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Influence of MK on the reaction kinetics in MK/lime and MK-blended cement systems at 20°C

Moisés Frías*, Joseph Cabrera[1]

Civil Engineering Materials Unit (CEMU), School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK

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Abstract

Metakaolin (MK)/lime and MK-blended cement pastes are studied in samples stored and cured at 20°C and up to 360 days of hydration. The nature of the reaction products and their sequence of appearance are obtained from differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques. The results show a different behavior of the pozzolanic reaction in both pastes. XRD data reveal the absence of crystalline phases in MK-blended cements up to 360 days of curing. MK shows high pozzolanic activity, which provides the quick formation of CSH, C_2ASH_8 (stratlingite), and C_4AH_{13} in MK/lime systems. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Lime; Blended cement; Hydrated phases

1. Introduction

During the present decade, metakaolin (MK) has been the objective of numerous investigations due to its capacity for reacting with the calcium hydroxide released during the hydration reaction.

The most important characteristics of this calcined product are: chemical composition ($SiO_2 + Al_2O_3$ about 90–95%), fineness (surface area between 15 and 20 m^2/g), and its poorly crystalline nature. These permit MK to show a high pozzolanic activity; sometimes it is compared to pozzolanic activity of the silica fume [1,2].

When MK reacts with calcium hydroxide, cementitious products are formed. It has been reported that the stratlingite (C_2ASH_8) and CSH gel are the most important hydrated phases formed [3]. Other studies [4,5] have also reported the appearance of C_4AH_{13} or C_4ACcH_{11} with C_2ASH_8 and CSH at 20°C.

Curing at 50°C or under hydrothermal conditions, hydrogarnet was produced [6,7]. Subsequently, the formation of this cubic hydrated phase (C_3AH_6) was detected in mixes of lower lime content at ambient temperature [3].

According to previous investigations, it is possible to deduce that the hydration phases and their stabilities with curing time are closely related to MK/lime ratio [8], temperature [9], and the presence of different activators [10].

These aspects are very important from the point of view of the engineering and microstructural properties, which could have associated a negative effect on the performance

Table 1
Chemical composition and physical properties of cementitious materials used

Oxide (%)/physical properties	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
Relative density (g/cm^3)	3.27	2.66
Surface area (m^2/g)	1.04	15.00

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* Corresponding author. Present address: Eduarto Torroja Institute (CSIC), 28033 Madrid, Spain. Tel.: +34-91-3020-440; fax: +34-91-3020-700.

E-mail address: mfrias@ietcc.csic.es (M. Frías).

[1] Joseph Cabrera died prior to the publication of this article.

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of the MK-blended cement. As for the temperature, De Silva and Glasser [10] reported that the C_2ASH_8 and the tetracalcium aluminate hydrates tend to be present as metastable phases, converting into hydrogarnet at longer curing times when temperature increases.

Recently, the authors of the current paper reported that hydrogarnet might be obtained as a result of the pozzolanic reaction between MK and lime and it did not originate from a transformation reaction [11].

Also, the development of hydration phases depends on the nature of the activator used [10,12]. De Silva and Glasser reported that in an MK/lime paste, the CSH was a major product of hydration in all activators studied while the nature of minor phases is much influenced by the system chemistry. In a system (at 180 days and 40°C) without the presence of secondary activators, C_3AH_6, C_2ASH_8, and C_4AH_{13} were formed. C_3AH_6 and C_4AH_{13} (traces) formed when sulfate was present, and finally using NaOH as activator, the content of the MK goes mainly toward the formation of C_2ASH_8 and C_4AH_{13} (traces).

Most of the studies carried out with MK were focused in MK/lime systems. However, there is a lack of investigations about the reaction kinetics in MK-blended cement. The chemical reactions taking place in MK-blended cement are

