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The effect of high curing temperature on the reaction kinetics in MK/lime and MK-blended cement matrices at 60 °C

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Abstract

It is well known that the pozzolanic reaction between metakaolin (MK) and calcium hydroxide produces CSH, C_2ASH_8 (stratlingite), C_4AH_{13} and C_3ASH_6 (hydrogarnet). However, the presence or absence of these hydrated phases depends on different parameters, such as curing temperature, matrix used, etc. This paper shows the results of a study in order to know the effect of high curing temperature (60 °C) on the kinetics of the pozzolanic reaction in different matrices. MK/lime (calcium hydroxide) and MK-blended cement matrices were studied in samples stored and cured at 60 °C and up to 123 days of hydration. The nature, sequence and crystallinity of the hydrated phases were analysed using differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques.

Results showed that the sequence and formation of the hydrated phases was different in both matrices cured at 60 °C. In an MK/lime matrix, C_2ASH_8, C_4AH_{13} and C_3ASH_6 were the main hydrated phases; while in an MK-blended cement, stratlingite was the sole hydrated phase issued from pozzolanic reaction. The DTA and XRD data also reveal an important fact: there is no evidence of the presence of hydrogarnet in blended cements.

Keywords: Metakaolin; Lime; Blended cement; High temperature; Hydrated phases

1. Introduction

During the last decade, particular attention has been paid to the reaction between metakaolin (MK) and calcium hydroxide. Previous works [1–3] showed the positive effect of MK on the properties of blended cements and/or concretes, mainly on the durability [4,5] as well as in new application fields, for example in immobilization of wastes [6] and in high-performance mortars [7]. The literature review shows that a few researches have reported about the role of MK in modifying the pore size distribution [8]. In this line, Frías and Cabrera [9] reported that the best evidence of the influence of MK on the refineness of the pore structure was detected in pores with radius smaller than 100 Å.

This positive effect of MK as a pozzolanic material is closely related to the hydrated phases produced during the reaction. It is known that the main phases produced during the pozzolanic reaction at ambient temperature are CSH, C_2ASH_8 and C_4AH_{13}. However, Silva and Glasser [10] reported significant changes of pattern in the development phase with curing temperature (20 and 55 °C). The C_2ASH_8 and C_4AH_{13} phases are not stable and can be transformed into hydrogarnets at long term. The consequence of a total transformation would produce a volume reduction of 13.3%, leading to an increase in porosity and a loss of microstructural compactness.

Nowadays, studies focus this research line in order to know more profoundly the influence of curing temperature on the development and stability of the main hydrated phases from pozzolanic reaction. Thus, in previous works carried out in MK/lime systems, Frías and Cabrera [11] reported that an increase of temperature from 20 to 60 °C had a direct influence on the reaction kinetics at short time. The rate constant obtained by Jander mathematical model at 60 °C of curing was about 68 times higher than that obtained at 20 °C and, on the other hand, the hydrogarnet was not formed from a transformation reaction, but as a result of the reaction between MK and calcium hydroxide at curing temperature of 60 °C [12].

Most of the works published up to now about reaction kinetics were carried out in MK/lime systems. However,

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Table 1
Chemical composition and physical properties of cementitious materials used

Oxide (%)	Cement	Metakaolin
SiO_2	20.40	51.60
Al_2O_3	5.02	41.30
Fe_2O_3	2.92	4.64
CaO	64.25	0.09
MgO	2.83	0.16
SO_3	2.63	–
Na_2O	0.39	0.01
K_2O	0.84	0.62
TiO_2	0.21	0.83
LOI	0.70	0.60

there is scant information about other systems submitted at high curing temperature; such as cement paste, which is characterized by the presence of some activators and minor elements present in its matrix. Those could alter the reaction kinetics as can be deduced from a previous work. De Silva and Glasser [13] reported that the presence of some activators (sulphates, NaOH) in MK/lime systems cured at 20 °C showed important structural modifications.

