Pergamon

Cement and Concrete Research 32 (2002) 133–138

CEMENT AND CONCRETE RESEARCH

The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime–water systems

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Received 29 August 1999; accepted 30 July 2001

Abstract

The paper presents the results of a study carried out to determine the effect of curing temperature on the kinetics of reaction of a metakaolin (MK)/lime mixture. MK and analytical grade $Ca(OH)_2$ were mixed in a ratio of 1:1 by weight and with a water/binder ratio of 2.37. Specimens were cured at 20 and 60 °C. In the first case, the curing time varied from 2 h up to 180 days and, in the second case, from 2 h up to 123 days. A mathematical model was applied to calculate the rate constant for the hydration reaction. The identity and the amount of the phases present were determined from thermal analysis (TG and DTA) data. The results showed that the rate constant for the samples cured at 60 °C was 68 times greater than the rate constant at 20 °C for the same curing period (up to 9 days). At 20 °C, the sequence of appearance of the hydrated phases was C–S–H, C_2ASH_8 and C_4AH_{13}; while at 60 °C, the sequence was C–S–H, C_2ASH_8, C_4AH_{13} and hydrogarnet (C_3ASH_6). There is no evidence of further C_2ASH_8 and C_4AH_{13} transformation into hydrogarnet in the mixture studied for 123 days at 60 °C. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Lime; Pozzolanic reaction; Reaction kinetics; High temperature

1. Introduction

In recent decades, pozzolanic materials have been used for construction, mainly because of their influence on the microstructure and durability of the blended concrete [1–3]. One such pozzolan is metakaolin (MK), material obtained under a carefully controlled process of thermal activation of kaolinite clay [4–6]. The kaolinite is dehydrated at 600–700 °C, which causes major structural disorganization and significant increase in pozzolanic activity. In the previous works [7–9], the positive effect of MK on the properties of blended cements has been shown. So, MK improves workability, microstructure, mechanical strength as well as less permeability, higher durability that the equivalent opc matrix. These advantages allow its use in new application fields, for example, immobilization of wastes [10].

Frías et al. [11] reported that MK exhibits lower pozzolanic activity than silica fume, but significantly greater pozzolanic activity than fly ash. This fact is related to chemical and mineralogical composition, pozzolanic activity, fineness, etc. It is well documented that the main phases that form during the pozzolanic reaction between MK and lime at ambient temperature are C–S–H, C_2ASH_8 and C_4AH_{13}. Different factors can influence the reaction kinetics and the amounts of the hydrated phases produced [6,12,13]. Among them, curing temperature is the most important factor because it influences on the stability and the transformation of the hydrates.

Silva et al. [14] reported significant changes 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 convert into hydrogarnet at elevated temperatures. However, Cabrera and Frías [15] made a detailed study of the pozzolanic reaction between MK and lime, showing that the main phases produced and their evolution at 60 °C and early hydration times (from 2 h to 9 days). 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.

The present investigation focuses on the influence of curing temperature on the mechanism of reaction in MK–

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PII: S0008-8846(01)00642-1

lime systems. This investigation reports the behavior of the MK/lime reaction at 60 °C, in the period between 0 and 123 days. These results are compared to similar results obtained at 20 °C (up to 180 days). A mathematical model is applied to calculate the reaction rate constants. The sequence, evolution and semiquantitative studies of the hydrated phases were followed by TG/DTA thermograms, which give valuable information about the nature of the reaction products and their stability with hydration time.

2. Experimental

An English commercial MK was used, with a content of 51.5% of SiO_2, 41.3% of Al_2O_3, 4.64% of Fe_2O_3, 0.1% of CaO, 0.16% of MgO, 0.63% of alkalis and 0.83% of TiO_2. A value of 15.5 m^2/g of specific surface and 130 Å of average pore diameter were obtained using BET technique. The mineralogical analysis obtained from XRD showed that MK is mostly amorphous, but includes small amounts of quartz and micas (muscovite) as crystalline compounds.