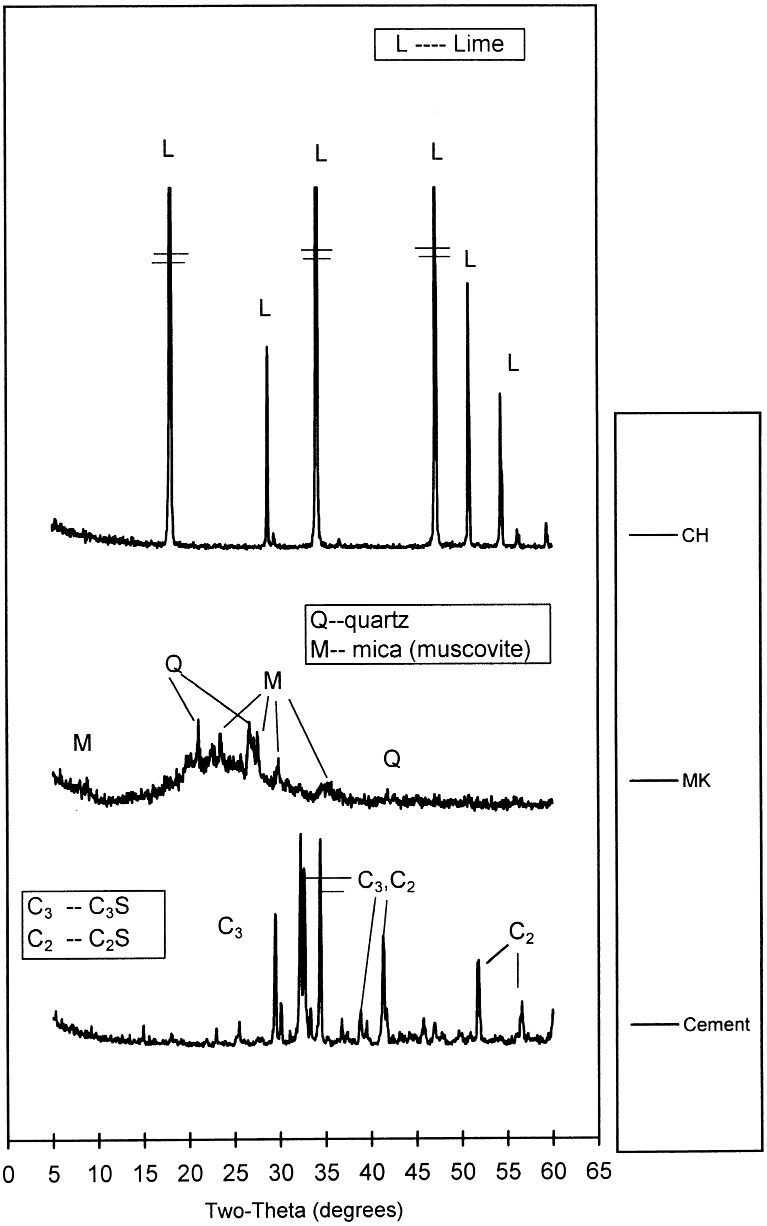

Fig. 1. Crystalline compounds in the raw materials used.

generally more complex than in the MK/lime system. It is due to the fact that cement is a mixture of phases reacting at different rates. This fact, in conjunction, with the presence of other compounds, such as sulfates, alkalis, chlorides, and minor elements (zinc, cadmium, lead, chromium, etc.), could provoke an alteration in the pozzolanic reaction rate and, therefore in the development and crystallinity of hydrated phases.

This research presents the results of an experimental study of the kinetics of the pozzolanic reaction in MK/lime and MK-blended cement at 20°C. The sequence and identification of the hydrates up to 360 days of hydration time are studied using differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques.

2. Materials and experimental techniques

A commercial MK and a white Portland cement available in UK were used for this study. Their composition and some

