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ALKALINE ACTIVATION OF METAKAOLIN
An isothermal conduction calorimetry study

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Abstract

The alkaline activation of metakaolin leads to high mechanical performance inorganic polymers.

A JAF conduction calorimeter was used to follow the reaction of metakaolin with NaOH solutions. The alkaline activation of metakaolin to yield a cementitious material is an exothermic process involving three steps: an initial and very fast process of dissolution, which is strongly exothermic, followed by an induction period in which the heat exchange rate decreases, and finally an exothermic step of reaction reactivation in which cementitious materials precipitate and after which the heat exchange rate decreases.

The calorimetric curves lead to the following findings:

– The induction period is lengthened as the NaOH solution concentration and the liquid percentage increase.

– The induction period is shortened as the temperature increases.

– The total heat increases as the liquid percentage and the NaOH concentration increase.

Keywords: activation, alkali, metakaolin

Introduction

When metakaolin (MK) is activated by alkali metal hydroxide solutions, a polycondensation reaction occurs, leading to the formation of a cementitious material with high mechanical strength [1, 2]. The starting aluminosilicate, the different compositional parameters, the curing time and the temperature all directly influence the final properties of the inorganic polymer formed [3].

The synthesis of this binder can be compared to zeolite synthesis. The structures of these materials involve a three-dimensional framework formed by SiO_4 and AlO_4 tetrahedra linked altenately by sharing all the oxygens, where the alkali metal cations from the activator solution are present to balance the negative charge of the four-coordinated Al [4]. However, in contrast with zeolites, the producte obtained is almost amorphous [5].

The aims of the present work were

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1) To establish the steps through which the process of activation of MK by sodium hydroxide solutions occurs, and to determine the nature of the reactions taking place in each step;

2) To study the modifications in the alkaline activation process in response to variations in the synthesis parameters (temperature, alkali concentration and activator volume).

Experimental

In the present study, a Spanish kaolin from Tudela (C) was used. A complete chemical and mineralogical characterization is given in a former work [6]. Table 1 details the chemical analysis of the kaolin. It contains some quartz as a secondary species and also small proportions of anatase and pyrophyllite.

Table 1 Chemical analysis of kaolin C

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	TiO_2	K_2O	I.G.
46.99	36.00	0.54	0.00	0.82	0.68	1.15	1.68	11.70

I.G. = ignition loss

The MK used as raw material for the polymer synthesis was prepared by thermal treatment of kaolin C at 750°C during 24 h [7].

A JAF conduction calorimeter was used to follow the reaction MK with NaOH solutions. Mixes prepared for this purpose are given in Table 2. Calorimetric data were obtained isothermally at 35 and 45°C with variable solution/solid ratios and different NaOH solution concentraions. As the mixes were prepared outside the calorimeter, the fast heat evolution peak reflecting the contact of solution and MK could not be registered.

Table 2 Compositions tested for calorimetric studies

Composition	[NaOH]/M	Sol./ml
T1220	12	3
T1230	12	4.5
T1250	12	7
T1520	15	3
T1530	15	4.5
T1550	15	7
T1820	18	3
T1830	18	4.5
T1850	18	7

Samples removed from the calorimeter were treated with acetone-ethanol, dried in vacuum to constant weight and treated with dilute hydrochloric acid and then a 5% Na_2CO_3 solution. The polymer formed was soluble in these solutions while the initial MK was insoluble. With this treatment, the MK remaining unreacted could be quantified and the insoluble residue (Insol. Res.) could be considered as a measure of the reaction degree. These samples were also analysed by XRD and FTIR.

On the other hand, in order to associate the different calorimetric signals appearing in the curves, a series of thermal suppressions of the samples were carried out. Two of the compositions tested in the calorimetric study were chosen for thermal suppression. For this purpose, 10 g of MK plus NaOH solution were placed ina sealed plastic bag and maintained at a constant temperature of 35°C in a water-bath during the times determined by the calorimetric peaks. The times at which the samples were thermally suppressed are shown in Table 3.

Table 3 Compositions and times for thermal suppression

Composition	T1230			T1530		
Time/h	9	13	40	17	26	40

The templating times correspond to the time before the appearance of the reaction peak, the time of the peak maximum and the time immediately after the reaction peak. Samples removed from the water-bath were treated with cold water, filtered, washed and dried in vacuum to constant weight. The solid was then treated with dilute hydrochloric acid according to the methodology described above for the Insol. Rev. measurement. The samples were finally analysed by XRD and FTIR.