The MK was mixed with analytical grade calcium hydroxide in the ratio 1:1 by weight. The water/binder ratio of 2.37 by weight was kept constant in all cases. Mixtures were placed in plastic airtight containers and cured in two ways. One set was left in a water bath at 60 °C for 0 h, 2 h, 6 h, 12 h, 21 h, 30 h, 2 days, 3 days, 5 days, 9 days, 23 days, 34 days and 123 days. The other set was placed in a curing room at 20 °C and 100% RH, and maintained for 2 h, 8 h, 21 h, 30 h, 2 days, 3 days, 5 days, 9 days, 23 days, 56 days, 90 days and 180 days. After the appropriate hydration times, small samples were taken from the plastic containers and dried during 9 min in a commercial microwave oven at 105 °C. Further information in Ref. [15].

3. Results and discussion

3.1. Influence of curing temperature on lime consumption

The reaction between MK and lime was studied at 20 and 60 °C. The analytical method consisted of measuring the amount of lime left at different time intervals. The amount of $Ca(OH)_2$ in cementitious materials can be measured quantitatively by thermal analysis. The amount of total calcium hydroxide present in the mixture was calculated from the weight loss due to the dehydroxilation of $Ca(OH)_2$ (at about 400–500 °C) and decarbonation of $CaCO_3$ (at about 600–750 °C). The results of lime consumption versus time are presented in Fig. 1. A different trend of decreasing lime content as the temperature increases is shown. In the samples cured at 60 °C, lime is rapidly consumed during the first 120 h (Fig. 1). Between 5 and 9 days, the amount of transformed lime at 60 °C is approximately 65% higher than that at 20 °C. Total lime consumption was 63%, 82% and 92% at 2, 9 and 34 days, respectively. Beyond 34 days (between 34 and 123 days) of curing time, there is only an additional 1% of lime reacted.

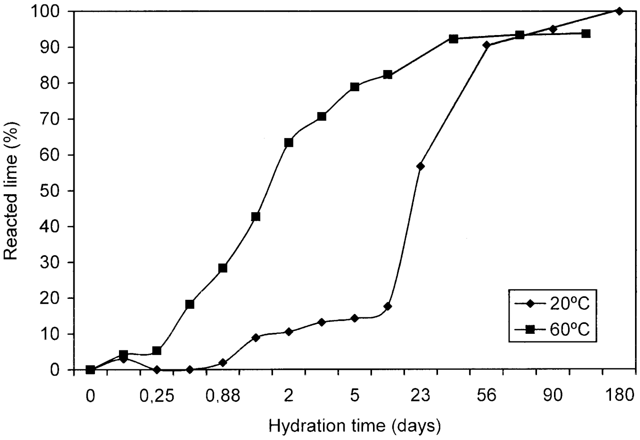

Fig. 1. Evolution of reacted lime with curing time at different temperatures.

The curve corresponding to the samples cured at 20 °C shows that lime is consumed at a slower rate than that at 60 °C. It is interesting to point out that the total consumption of lime was 10%, 17% and 90% at 2, 9 and 56 days, respectively. However, at 180 days of curing time, lime had totally reacted by pozzolanic reaction.

These results reveal an important increase in the activity of MK between 7 and 56 days at 20 °C, while in the same samples cured at 60 °C, the interval of maximum pozzolanic activity is detected between 6 h and 2 days. The results seem to shed some light on previous works. Kostuch et al. [8] reported that the presence of MK 10 and 20% in blended concrete increased its compressive strength between 7 and 90 days of curing compared with the conventional concrete. Wild et al. [16] also reported the positive effect of MK on the strength of concrete beyond 7 days.

3.2. Reaction rate constants

Ramezanianpour and Cabrera [17] and Plowman and Cabrera [18] showed that both pozzolanic and hydration reaction mechanisms are controlled by the diffusion phenomenon. During this investigation, two possible mechanisms based on the dissolution models developed by Jander [19] and Ginstling and Brounshtein [20] were investigated. The kinetic model that best fit the present results, both 20 and 60 °C, was that of Jander. This model is based on a variation of Fick's law, assuming that the rate of thickening of the reaction products is inversely proportional to its thickness. The Jander equation is:

$$[1-(1-x)^{1/3}]^2 = 2kt/r^2 = Kt$$

where: x = fraction of sphere which has reacted, t = time of reaction (h), r = radius of reacting sphere, k = parabolic rate constant, K = constant proportional to k.