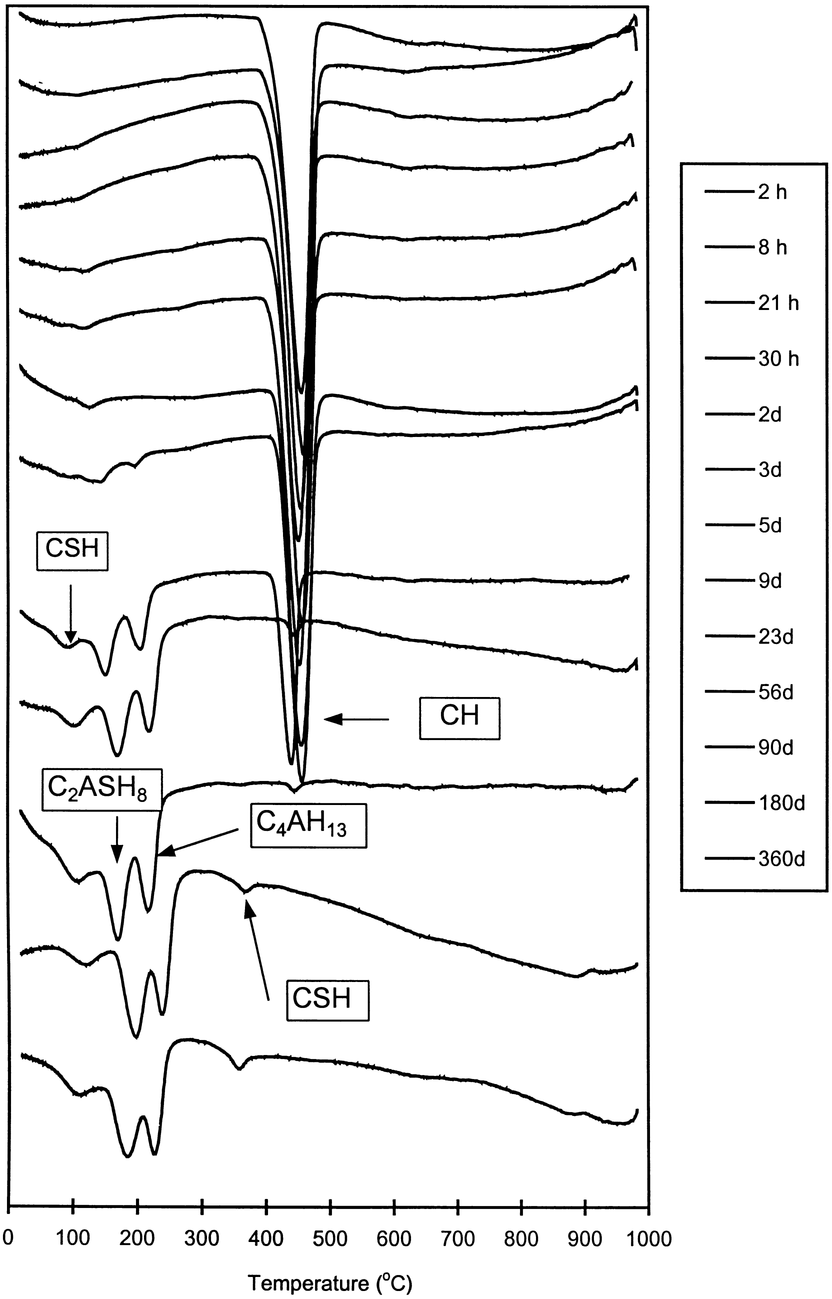

Fig. 2. DTA curves for MK/lime pastes at 20°C.

of their physical properties are given in Table 1. The lime used was analar $Ca(OH)_2$.

The mineralogical characterization for these materials is illustrated in Fig. 1. It shows the low crystalline nature of MK, with low-intensity peaks corresponding to quartz and mica (muscovite).

MK and analar $Ca(OH)_2$ were mixed in the ratio of 1:1 by weight and 2.37 of water/binder. The hydration times selected for the study were from 2 h to 360 days.

Five pastes containing 0%, 10%, 15%, 20%, and 25% of MK were prepared. The water/binder was 0.55 by weight. The hydration times were from 1 to 360 days. These MK percentages were selected on the basis that pozzolan contents in typical blended cements are normally in the range 0–25%. This last value is in the range of the total portlandite content in fully hydrated cement.

All mixtures were placed in plastic airtight containers and then left in a curing room at 100% RH and