The present research shows the results of an experimental study on the kinetics of pozzolanic reaction in MK/lime binder as well as MK-blended cement at 60 °C. A comparative study in both systems was carried out. The sequence, development and crystallinity of hydrated phases up to 123 days of curing time were studied by means of DTA and XRD techniques.

2. Materials and experimental techniques

A commercial MK was used in the present work. The BET surface area of MK was 15.5 m^2/g. The mineralogical characterization of MK showed very low crystalline nature, with the presence of low intensity peaks corresponding to quartz and mica (muscovite). The lime used was $Ca(OH)_2$. A commercial white Portland cement available in UK was also used for this study. The BET surface area of cement was 1.04 m^2/g. The chemical composition for MK and white cement is given in Table 1.

MK and $Ca(OH)_2$ were mixed in the ratio of 1:1 by weight and the water/solid ratio that resulted in a satisfactory slurry mix was 2.37. Four different pastes were prepared. White OPC was partially replaced by 0%, 10%, 20% and 25% of MK. The water/binder was 0.55 by weight.

For both cases, all mixtures were placed in plastic airtight containers and then left in a water bath at a temperature of 60 °C. Different hydration times were applied: 0, 2, 6, 12, 21 and 30 h and 2, 3, 5, 9, 34, 62 and 123 days for MK/lime mixes and 30 h, 3, 9, 34 and 123 days for MK-blended cements. After the appropriate hydration time, samples were taken from the plastic containers and dried in an oven at 105°C for 24 h.

Differential thermal analysis (DTA) and X-ray diffraction (XRD) were used to provide information about the effect of temperature on the pozzolanic reaction kinetics in different matrices. X-ray diffraction patterns were obtained with a Philips model PW-1700 with a X-ray tube containing a copper anode, while DTA thermograms used a Stanton Redcroft STA 1000 Simultaneous Thermal Analyses Series, with a heating rate of 20 °C/min in an inert atmosphere (N_2).

3. Results and discussion

3.1. Reaction kinetics in an MK/lime system at 60 °C

Fig. 1 shows DTA thermograms for the MK/lime matrix as a function of curing time at 60 °C. This figure shows the presence of C–S–H at 6 h, C_2ASH_8 and C_4AH_{13} appeared as predominant phases beyond this time. At 30 h, a new endothermic peak appeared at about 310 °C, which was attributed to hydrogarnet. It is important to indicate that above 9 days of curing time, the two peaks corresponding to the metastable phases (C_2ASH_8 and C_4AH_{13}) created an evolution, forming a wide band with a maximum situated at about 215 °C. This phenomenon might be indicating an evolution from C_2ASH_8 to C_4AH_{13}. However, studies

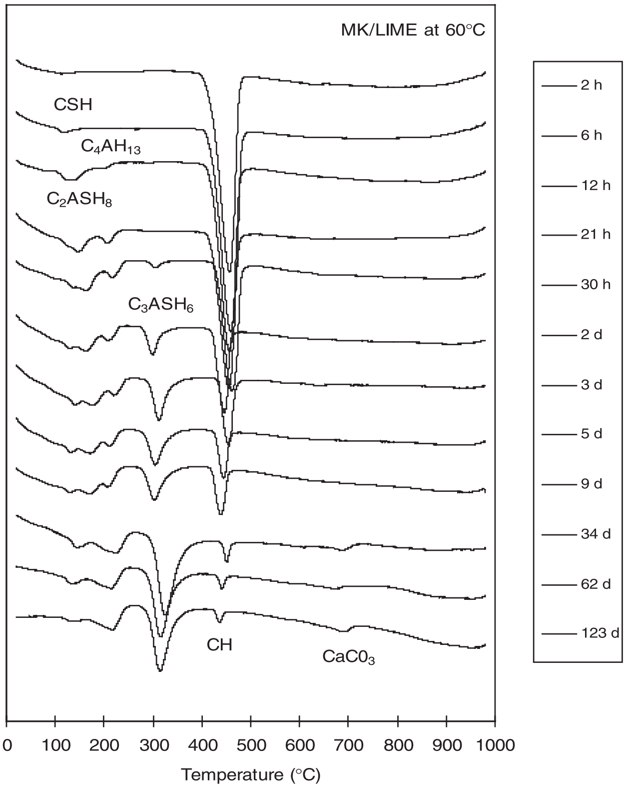

Fig. 1. DTA thermograms for MK/lime matrix at 60 °C of curing temperature.

carried out by XRD showed no evidence of this evolution or disappearance.