Fig. 2 shows the $F(x)$ values versus curing time, regression lines and correlation coefficients at 20 and 60 °C that we obtained using this model. The slopes of the lines were used to determine the reaction rate constants (K) for MK. The experimental points were separated into two groups (0–120 h and beyond 120 h up to the end to the curing time). Linear regression analysis was carried out on each group. Values of the rate constants (K) for MK are:

	K_1 (1st group)	K_2 (2nd group)
For 20 °C	0.22×10^{-4}	2.48×10^{-4}
For 60 °C	15.1×10^{-4}	2.87×10^{-4}

The maximum values of K show clearly the difference on pozzolanic reaction rate with curing temperature. At 60 °C, the reaction rate constant (K) was 15.1×10^{-4}, while at 20 °C it was only 2.48×10^{-4}. It is important to highlight the fact that pozzolanic reaction rate at 60 °C (between MK and lime) is very high during the first 120 h of hydration compared to that at 20 °C for the same curing period (K_1 values). The results showed that the pozzolanic reaction rate was 68 times higher in samples cured at 60 °C than those cured at 20 °C. At longer curing times (beyond 120 h), the pozzolanic reaction rate at 60 °C is nearly identical to that at 20 °C (2.48 against 2.87×10^{-4}).

3.3. Influence of temperature on the kinetics of reaction

Fig. 3 shows the DTA thermograms for the MK/lime system as a function of curing time at 20 °C. At the first hours of reaction (up to 2 h), the thermogram shows only one endothermic peak at about 450 °C which it is attributed to the decomposition of $Ca(OH)_2$. At 2 days, a very weak endothermic peak about 110–120 °C is detected. This effect indicates the presence of hydrated calcium silicate. Between 5 and 9 days of curing time, it is possible to detect the presence of C_2ASH_8 (stratlingite) and C_4AH_{13} at about 160 and 210 °C, respectively. For prolonged hydration (up to 180 days), the amounts of these phases increase.

After 90 days, a new endothermic peak appears at about 350 °C, which is also interpreted as loss of water molecules from the C–S–H gel; since X-ray data published in Ref. [21], there is no evidence of the presence of hydrogarnet as crystalline compound.

The temperature of 60 °C accelerates the rate of hydration (Fig. 4). Important changes in the phase development pattern are detected between 60 and 20 °C. At 60 °C and 6 h, the presence of C–S–H is detected and, 6 h later, C_2ASH_8 and C_4AH_{13} appear as predominant phases. Beyond 21 h, a new endothermic peak appears at about 310 °C, which was attributed to hydrogarnet. Beyond 9 days, a weak band

