Pergamon

Cement and Concrete Research 31 (2001) 25–30

CEMENT AND CONCRETE RESEARCH

Calorimetric study of alkaline activation of calcium hydroxide–metakaolin solid mixtures

Santiago Alonso, Angel Palomo*

Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), Serrano Galvache s/n, 28033 Madrid, Spain

Received 1 July 1999; accepted 14 September 2000

Abstract

The products originated in the alkaline activation reaction of metakaolin (MK) in calcium hydroxide presence vary as a function of the concentration of the alkaline hydroxide that activates the solid mix. In order to study these reaction products, a series of MK + calcium hydroxide mixes were activated in 1:1 proportion, with different sodium hydroxide concentrations: 5, 10, 12, 15 and 18 M at 45°C during 24 h. The activation steps were examined through isothermal conduction calorimetry and the reaction products characterisation was carried out by means of chemical analysis and instrumental techniques (XRD, FTIR and nuclear magnetic resonance (NMR)). When the activator concentration is 5 M or less, MK activation in the conditions previously described occurs only to a minor extent and the main reaction product is CSH gel. If activator concentration is 10 M or higher, MK dissolution is very fast and the main reaction product is an aluminosilicate with high mechanical performance. In all cases, the formation of CSH gel as the secondary reaction product is also observed.

Keywords: Alkaline activation; Alkaline polymer; Metakaolin; Isothermal conduction calorimetry; NMR; CSH gel

1. Introduction

Metakaolin (MK) is essentially an anhydrous aluminosilicate obtained from kaolin, after a thermal treatment that enables the OH^- groups elimination from the crystalline clay.

Murat and Dirouche [1] concluded that between 730°C and 760°C, kaolin calcination generated a high-disordered MK that was more reactive.

Davidovidts [2] described alkaline activation of MK in alkaline media (sodium and potassium hydroxides) in terms of a polymeric reaction characterised by the formation of materials with high mechanical strengths. The inorganic polymers developed have the general formula:

$$M_n\{-(Si-O_2)_z-Al-O-\}_n \cdot wH_2O$$

where - is a bond; z may be 1, 2 or 3 and n is the polymerisation degree. Similar structures have been proposed for zeolite formation.

The main difference between zeolites and the product obtained from the alkaline activation of MK is related with the structure order. While those are perfectly crystalline species, the inorganic polymer is amorphous. However, numerous similarities exist with respect to the syntheses of both materials: for example, the formation process needs OH^- presence to activate reactions. Actually, the amorphous polymer is considered to be the precursor of crystalline zeolitic species [3].

The study of the mechanisms of the alkaline activation process is one of the fields more difficult to deal with. Diverse works [4–6] suggest the process evolution through three steps: The first step is the dissolution of soluble species in the alkaline phase; the second step is a reorganisation and a diffusion of dissolved ions with the formation of small coagulated structures; and the third step is the growth and condensation of these structures to form the hydrated products.

IR absorption spectroscopy seems to be a suitable tool to characterise these type of materials. Their IR spectrum is characterised by the shift of the bending

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* Corresponding author. Tel.: +34-91-30-20-440; fax: +34-91-30-26-047.

E-mail address: palomo@fresno.csic.es (A. Palomo).

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PII: S0008-8846(00)00435-X

Table 1
Samples activated and studied by conduction calorimetry

Sample	[NaOH] (M)	MK/$Ca(OH)_2$ (weight ratio)	T (°C)
A	5	1:1	45
B	10	1:1	45
C	12	1:1	45
D	15	1:1	45
E	18	1:1	45

band of the Si-O bond (1050 cm^{-1}) from MK to lower frequencies (990 cm^{-1}), and the progressive decrease of the 800 cm^{-1} band with the formation of a new band at about 720 cm^{-1} that is characteristic of the polymer formed [7].

Davidovits [8] studied the ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) spectra giving more data about the polymer structure. For this author, the appearance of a unique peak at 55 ppm in the aluminium spectrum indicates the presence of a three-dimensional structure of aluminosilicate polymeric units, excluding the presence of low molecular weight polymeric units such as dimmers or trimers.

