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The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars

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Abstract

The hydration heat of mortars or concretes may be decreased by means of pozzolanic additions. Materials that exhibit pozzolanic activity can decrease the hydration heat by means of cement substitution, which increases the heat generated in hydration due to the pozzolanic reaction. Thus, the evolution of the hydration heat with time represents a reference point when establishing the pozzolanic activity of materials; by monitoring this heat, the behaviour of mortars or concretes during hydration can be established. In this work, the influence of the pozzolanic activity of the metakaolin (MK) on the hydration heat has been studied in comparison to the behaviour of other traditional pozzolanic materials such fly ash and silica fume. The results revealed that MK mortars produce a slight heating increase when compared to a 100% Portland cement mortar, due to the high pozzolanic activity of MK. With respect to the hydration heat, MK-blended mortar showed closer behaviour to silica fume than to fly ash. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Heating; Heat of hydration; Mortar; Pozzolanic reaction

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1. Introduction

In a previous work the authors have studied the effect of different pozzolanic materials on the hydration heat developed by cements mixed with the pozzolanic materials, in comparison to a control cement. These results have shown that pozzolanic materials do not cause a reduction in the heat evolution in proportion to the amount of cement substituted [1].

Pozzolanic materials react with calcium hydroxide released in the hydration of Portland cement (PC), increasing the hydration heat due to the exothermic effect of the pozzolanic reaction. This fact becomes more evident in materials with high pozzolanic activity as the case of silica fume (SF), which produces an increase in heat evolution of hydrating cement, compared to the 100% PC. However, materials with low initial activity, such as fly ashes (FA), decrease the hydration heat [2], as do natural pozzolanic materials [1].

In other work [3], opaline rock, FA, and SF were studied using different methods: a quick method of detection and quantification of pozzolanic activity with time [4] and the method of Langavant calorimeter to control the hydration heat of mortar [5] collected in the Spanish Standard [6]. The results reported showed that both methods offer similar data on the behaviour of the materials considered, since there was a good correlation between both, despite the fact that they are different methods based on the observation of different properties and effects.

Mineral additions for the manufacture of concrete generally include both natural pozzolans of volcanic origin and artificial pozzolans such as FA and SF. Currently, other alternatives to these materials are being investigated using clay minerals (i.e., kaolinite, montmorillonite, illite that can be thermally activated by dehydration in the temperature range of 700 to 800°C). The most typical example is kaolin, which upon heating produces metakaolin (MK). The properties of MK as a pozzolanic material have been reported previously [7–10]. Also, the influence of curing temperature on reaction rate constants and on the behaviour and stability of hydration phases have been studied [11,12]. MK shows a high level of pozzolanic activity, similar to SF. For this reason, it is very important to quantify the heat evolution during hydration in MK/cement systems.

It is well known that finely divided materials can accelerate PC hydration. Moreover, if the material shows high pozzolanic activity, the heat produced during hydration is higher in the blended mortar than in an equivalent reference

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mortar (a typical example is SF) [2]. Due to this fact, an increase in the hydration heat released can have a negative effect on performance (durability) of the mortars and concretes, mainly due to volume changes (shrinkage) and microcrack formation.

In the particular case of MK, it appears to have excellent potential as an active addition for producing mortars and concretes [13]. However, this material shows a particular nature in its chemical and mineralogical composition. The hydrated phases (C_2ASH_8 and C_4AH_{13}), formed during the pozzolanic reaction at early curing periods, tend to be present as metastable phases. With longer curing times, the conversion of these hydrates to hydrogarnet (stable phase) can be expected [14]. This transformation will depend on different factors (for example, temperature reached inside the specimen).

Few references to studying the heat evolution of MK-blended mortars exist. However, in previous work [15], a maximum temperature of 49°C was reported in blended mortar with 10% MK and at a curing temperature of 20°C. In other work, different accelerated tests in MK-blended specimens were applied to observe the influence of the temperature on the evolution and stability of the hydrated phases. Curing temperatures between 40 and 60°C have been used. According to the bibliography, it is very important to take into account the fact that different curing temperatures can modify the behaviour of mortars and concretes. In most cases, the curing temperature was chosen either randomly or from the Standards, which are used for particular objectives. For this reason, it is necessary to unify the curing temperature to establish the true temperature rise inside the specimens.

