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Mechanism of hydration of the metakaolin–lime–water system

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Abstract

The reaction kinetics of a mixture of metakaolin and lime (calcium hydroxide) in water at 60°C has been investigated using thermal analysis. The numerical results have been used to determine the nature of the reaction. It is shown that, on the whole, this pozzolanic reaction is diffusion controlled and can be represented by the Jander diffusion equation. The paper discusses a new rapid method for monitoring the reaction, utilizing a microwave oven to stop it at any desired reaction time. The nature and quantity of the reaction products were determined by differential thermal analysis (DTA), thermogravimetry (TG) and X-ray diffraction (XRD). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Lime; Microwave; Reaction kinetics; High temperature

1. Introduction

Natural pozzolans have been used since antiquity with excellent results for the production of durable concrete [1]. By-products as pozzolanic additions are now routinely used for the production of high-performance concrete. Fly ash and silica fume is used to improve the resistance of concrete to the attack in aggressive environments [2,3]. Recently, some activated materials such as metakaolin, which is produced by heating kaolinite, have been shown to be an excellent pozzolan. The abundance of kaolinite in known commercial deposits and in the C horizon of soil profiles in tropical regions make it not only economically attractive, but environmentally desirable for use as an addition or part replacement of ordinary Portland cement in the manufacture of concrete [4,5].

The lime reactivity of a pozzolanic material depends on its particle size and surface area and on its mineralogical make-up. Pozzolans containing large proportions of amorphous silico-aluminates, having particles of small average mean diameter and relatively high specific surface, exhibit high reactivity. There are a number of methods for the measurement of the lime reactivity of pozzolans; these have been reviewed by Massazza [6], Kokubu [7], Sersale [8] and Taylor [9]. In general these methods are classed as indirect or direct methods. Greenberg [10], for example, describes a method based on the use of a conductometric technique to indirectly monitor the depletion of lime by measuring the electrical conductivity of the test solution as the reaction proceeds. Other indirect methods are based on the strength development occurring with reaction time. Direct methods are based on the measurement of the amount of lime reacted. Instrumental techniques currently used include thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction (XRD) and calorimetric analysis.

The results obtained by these techniques provide information on the pozzolanic potential of the material and can be used effectively for studying the kinetics of the pozzolan–lime reaction.

When direct methods are used, it is necessary to stop the reaction before determining the calcium hydroxide content. Methods commonly used include drying in an oven for 24 to 36 h at 105°C, use of organic liquids to drive off the water, and freeze-drying. These methods are time consuming and have a number of drawbacks. For example: drying in an oven for 24 to 36 h can accelerate the reaction during drying prior to the total evaporation of water. However, this method has been used with a certain degree of success [11] and will be used here as a reference to compare with the new drying procedure. Drying using organic liquids can produce reac-

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Table 1
Chemical composition and physical properties of the metakaolin used

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	NaO_2	K_2O	TiO_2	LOI
Percent by weight	51.6	41.3	4.64	0.09	0.16	0.01	0.62	0.83	0.60
Passing 10 μm (% by weight) = 88									
Passing 2 μm (% by weight) = 37									
Surface area (m^2/g) = 15									

tion with the lime, forming carbonate ions that can alter the thermogravimetric results [12].

On the other hand, the hydration temperature plays an important role on reaction kinetics and stability of hydrated phases. For this reason, it was very important to establish the real temperature inside samples during hydration. Temperatures of 40–60°C are reported in the bibliography [13,14] for highly reactive pozzolans. Latterly in a previous paper, the authors reported that the maximum temperature reached for metakaolin mortar was between 58°C and 60°C, as found by the Langavant Calorimetric method [15]. Therefore, the hydration temperature of 60°C was selected in the current work.

This paper describes the results of a rapid method for the determination of lime by TG and DTA in a mixture of lime and metakaolin. The reduction in time for this determination is achieved by drying the samples using a microwave oven, which reduces the time of drying to 9 min for any reactant for a selected time.

The results are also used to determine the mechanism of the reaction at 60°C. XRD and DTA give valuable information on the nature of the reaction products and their stability with reaction time.

2. Material and experimental techniques

A commercial metakaolin available in the UK was used. Table 1 gives its composition and some of its physical properties. The lime used was analytical grade $Ca(OH)_2$.

The metakaolin and $Ca(OH)_2$ were 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 mixes were placed in plastic containers and immersed in a water bath maintained at 60°C until required for testing. The hydration times selected for the study were 0, 2, 12, 21, 30, 48, 72, 120 and 216 h. After the appropriate hydration time, samples were taken from the plastic containers and dried in a commercial microwave oven.