When the system MK–calcium hydroxide is activated with low concentration solutions, CSH gel is obtained, although in this case, the proportions of calcium aluminate hydrate C_4AH_{13} and hydrated ghelenite (C_2ASH_8) in the final product increase [9].

The objective of the present work is to study MK activation with highly concentrated NaOH solutions in the presence of calcium hydroxide.

2. Experimental

2.1. Materials

The MK used for this study was obtained by thermal treatment of Spanish kaolin at 750°C during 24 h. The chemical composition (wt.%) of MK is as follows:

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO
57.00	41.55	0.58	0.17	0.00

With respect to other materials used in the present work, $Ca(OH)_2$ and NaOH pellets, were high-purity chemicals.

2.2. Method

The solid mix of MK with calcium hydroxide was carried out in a humid medium, using acetone as dispersant. The weight ratio was 1:1. This solid mixture was alkaline activated with NaOH solutions with concentrations of 5, 10, 12, 15 and 18 M.

In order to follow the activation reactions, conduction calorimetry technique was used. The samples studied are described in Table 1.

To carry out the calorimetric test, mixing of the solids with the activator solution was done outside the cell impeding the obtention of a perfect resolution of the first signal corresponding to the solid species dissolution in the aqueous medium.

All the samples were extracted from the calorimetric system after 24 h reaction and quenched by acetone treatment. The product characterisation was carried out by XRD,

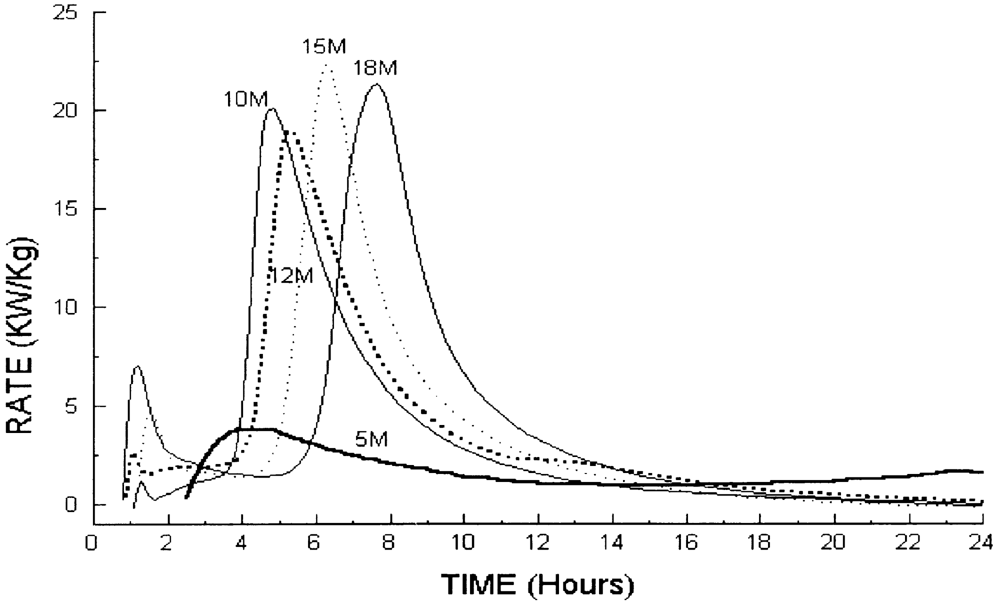

Fig. 1. Curves of rate of heat evolution in samples activated with different NaOH concentrations. MK/$Ca(OH)_2$ ratio of 1:1 and working temperature 45°C.

Table 2
Crystalline components identified by XRD

Sample	Portlandite	Quartz	Calcite	Termonatrite	HS
A	++	+	+		
B	++	+		+	
C	++	+		+	+
D	++	+		+	+
E	++	+		+	+

HS: hydroxysodalite; (+++) intense signal; (++) moderate signal; (+) weak signal.

FTIR and NMR. At the same time, samples were submitted to an HCl and Na_2CO_3 attack in order to dissolve all the reaction products and leave unaltered the initial MK that remains [10].