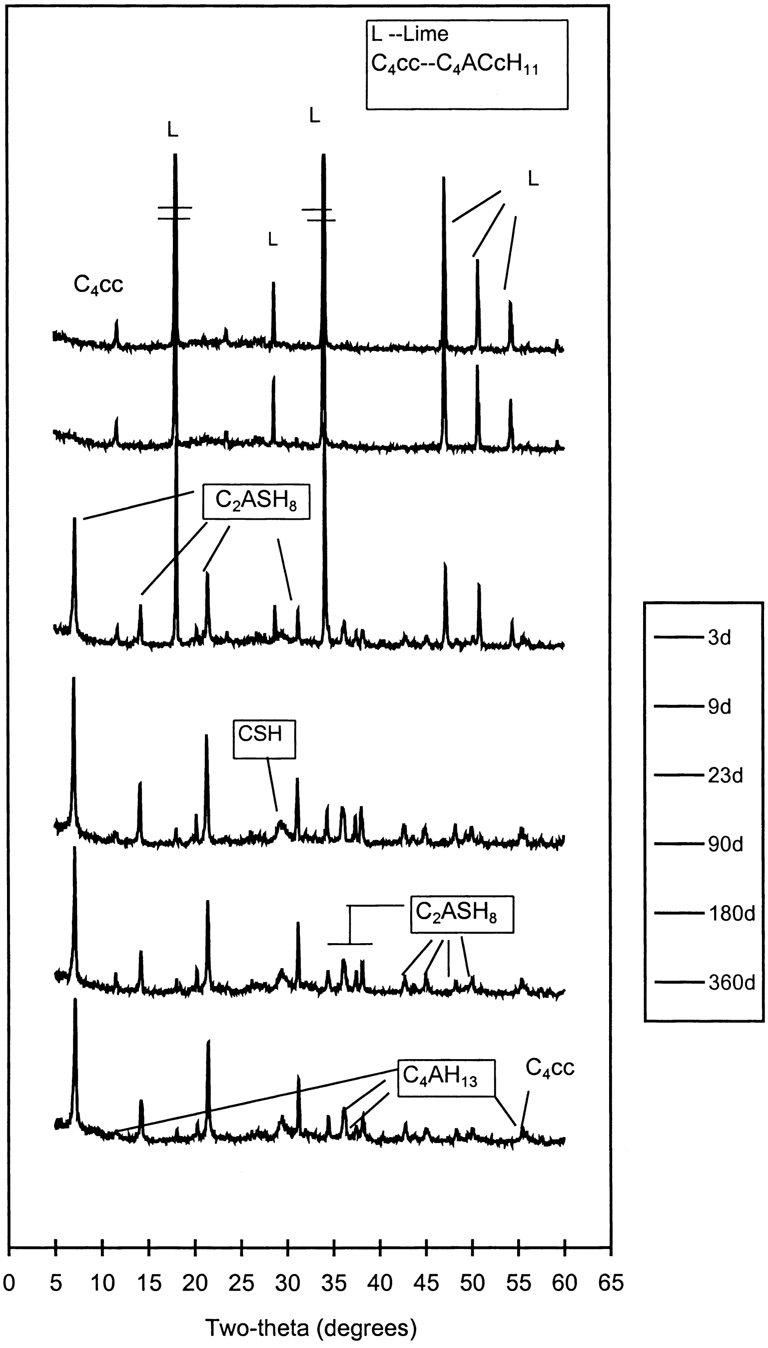

Fig. 3. XRD patterns for MK/lime pastes at 20°C.

20°C. After each predetermined curing time, the hydration reaction was stopped using a microwave oven [12].

DTA and XRD were used to provide information on the kinetics of the pozzolanic-lime as well as MK/cement reactions.