Results

Results obtained in a calorimetric studies are detailed in Table 4. The results of measurements of Insol. Res. in acid medium at the end of the calorimetric test are also given in Table 4.

Figures 1–3 depict maximum rate *vs*. time curves for MK at the three NaOH concentrations and the three liquid percentages tested.

The results permit the following findings:

– The rate evolution curves reveal the appearance of a first dissolution peak that is not always registered, mainly at the highest temperature (45°C). After this, a period of scarce heat interchange or an induction period can be observed. A second reaction peak appears, with a shoulder immediately after the reaction peak, which is seen more clearly at 35°C (because the reaction rate is lower). This could indicate that two overlapping processes are taking place.

Table 4 Results of calorimetric tests and Insol. Res. in HCl(1:10)+5%Na_2CO_3

Sample	Insol. Res./ %wt.		Total heat/ kJ kg^{-1}		Rate/ W kg^{-1}		Time/h (max. rate)	
	35°C	45°C	35°C	45°C	35°C	45°C	35°C	45°C
T1220	51.34	49.97	90.2	230.4	4.87	16.0	10.5	3.6
T1230	37.96	30.62	328.4	365.7	4.33	16.5	13.0	3.4
T1250	18.48	20.39	400.8	434.7	4.51	16.9	12.6	3.8
T1520	43	41.81	462.5	314.3	3.85	15.1	26	5.8
T1530	23.42	23.93	452.9	441.8	4.31	14.8	26.1	7.9
T1550	17.13	18.45	619.0	442.6	5.65	15.1	34.5	8.4
T1820	41.43	34.67	395.6	374.0	3.15	13.0	91.0	9.4
T1830	22.76	20.80	475.9	418.0	2.96	9.4	110	32.8
T1850	15.37	15.95	562.5	471.2	3.90	8.2	63	45

– The induction period is lengthened as the NaOH solution concentration increases and shortened with the rise of temperature.

– The induction period becomes longer as the liquid percentage increases (except for compositions with 12 M NaOH, which there is little variation).

– Total heat increases as the liquid percentage and the NaOH concentration increase.

– In many cases, the total heat registered at 35°C is higher than that at 45°C. This could be explained by considering the higher reaction rate at 45°C. Then, when the calorimetric curve recording is started, the reaction has progressed

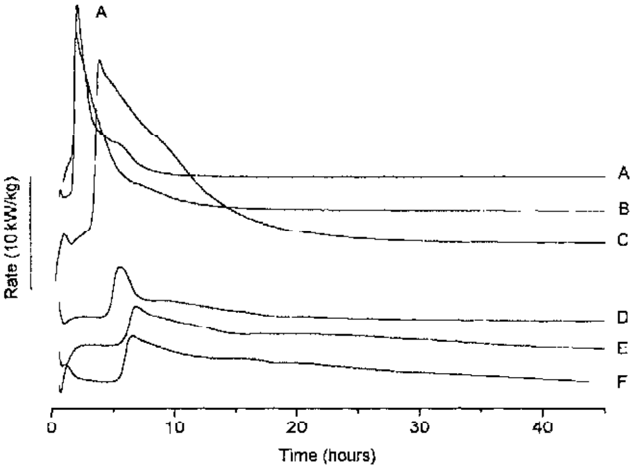

Fig. 1 Rate of heat evolution *vs.* time for samples with [NaOH]=12 M. A, T1220/45°C; B, T1230/45°C; C, T1250/45°C; D, T1220/35°C; E, T1230/35°C; F, T1250/35°C

more at 45 than at 35°C, involving a lack of calorimetric data during the first few of minutes of reaction.

– Insol. Res. decreases as both the NaOH concentration and the liquid percentage (% Na_2O increases) increase.

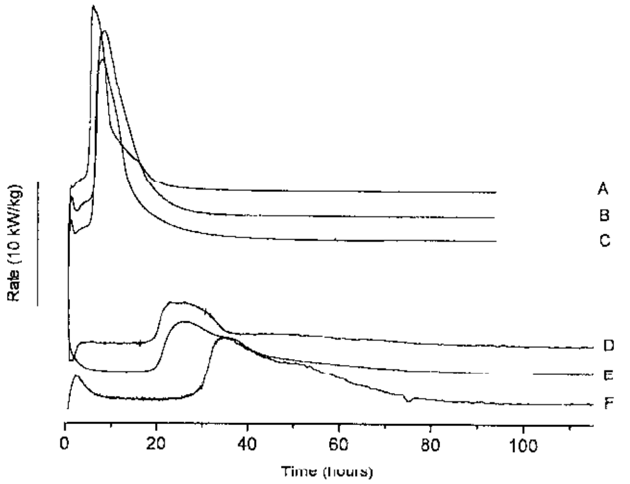

Fig. 2 Rate of heat evolution *vs.* time for samples with [NaOH]=15 M. A, T1520/45°C; B, T1530/45°C; C, T1550/45°C; D, T1520/35°C; E, T1530/35°C; F, T1550/35°C