The current paper reports data for the hydration heat developed in MK-blended mortars, compared with other pozzolanic materials normally used in the manufacture of mortars and concretes (FA and SF).

The results obtained in the present paper are important in that they provide data to enable an assessment of temperature rise in mortars and concretes to be made in practice. It is very important to emphasize that the temperature reached in MK mortars has an important effect on engineering properties, mainly on durability, as mentioned previously.

2. Methods

2.1. Materials

The materials used in this study were: cement, sand, SF, FA and MK. Table 1 shows the chemical composition of these materials.

Base cement: According to the Spanish UNE 80 301 standard [16], the base cement was a CEM I/42,5 R cement with a clinker content equal to or above 95%, and could have up to 5% additional components.

Sand: The sand used had a silica content of more than 98% and maximum particle size of less than 2 mm.

Table 1
Chemical composition

Content	SF (%)	FA (%)	MK (%)
SiO_2	91.92	49.50	51.60
Al_2O_3	0.20	27.90	41.30
Fe_2O_3	0.10	7.82	4.64
MgO	0.30	2.03	0.16
CaO	0.32	2.00	0.09
TiO_2	–	0.82	0.83
$K_2O + Na_2O$	0.58	5.20	0.63
SO_3	0.18	0.29	–
Loss on ignition	6.30	3.30	0.60

Pozzolanic materials: These materials were characterized using chemical and mineralogical analysis and pozzolanic characteristics.

SF: A commercial SF (nondensified) was used. It was comprised of 91 or 92% silica. X-ray diffraction (XRD) pattern (Fig. 1a) indicates the low crystallinity of the SF, with low intensity peaks corresponding mainly to quartz (Q), silicon carbide (SiC), and silicon (Si).

FA: FA was generated in a power plant that burns bituminous coal. The loss on ignition value (3.3%) reflects its unburnt carbon content. The main chemical constituents were silicon oxide (49.5%), aluminium oxide (27.9%), and iron oxide (7.82%). It had a low calcium content (2.0%). The main crystalline components were quartz (Q), mullite (Mu), and hematite (He) (Fig. 1b).

MK: This product was produced by calcination of kaolinite. It had an $Si0_2$ content of 51.60% and an Al_2O_3 content of 41.30%. It was studied by means of XRD and showed a product of low crystallinity. Crystalline phases consisted of quartz (Q) and mica (M), mainly muscovite (Fig. 1c).

The fineness of these materials was determined by laser granulometry (in wet suspension with isopropilic alcohol) [17] and the results obtained are shown in Fig. 2. It can be verified that the fineness of MK is between that of SF and FA. Both the fineness and the mineralogy are important factors in determining pozzolanic activity.

2.2. Mixed cements

The mixed cements were prepared in a high-speed powder mixer to ensure homogeneity and dispersion. Mixtures were made up by weight to the following compositions:

Cement/SF: 90/10 and 70/30
Cement/MK: 90/10 and 70/30
Cement/FA: 90/10 and 70/30
100% PC: 100/0

These mixed cements were used to prepare mortars with sand/cement proportion of 3/1 and water/cement ratio of 0.5.