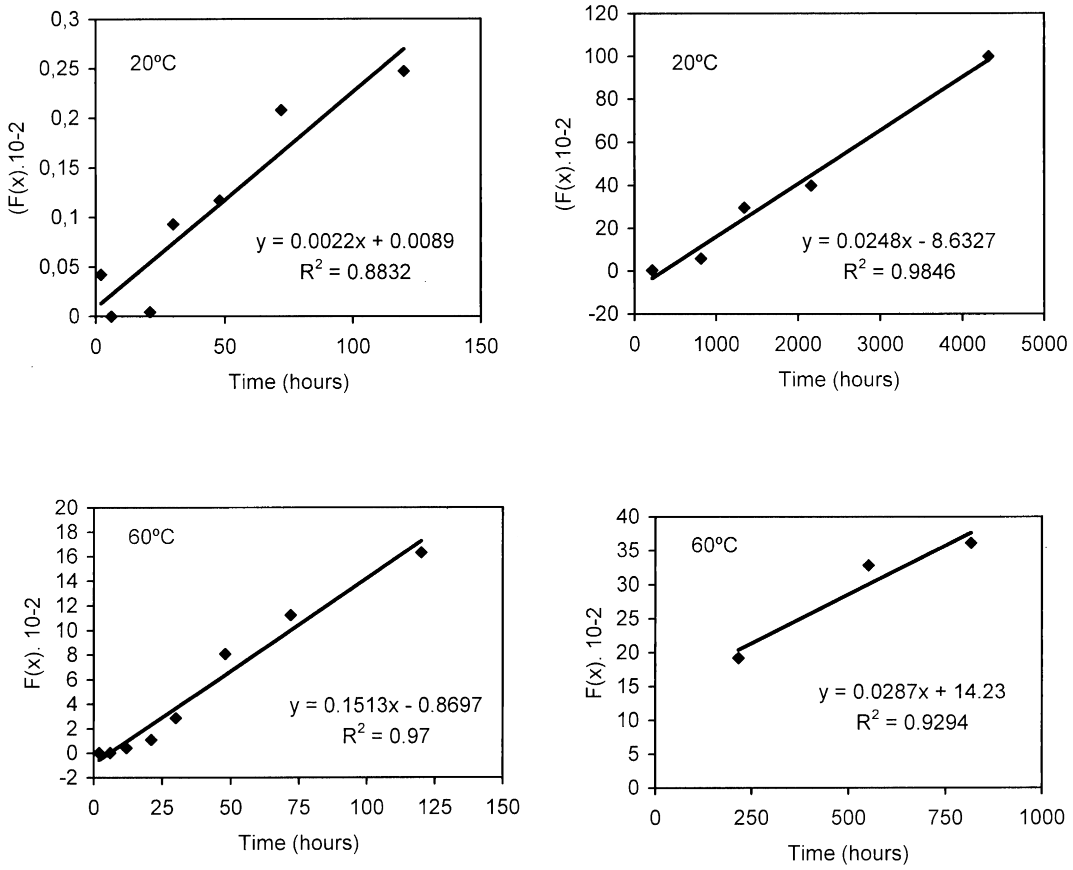

Fig. 2. Regression lines for the results obtained at 20 and 60 °C of curing temperature.