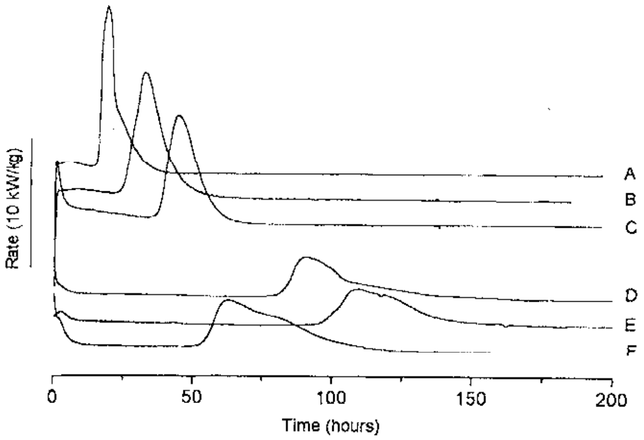

Fig. 3 Rate of heat evolution *vs.* time for samples with [NaOH]=18 M. A, T1820/45°C; B, T1830/45°C; C, T1850/45°C; D, T1820/35°C; E, T1830/35°C; F, T1850/35°C

The XRD and FTIR analyses of these samples lead to the following results:

On XRD of these compositions, a broad halo at about $2\Theta=26°$, together with some diffraction lines of a sodalite type zeolite $Na_8(AlSiO_4)_6(OH)_2 \cdot H_2O$ are observed; the lines corresponding to the zeolite become more intense as the liquid percentage increases, but this effect is not seen when the NaOH concentration increases.

In the IR spectra of alkaline-activated MK, as the aggressivity of the treatment increases (higher concentration or liquid percentage), a progressive shift of the MK Si–O band at 1090 cm^{-1} towards lower frequencies (>990 cm^{-1}) is observed with a progressive decrese of the 800 cm^{-1} Al–O band until its disappearance and the formation of a new band at about 720 cm^{-1}, characteistic of the polymer formed, can be observed. In these spectra, the bands corresponding to dehydroxylated pyrophyllite and the zeolites identified by XRD remain. The stronger the treatment, the weaker the original MK bands are.

Insol. Res. measurements on the thermally suppressed samples are shown in Table 5.

Table 5 Insol. Res. of thermally suppressed samples at different times (35°C)

Composition		T1230			T1530	
Time/h	9	13	40	17	26	40
Insol. Res.	90.42	87.84	49.82	90.4	71.31	49.82

The XRD and FTIR analyses of these samples furnish the following results:

– Diffractograms of the sample thermally suppressed at the end of the induction period correspond to an amorphous product and the smaple is in a plastic state. No shift in the Si–O band at about 1050 cm^{-1}, nor any evolution in the Al–O band at about 800 cm^{-1} for the original MK, can be seen.

– When the samples are thermally suppressed at the time of the maximum rate of evolution of heat, their diffractograms are very similar to that found at the end of the induction period. A small shift in the Si–O band from about 1050 cm^{-1} towards 1015 cm^{-1}, and a decrease in the intensity of the Al–O band at about 800 cm^{-1}, are observed.

– Samples thermally suppressed immediately after the shoulder (which appears after the reaction peak) the amorphous halo, but the peaks corresponding to a zeolite of sodalite type ($Na_8(AlSiO_4)_6(OH)_2 \cdot H_2O$). The FTIR spectra confirm these results.

Discussion

The alkaline activation of MK up to the production of cementitious material is an exothermic process. The calorimetric curve corresponding to this process displays an initial and very fast strong exothermic peak that can not always be recorded, mainly at the highest temperature of study (45°C). The first step is followed by an induction period in which the heat exchange rate decreases. After the induction period, a strong asymmetric exothermic peak appears (first an intense signal, followed by a shoulder), which corresponds to the sum of two overlapping signals reflecting the two processes taking place. The two signals are observed more clearly at the lower reaction temperature (35°C) because of the lower reaction rate.

