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Study of hydrated phases present in a MK–lime system cured at 60 °C and 60 months of reaction

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Abstract

This research presents the experimental results of a study carried out to determine the effect of curing temperature on the reaction kinetics in a metakaolin/lime mixture cured at 60 °C and after 60 months of hydration. The stabilities of hydrated phases formed during the pozzolanic reaction in these working conditions were evaluated. The results obtained in current paper showed that metastable hexagonal phases (C_2ASH_8 and probably C_4AH_{13}) coexist with stable cubic phase (hydrogarnet) in the absence of lime. Also, there is evidence of the possible presence of a calcium aluminum silicate hydroxide hydrate (vertumnite).

Keywords: Metakaolin; Lime; Hydrated phases stability; High curing temperature; Long hydration times

1. Introduction

Many studies have showed the positive benefits of metakaolin, incorporated in blended cement pastes, mortars and concretes [1–5]. When MK reacts with calcium hydroxide, cementitious products are formed. 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, de Silva and Glasser [6] reported significant changes in phase development between with curing temperatures of 20 and 55 °C. The C_2ASH_8 and C_4AH_{13} phases are not stable and can transform 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.

Similarly, Khabit and Wild [7] and, Frías et al. [8,9] reported refinement of the pore structure and an increase of total intruded pore volume in MK-blended pastes cured at 20 °C. Also, Sabir et al. [10] reported that the MK is a very effective pozzolan, altering the pore structure of the cement paste and greatly improving its resistance to the transport of water and diffusion of harmful ions leading to degradation of the matrix. Frías et al. [11] reported that MK exhibits lower pozzolanic activity than silica fume, but significantly greater pozzolanic activity than fly ash.

In spite of the excellent qualities showed by MK as pozzolanic material, its use is in part conditioned by a generalised concern about possible conversion of metastable hexagonal hydrates (C_2ASH_8 and C_4AH_{13}) to stable cubic phase (siliceous hydrogarnet with variable composition, $C_3AS_zH_{6-2z}$), when samples are submitted to high curing temperatures [6]. This phenomenon may lead to a negative influence on the performance of MK blended matrixes, mainly on durability.

Recent researches carried out by Frías et al. [12–14] found metastable hexagonal phases coexisting with stable cubic phase in MK/lime system cured at 60 °C for both short and medium terms (up to 9 and 123 days of curing). This suggested that the hydrogarnet formed directly from pozzolanic reaction and not as result of a conversion reaction. Furthermore, these authors noted the absence of hydrogarnet in MK blended cement systems. These findings were very important from what the microstructural point of view had on implications for durability.

Nowadays, researching works on reaction kinetics between MK and lime at very long hydration periods were not found in bibliography and on the other hand, factors as curing

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Table 1
Chemical composition for starting metakaolin

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	L.O.I.
MK(%)	51.6	41.6	4.64	0.09	0.16	–	0.01	0.62	0.83	0.6

temperature and hydration time are well known of playing an important role in pozzolanic reaction. For this reason, the current work shows the results of an experimental study on the reaction kinetics of pozzolanic reaction in MK/lime mix cured at 60 °C for up to 60 months in order to evaluate the effect of high curing temperature and long hydration times on the formation and stability of hydrated phases formed during pozzolanic reaction.

2. Experimental

A commercial metakaolin available in the UK was used. Its chemical composition is given in Table 1. The lime used was commercial analytical grade calcium hydroxide (minimum 95% of purity).

The metakaolin and $Ca(OH)_2$ was mixed in the ratio of 1 : 1 by weight and enough distilled water was added to produce a slurry. The water/solid ratio that resulted in a satisfactory slurry mix was 2.37. The mix was placed in sealed plastic containers, introduced in a glass bottle with water and maintained in an oven at 60 °C until testing. The hydration time selected for the study was 60 months. After the appropriate hydration time, sample was taken from the plastic containers and dried to constant weight in a commercial oven at 60 °C.

3. Results and discussion

3.1. Hydrated phases present by thermal methods

DTA and TG thermogravimetric analyses were used to identify and estimate the presence of hydrated phases after 60 months of testing. The curves were obtained on 28.08 mg of sample, using a thermal analyzer in nitrogen with a heating rate of 10 °C/min.