For this work, a satisfactory method of drying was developed by monitoring the temperature of the sample against the drying time. The metakaolin/lime slurries were dried for times of 1–11 min. The experimental results showed that the temperature reached by the samples was 106°C after 9 min of exposure. This temperature is very close to that used in the reference method (105 ± 2°C). In order to ensure that free water was eliminated, the samples were remixed in their containers after 6 min of drying.

The weight losses obtained from both methods of drying can be determined by different ways, as for example: comparing the weight losses of the samples before and after drying or using thermal analysis. The authors selected the latter because this technique provides additional valuable information on the nature of the reaction products and their stability with reaction time.

The evolution of sample weight (% residue) obtained once TG analysis was finished (% original weight − % weight loss = % residue) for both microwave and oven drying was used to deduce that a microwave drying time of 9 min was an appropriate drying time (Fig. 1).

3. Results and discussion

3.1. Mechanism of the metakaolin–lime reaction

To study the mechanism of the metakaolin–lime reaction, measurements of lime consumed at different reaction times were obtained using TG. Fig. 2 includes results for samples dried in the microwave and in a conventional oven (at 105°C for 24 h). It can be seen that close to 60% of the

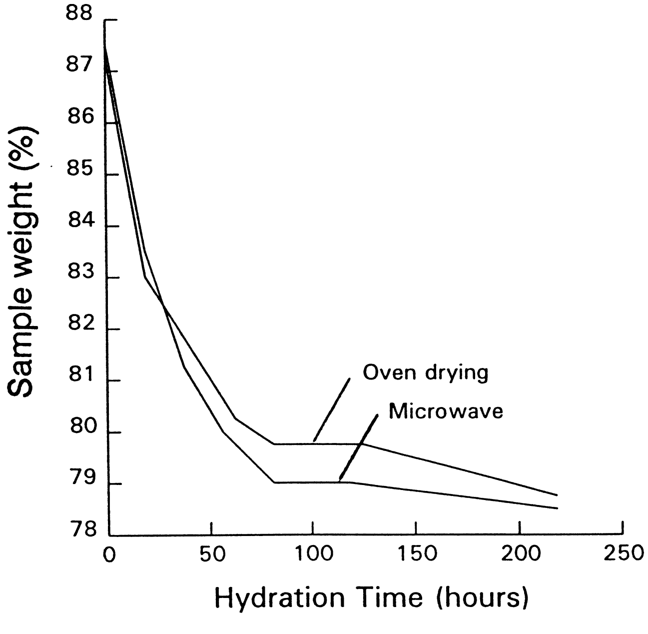

Fig. 1. Sample weight versus hydration time.

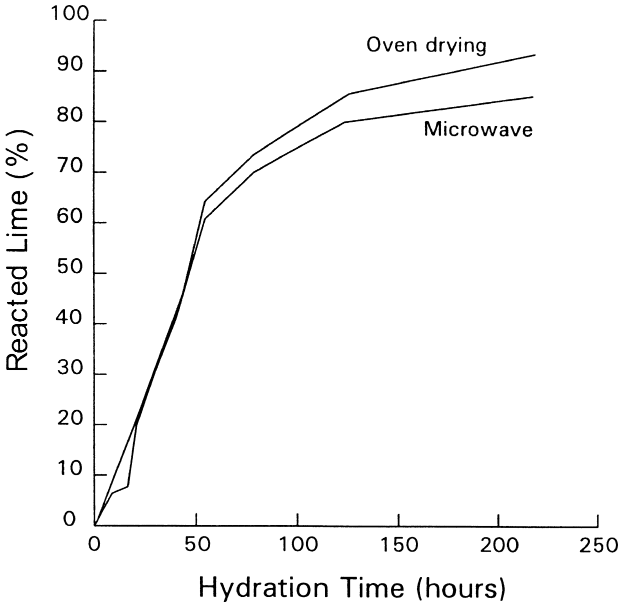

Fig. 2. Amount of lime reacted at different hydration times as determined from TG.

lime has reacted at 50 h. From 50 h onwards the rate of lime consumption decreases. After 50 h the amount of lime reacted as determined in samples dried by the microwave technique is slightly less than that of samples dried in the conventional oven. This difference increases with time and although there is no clear explanation, it might in part be due to the continuation of the reaction in the oven prior to the total evaporation of water during the 24–36 h of drying.