These same samples were also subjected to a process of extraction with methanol–salicylic acid that selectively complexes the calcium present [11], dissolving the calcium silicate formed and leaving unaltered the alkaline polymer.

The measurement of the silicon extracted in this organic matrix by ICP provided the quantification of the silicon fixed as hydrated calcium silicate.

3. Results

The results obtained by calorimetry in the study of A, B, C, D and E samples are shown in Fig. 1.

The curves of rate of heat evolution present a first peak (not totally registered) corresponding to the dissolution of solid species in the alkaline solution; a short induction period where the rate of heat evolution is considerably reduced and a broad and well-defined peak corresponding to the formation of the reaction products.

In these curves, a great difference between the activation reaction carried out with NaOH 5 M and those carried out with the other solution concentrations can be observed. When $[NaOH] \geq 10$ M, curve profiles are very similar in all cases. The intense signal of those curves corresponds to the massive precipitation of reaction products, and it appears at similar activation times. On the contrary, the calorimetric signal corresponding to the activation with 5 M NaOH is sensibly lower in intensity.

XRD diffractograms of the reaction products (see Table 2) show quartz and portlandite as the main crystalline compounds, regardless of the activator concentration. Portlandite indicates the calcium hydroxide excess (unreacted), and quartz is an impurity of the initial MK.

Other signals detected are of very low intensity. Those corresponding to zeolitic structures of the type of zeolite A and hydroxysodalite and some carbonates (calcite, termonatrite) can be mentioned. When activation is carried out with $[NaOH] = 5$ M, no lines are observed corresponding to zeolitic species.

Finally, in all diffractograms, a shift of the halo at about $2\theta = 28°$ can be observed, characteristic of amorphous compounds.

Infrared spectra of these reaction products (see Fig. 2) confirm the $Ca(OH)_2$ excess (see the sharp band at 3640 cm^{-1}) and the presence of carbonates (bands between 1420–1480 and 865–875 cm^{-1}). Besides, if these spectra are compared with that of the initial MK, a shift of the asymmetric bending of the bonds O-Si-O and O-Al-O to lower frequencies can be observed, which is in accordance with previous studies [7] about the characterisation of the alkaline polymer by infrared spectroscopy.

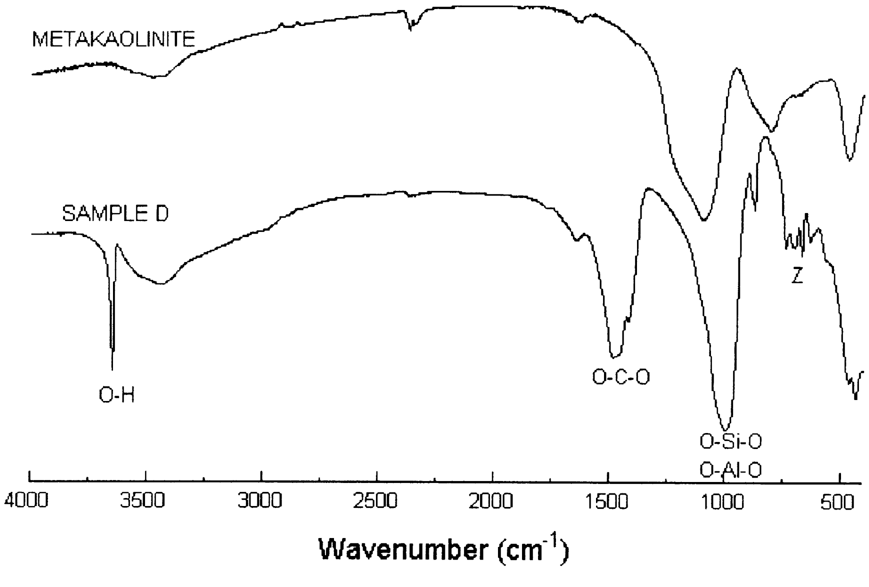

Fig. 2. Infrared spectroscopy spectra of the initial MK and D sample.