Fig. 1 shows the evolution of TG curve. Two main weight losses were detected. From 100 to 330 °C with a weight loss of 11.86%, observing an inflexion point at 220 °C and, between 635 and 733 °C the second weight loss (4.4%) was observed.

According to Fig. 2, these weight losses correlate with the different endothermic effects: in the first interval, an endothermic band appears as a wide shoulder of main endothermic peak (up to 160 °C, inflexion point), indicating the presence of calcium silicate hydrate (CSH) and, finally an endothermic maximum peak (230–330 °C) localized at 292 °C, corresponds to decomposition of hydrogarnet, $C_3Al_2\,(Si0_4)\,(0H)_8$ [15]. Finally, the endothermic peak at 635–733 °C is related to the decomposition of calcium carbonate. No calcium hydroxide was detected in the DTA thermogram.

The endothermic effect at 215 °C corresponds to a wide band which could indicate the coexistence of metastable hydrated phases (C_2ASH_8 and C_4AH_{13}), identified in a previous paper. Frías et al. [12,14] reported on the reaction kinetics for the MK/lime system that at very short term (9 days) C_2ASH_8 and C_4AH_{13} phases appeared resulting in as two well defined endothermic peaks in DTA thermogram (160 and 210 °C, respectively). But for longer curing times (123 days), both peaks merged forming a wide band with a maximum situated around 215 °C and where traces of lime was only detected.

Therefore, this peak still persists after 60 months of curing.

It is important to note that the endothermic peaks correspond to the metastable phases (215 °C) and cubic phase (292 °C) showed a similar weight loss, 4.8 and 4.3 respectively. This tendency is different to that observed in Ref [12] in which hydrogarnet was the predominant cubic phase with respect to the metastable phases.

3.2. Hydrated phases present by XRD

Fig. 3 illustrates the XRD pattern for a MK/lime system at 60 °C of curing temperature. Stralingite was clearly detected as a predominant crystalline phase at 60 months of reaction.

A hydrogarnet belonging to the C_3AH_6–C_3AS_3 series was identified as stable phase in the $Ca0$–Al_20_3–$Si0_2$–H_20 system at high temperatures. The diffraction peaks situated at 17.4, 20.2,

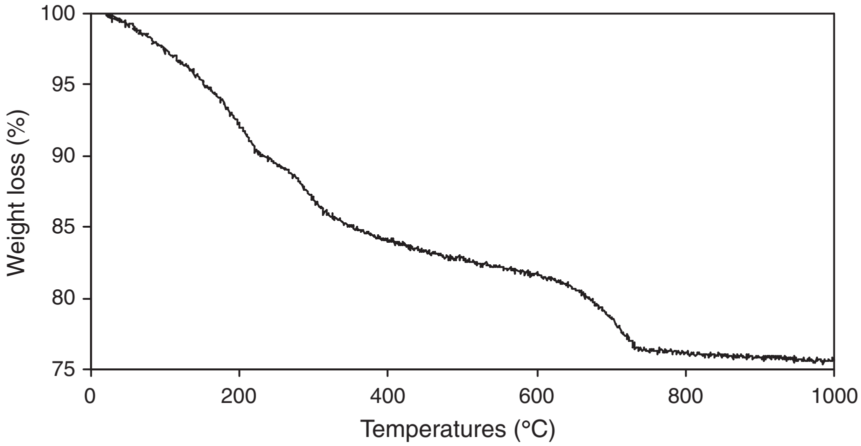

Fig. 1. TG curve for MK/lime paste.