Previous research has shown that the mechanism of the pozzolanic reaction can be satisfactorily described by a diffusion equation [11]. The Jander equation [16], which is based on Fick's parabolic law of diffusion, has been used satisfactorily. Ramezanianpour and Cabrera [11] used a modification of this equation, proposed by Ginstling and Brounshtein, to describe the mechanism of reaction in microsilica–lime and trass–lime systems.

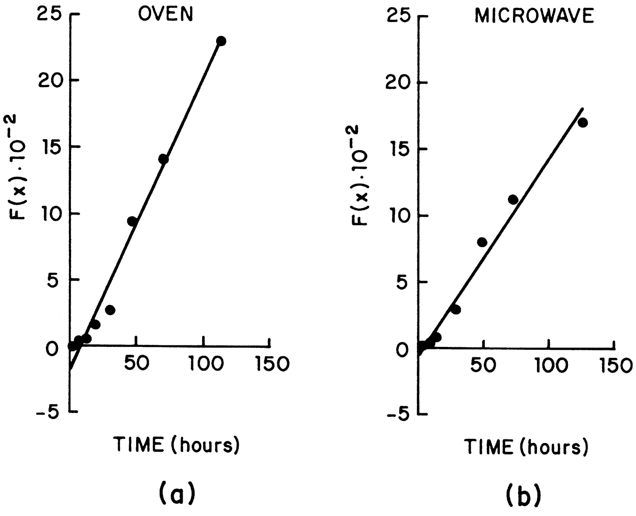

Fig. 3. Regression lines for the results obtained by (a) conventional oven drying and (b) microwave drying. For fraction of sphere reacted, *F*(*x*) as a function of time.

The kinetic model that best fitted the present results was that proposed by Jander [16]. It assumes that the reaction interface is a contracting sphere and leads to the well-known equation (Eq. (1))

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

where: x = fraction of the sphere that has reacted; r = initial radius of the starting sphere; K = constant proportional to k; k = parabolic rate constant.

This linear equation implies that a plot of $F(x)$ against time would be a straight line whose slope is equal to K, the reaction rate constant. The linearity of a plot of $F(x)$ based on the lime consumed against time provides a good criterion to see if the reaction is diffusion based. Fig. 3 shows the plots of $F(x)$ versus time of hydration for the microwave dried and the conventional oven-drying procedures. The regression equations obtained are:

$$\text{For conventional oven}: F(x) = 0.206t - 1.641 \quad r^2 = 0.980,$$

$$\text{For microwave}: F(x) = 0.151t - 0.800 \quad r^2 = 0.970.$$

The last data point for lime consumed, i.e. 216 h, was not used in calculating the regression lines (because they no longer fitted the linear relation), so that the reaction constant represents the reaction rate up to 5 days. The rate constants are then:

Conventional oven 20.6×10^{-4},

Microwave oven 15.1×10^{-4}.

The values obtained in this study are similar to those found by other investigators (Table 2). The present results show that the kinetics of reaction of the metakaolin–lime system up to 120 h is clearly consistent with diffusion control.

3.2. Hydration products

DTA, TG and XRD were used to study the nature of the reaction products as they develop with time of hydration.

Table 2
Lime reactivity of various pozzolans

Pozzolan	Lime reactivity ($K \times 10^{-4}$)
Natural trass	1.60
Activated trass	3.64
Natural Kaolin (tropical profile)	2.40
Metakaolin (tropical profile)	25.00
Fly ash (very fine)	20.00
Fly ash (BS 3890 pat 1)	5.00–12.00
Microsilica	27.00
Metakaolin (this study)	15.00–20.00

Many investigators have studied the kinetics of the metakaolin–lime reactions detailing the nature of the hydration products formed [4,17–20]. It is agreed that the times at which different hydration products are formed, their stabilities and the mineralogical transformations that occur with hydration time depend on the metakaolin–lime ratio, the temperature and the presence of such activators as NaOH or Na_2SO_4.

Murat [4] studied metakaolin/lime mixtures with different ratios. For a mass ratio of 1:1, he suggested that the metakaolin, $Ca(OH)_2$ and water reacted to give CSH and C_2ASH_8.

Da Silva and Glasser [17,21] reported that in a metakaolin/lime mixture of the same composition at 55°C, C–S–H develops after 24 h of hydration and that after 90 days the hydration products were C_2ASH_8, C_4AH_{13}, hydrogarnet and C–S–H. They indicated that C_2ASH_8 and C_4AH_{13} are probably present as metastable phases that after long curing periods convert to hydrogarnet. They also believed that the appearance of C_4AH_{13} at early ages of hydration is a metastable phenomenon caused by supersaturation of the aqueous phase with respect to CH. High concentrations of Ca^+ and OH^- in the pore solution maintained a pore fluid composition that allowed C_4AH_{13} to precipitate.