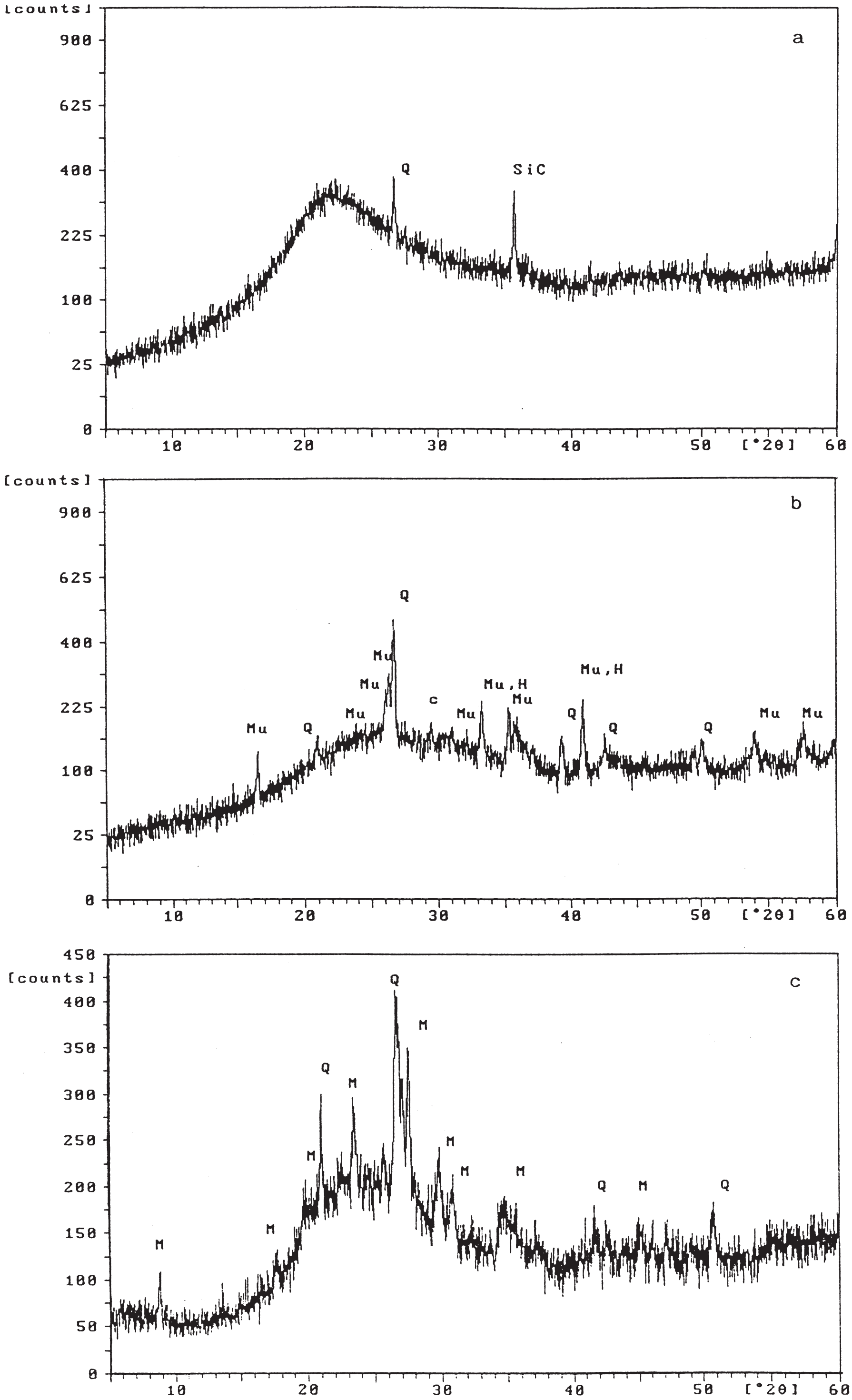

Fig. 1. XRD patterns: (a) SF, (b) FA, (c) MK.

2.3. Test methodologies

To carry out qualitative or quantitative determinations of the pozzolanic activity, many experimental methodologies have been developed. However, most of them are based on the measurement of the reaction of pozzolanic materials with the calcium hydroxide released during cement hydration.

In this work, as in other studies carried out by the authors, an accelerated method was used to study the pozzolanic activity of these materials. This followed the material-lime reaction with time. The test consisted of putting the different pozzolanic materials in contact with a saturated lime solution at 40 ± 1°C for 2 h, and 1, 7, 28, and 90 days.