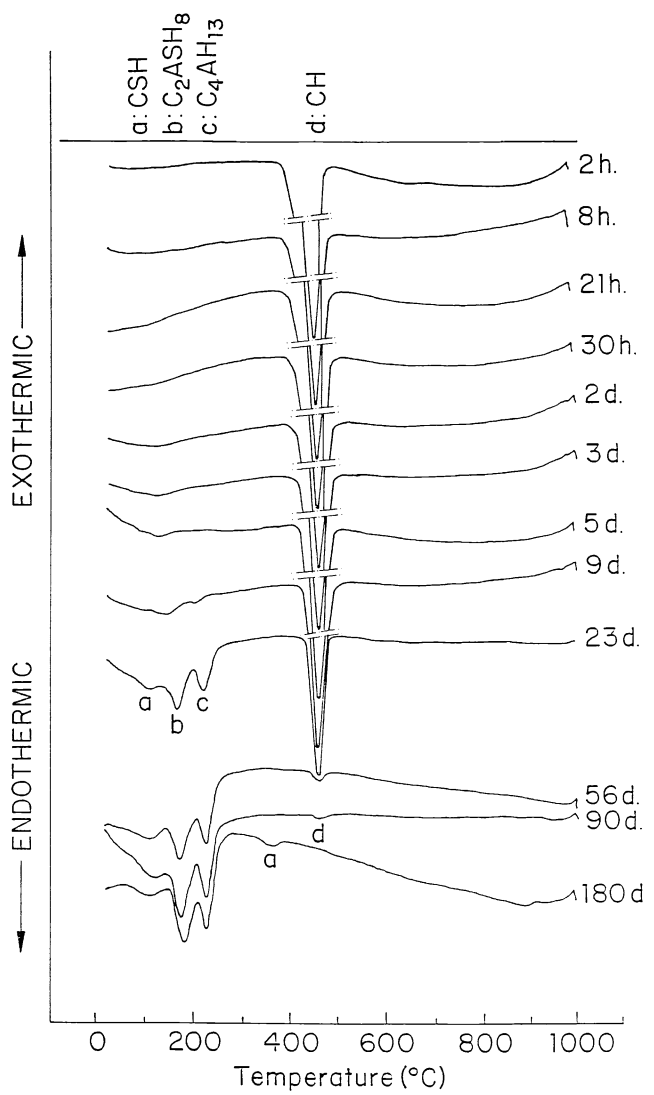

Fig. 3. DTA curves: evolution of hydrated phases with the time of hydration at 20 °C.

appears at about of 650–700 °C, corresponding to calcium carbonate. It is important to indicate that the two peaks corresponding to the metastable phases (C_2ASH_8 and C_4AH_{13}) experience a slight change, forming a wide band with a maximum situated at about 215 °C. This phenomenon might indicate an evolution from C_2ASH_8 to C_4AH_{13}. At this time, there is no explanation for this phenomenon, further studies at longer times of curing time are being carried out.

The hydration mechanism of MK/lime mix can be studied by the quantitative determination of hydrated phases from the results of TG analysis. Figs. 5 and 6 show the percentages of reaction products of the mixture under investigation calculated by this technique. At 20 °C (Fig. 5), the results indicate that the C–S–H appears at 2 days of hydration. It is clear that C_2ASH_8 and C_4AH_{13} are formed after 5 days (Fig. 5, right). In all cases, the C–S–H, C_2ASH_8 and C_4AH_{13} contents are sharply increased after 5–9 days until 60 days, followed by a slow increase (Fig. 5, left). This phenomenon corresponds to a pronounced decreasing in the $Ca(OH)_2$ content. According to the data exposed in Fig. 1, the 75% of lime is transformed in hydrated phases at this time period.

When the curing temperature increase (60 °C), a great difference on the hydration kinetic exists (Fig. 6). At the beginning of the reaction (up to 12 h), the predominant phase is the C–S–H gel. The figure shows also that rate of formation of C_2ASH_8 and C_4AH_{13} are notably influenced by curing temperature. The C_2ASH_8 and C_4AH_{13} appear after 6 h of reaction. The hydrogarnet is formed after 21 h and its amount increases with time. After 50 h (Fig. 6, left), this compound is the predominant phase, increasing with the decrease of the lime content up to 34 days. At longer times, the evolution is practically constant.

These findings are not totally in agreement with the investigations carried out by other researchers about stability of C_2ASH_8 and C_4AH_{13} with increase of temperature [14]. In the current paper, authors show that the phases C_2ASH_8 and C_4AH_{13} are metastable up to 123 days at 60 °C under the circumstances studied. This could be an indication