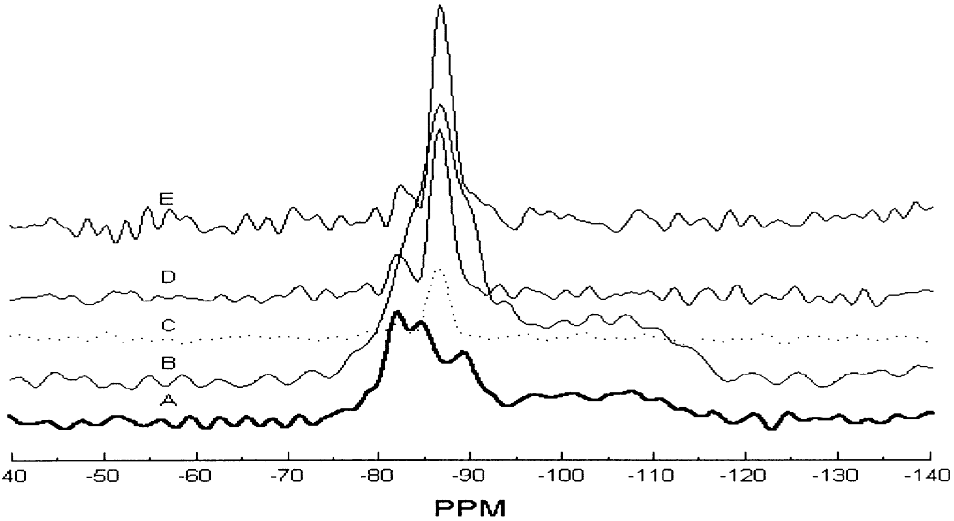

Fig. 3. ^{29}Si NMR spectra of the samples activated with different NaOH concentrations.

When sharper and better-defined bands appear corresponding to zeolites, the polymer identification and characterisation is more difficult. When the activation is carried out with 5 M sodium hydroxide, the presence of bands associated to MK can be observed, as well as the absence of signals corresponding to crystalline zeolites.

In Fig. 3, ^{29}Si NMR spectra are shown. These spectra are modified depending on the activator concentration: When [NaOH] = 5 M (sample A), signals appear at − 82, − 84, − 89 and a broad peak at about − 107 ppm, associated to Q_2(1Al), Q_2, Q_3 and Q_4 structures, respectively.

When the concentration is 10 M (sample B), the main signal appears at − 86.4 ppm, which is assigned to a Q_4(4Al) structure. This peak presents shoulders at − 82 and − 89 ppm. Finally, also observed is a little defined peak at about − 107 ppm.

When activator concentration is increased, spectra are very similar, which are similar to that of sample B: A sharp peak appears at about − 86 ppm (Q_4(4Al)) and also a less intense peak at − 82 ppm (Q_2(1Al)).

The interpretation of the ^{27}Al spectra (see Fig. 4) is more difficult. When [NaOH] = 5 M, two signals appear at 9 and 59 ppm, respectively, corresponding to the aluminium octahedral and tetrahedral coordinations. When the concentration is increased, only the signal corresponding to the lower coordination is observed. This signal varies as a function of the activator concentration.

Finally, the results obtained in the study of the chemical attack of the reaction products are shown in Table 3.

When the activation is carried out with [NaOH] = 5 M, MK reacts to a minor extent only. The opposite occurs with concentrations higher that 10 M, where it reacts almost