At the beginning of the reaction (up to 12 h), the predominant phase was the C–S–H gel. The C_2ASH_8 and C_4AH_{13} appeared after 6 h of reaction. The hydrogarnet was formed after 21 h and its amount increased with curing time. After 30 h, this compound was the predominant phase, increasing with the decrease of the lime content up to 34 days. Later (from 34 to 123 days), the C_3ASH_6 content was practically constant.

From the results stated before, together with those of a prior paper [14] published by the same authors, it is possible to conclude that the hydrogarnet content is closely related to the lime content. This fact is perfectly identified in the formation sequence of hydrogarnet (Fig. 1). When the lime content decreased with curing time, the hydrogarnet content increased; however, when the lime content was practically constant (about 1% left), the hydrogarnet content remained constant (period between 34 and 123 days of curing time).

Fig. 2 shows the XRD patterns for the MK/lime systems as a function of curing time at 60 °C. At 21 h, gehlenite is clearly detected as the predominant crystalline phase from pozzolanic reaction between MK and lime. C_4AH_{13} is not clearly observed due to either its low crystallinity degree or the overlapping of the reflection peaks, mainly with C_2ASH_8 and C_4AcH_{11}. According to De Silva and Glasser [15], the C_3ACcH_{11} and C_4AcH_{12} had the same thermodynamic properties as C_4AH_{13} and at low CO_2 contents were miscible with it.

At 30 h of curing time, the first signs of the hydrogarnet appearance were observed. Above 9 days of curing, the presence of C_2ASH_8 and hydrogarnet as predominant crystalline phases from pozzolanic reaction at 60 °C of curing temperature was clearly established.

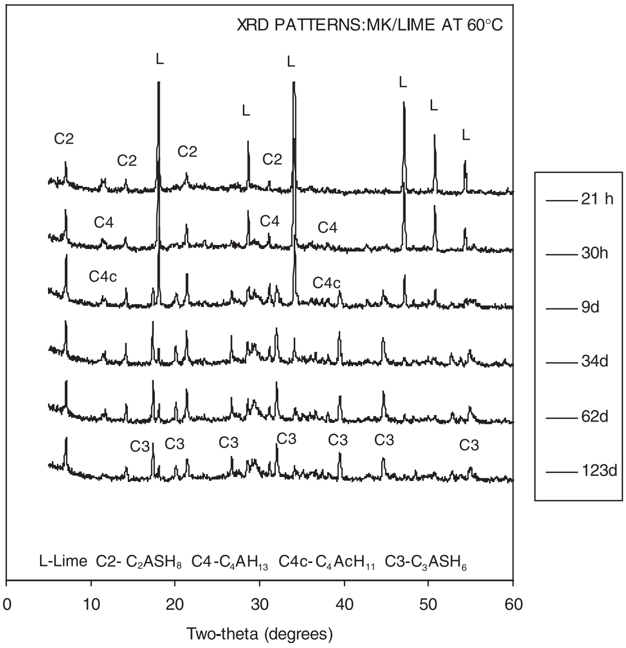

Fig. 2. XRD patterns for MK/lime matrix at 60 °C of curing temperature.

From DTA and XRD data exposed above, it is important to highlight the fact that there is no evidence of a possible transformation of C_2ASH_8 and C_4AH_{13} into hydrogarnet in conditions tested here.

