}{(CH_C * C_{\%})} * 100 \quad \text{(E2)}$$

where CH_C is the amount of CH in the control paste for a given curing time, CH_P is the amount of CH present in the pozzolan paste at the same curing age and C% is the proportion of cement present in the pozzolan paste (in per unit mass). Both CH_C and CH_P determinations are stoichiometrically calculated by using the following equation:

$$CH_p = \frac{H}{m_H} * m_{CH} \quad \text{(E3)}$$

where H is the water loss related to portlandite decomposition, m_{CH} is the molecular mass of $Ca(OH)_2$ and m_H is the molecular mass of H_2O.

The total weight loss (P_T) in the range 35–600 °C can be obtained by means of thermogravimetric analysis. The percentage of water related to the hydrated products (P_H), except portlandite, is calculated as follows:

$$P_H = P_T - P_{CH} \quad \text{(E4)}$$

where P_{CH} is the amount of water released in the decomposition of portlandite.

CH_P and P_H calculated values for pozzolan pastes with 15% of FCC or MK are summarized in Table 2.

Using data from portlandite present in the control paste and FCC and MK pastes, and with Eq. (E2), fixed lime percentage values were calculated for pozzolan pastes (Fig. 3).

From the analysis of fixed lime percentages by the FCC and MK pastes, it can be concluded that:

- For pastes cured at 5 °C, it is noted that FCC is able to fix portlandite for all curing times. In contrast, for MK and the earliest curing times (3 and 7 days), negative fixed lime percentages are obtained because an acceleration in the hydration process of cement is produced which is more relevant than the pozzolanic reaction. After 14 days the pozzolanic reaction becomes more important. At this temperature, the particle effect produced by MK particles contributes to the acceleration of the cement hydration process.
- For pastes cured at 10 °C, a similar behaviour is shown. For the earliest curing times, MK accelerates the cement hydration process but in this case, fixed lime data are less negative than those found at 5 °C. Fixed lime for FCC pastes are always positive and these values are higher than those found for pastes cured at 5 °C.
- MK pastes cured at 15 °C presents a positive fixed lime percentage (%CH) since 7 days of curing, and yields 30% of fixed lime for 28 curing days. The behaviour of FCC paste is similar to that found for lower temperatures (5 and 10 °C), and positive values of fixed lime are always obtained, although for 28 curing days there are slightly lower than MK pastes.
- Finally, for pastes cured at 20 °C both pozzolan pastes yielded positive values of fixed lime for all curing times studied. For this curing temperature, the particle effect is lower compared to the pozzolanic reaction.
- Therefore, it can be concluded that at low temperatures, the FCC has a higher pozzolanic reactivity than that of MK, although the latter has a smaller mean particle size. Thus, especially for pastes cured at 5 and 10 °C, positive values of lime fixed can be obtained, even for early curing times.

To analyze the index of hydration products formation in the pastes containing pozzolans, the difference of the percentage of combined water in pozzolan pastes compared to those for the paste control, are calculated by using the following equation:

$$\Delta PH(T,t) = (P_H)_{poz,T,t} - (P_H)_{con,T,t} \quad \text{(E5)}$$

where $(P_H)_{poz,T,t}$ is the value of the percentage of water combined for pozzolan paste for a given curing time (t) and temperature (T), and $(P_H)_{con,T,t}$ is the percentage of combined water value for the control paste at these same age and temperature.

The data obtained calculated with Eq. (E5) are shown in Fig. 4, which represents ΔPH versus curing time.

Fig. 4 shows that, at early curing time and low temperatures, combined water percentages for pozzolan pastes are lower than those obtained by the control paste. However, with increasing curing time, this trend changes and high positive values for ΔPH are obtained due to the presence of more hydration products resulting from the pozzolanic reaction. After 14 days of curing, except for 5 °C, ΔPH values are always positive. For 20 °C test, positive values are always reached, which indicates that the decrease in temperature not only affects the cement hydration reaction but also the pozzolanic reaction.