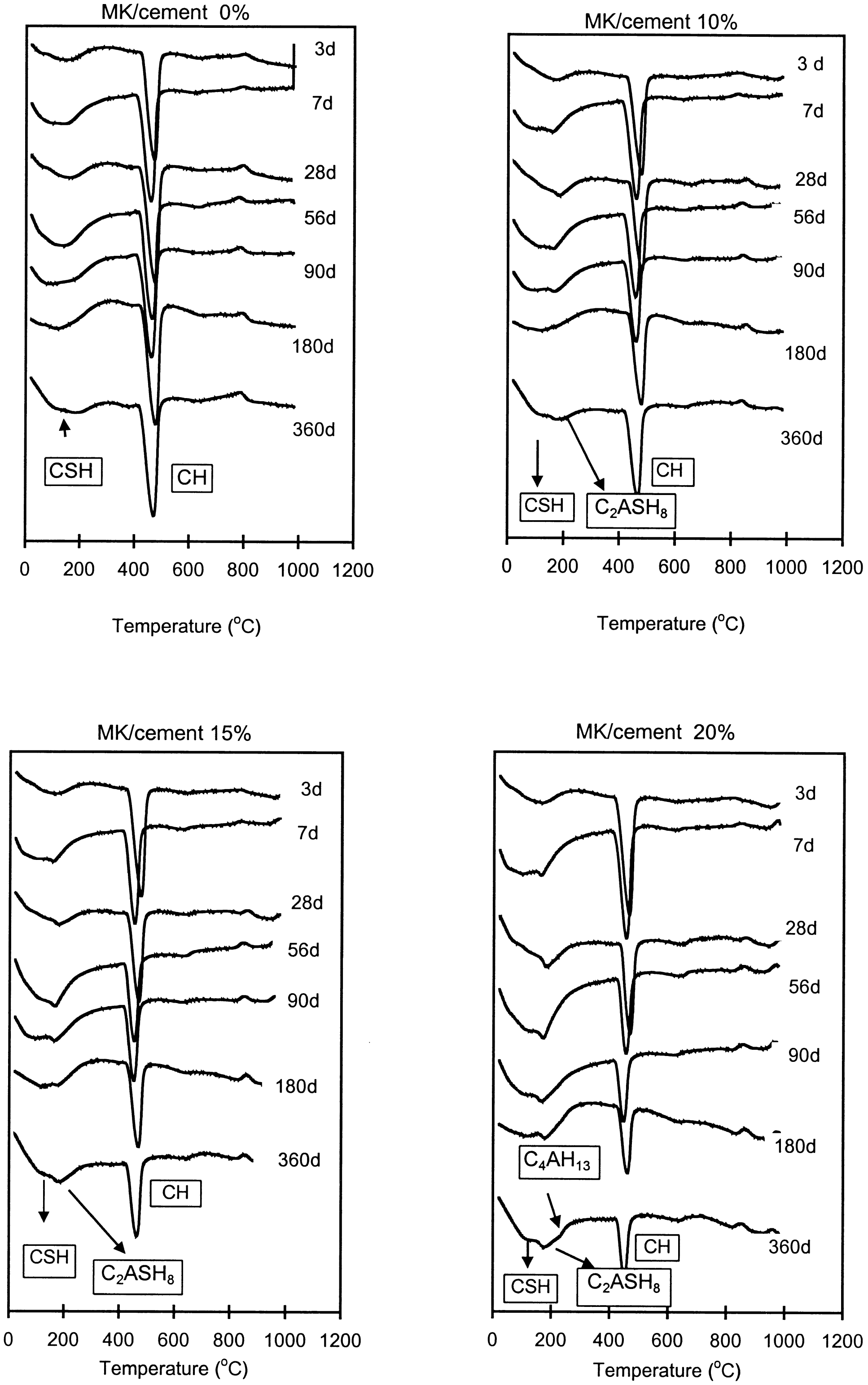

Fig. 4. DTA curves for blended cements containing 0%, 10%, 15%, and 20% of MK.

3. Results and discussion

3.1. Reaction kinetics in an MK/lime system

Fig. 2 shows the evolution in the DTA thermograms as hydration progressed. In a previous paper, we [13] reported that the rate constant obtained by the Jander mathematical model in MK/lime system at 20°C was 83.3 times smaller than that obtained at 60°C. Due to this fact, important differences in consumed lime contents and in the appearance of hydrated phases between 20°C and 60°C were detected.

CSH appears at 2 days, while C_2ASH_8 and C_4AH_{13} occur at 9 days of curing time. The content of both calcium aluminate hydrates increases with curing time, further information in Ref. [13].

Beyond 90 days of curing time, the lime is totally consumed by pozzolanic reaction, fact will be in agreement with a prior study [14], which reported that MK reacts with 1.2 times its mass of portlandite. Subsequently, another endothermic peak was detected about 360°C, which could be attributed to CSH [15].

Fig. 3 illustrates the XRD patterns in MK/lime pastes at 20°C. Gehlenite is clearly detected as a predominant crystalline phase beyond 9 days, C_4AH_{13} is not clearly observed, on the one hand due to its low degree of crystallinity and the overlapping of the reflection peaks; mainly with C_2ASH_8 and C_4ACcH_{11}. According to De Silva and Glasser [10], the C_4ACcH_{11} has thermodynamic properties similar to the C_4AH_{13}. Hydrogarnet is not detected up to 360 days, indicating this phase to be associated with high curing temperature. Further information about the influence of the temperature on the kinetic reaction in MK–lime–water system is shown in Refs. [12,13].