3.2. Reaction kinetics in MK-blended cement systems at 60 °C

Fig. 3 shows the evolution of hydrated phases with the curing time for the cement pastes containing between 0% and 25% of MK. These curves illustrate that the main hydrates in a white Portland cement were CSH gel and CH (portlandite). In MK-blended cements also appeared a peak about 170–175 °C, which is attributed to the C_2ASH_8 phase. Statlingite appeared as the predominant phase of the pozzolanic reaction between MK and calcium hydroxide released from hydration reaction. The content of this phase increased with the decrease of the lime content, hydration time and with the increase of MK contents. In all cases, the stratlingite was detected at 30 h of curing time.

An important aspect obtained from DTA curves was the absence of other hydrated compounds, such as C_4AH_{13} and hydrogarnet, main phases clearly identified in MK/lime systems cured at 60 °C. With respect to this phenomenon, the DTA curves corresponding to 10% and 20% of MK (mainly) showed the presence of a very weak endothermic peak at about of 300 °C. This peak might be assigned to the hydrogarnet phase, the decomposition temperature of this phase found in MK/lime system at 60°C (Fig. 1).

Comparing the DTA results with those obtained from MK/lime system at the same curing temperature, it is possible to observe a very important fact on the reaction kinetics and evolution of hydrated phases at 60 °C. In MK-blended cement, C_2ASH_8 was the only phase obtained from pozzolanic reaction, while that in MK/lime C_2ASH_8, C_4AH_{13} and C_3ASH_6 were found.

Figs. 4–6 (up) show the evolution of the crystalline phases in MK-blended cements up to 123 days of hydration time. The presence of portlandite and unhydrated cement particles is clearly detected. The intensity of the portlandite peak decreased with the hydration time (except for 0% of MK) and with the MK percentages incorporated. Blended cement with a 10% of MK, lime contents decreased up to 3 days of curing; later, its content increased due to the total consumption of MK (Figs. 3 and 4).

With respect to unhydrated cement particles, the intensity of the peaks showed a different behaviour in function of MK contents. Cement samples with 0% and 10% of MK and unhydrated calcium silicates decreased quickly with curing time (Fig. 4), observing the complete reaction at 124 days of curing time (Fig. 6 up). In the cases of 20% and 25% of MK, the evolution of hydrated compounds was different (Figs 5 and 6 up). The intensity of peaks decreased slowly,