3.2. Mechanical strength results

3.2.1. Mortars with cement substitution

The aim of this study is to test the effect of the low curing temperature process on the mechanical strength development of mortars. Mortars with 15% substitution of cement by MK or FCC were prepared and cured at 5 and 20 °C. Particularly, in this case, limestone filler (LF) is also used in order to analyse the influence of particle effect for these experimental conditions. Mixture proportions used for the control and cement replaced mortars are shown in Table 3.

Compressive strength values (MPa) of control and replaced mortars at 5 and 20 °C are listed in Table 4.

Table 2
Portlandite percentages, CH_P and combined water in hydrates P_H for the control, FCC and MK pastes.

	5 °C						10 °C					
	CON		FCC		MK		CON		FCC		MK	
	CH_P	P_H	CH_P	P_H	CH_P	P_H	CH_P	P_H	CH_P	P_H	CH_P	P_H
3	7.92	11.56	5.97	11.43	7.91	11.14	9.84	13.41	6.90	13.28	8.48	12.73
7	11.30	14.31	9.03	13.98	10.63	13.30	11.97	13.85	9.10	13.78	10.57	14.31
14	14.29	15.78	9.49	15.72	10.16	15.32	12.75	15.10	7.47	16.50	9.34	18.88
28	14.23	16.72	9.52	17.81	10.17	18.71	14.86	16.48	9.49	18.75	8.23	18.30
	15 °C						20 °C					
3	9.58	13.25	7.17	13.50	8.92	13.18	12.28	13.67	8.60	14.16	9.09	13.81
7	12.64	15.41	7.51	14.64	10.17	14.14	13.30	16.07	9.12	16.08	7.89	16.61
14	13.94	15.50	10.03	17.21	8.54	16.85	13.65	16.92	8.87	18.55	6.74	19.67
28	14.19	16.88	8.47	17.69	4.80	17.97	13.17	17.69	8.23	22.66	6.51	20.36

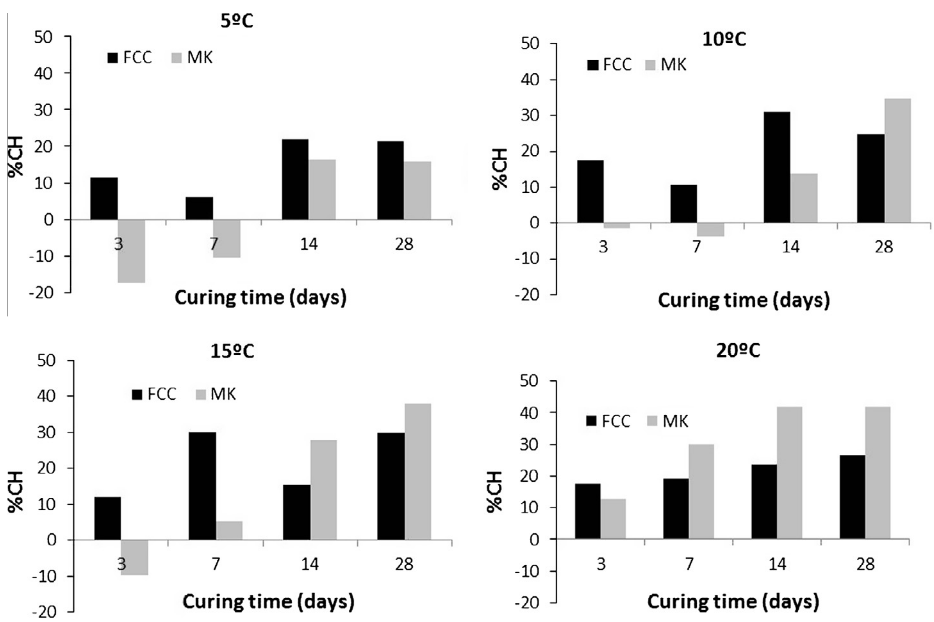

Fig. 3. Fixed lime percentage (%CH) in FCC and MK pastes at 5, 10, 15 and 20 °C.