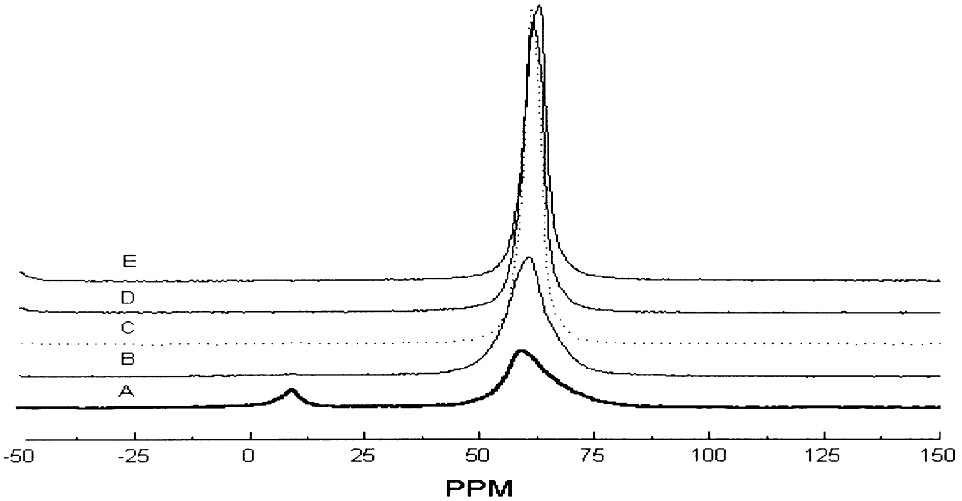

Fig. 4. ^{27}Al NMR spectra of the samples activated with different NaOH concentrations.

Table 3
Inert percentage of SiO_2 and SiO_2 fixed as CSH gel with respect to the initial silica as a function of the alkaline activator concentration

Sample	Inert SiO_2[a] (wt.%)	SiO_2[b] fixed as CSH (wt.%)
A	80.1	17.5
B	40.2	24.7
C	17.9	20.4
D	18.1	26.6
E	19.9	31.7

[a] Insoluble residue of the acid attack.

[b] Soluble silica in methanol–salicylic acid.

completely (between 12% and 13% of inert crystalline silica exists as quartz).

The percentage of fixed silicon as hydrated calcium silicate indicates that CSH gel is formed in all the activations.

4. Discussion

From previous experiences [6,11,12], we think that we can relate the intense signal found in conduction calorimetry with the process of formation of the alkaline polymer similar to the "geopolymer" synthesised by Davidovits [2].

If all the data obtained by XRD are considered (the minor amount of crystalline species and the presence of an halo at about $2\theta = 28°$), the formation of an amorphous product seems to be evident.

On the other hand, the identification of crystalline phases of zeolitic type in samples activated with sodium hydroxide solutions of concentration higher than 5 M leads us to think that adequate conditions for the formation of an alkaline aluminosilicate, of polymeric character, amorphous and precursor of a crystalline structure, are being set.

The bands observed in FTIR spectra of each of the samples (see Fig. 2) are in accordance with the bands established in the bibliography [7,13] for the inorganic polymer formed in the alkaline activation of MK. However, when the crystalline zeolites are formed, these yield to more intense and better-defined bands that overlap, in many occasions, those corresponding to the amorphous polymer.

At the same time, and considering the pozzolanic properties of the MK, it may be thought that the possibility of the formation of a hydrated calcium silicate of the CSH gel type originated during the activation in calcium hydroxide presence [9]. This product is also difficult to characterise by XRD and infrared spectroscopy due to its amorphous character and also because of the interference of minor products.

However, the analysis by ICP of the liquids from the sample attacked with methanol–salicylic acid confirms the formation of this CSH gel. This selective attack method dissolves the calcium gel, whereas it leaves unreacted the inorganic polymer and the unreacted MK [11]. Thus, it can be deduced that the SiO_2 amounts obtained in this organic matrix are those fixed by the hydrated calcium silicate.

If this silica fixed as CSH gel is summed to the unreacted SiO_2 during the activation process (obtained from the insoluble residue data), it is observed that 100% is not reached in any case (see Table 3). This will justify the fact of assigning the rest of silicon to the formation of the amorphous aluminosilicate.

Analysing the values from this table, the difference between the silicon fixed as CSH gel when the activation is carried out with 5 M sodium hydroxide and with higher concentrations can be observed.

The main reaction product in the first of the activations (sample A) is the formation of the CSH gel, while when the concentrations of activator solution are ≥ 10 M, the formation of the alkaline aluminosilicate is the main process of the activation reaction. This explains the differences observed among the calorimetric curves in Fig. 1.

Simultaneously, the results of the chemical attack are in accordance with those obtained by NMR. When the MK activation is carried out with 5 M NaOH concentration, the main signals of the ^{29}Si spectrum are Q_2 and $Q_2(1Al)$ corresponding to linear structures in silicate chains with some aluminium substitution similar to the expressed in the bibliography [14,15] for the CSH gel.