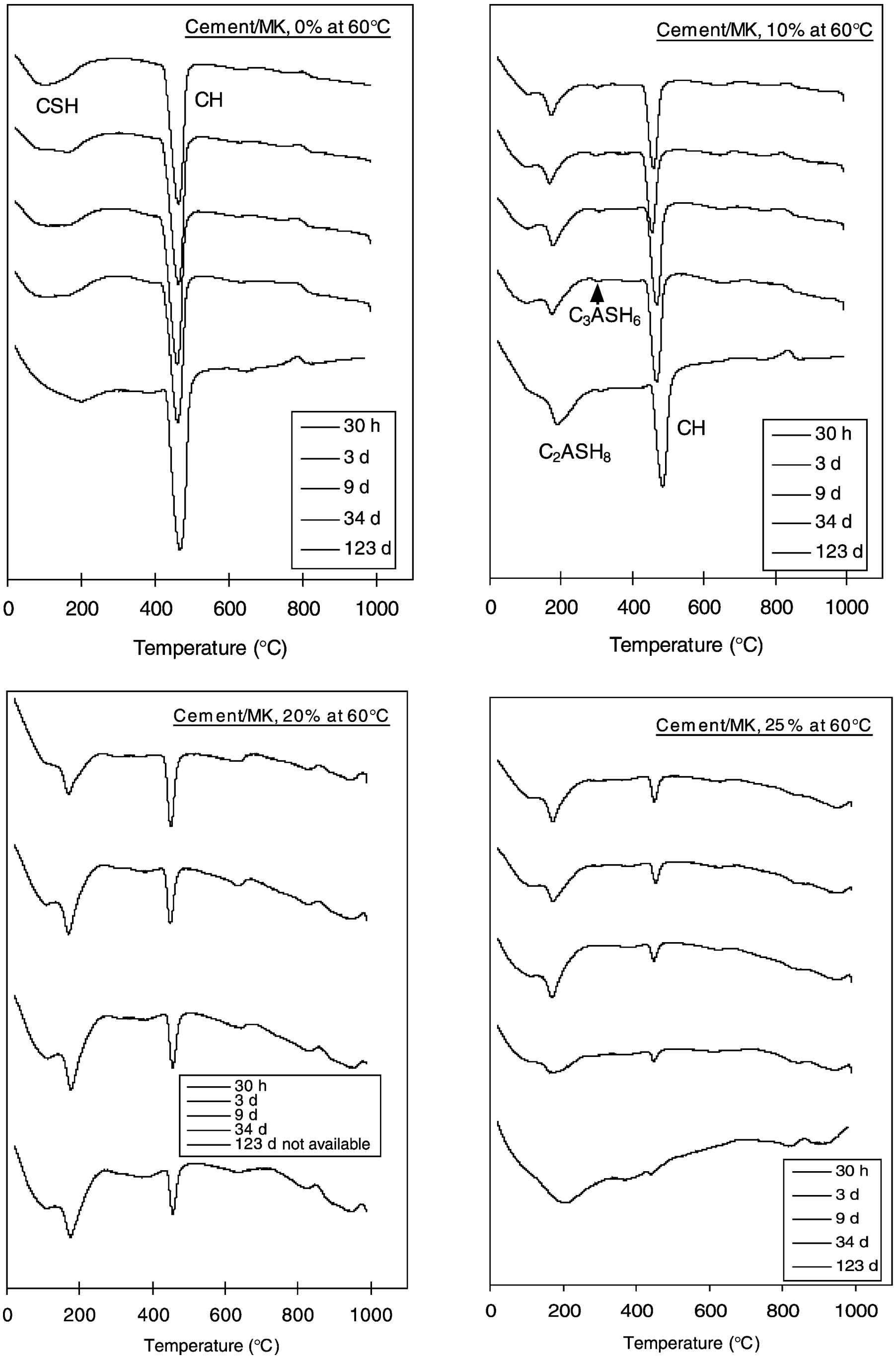

Fig. 3. DTA thermograms for MK-blended cements containing 0%, 10%, 20% and 25% of MK at 60 °C of curing temperature.

detecting high contents after 124 days of reaction at 60 °C; therefore, the hydration reaction showed a delay, which depends on high MK contents. This fact could have a contradictory side since it is well known that the curing temperature accelerates the hydration reaction as well as the incorporation of pozzolanic material due to its filler effect. The data exposed here could sometimes contradict this fact. It might be related to, on the one hand, the absence of humidity in MK-blended cement with high MK contents (20–25%) due to the pozzolanic reaction and, on the other, the physical barrier of the hydrated compounds produced in the first layers of cement particles, which could impede or delay the access and mobility of water molecules towards the inside of the particle.

With respect to the hydrated phases from pozzolanic reaction, the XRD patterns did not supply any information about the formation of C_2ASH_8, C_4AH_{13} and C_3ASH_6. In the case of blended cement containing 20% of MK (Fig. 6 down) it was only possible to detect a weak peak localised at 17.5° (2θ), which was attributed to the hydrogarnet phase.