A natural logarithmic fitting equation (Eq. (E6)) for strength values (R_c) versus time (t) has been performed, considering these data. Mortars containing pozzolans as fly ash [35] have been found in this setting. Coefficients for the obtained equation are summarized in Table 5 (the regression coefficient R^2 is also given):

$$R_C = a + b * \ln t \tag{E6}$$

Taking into account mechanical strength values and the fitting data for different mortars, it can be noted:

- Compressive strength data for early age curing mortars at 5 °C are much lower than those obtained for mortars cured at 20 °C. This behaviour is found for all mixtures studied.
- At 5 °C, compressive strength values for control mortar and for FCC mortar are very similar, and consequently the "a" and "b" constants. The mortar containing limestone filler (LF) shows compressive strengths lower than those found for the control one, which is reflected in lower values for "b" in the logarithmic fitting equation. Finally, the mortar with MK reaches mechanical strength higher than the control one in the 1–7 days period, which results in a higher value of the parameter "a", and slightly lower for the parameter "b", with respect to parameters for control mortar.

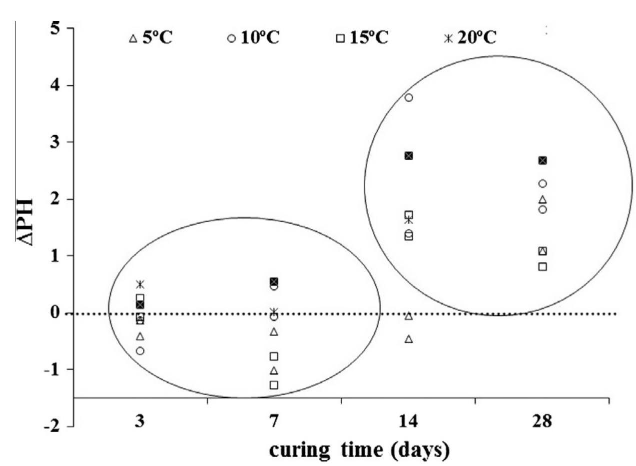

Fig. 4. Differences in the percentage of hydration products versus curing time.

- At 20 °C, as a result of a high reaction rate in the cement hydration process, a larger value for parameter "a" is obtained for the control mortar (3.53 for 5 °C test versus 18.93 for 20 °C). The highest value for parameter "b" is obtained for FCC and MK mortars, which represent the increase in compressive strengths

Table 3
Dosages for control and blended mortars.

	Cement (g)	Addition (g)	Aggregate (g)	Water (g)
CON	450	–	1350	225
FCC	382.5	67.5	1350	225
MK	382.5	67.5	1350	225
LF	382.5	67.5	1350	225

Table 5
Coefficients within equation E6 for control and blended mortars cured at 5 and 20 °C.

	5 °C			20 °C		
	a	*b*	R^2	*a*	*b*	R^2
CON	3.28	11.62	0.986	20.24	9.63	0.993
FCC	3.65	11.89	0.995	12.39	14.79	0.975
MK	7.89	10.38	0.972	17.08	13.03	0.981
LF	2.36	9.92	0.976	15.58	9.81	0.989

with the curing time. Compressive strengths of mortars with pozzolans are clearly higher than control mortar ones at long curing times due to pozzolanic contribution.

- R_c values for LF mortar are always lower than control mortar, which corresponds to the behaviour of an inert material. Therefore, no pozzolanic activity for LF is related to "*b*" value for 20 °C which is very similar to that found for control mortar.