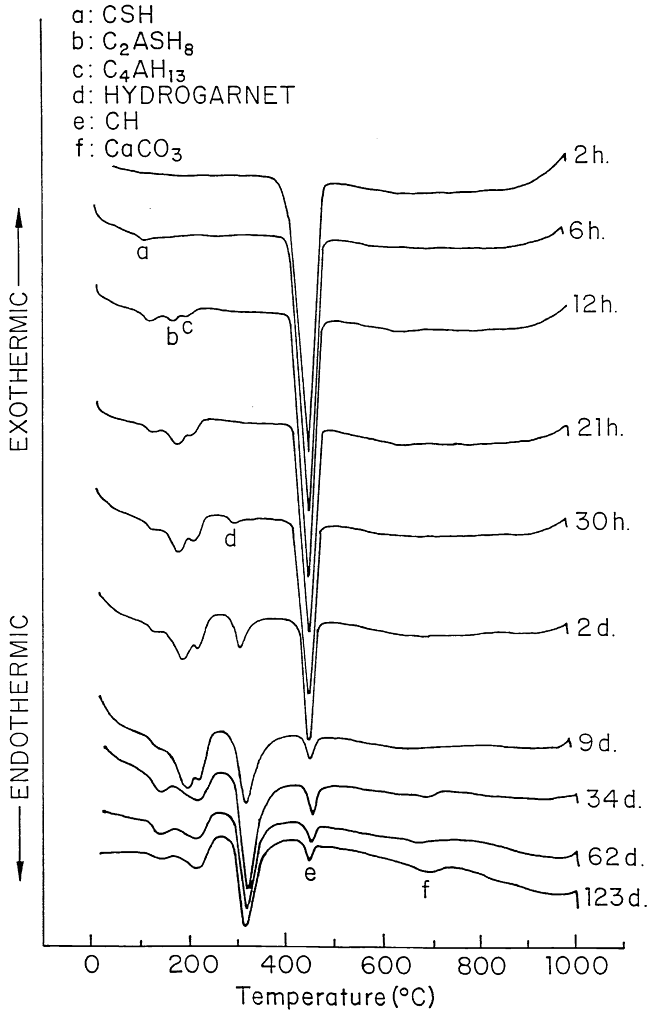

Fig. 4. DTA curves: evolution of hydrated phases with the time of hydration at 60 °C.

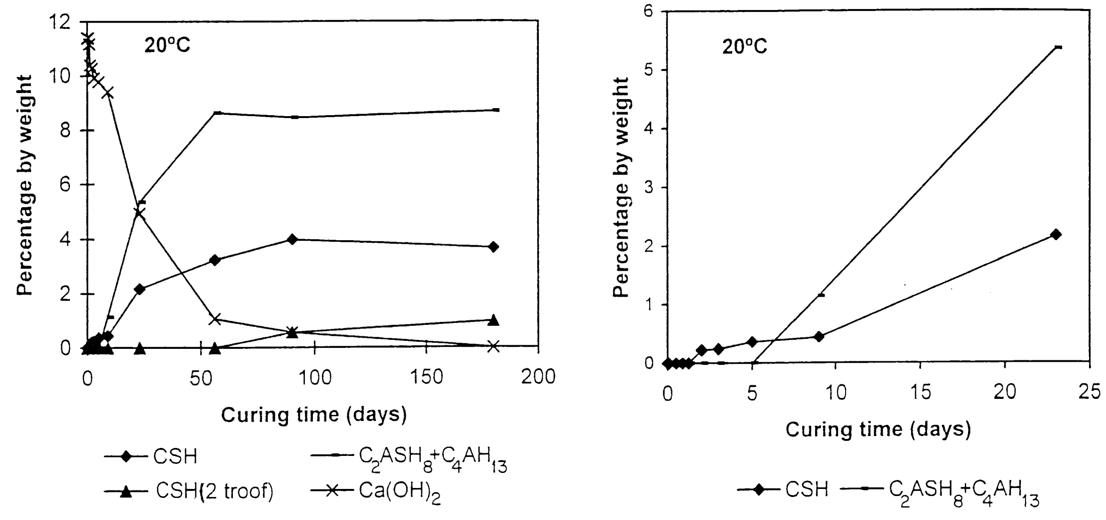

Fig. 5. Quantity of reaction products calculated from thermal analysis at 20 °C.

that C_3ASH_6 (hydrogarnet) is produced as a result of the pozzolanic reaction of MK and lime and not through a transformation reaction.

Also, Silva et al. [14] reported the disappearance of C_4AH_{13} at 90 days in specimens cured at 20 °C and in MK/lime mixes with a molar ratio of 1:3. This fact was due to the loss of saturation of the aqueous phase with respect to lime. However, the present investigation shows the presence of C_4AH_{13} up to 180 days, notwithstanding the fact that lime is not present after 90 days. This might be indicating that this compound could be a stable phase in absence of lime.

In general, the studies carried out here do not show any evidence of a possible decrease of the hexagonal hydrated phases amounts ($C_2ASH_8+C_4AH_{13}$) to cubic phase (C_3ASH_6) in samples curing at 60 °C. This phenomenon might be indicating the coexistence of different hydrated phases in presence of Ca $(OH)_2$ and, therefore, during this period, the presence of hydrogarnet in MK/lime mixture would not suppose a negative effect on the MK-blended concrete performance. However, long-term studies are being carried out to know the evolution of these metastable phases.