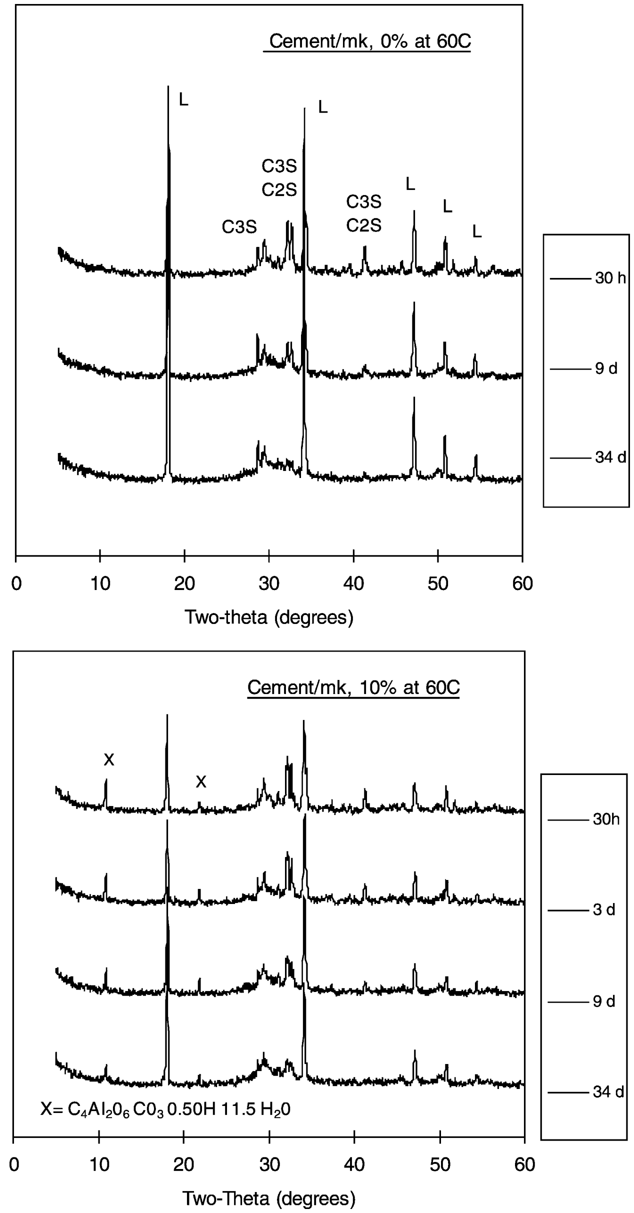

Fig. 4. XRD patterns for blended cements containing 0% and 10% of MK and up to 34 days of hydration.

In the rest of cases (i.e., 25% of MK), hydrogarnet appeared as traces.

Also, it is important to indicate the appearance of a hydrated phase located at 10.9° (2θ) in blended cements with 10% of MK, mainly (Figs. 4 and 6 up). At first sight, this peak could correspond to C_4AH_{13} phase; however, the presence of another peak at 21.8° (2θ) confirmed the existence of a carbonated phase named calcium aluminum oxide carbonate hydroxide hydrate [$Ca_4Al_2O_6(CO_3)\cdot 0.5(OH)\cdot 11.5H_2O$]. The formation of carbonated hydrate is due to the presence of CO_2 and/or $CaCO_3$ in pastes, which can come from different sources: the presence of atmospheric CO_2 during the elaboration and mixing stages, a slightly carbonated lime of starting and a bit amount of carbonic gas dissolved in mixing water.

From results obtained here, important differences have been found in both matrices submitted at 60 °C of curing temperature. In MK/lime systems, stratlingite was formed in parallel with C_4AH_{13} (above 6 h, from DTA curves), increasing its content with the hydration time. At 30 h of curing, hydrogarnet appeared as hydrated phase. However, data obtained from XRD, gehlenite and hydrogarnet only appeared as crystalline compounds.

In MK-blended cements systems, results from STA data showed clearly the formation of stratlingite as the main and only hydrated compound, and in some cases, the hydro-