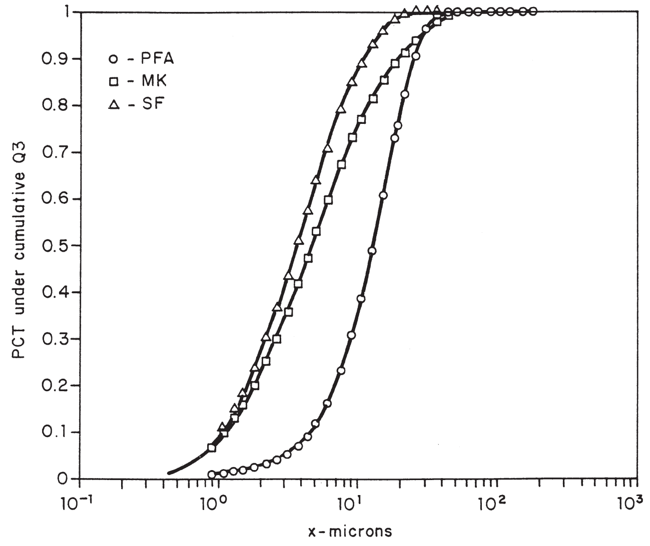

Fig. 2. Granulometric distribution curves: (a) FA, (b) MK, (c) SF.

At the end of each period, CaO concentration in the solution was established. The fixed lime (mM/L) was obtained by the difference between the concentration in the saturated lime solution and the CaO found in the solution in contact with the sample at the end of a given period.

The method given for determining hydration heat in the Spanish Standard [9] is based on the Langavant Calorimeter [4]. This semi-adiabatic method consists of quantifying the heat generated during cement hydration using a Dewar flask, or more exactly, a thermally isolated bottle. Since the exterior conditions are very influential, the test is carried out in a climatized room at 20 ± 2°C.

Heating (°C) is defined as the difference between the temperature of the mortar tested and the inert mortar (minimum 3 months old). This value of heating is used to calculate the hydration heat developed by the test sample.

The measurements were made over 5 days as indicated in the standard [4], since the heat increase is observed to be very low at later times, and also since the relative error of the measurement increases beyond that time.

3. Results and discussion

The results obtained for pozzolanic activity are shown in Fig. 3. After 2 h both the SF and MK show pozzolanic activity, since the samples have fixed significant amounts of calcium ions (lime), while the FA, due to its lesser activity at early stages [1], hardly shows any reaction with lime before day 28.

Fig. 4 shows the evolution of heating for the different mortars analyzed. Results obtained show how the maximum heating occurs at around 15 to 20 h and depends on the type of addition. FA delays this maximum with respect to the 100% PC mortar, while SF, especially when 10% is incorporated, advances this maximum. In the case of MK, these variations are not significant. In both mortars with 10% and 30% MK, the “heating” developed is greater than that of the 100% PC mortar.

These results indicate that there are two different effects to be considered regarding the behaviour of materials: on one hand, its pozzolanic activity, and on the other hand, the influence of substituting PC by additions, which may simply dilute the effects of PC hydration (effect of dilution) or may accelerate PC hydration.

In the case of FA, the effect of cement substitution is the determining factor relative to the 100% PC in that no temperatures rise is observed and the “heating” decrease is equivalent to the amount of cement substituted. In the case of SF, pozzolanic activity is the principal factor with 10% SF and the “heating” increases with respect to the 100% PC mortar. In the mix with a 30% SF both effects are significant and there is a slight decrease of the heating with respect to the 100% PC mortar.

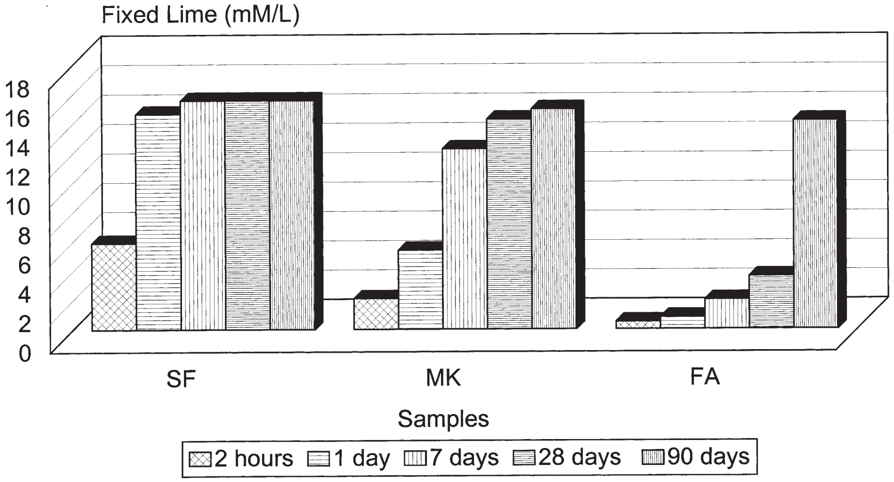

Fig. 3. Pozzolanic activity: fixed lime over time.