The differences in compressive strength between control and replaced mortars for all curing ages were calculated in order to analyse the influence of replacing part of cement by FCC, LF and MK. These graphics are depicted in Fig. 5. The control mortar strength data are multiplied by 0.85, because the mineral admixture mortars contain 15% less of cement. The increase strength value ΔR is calculated as follows:

$$\Delta R = (R_C)_A - 0.85 * (R_C)_0 \quad \text{(E7)}$$

where $(R_C)_A$ is the strength value for mortars containing FCC, MK and LF, and $(R_C)_0$ is the value for control mortar, at the same curing temperature and curing time.

From the analysis of these graphs, it can be noticed that:

- MK mortar shows the best behaviour at 5 °C for all curing ages, except for 28 curing days. In previous thermogravimetric studies, it is assumed that MK, due to its small particle size, has a very important effect on the acceleration of cement hydration. Thus, the matrix is densified and therefore the obtained strength is improved when compared to the control mortar. FCC mortar also showed an improvement on strength values. In this case, the increase can be mainly attributed to the pozzolanic reaction.
- At 20 °C, mortars containing MK always yield positive ΔR values, whereas for FCC mortar ΔR was positive at 7 and 28 curing days. For mortars samples cured for 28 days, ΔR values for FCC and MK mortars are higher than those obtained at 5 °C, suggesting that the pozzolanic reaction is more important and occurs in a greater extent at higher curing temperatures. This fact was confirmed when comparing the values of ΔR for both curing temperatures: at 20 °C, ΔR values reached about 20 MPa for both FCC and MK mortars; however, at 5 °C ΔR values were about 8 MPa.
- The limestone filler (LF) mortar cured at 5 °C presented negative ΔR values, because the particle effect cannot compensate the dilution effect due to substitution of 15% of cement by this inert material. The replacement of cement by LF at 20 °C can achieve low positive ΔR values at 28 days, confirming the behaviour of LF as an inert material.

3.2.2. Mortars with aggregate substitution

Once analyzed the behaviour of the different mineral additions in the replacement of cement in mortars, the study with aggregate replacement mortars (addition mortar) was performed in order to analyze the behaviour of mortars when the cement content and the water/cement ratio remains constant. As indicated in Section 2, in this type of mortar, 10% of aggregate (sand), is replaced by FCC, MK and LF. Thus, mortars have the same water/cement ratio (0.5). In this type of mortar, it was necessary to add a plasticizer to maintain similar workability than that for control mortar (145 ± 10 mm). Table 6 shows mixture proportions used in the production of addition mortars.

In Table 7, compressive strength (MPa) values of control and addition mortars cured at 5 and 20 °C are shown. As in the mortar substitution section, a logarithmic fitting equation of strength values versus curing time has been established. In Table 8, fitted coefficients are shown. It can be noticed that:

- For all mortars with addition, compressive strengths are higher than those obtained for control mortar. This fact is evidenced on high parameters "*a*" and "*b*" obtained from the natural logarithmic equation.
- At 5 °C and 20 °C, FCC and MK addition mortars have the highest values of coefficients "*a*" and "*b*", thereby demonstrating that the pozzolanic effect for these mixtures is very important for all tested curing conditions.

The increase strength (ΔR) was also calculated; however, in this case no correction to the data of control mortar strength was applied since all mortars have the same one. The equation used was:

$$\Delta R' = (R'_C)_A - (R_C)_0 \quad \text{(E8)}$$

where $(R'_C)_A$ is the compressive strength for mortars with FCC, MK and LF; and $(R_C)_0$ is the compressive strength value for the control mortar. In Fig. 6, the results obtained are shown.

From the study of the graphs of increased strength, it can be concluded that:

Table 4
Compressive strength data (MPa) for the control and blended mortars at 5 and 20 °C.