These results indicate that C_4AH_{13} does not disappear with curing time. De Silva and Glasser [9] reported that in a mixture of 50/50 wt.% of MK/lime, the C_4AH_{13} tended to disappear after 180 days. This phenomenon reported to be due to the loss of supersaturation of the aqueous phase with respect to calcium hydroxide.

The results of this investigation show some differences with the results of De Silva and Glasser. $Ca(OH)_2$ is consumed by 90 days of hydration time (Fig. 2); therefore, the persistence of C_4AH_{13} phase at 20°C is not clearly associated with the evolution of the lime content.

3.2. Reaction kinetics in MK/cement system

Figs. 4 and 5 show 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 hydrates present in a Portland cement are: CSH gel and CH (portlandite). In MK-blended cements, a peak also appear at about 170°C, which is attributed to the C_2ASH_8 phase.

C_2ASH_8 appears as the predominant phase of the pozzolanic reaction between MK and calcium hydroxide. The amount of this phase increases with the decrease of the lime content, hydration time, and mainly with the increase of MK contents. In all cases, C_2ASH_8 is detected at 7 days of curing time, except for MK contents between 20% and 25%, in which this hydrated phases appears at 3 days.

Comparing the results with those obtained from MK/lime system, it is possible to observe that MK shows an accelerating effect on the hydration reaction. In MK/lime systems, C_2ASH_8 appears at 9 days of hydration, while in blended cements this phase is detected between 3 and 7 days, depending on the MK contents.

Another important aspect obtained from DTA curves is the appearance of a weak endothermic band at 220°C and after 180 days in blended cement with a 20% and 25% of MK. This band is assigned to the C_4AH_{13} phase.

Fig. 6 shows the evolution of the crystalline compounds of MK-blended cements at 180 and 360 days of hydration time. Portlandite and unhydrated cement particles are present. The intensities of the portlandite peaks decrease with the amount of MK and with hydration time.

In the case of blended cements containing 20% and 25% of MK (Fig. 7), the XRD patterns show traces of C_2ASH_8 phase (weak peak at 7.2 (2θ)). This fact means the very low crystallinity of C_2ASH_8 phase in blended cements with respect to MK/lime pastes.

These findings totally agree with prior results. Ambroise et al. [16] only detected the presence of C_2ASH_8 in blended cement with MK contents of 30% or more at 28 days of curing time. SEM examinations showed that the matrix was poorly crystalline. However,

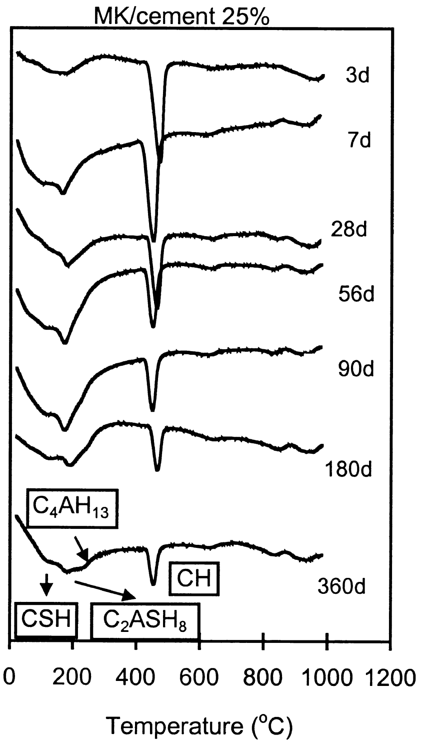

Fig. 5. DTA curves for blended cement containing 25% of MK.