The results of the present investigation are summarized in Fig. 4 and Table 3. They differ in some respects from those reported in other references. The first product of hydration is C–S–H, which is detected clearly at 6 h. At 12 h of hydration C–S–H, C_2ASH_8 and C_4AH_{13} are clearly detected. Hydrogarnet appears after 21 h of hydration.

Comparing the results to those of Ref. [21], the main difference is that C_4AH_{13} is still present at 3 days and

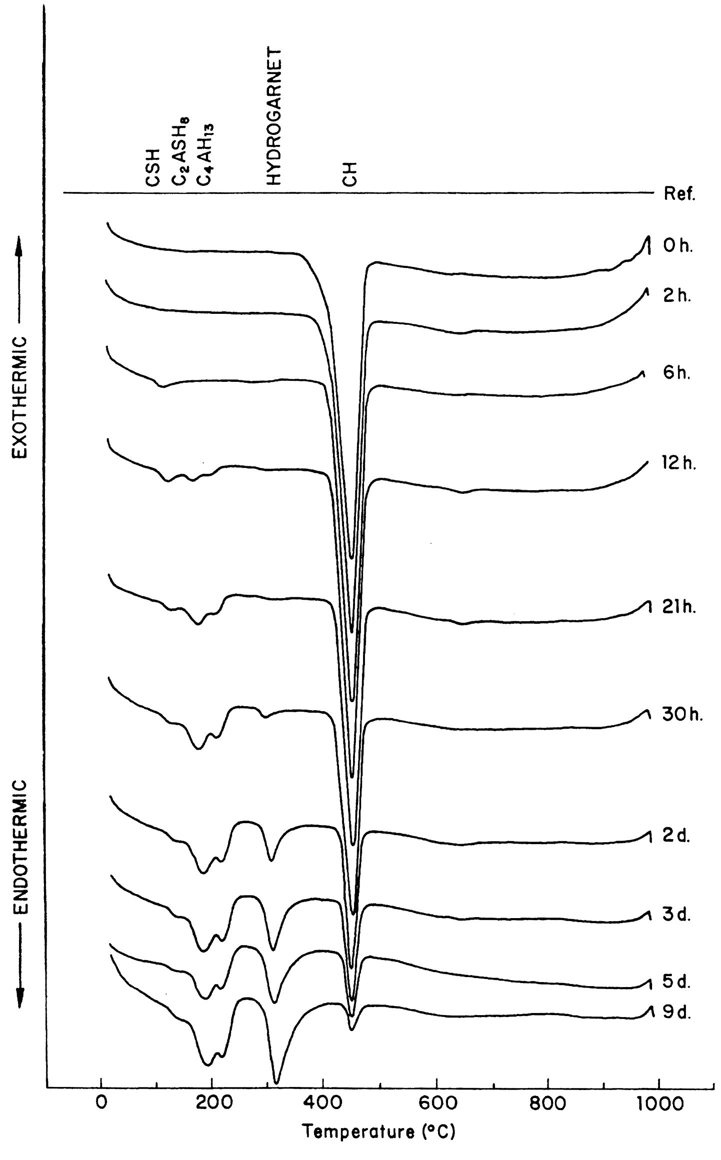

Fig. 4. DTA curves shows the formation of reaction products with time of hydration at 60°C.

Table 3
Hydration products of the metakaolin–lime reaction reported by various authors and in the present investigation

Temperature (°C)	Time	C_2ASH_8	C_4AH_{13}	Hgt	CH	C–S–H	Reference
20	10 days	+	+		+	+	[4]
	90 days	+	tr		+	+	
	180 days	+	tr		tr	+	
55	3 days		+	+	+	+	[21]
	28 days		tr	+	tr	+	
	90 days		tr	+		+	
60	6 h				+	+	This investigation (DTA)
	12 h	+	+		+	+	
	21 h	+	+		+	+	
	30 h	+	+	+	+	+	
	2 days	+	+	+	+	+	
	3 days	+	+	+	+	+	
	5 days	+	+	+	+	+	
	9 days	+	+	+	+	+	
60°	21 h	+	+		+	?	This investigation (XRD)
	30 h	+	+	+	+	?	
	9 days	+	+	+	+	?	