	5 °C				20 °C			
t (days)	1	2	7	28	1	2	7	28
CON	3.53(±0.16)	12.55(±0.38)	22.98(±0.42)	43.46(±0.94)	18.93(±0.21)	28.54(±0.36)	39.02(±0.27)	51.96(±0.91)
FCC	3.61(±0.08)	12.89(±0.11)	25.02(±0.38)	44.12(±1.29)	14.12(±0.09)	23.09(±0.17)	36.16(±0.34)	64.52(±0.96)
MK	5.20(±0.09)	17.34(±0.32)	30.29(±1.18)	40.75(±0.68)	19.38(±0.15)	24.86(±0.28)	39.28(±0.81)	62.60(±0.70)
LF	3.00(±0.09)	10.17(±0.18)	18.36(±0.70)	37.16(±0.86)	16.04(±0.12)	22.96(±0.25)	32.46(±1.01)	49.43(±0.94)

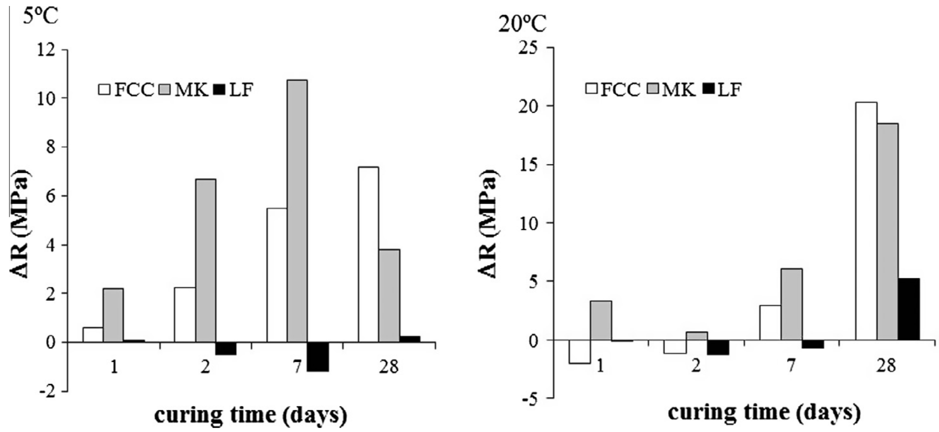

Fig. 5. Increase in compressive strength (ΔR) related to the replacement of cement by FCC, MK and LF, cured at 5 and 20 °C.

Table 6
Dosages of control mortar and mortars with partial replacement of aggregates by FCC, MK, and LF.

	Cement (g)	Addition (g)	Aggregate (g)	Agua (g)	Plasticizer (g)
CON	450	0	1350	225	–
FCC	450	135	1215	225	3
MK	450	135	1215	225	3
LF	450	135	1215	225	–

Table 8
Coefficients for adjusted logarithmic equations of control and addition mortars cured at 5 and 20 °C.

	5 °C			20 °C		
	a	*b*	R^2	*a*	*b*	R^2
CON	3.28	11.62	0.986	20.24	9.63	0.993
FCC	11.43	13.83	0.953	24.61	16.78	0.987
MK	12.69	14.71	0.952	25.87	16.18	0.997
LF	6.67	14.07	0.985	24.41	10.30	0.984

- The values for both pozzolan mortars are very similar, reaching $\Delta R'$ values higher than 20 MPa at 5 °C curing temperature and higher than 25 MPa at 20 °C.
- The LF mortars also obtained positive $\Delta R'$ values, being these much lower than those obtained by FCC and MK. This fact shows for both curing temperatures, the increase in the content of fine materials has an important role in the strength gain at all curing times. This fact was not observed in mortars with cement replacement, where even its presence had a negative effect ($\Delta R' < 0$). With the increase in fines, the matrix becomes denser and this will be observed in the mechanical strength improvement.
- The highest strengths obtained by FCC and MK are a consequence of the sum of the filler effect and the contribution of the pozzolanic reaction, for both 5 °C and 20 °C temperatures.

Table 7
Compressive strength data (MPa) of control and addition mortars cured at 5 and 20 °C.