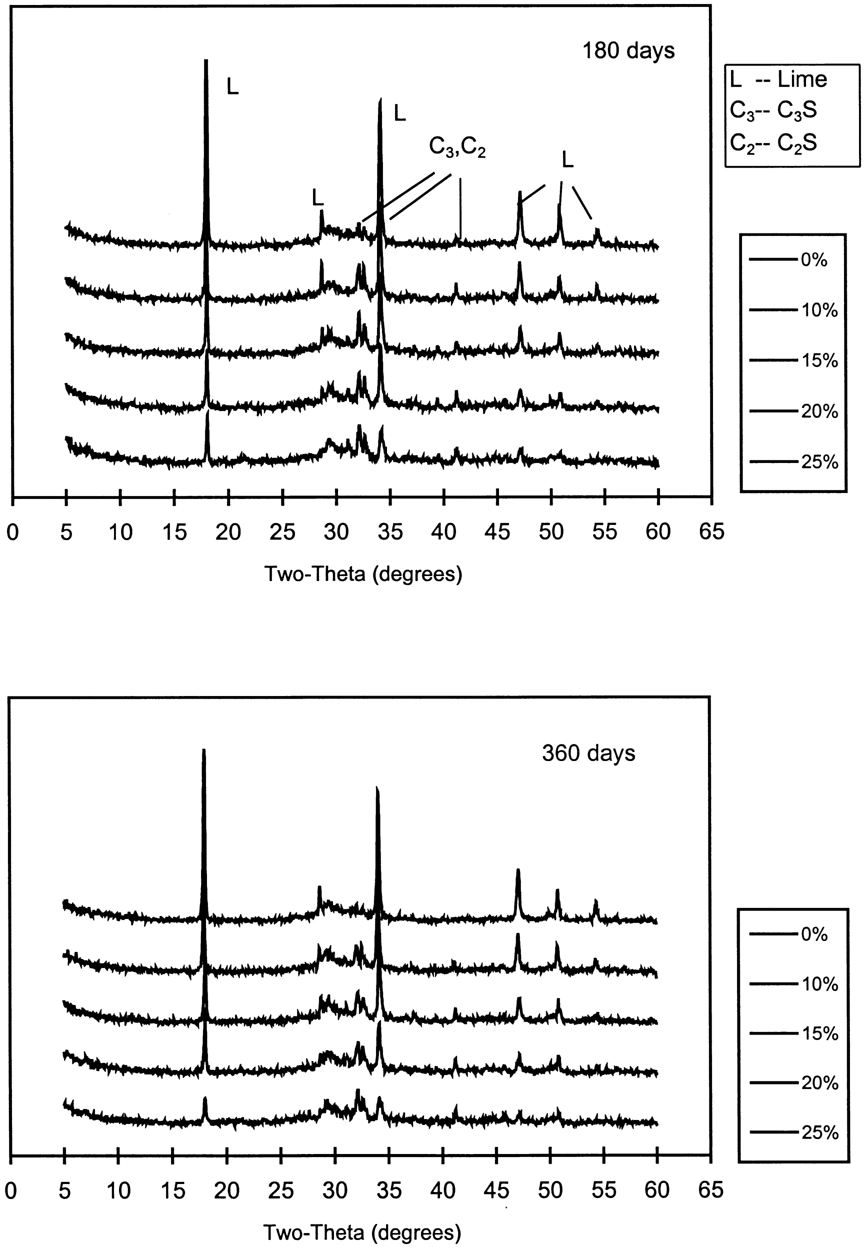

Fig. 6. XRD patterns for MK-blended cements at 180 and 360 days of hydration time.

the study carried out at different C_3S/MK ratios, C_2ASH_8 was identified in all mixes.

The results obtained here from DTA analysis indicate the sequence of phase development, C_2ASH_8 and C_4AH_{13}, to be closely related to matrix used. In the MK/lime matrix (1:1 in weight), C_2ASH_8 is formed in parallel with the C_4AH_{13}, increasing their contents with the hydration time. However, in blended cement matrices (up to 25% of MK), C_2ASH_8 is the main hydrated aluminate compound and only a small amount of C_4AH_{13} is detected in matrices cured longer than 180 days and with MK contents at least 20%.

These results differ from those of Sersale and Orsin [17]. They studied different pozzolans with saturated calcium hydroxide at 20°C, reporting that high concentration of SiO_2 and Al_2O_3 favors the formation of the C_2ASH_8, while the C_4AH_{13} is formed from glasses high in SiO_2 and low in Al_2O_3, except for slag glasses.