Hgt = hydrogarnet.

does not transform even at 9 days. Da Silva and Glasser [17] have indicated that hydrogarnet forms slowly from strätlingite and C_4AH_{13} in the absence of sulfates. Fig. 5 shows the percentages of the reaction products calculated from the TG curves. Here there is no indication of a transformation, but hydrogarnet is formed without a decrease of C_2ASH_8 and C_4AH_{13} weight. It is important to indicate that these results are at relatively short hydration times since mixtures of C_2ASH_8 and calcium hydroxide are known to be incompatible and would therefore form hydrogarnet under prolonged curing [21]. Oriol and Pera [22] reported that specimens produced by microwave heating were more homogeneous and of lower porosity than conventional oven-dried specimens.

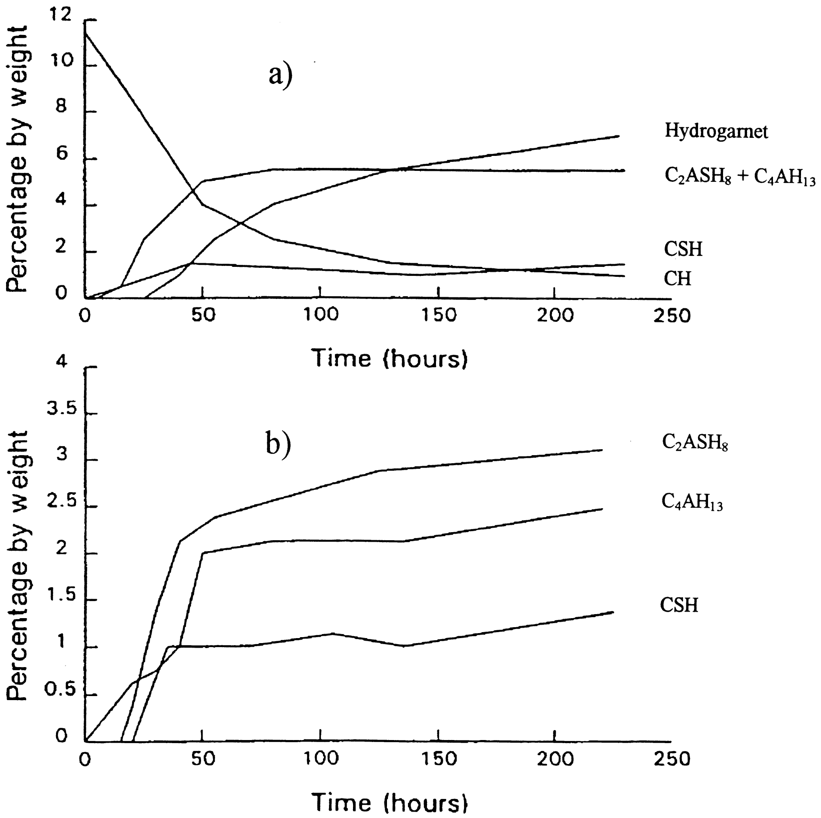

Fig. 5. Quantities of reaction products calculated from the TG experiments, (a) includes CH depletion; (b) shows clearly that the C_2ASH_8 and C_4AH_{13} do not decrease up to 9d.

XRD traces were also obtained for hydration times of 2 h up to 9 days. Table 3 is a summary of the crystalline products at 21 h, 30 h and 9 days hydration time. It is emphasized that there is no evidence of transformation of C_2ASH_8 and C_4AH_{13} into hydrogarnet in the mixtures studied for short hydration times. Studies of hydration for longer times and at 20°C are in progress and will be reported in a separate paper.

4. Conclusions

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

(1) Microwave drying to stop the hydration process has been shown to be a very practical and useful method that does not alter the nature of the reaction products. A drying time of 9 min was found to be adequate to drive off the free water from the metakaolin–lime–water mixture.

(2) Lime is consumed at a very rapid rate in the initial period of reaction (up to 50 h). The mechanism of reaction is consistent with diffusion control for the first 120 h; the calculated rate of reaction constant from the Jander equation shows that the metakaolin tested was very reactive and comparable in reactivity to silica fume.

(3) The reaction products detected from 2 h up to 9 days indicate that C_2ASH_8 and C_4AH_{13} phases are metastable for up to 9 days at 60°C under the circumstances studied, notwithstanding the fact that hydrogarnet is also present from 30 h up to 9 days. This might be an indication that hydrogarnet is not formed from a transformation reaction, but results from direct reaction between metakaolin and lime.

(4) The XRD results confirm the results of DTA and TG studies.

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