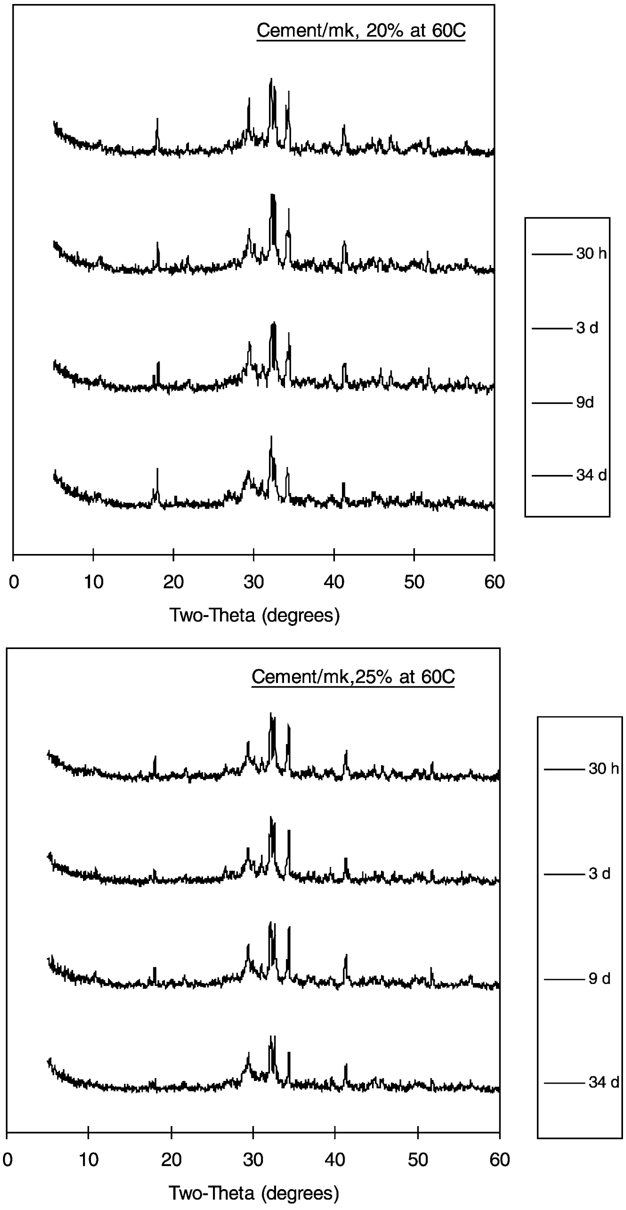

Fig. 5. XRD patterns for blended cements containing 20% and 25% of MK and up to 34 days of hydration.

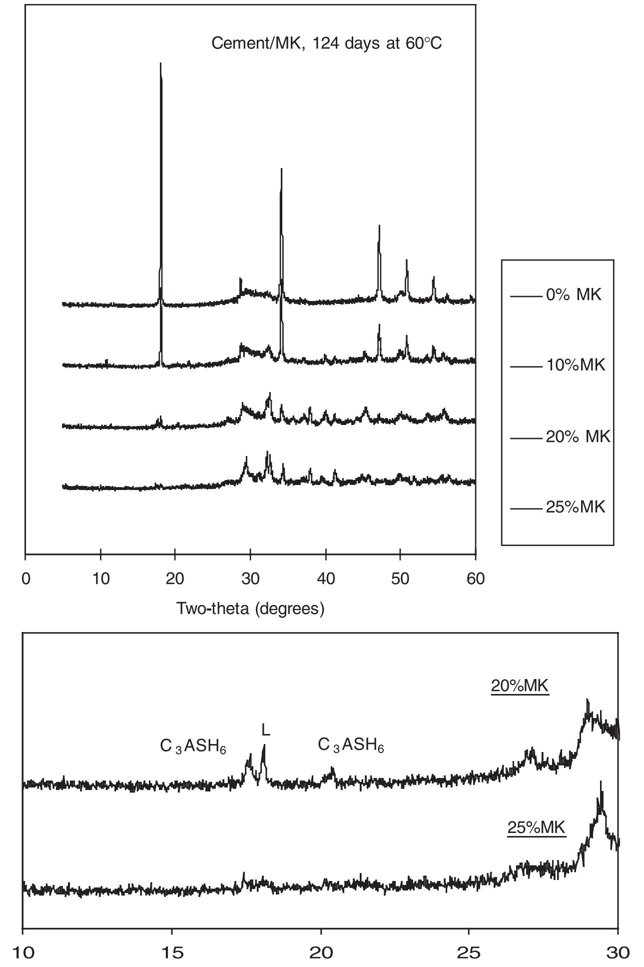

Fig. 6. XRD patterns for blended cements (up) with 0%, 10%, 20% and 25% of MK and at 124 days of hydration, (down) with 20% and 25% of MK for angle interval between 10° and 30° (2θ).

garnet was weakly identified. XRD results showed that blended cement matrices submitted to high temperature were poorly crystallized. Stratlingite was not detected as crystalline phase.