However, when sodium hydroxide concentration is 10 M or higher, the main signal in the ^{29}Si spectrum corresponds to a three-dimensional structure Q_4 of Si (4Al), very similar to that assigned to the alkaline polymer in the study carried out by Granizo [6] about the alkaline activation of MK.

Although the most important signal of the samples is that corresponding to the alkaline aluminosilicate (see Fig. 3), the spectra also present a Q_2 signal of a small CSH gel formation. Additionally, it is also deduced from the NMR spectra the presence of unreacted MK (broad signal at -107 ppm). That signal is very significant for 5 M NaOH solutions and considerable for 10-M solutions (see Fig. 3), which confirms the analysis of the insoluble residues in Table 3.

There exists different reactions occurring at different rates as a function of the medium OH^- concentration:

$$\begin{aligned}&\mathrm{MK} + \mathrm{Ca(OH)_2} \xrightarrow{[\mathrm{NaOH}]=5\ \mathrm{M}} \mathrm{CSH\ gel}\\&\quad + \text{Unreacted initial products (Mainly)}\end{aligned}$$

$$\begin{aligned}&\mathrm{MK} + \mathrm{Ca(OH)_2}\\&\quad \xrightarrow{[\mathrm{NaOH}]\geq 10\ \mathrm{M}} \text{Amorphous alkaline aluminosilicate}_{\text{(Main)}}\\&\qquad + \text{CSH gel}_{\text{(Secondary)}} + \text{unreacted product}\end{aligned}$$

When the activator concentration is high, a great amount of hydroxyl ions is in the liquid phase, impeding the dissolution of calcium hydroxide. The amounts of calcium cation present will be low and, thus, not enough to produce the precipitation of hydrated calcium silicate.

However, the reactant concentration in the aqueous phase is enough, and the conditions are adequate to the synthesis of the sodium aluminosilicate.

This alkaline polymer fixes OH^- groups in its structure, decreasing the aqueous phase pH with the subsequent favouring of the calcium hydroxide dissolution. Therefore, the calcium cation concentration may increase to the precipitation in form of hydrated calcium silicate.

For these high activator concentrations, the formation of the alkaline aluminosilicate is the factor that provokes the formation of the hydrated calcium silicate. Both precipitations are simultaneous; it explains the appearance of an unique calorimetric signal corresponding to the formation of both products.

However, when the activator concentration is 5 M or less, the OH^- amount notably decreases and calcium hydroxide dissolution is not so difficult. The Ca^{2+} amount in solution will be enough to precipitate in the form of hydrated calcium silicate. Besides, the synthesis of this gel will be favoured upon the formation of the alkaline polymer, because MK dissolution is slower in low OH^- concentration media. This makes that the initial amount of dissolved aluminates is not enough to produce the formation of the alkaline aluminosilicate and, consequently, silica will precipitate as CSH gel.

5. Conclusions

- When sodium hydroxide concentration is 5 M or lower in the MK activation in calcium hydroxide presence, the main product formed is CSH gel, although at the reaction time studied the MK activation is not completed.
- When the activation is carried out with 10 M or higher NaOH concentrations, the main reaction product is the alkaline aluminosilicate, with polymeric character, similar to that obtained in the MK activation with this same activator but in calcium hydroxide absence. As secondary reaction product (between 20% and 30%), CSH gel is obtained.
- A threshold OH^- concentration exists above which, the alkaline polymer is mainly formed, and beneath which, the CSH gel is the main reaction product.
- A high hydroxyl group concentration impedes the calcium hydroxide dissolution, Ca^{2+} concentration is small and the dissolved silicates are fixed as sodium aluminosilicate. When $[OH^-]$ is not so high, $[Ca^{2+}]$ in solution increases and it precipitates as hydrated calcium silicate.
- The chemical analysis of the samples treated with selective solutions, as well as the data collected from the NMR, gives a suitable information to differentiate both amorphous products obtained in the alkaline activation of MK in calcium hydroxide presence.

Acknowledgments

The authors of the present work wish to thank to the CICYT for funding this study through the projects MAT 93-0282 and MAT 96-0598.

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