The absence of C_4AH_{13} in MK-blended cement studied in this work is difficult to interpret and might be related to different phenomena, which could be compatible at the same time:

1. The cement used in this study contained 24% (value obtained from TG analysis) of calcium hydroxide after 1 year of curing. Assuming that the calcium hydroxide liberated by a fully hydrated cement could be about 24–25%, the MK/lime ratio would be equal or above

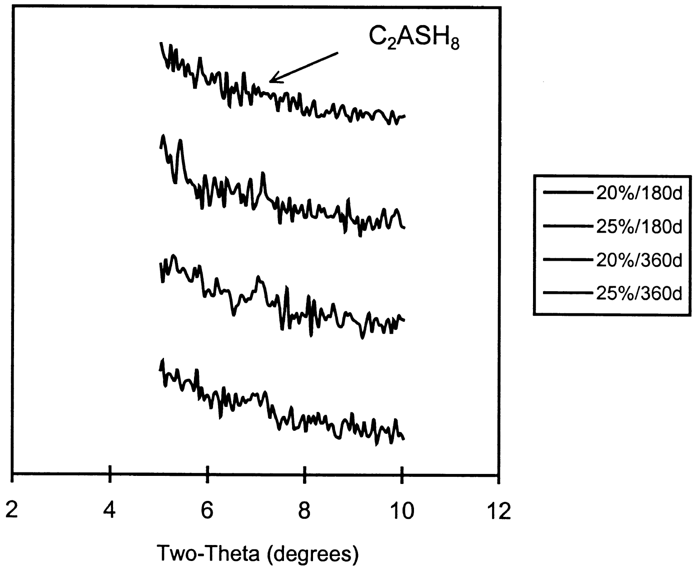

Fig. 7. XRD patterns (between 2 and 12 (2θ)) for blended cements with 20% and 25% of MK at 180 and 360 days of hydration time.

1. This ratio would favor the C_2ASH_8 formation, taking in account the competitive of hydration reaction proposed by Murat [4].
2. The presence of alkalis from cement as well as MK can increase the pH value above 12.5 (value supplied by $Ca(OH)_2$). This decrease the solubility of calcium hydroxide and therefore, the soluble portlandite content could be insufficient to form the C_4AH_{13}.
3. Another important aspect of the absence of C_4AH_{13} in the reaction kinetics of MK-blended cement could be related to the presence of SO_4^{2-} ions in matrix (from Portland cement). This fact is in agreement with the observations realized by De Silva and Glasser [10] that the tetracalcium aluminate hydrated phase either is not present or is present only in traces in the sulfate-activated systems.

Thus, the presence of some activators (from Portland cement) in the pozzolanic reaction (alkalis, SO_4^{2-}) can alter the pozzolanic reaction kinetics, impeding or delaying the C_4AH_{13} formation and favoring the C_2ASH_8 formation, as a poorly crystalline phase.

4. Conclusions

From the results presented in this paper, the following conclusions are offered:

1. The mechanism of hydration of the pozzolanic reaction is closely related with the matrix used.
2. In an MK/lime system (1:1 in weight), the sequence of appearance of hydrated phases is clearly showed in Fig. 2. The CSH is detected at 2 days of hydration time, followed by C_2ASH_8 and C_4AH_{13}. These two phases are detected at the same time.
3. In an MK/cement system (up to 25% of MK), the development of the hydrated phases presents a different behavior to the MK/lime system. The C_2ASH_8 is detected between 3 and 7 days of curing time and it depends on MK contents. Subsequently, the C_4AH_{13} is possibly formed between 180 and 360 days. This phase is only detected with high MK contents, mainly with 25% of MK. Below 20% of MK, this phase is not identified.
4. In the XRD patterns for the MK/lime systems, the C_2ASH_8 is only identified as a crystalline hydrated phases, but not the C_4AH_{13}. This fact indicates very low crystallinity of the C_4AH_{13} with respect to the C_2ASH_8 phase.

   In MK-blended cement, XRD show that the C_2ASH_8 formed during the pozzolanic reaction is an amorphous compound (Fig. 7) and on prolonged hydration it is possible to identify a very weak peak with high MK contents.
5. As was mentioned before, the pozzolanic reaction in a blended cement matrix is more complex that in an MK/lime matrix, because of the presence of different ions (CO_2^{2-}, SO_4^{2-}, alkalis, chlorides), which could alter the kinetics as well as the development and crystallinity of the hydrates phases. It is due to the changes in solubility and evolution of the concentrations of the majority compounds (CaO, Al_2O_3, and SiO_2). The final result from all these is that there is no formation of the C_4AH_{13} up to 180 days and the formation of an amorphous C_2ASH_8.

In spite of these investigations, it is necessary to carry out further research on this matter, which will provide more details about the agents' or mechanisms' influence in pozzolanic reaction.

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