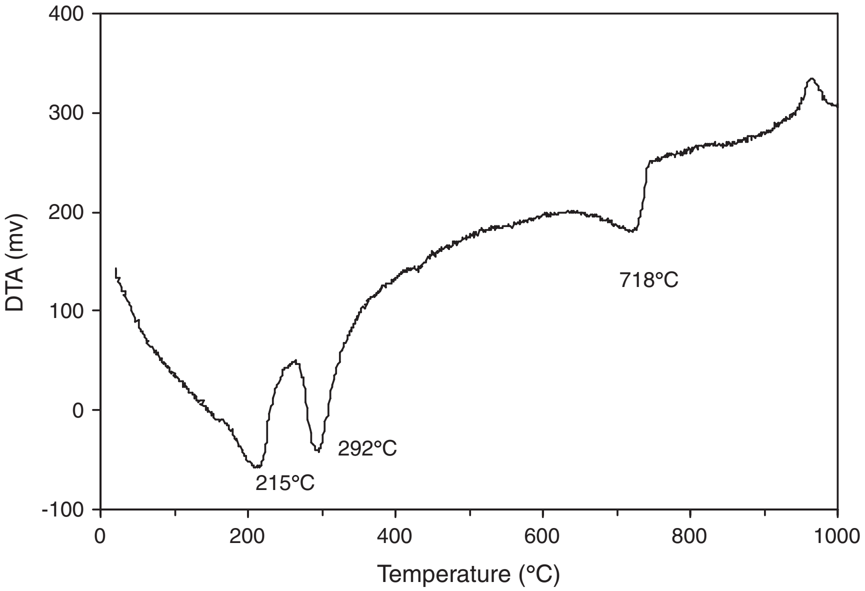

Fig. 2. DTA curve for MK/lime paste.

26.7, 32.1 (2-theta) corresponds to the hydrogarnet composition termed katoite $Ca_3Al_2(Si0_4)(0H)_8$, in which 4 hydroxyls in C_3AH_6 are replaced by silicate Si04.

The location of other reflection peaks situated at 36.6 and 52.55 (2-theta) could be also indicating traces of a hydrogrossular phase (nominally C_3AH_6) in these testing conditions, not detected in previous works. In forthcoming researches at longer hydration times (>60 months), a deeper study will be carried out in this research line in order to know the evolution of katoite and the possible mixture with other garnet phases.

Also, from the XRD diffractograms for the MK/lime system in these curing conditions, the authors of current paper note the possible existence of other crystalline compound, different to those reported before. Reflection intensities at 7, 14.1 and 21.2 (2-theta) could be attributed to vertumnite ($Ca_4Al_4Si_40_6$ $(OH)_{24}$ $3H_20$). Their reflection peaks are similar to the stratlingite which makes its identification difficult. Rinaldi et al. [16] showed that, the crystal structures of stratlingite and vertumnite are made up of the same structural modules consisting of: a) an "octahedral" or "brucite type" and b) a double tetrahedral layer.

According to the reflection peak list, there is a peak situated at 36.8 (2-theta) which appears for vertumnite but and not for stratlingite. The appearance of this peak in XRD curve (Fig. 4) would indicate the possible presence of a calcium aluminum silicate hydroxide hydrate not detected up till now in a MK/lime system cured at elevated temperatures. From studies reported by Van Aardt and Visser [17] and Regourd et al. [18] about the different vertumnite formation mechanisms , the MK/lime system has the suitable conditions (C_4AH_{19} is structurally derived from C_4AH_{13} by addition of an extra layer of H_20

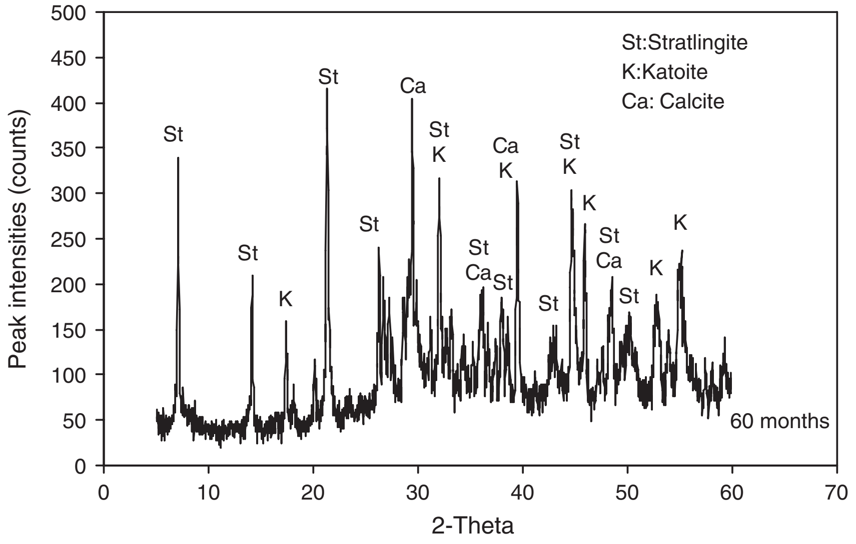

Fig. 3. XRD pattern for MK/lime paste.