These findings are in accordance with results obtained in a previous paper by the same authors [14]. They reported that stratlingite was identified as the main hydrated phase in MK-blended cement submitted at 20 °C of curing temperature, but also showed absence of crystallinity. According to the results obtained by Ambroise et al. [2], it was only possible to detect the crystalline C_2ASH_8 in blended cement with MK content of at least 30%.

As mentioned above, other important aspects observed in present work was the total absence of hydrogarnet in MK-blended cements (only traces with 20% and 25% of MK). Therefore, the formation of this hydrated phase will be related to curing temperature as well as matrix used.

The absence of hydrogarnet in MK-blended cement cured at 60 °C is difficult to interpret. One possible explanation about this might be related to different phenomena, which could be compatible at the same time.

1. At each curing time, the calcium hydroxide liberated from cement is not enough to form hydrogarnet due to the competitive hydration reaction proposed by Murat [16]; the formation of hydrogarnet would need 5 mol of lime for each mole of MK. For this reason, this phase was only detected in MK/lime samples at 60 °C (Fig. 1).
2. Decrease of the solubility of calcium hydroxide due to the presence of alkalis, which provokes an insufficient calcium ion amount to react with MK.
3. The presence of some activators and/or ions in cement paste (i.e., sulphates) could alter the pozzolanic reaction kinetics, impeding or delaying the hydrogarnet formation in blended cement systems.

4. Conclusions

The following conclusions are offered.

1. The reaction products of the pozzolanic reaction between MK and calcium hydroxide are closely related to the matrix used. The pozzolanic reaction in a blended cement paste at 60 °C of curing temperature and up to 123 days of hydration, does not necessarily have to imply the formation of hydrogarnet.
2. In an MK/lime system (1:1 in weight), hydrated phases formed at high temperature (from DTA data) were essentially CSH, C_2ASH_8, C_4AH_{13} and C_3ASH_6. CSH is detected at 6 h of hydration time, followed by C_2ASH_8 and C_4AH_{13} at 12 h of curing and finally C_3ASH_6 at 30 h of age.
3. In a MK-blended cement system (10%, 20% and 25% of MK), the development of hydrated phases presents a different behaviour from the MK/lime system. Stratlingite was detected in all cases as the sole reaction product from pozzolanic reaction. There was no evidence of formation of C_4AH_{13} and hydrogarnet (only traces).
4. XRD patterns for the MK/lime systems, stratlingite and hydrogarnet were identified as crystalline hydrated phases but not C_4AH_{13}.
5. In MK-blended cement at 60 °C, XRD showed important changes with respect to the crystallinity of hydrated phases. Stralingite did not appear as a crystalline phase; therefore, this fact is indicating a very low crystallinity of this compound in blended cements. At 20% and 25% of MK, the presence of hydrogarnet traces was observed (Fig. 6 down).

From results mentioned above and under the conditions tested in the present paper, it is possible to summarize that formation, sequence of phase development and crystallinity of the hydrates produced during pozzolanic reaction between MK and calcium hydroxide depend on different parameters, one of the most important of which is the nature of the matrix. The presence of different ions in the matrix alters the equilibrium between solid phase and liquid phase, provoking alterations on reaction kinetics, as demonstrated in the present paper. The final result was the absence of hydrogarnet in MK-blended cements, a very important aspect towards the durability of mortars and concretes elaborated with MK (up to 25%). In those cases, there is no evidence of the formation of hydrogarnet and therefore, of a possible transformation from hexagonal hydrated phases (C_2ASH_8 and C_4AH_{13}) to cubic phase (C_3ASH_6).

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