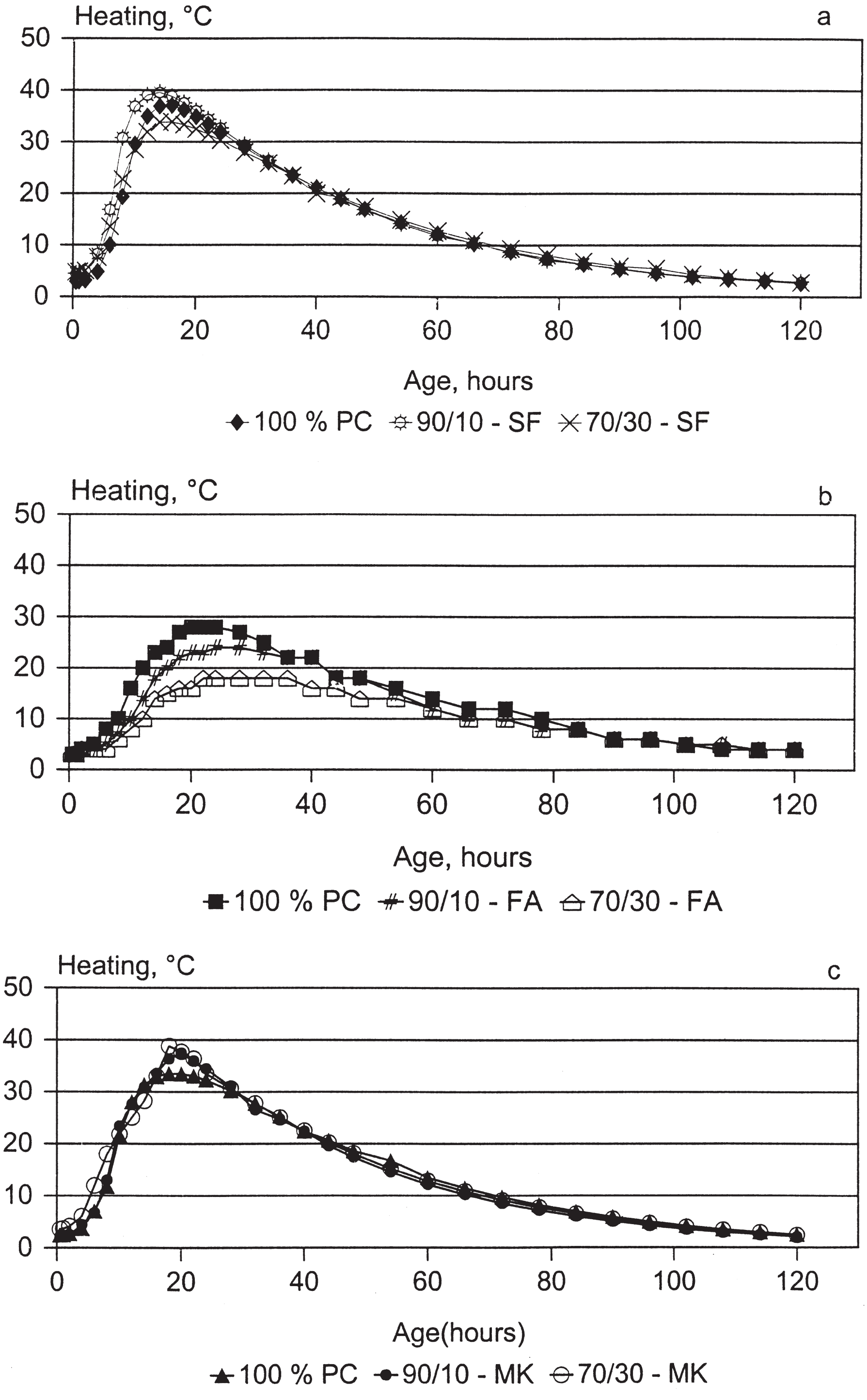

Fig. 4. Heating over time: (a) SF, (b) FA, (c) MK.