	5 °C				20 °C			
t (days)	1	2	7	28	1	2	7	28
CON	3.53(±0.16)	12.55(±0.38)	22.98(±0.42)	43.46(±0.94)	18.93(±0.27)	28.54(±0.63)	39.02(±0.41)	51.96(±0.28)
FCC	8.57(±0.40)	21.39(±0.55)	44.51(±0.63)	53.85(±0.46)	22.15(±0.35)	37.67(±0.51)	60.48(±0.75)	78.35(±0.78)
MK	8.47(±0.32)	25.25(±0.58)	46.98(±0.37)	57.92(±0.74)	27.21(±0.52)	35.81(±0.43)	56.58 ± 0.82)	80.52(±1.02)
LF	5.11(±0.08)	16.58(±0.39)	37.59(±0.65)	51.50(±0.80)	24.49(±0.07)	32.89(±0.28)	41.73(±0.31)	60.07(±0.96)

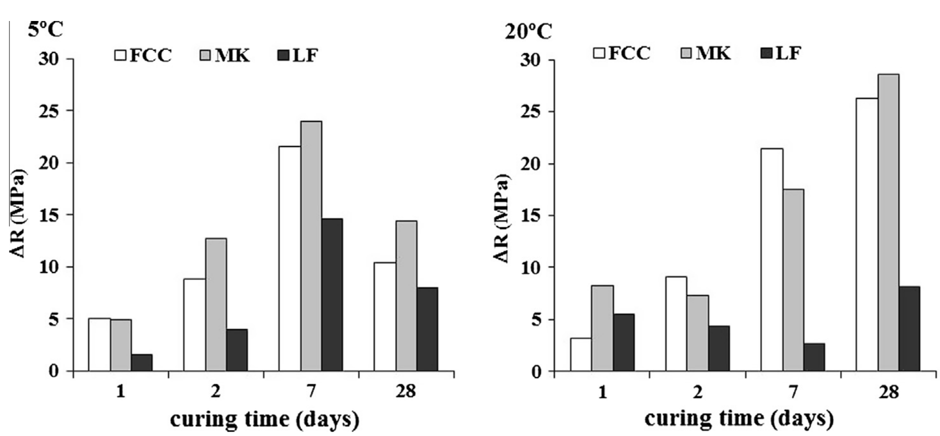

Fig. 6. Increase strength values ($\Delta R'$) in addition mortars with FCC, MK and LF, cured at 5 and 20 °C.

4. Conclusions

The following conclusions have been proposed from the study of the effect of curing temperature on pastes and mortars containing fluid catalytic cracking catalyst residue (FCC), metakaolin (MK), and limestone filler (LF):

- From the thermogravimetric study on pastes with 15% replacement of cement by MK and FCC, it can be concluded that FCC pastes always present positive fixed lime percentages for all curing times and all selected curing temperatures. This means that the pozzolanic reaction also occurs at low temperatures. On the contrary, MK paste, at early curing age and low curing temperatures showed negative fixed lime percentages. In this case, MK behaves as filler which accelerates the cement hydration process due to its high fineness.
- The replacement of cement by MK and FCC produced an increase in strength with respect to the control mortar. This improvement is mainly related to the strength gain due to the pozzolanic reaction. In addition, in the case of MK, at low curing temperatures, there is an acceleration contribution on the cement hydration.
- The mortars with addition (replacement of aggregate by MK, FCC and LF) obtained in all cases positive $\Delta R'$ values. For both temperatures studied (5 °C and 20 °C) the behaviour of the FCC and MK were similar and higher than mortar with LF, thus confirming once again that the pozzolanic reaction contributes greatly to the gain in strength.
- In general, the use of pozzolans such as FCC or MK has a positive effect on mortars cured both at 5 °C and 20 °C. Their use is recommended in cold weather mixing, especially for partial aggregate replacement.

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