According to the results in Table 5, when the activation reaction is stopped at the end of the induction period, samples T1230 and T1530 present an Insol. Res. of 90% (which indicates a very low reaction degree). By XRD analysis, the formation of crystalline species is not observed. At the same time, in the FTIR spectra, the shift in the MK Si–O vibration band at 1090 cm^{-1} towards lower frequencies is not observed, and the MK Al–O vibration band in the 800 cm^{-1} region remains.

When the activation reaction is stopped at the times of maximum rate of interchange, the reaction has progressed more, but the presence of crystalline species is not observed. In samples activated during 40 h, i.e. immediately after the reaction peak, a strong increase in reaction degree (lower Insol. Res. values) is observed with the simultaneous appearance of low-intensity zeolite reflections in the XRD patterns. Thus, it seems that the second exothermic peak may be associated with polymer formation, whereas the shoulder overlapping, with this peak could correspond to zeolite crystallization.

During the first and second steps, the material is in a plastic state; after the third step, the material hardens by precipitation of cementitious material together with some zeolite. The material obtained after alkaline MK activation is mainly an amorphous sodium aluminosilicate, which can be characterized by FTIR, via its bands at 990 and 720 cm^{-1} [1]. Its XRD pattern displays an intense halo at around $2\Theta=26°$, characteristic of siliceous amorphous materials. Together with this halo lengthening, small zeolite peaks can be seen.

The mechanism governing the induction period, and the kinetics in each process step, are unknown, but the lengthening of this period when the water/solid ratio is increased, suggests that a critical concentration (oversaturation) of ionic species must be reached before cementitious material precipitation occurs. On the other hand, the concentration of ionic species necessary for precipitation would be higher when a medium ionic force increases. This would justify the increase in the induction period when the Na concentration of the activator solution is increased. Later studies must be carried out on this.

Insol. Res. could be a good way to measure the reaction degree attained, if this is understood as the MK amount that remains unreacted. However, this parameter is not a direct measurement of the polymer formed, because it also contains the amount of zeolites formed. The induced error when Insol. Res. is regarded as the reaction degree of polymer formation is very small in those samples in which the lower liquid proportion is used (and even for the intermediate proportion), no matter what the NaOH concentration, because they contain only traces of zeolites.

The reaction degree depends on the activator solution concentration and on the liquid/solid ratio. Accordingly, if Insol Res. is taken as the reaction degree and represented *vs.* % Na_2O, a non-linear dependence will be observed, obeying the following equations:

$$y=124.75-12.006x+0.3319x^2\ (T=45^\circ\mathrm{C})\ \text{with}\ R^2=0.937 \quad (1)$$

$$y=132.89-12.939x+0.3560x^2\ (T=35^\circ\mathrm{C})\ \text{with}\ R^2=0.950 \quad (2)$$

where y is the insoluble and x is the percentage of Na_2O.

Insol. Res. decreases as the Na_2O concentration in solution increases. Hence the reaction degree increases as the NaOH concentration or liquid amount increases.

The kinetics of the process of MK activation cannot be determined from the total heat data obtained by this procedure. As it clearly has been seen from the Insol. Res. values, the reaction degree does not depend on the temperature of the process, and consequently the total heat is also independent of temperature. As the total heat data obtained differs from one temperature to another, the loss of data in the first stages of the reaction at the highest temperature is confirmed. Another calorimetric technique should be used to determine the values of total heat, and the kinetics of the process will be determined.

Conclusions

1) MK activation is an exothermic process. The calorimetric curve of this process shows a dissolution peak followed by an induction period. After this induction period, a strong asymmetric peak appears, which corresponds to the sum of two overlapping signals showing the two processes taking place.

2) The strong asymmetric peak has been associated with amorphous inorganic polymer formation, responsible for the mechanical strength of the material, whereas the shoulder overlapping with this peak corresponds to a zeolite crystallization process.

3) The lengthening of the induction period when the water/solid ratio is increased suggests that a critical concentration of ionic species must be reached before cementitious material precipitation occurs. The concentration of ionic species necessary for precipitation would be higher when the medium ionic force increased. This would justify the increase in the induction period when the Na concentration of the activator solution is increased.

4) Insol. Res. could be a good way to measure the reaction degree, which depends on the activator solution concentration and the liquid/solid ratio. Thus, in representations *vs.* the Na_2O concentration, a non-linear dependence can be observed. Isol. Res. decreases as the %Na_2O in solution increases, according to Eqs [1] and [2] for each study temperature.

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