With the incorporation of MK as pozzolanic material (10 and 30%) (Fig. 4c), a different behaviour with respect to the other materials was observed. This pozzolanic material is a typical example where the effect of the pozzolanic reaction is compensated for by the dilution effect (30% MK). There are some differences with the results reported in the references [15]. At 20 h an increase of the "heating" is observed in MK mortars. The maximum temperature reached for both MK mortars was between 58 and 60 °C (according to the "heating" definition, 38–40°C of heating plus 20°C of the inert mortar).

Binders with pozzolanic material usually increase the hydration heat with respect to the base cement. During the first hours of the test, that is between the fifth hour and up to the first 12 h, reactions due to the PC are strongly exothermic, which makes the ascending slope of the curves very steep;

after 48 h the hydration heat begins to stabilize and the heat released is of little significance.

Fig. 5 shows the hydration heat (J/g of binder) for the three mortars with each pozzolan [i.e., SF (Fig. 5a), FA (Fig. 5b), and MK (Fig. 5c)].

SF, a product of high activity, represents the opposite case of that of FA (Fig. 5a). In this case, the mortar with 10% SF produces the highest hydration heat, followed by the 100% PC mortar. In the mortar with 30% substitution, the dilution effect is dominant at early ages, although this level of substitution does not produce a decrease in hydration heat relative to the 100% PC at long periods (130 h). The reduced level of the hydration heat relative to the 100% PC at an early age may be due to a lack of availability of CH.

As has been mentioned previously, pozzolanic materials can decrease the hydration heat due to cement substitution and the dilution effect. This fact is observed in the mortars with FA, in that the lowest hydration heat is produced by the mortar with