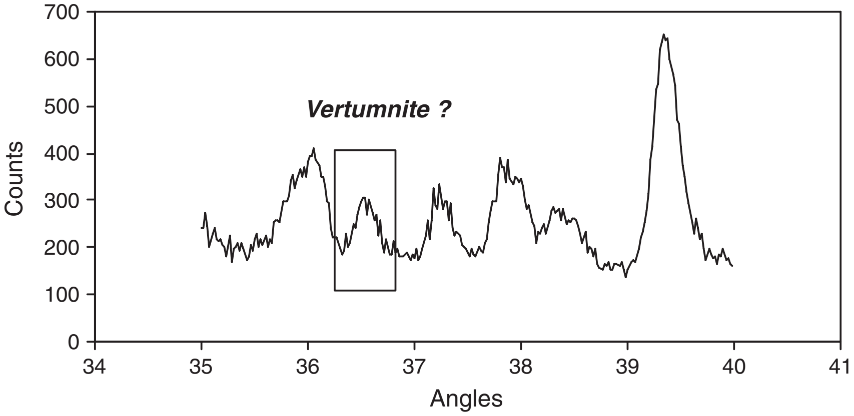

Fig. 4. XRD pattern for MK/lime paste in the interval 35–40 (2-theta).

molecules, amorphous silica coming from MK in excess and total absence of lime after 60 months of reaction) so that a possible formation of vertumnite can not be excluded at the present.

Calcite is also present in the sample as crystalline compound due to possible carbonation of the lime during the different stages before testing (manufacture, hydration period, dried in oven, grinding and sifted, etc.) without forgetting the presence of carbonates as $CaCO_3$ in starting sample, according to the certificate of analysis (maximum 5%). C_4AH_{13} hexagonal phase was not observed by XRD pattern, probably due to its low degree of crystallinity.

From DTA and XRD data, it is possible to confirm that after 60 months of reaction and 60 °C of curing temperature, the stratlingite and hydrogarnet were the predominant hydrated phases produced during the pozzolanic reaction in the absence of portlandite. These phases, metastable (stratlingite) and stable (hydrogarnet), persisted in these conditions. This fact supports the results published previously by authors of present paper in previous works (up to 123 days of curing), that hydrogarnet is produced directly from pozzolanic reaction, not through a transformation reaction.

There is no a clear evidence of the presence of C_4AH_{13}. This can be due to a very low crystallinity of this phase which is difficult to identify by XRD as well as its endothermic peak will be overlapped with the endothermic peak of stratlingite according to Serry et al [19]. They reported that the endothermic peak for the stratlingite moved toward higher temperatures with the hydration time increased in 50 : 50 MK/lime mixes.

With respect to the possible formation of vertumnite which cannot be excluded this could have the following explanation: in these testing conditions and in absence of lime, could produce the reaction between C_4AH_{13} and the excess of amorphous silica from MK (mixes 50 : 50) to produce other metastable phase named vertumnite. If this fact happens this way, no presence of C_4AH_{13} in XRD and DTA data will be justified. Further researching is being carried out to know this possible alternative.

4. Conclusions

Based on the results obtained in this paper, the following conclusions are raised:

1. DTA curve showed the presence of CSH and the coexistence of metastable and stable phases in a MK/lime system cured at 60 °C for 60 months of hydration.
2. The metastable phase was assigned to stratlingite (C_2ASH_8) and probably to C_4AH_{13}. The stable phase was attributed to katoite, a hydrogarnet structured phase.
3. XRD pattern confirmed the presence of stratlingite and katoite as main crystalline compounds present under tested conditions.
4. From these results, it does not discard the possibility of what is forming as a tetra calcium aluminum silicate hydrate as metastable phase. This research line needs deeper studies in order to clarify the mechanism of its formation.

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