4. Conclusions

Studies carried out in the present paper showed that curing temperature plays an important role on the rate of formation of hydrated phases as well as in the amounts produced.

The following conclusions are deduced from the above studies.

(1) For the same curing period (9 days), the samples cured at 60 °C showed an 82% of reacted lime, while for the sample cured at 20 °C, it is only 18%. In the last case, the $Ca(OH)_2$ content disappears at 180 days (Fig. 3). However, the specimens cured at 60 °C show 6% left of lime at 123 days (Fig. 4).

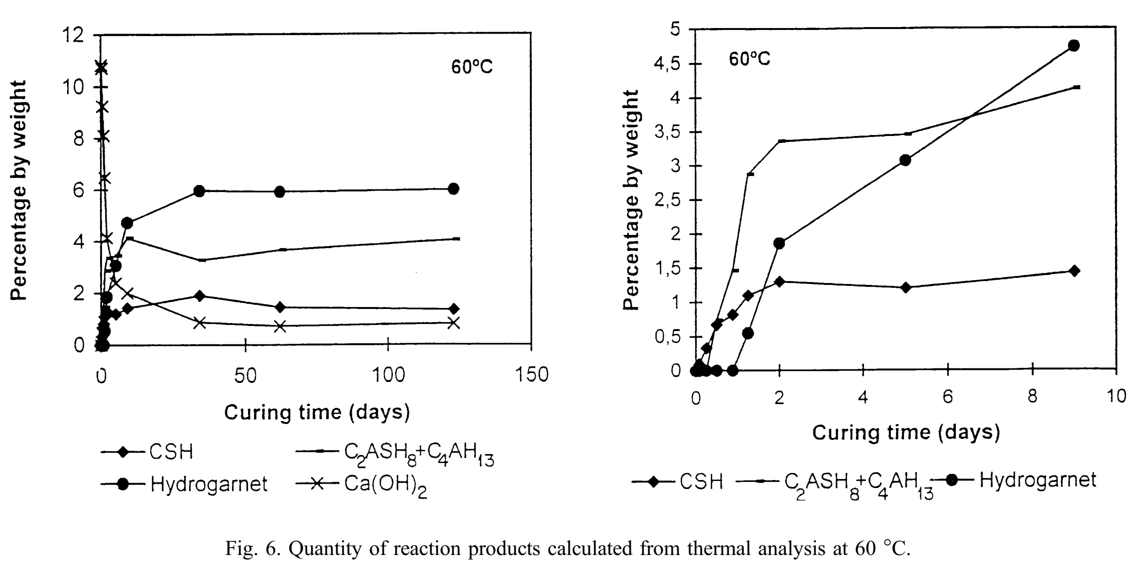

Fig. 6. Quantity of reaction products calculated from thermal analysis at 60 °C.

(2) The rate constant obtained by Jander model at 60 °C and up to 5 days of curing was 68 times higher than that obtained at 20 °C.

(3) At early stages of the reaction, the C–S–H was the main phase for both temperatures. Subsequently, C_2ASH_8 (stratlingite) and C_4AH_{13} appear, and finally the C_3ASH_6 (hydrogarnet) was the predominant phase in the samples cured at 60 °C. No hydrogarnet formation was detected at 20 °C.

(4) At 60 °C of curing temperature, there is no clear evidence of a transformation of metastable phases (C_2ASH_8 and C_4AH_{13}) into hydrogarnet under the conditions studied (up to 123 days), as was reflected in Fig. 6 (right). In the figure, it is clearly observed that C_2ASH_8, C_4AH_{13} and C_3ASH_6 amounts increase with curing time. This is indicating the fact that hydrogarnet is produced as a result of the pozzolanic reaction between MK and lime and not through a transformation reaction.

(5) At 20 °C, there is clear evidence of the existence of C_4AH_{13} in the absence of calcium hydroxide.

Acknowledgments

The authors are very grateful to the TMR Marie Curie Grant (European Commission), which supported the present research.

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