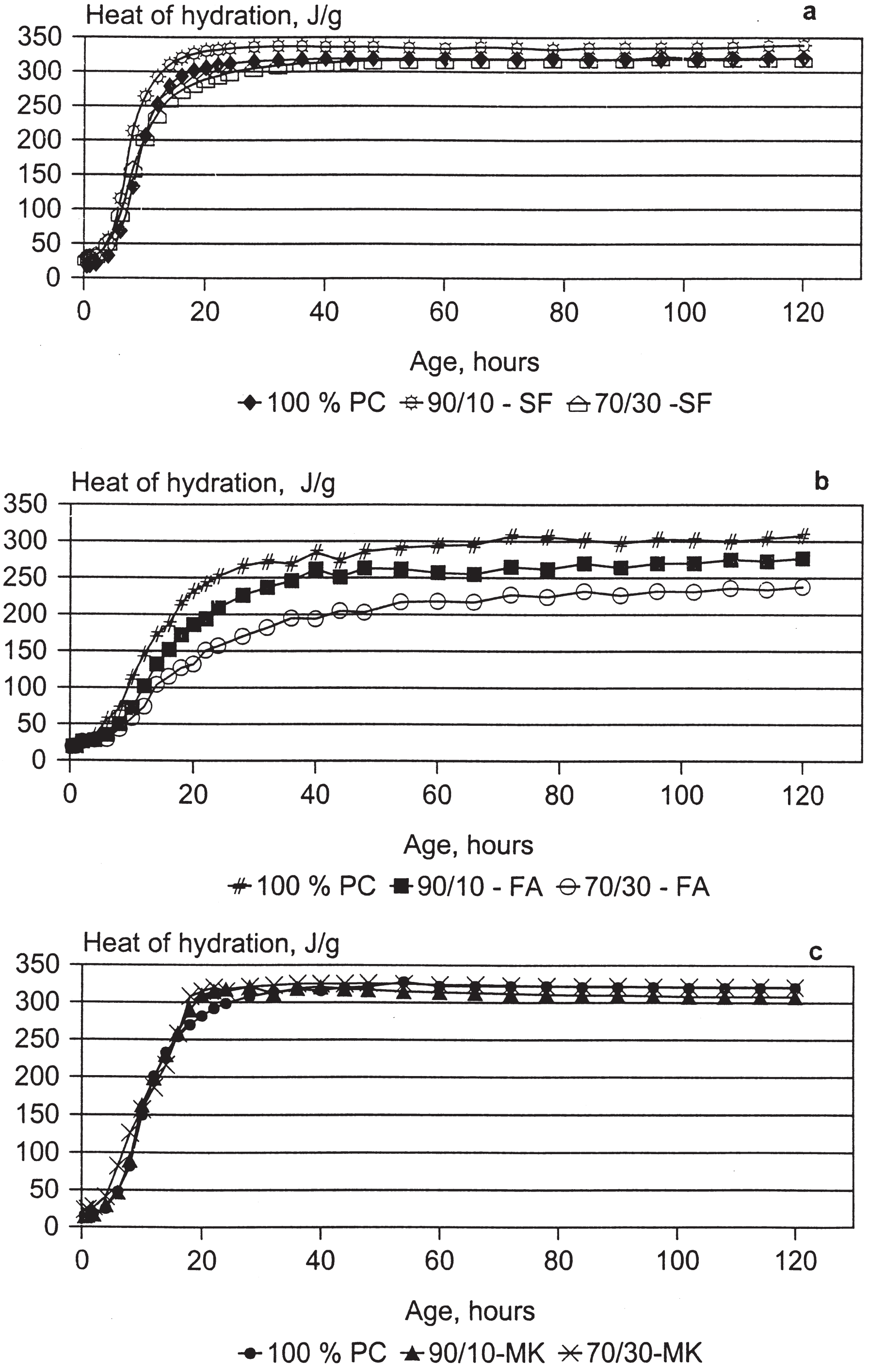

Fig. 5. Effect of different materials on the hydration heat: (a) SF, (b) FA, (c) MK.

30% substitution of PC with FA, followed by the mortar with 10% substitution, and finally, the 100% PC mortar (Fig. 5b).

The substitution of cement by MK produces an intermediate effect (Fig. 5c). The hydration heat of mortars with MK is similar to that of the 100% PC mortar. It is important to indicate that both MK contents (10 and 30%) produce a slight increase of the hydration heat between 18 and 30 h. This behaviour of the MK is in agreement with the results obtained by some of the authors in previous work [11]. J. Cabrera and M. Frías reported that the maximum pozzolanic activity of the MK occurred between 12 and 30 h, when the pastes (MK/lime) were subjected to curing temperatures of 60°C.

Fig. 6 represents the evolution of the hydration heat of mortars made with the different pozzolanic materials relative to 100% PC mortar, with a reference point of zero being assigned to the hydration heat developed by the 100% PC mortar. This graph covers the first 78 h of the test, when the pozzolanic materials often produce an increase in hydration heat in comparison to the base cement. It can be seen that after 30 h, the relative effects of the two active pozzolans on the heat released becomes less dominant. In the case of FA, substitution of PC with this pozzolan appears to produce a permanent drop in hydration heat output, although a slight increase of hydration heat at curing time above 30 h may indicate the first signs of pozzolanic reaction of this by-product.

It can be seen from Fig. 6 how during the first hours SF and MK (30%) show a similar behaviour, increasing hydration heat (positive values), while the FA decreases the hydration heat with respect to the 100% PC mortar (negative values). Ten percent MK has a small positive effect, but practically keeps its value similar to the 100% PC mortar.

At 8 h, the figure shows a maximum in hydration heat for the mortar with 10% SF, which produce a higher hydration heat in comparison to that of the 100% PC mortar, followed by MK (30%), SF (30%), and finally MK (10%).

Beyond 8 h, mortars with SF and MK show different behaviours. In the SF-blended mortars, the relative hydration heat rapidly decreases up to 20 h and subsequently stabilizes. While the data for mortar with 10% SF are always positive, the data give negatives values for mortar with 30% SF.

In mortars containing MK, the relative hydration heat decreases toward negative values for up to 16 h. Subsequently, values increase again (toward positive values) for up to 18 to 20 h of curing, where a second maximum is produced. At longer periods of testing, the mortar with MK (30%) shows positive relative hydration heat values, whereas negative values were obtained for mortar with 10% MK.

Fig. 3 established that SF shows a high pozzolanic activity that enhances the hydration heat with respect to the 100% PC mortar during the first hours of the test. Therefore, the pozzolanic activity is more important that the dilution effect. When the proportion of pozzolan was 30%, the hydration heat was below that of 100% PC mortar, indicating that the substitution effect predominates over the effect of the pozzolanic activity. At these high substitution levels the pozzolanic activity may be inhibited due to the reduced availability of CH.

In FA-blended mortar, an opposite behaviour prevailed. Due to its slow pozzolanic activity the limited heat released during this reaction cannot compensate for the decrease in heat caused by the cement substitution.

When cement mortars are partially substituted by MK, the pozzolanic effect is intermediate between SF and FA, according to the fixed lime data (Fig. 3). However, the positive values of relative hydration heat obtained during the first few hours showed that MK is closer in its behaviour to SF than it is to FA, due to its high pozzolanic activity.

The appearance of two maxima in relative hydration heat at 8 and 20 h of testing time (Fig. 6) confirms that MK displays a unique characteristic behaviour. At this moment, there is no clear explanation for this and further research would be necessary to identify the cause.

According to data obtained from differential thermal analysis results [11,12], some authors of the present paper reported that in MK/lime samples submitted to 60°C curing temperature, CSH gel was first formed (at 6 h) and subse-

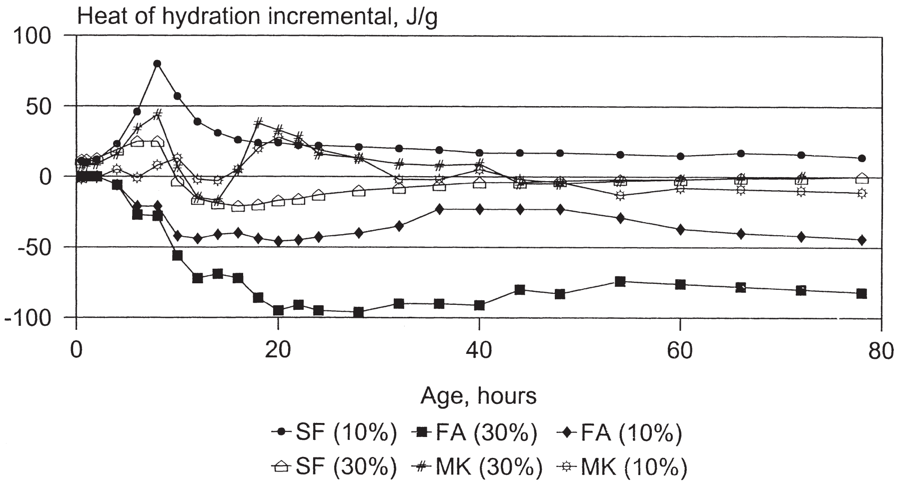

Fig. 6. Heat of hydration incremental over time.

quently gehlenite hydrate (C_2ASH_8) and hydrated calcium aluminate (C_4AH_{13}) (at 13–20 h) were formed. From these results, it is proposed that the first maximum might be due in part to the quick reaction of the amorphous silica in MK (51.60% SiO_2), while the second peak could be due to reaction of the amorphous alumina (41.3% AL_2O_3). According to the XRD pattern, MK is practically an amorphous material.

4. Conclusions

From the results presented in this paper, the following conclusions can be made:

1. MK is a pozzolanic addition showing pozzolanic activity below that of SF, but significantly greater than FA. This has been confirmed by the tests carried out on pozzolanic activity and hydration heat.
2. The pozzolanic activity results (fixed lime, Fig. 3) showed that the capacity for fixation of lime for MK at 1 and 7 days was 63.3 and 21.2% lower than for SF and 85.2 and 83.7% higher than for FA, respectively.
3. According to the heating definition, the blended mortar with 10 and 30% MK can reach higher "heating" with respect to 100% PC. "Heating" between 55 and 60°C was detected. This fact can assume temperatures of about 58 to 60°C inside blended mortar. It means an increase in temperature of between 10 and 15% with respect to the 100% PC.
4. Hydration heats for the SF and MK are similar, generally producing increased values (positives values), while the FA produces decreased values (negatives values) with respect to the 100% PC mortar.
5. Finally, even though MK is a highly pozzolanic material, MK mortars with similar relative hydration heats to 100% PC mortars can be obtained. This is possible with MK amounts below 10 to 12% wt.

Acknowledgments

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