JOURNAL OF MATERIALS SCIENCE **35** (2000) 6309–6315

Influence of the starting kaolin on alkali-activated materials based on metakaolin. Study of the reaction parameters by isothermal conduction calorimetry

M. L. GRANIZO, M. T. BLANCO-VARELA, A. PALOMO
C.S.I.C., Serrano Galvache-S/N 28033, Aptdo 19002, 28080 Madrid, Spain

The properties of the product obtained through alkaline activation of metakaolin are directly influenced by the characteristics of the starting kaolin. For the study of this influence, a complete characterization of two spanish kaolins used to synthesised the material has been carried out. A JAF conduction calorimeter was used to follow metakaolin reaction with NaOH solutions. Calorimetric data were obtained isothermally at 45°C with variable solution/solid ratio and NaOH solution concentrations varying from 12 to 18 M.

1. Introduction

Thermal treatment of kaolin at temperatures between 450 and 750°C produces its complete dehydroxylation. This process involves the breakdown of the kaolin structure and formation of a quasi-amorphous material in which Al changes its octahedral coordination to lower coordinations (tetra and pentacoordination) and Si changes from Q^4 (sharp NMR bands indicating an ordered environment) to broad NMR bands characteristical of an amorphous material named metakaolin [1]. Through metakaolin alkaline activation at temperatures below 100°C, cementitious materials with high mechanical properties can be achieved [2]. Characterisation studies of the obtained cements are reported from the microstructural and mechanical point of view [3, 4].

Although kaolin and metakaolin are able to be activated by alkaline hydroxide solutions, the rate at which the process occurs, likewise the characteristics of the obtained materials, depend on the reactivity of the raw aluminosilicate. Metakaolin (MK) dissolution rate is much higher than that of the kaolin due to the higher reactivity in basic medium of amorphous aluminosilicates or those poorly crystalline upon crystalline ones [2].

The metakaolin activation involves a dissolution step followed by a step of polycondensation that could be assigned to those described for zeolites which form when kaolinites or metakaolinites are attacked by NaOH solutions [5]. However, while in zeolite synthesis, an excess activator volume is used to permit crystalline products to be separated by filtrating, in the case of MK activated cements, a minimum activator solution volume must be used to obtain pastes with suitable plasticity and workability, obtaining practically amorphous materials. As in zeolite synthesis, compositional parameters, temperature and time of reaction, components mix order and siliceous source reactivity control the products properties [6].

In the literature, only a few studies are found about metakaolin alkaline cements in which the influence of parameters such as temperature, and curing time, mix order, compositional parameters, etc. are analyzed. [3, 4]. Davidovits [7], suggests composition limits to obtain optimum alkaline cements with high mechanical strengths, indicating the following molar ranges: M_2O/SiO_2, 0.2 to 0.8; SiO_2/Al_2O_3, 3.3 to 4.5; H_2O/M_2O, 10 to 25; M_2O/Al_2O_3, 0.8 to 1.6.

However, few references have been found relating raw kaolin characteristics to obtain alkaline cementitious materials with high mechanical properties.

The objective of this work is to relate different MK reactivity upon high alkaline solutions with the characteristics of raw kaolins.

2. Experimental

In the present work, two spanish kaolins from Guadalajara (C1) and Tudela (C2) were used. Table I, shows their chemical analysis.

Kaolins mineralogical characterization was carried out through Fourier transform IR absorption spectroscopy (FTIR), likewise by XRD, measuring their crystallinity degree (Hinckley index) [8]. Quartz contamination was determined by XRD using the method of known addition.

Thermal behaviour of the two kaolins was studied through DTA-TG, being heating rate 4°C/min.; 50 mv the DTA sensitivity; 400 mg sample weight; 1050°C the maximum heating temperature and kiln atmosphere, dry air without CO2.

The dehydroxilation isothermal weight loss curves behaviour was determined. Both kaolins were dried

TABLE I Chemical analysis of the two kaolins studied

	C1	C2
SiO_2	49.85	46.99
Al_2O_3	36.34	36.00
Fe_2O_3	0.57	0.54
MgO	0.15	0.00
CaO	0.00	0.82
P.F.	12.65	11.70

TABLE II Compositions tested for calorimetric studies

COMPOSITION	[NaOH] (M)	sol. ml/ 10g MK	METAKAOLIN (10g)
T1220	12	3	MK2
T1230	12	4.5	”
T1250	12	7	”
G1250	12	7	MK1
T1520	15	3	MK2
T1530	15	4.5	”
T1550	15	7	”
G1550	15	7	MK1
T1820	18	3	MK2
T1830	18	4.5	”
T1850	18	7	”
G1850	18	7	MK1

at 105°C and their weight loss curves were registered at 480, 520 and 560°C (points taken from the arising branch, at the top and in the decreasing branch of DTA curve). Heating rate until the fitted temperature was 25°C/min. Kaolin fraction (α) undergoing dehydroxylation at a time t is calculated dividing weight loss at that time by total water loss calculated in TG curve of the corresponding kaolin.

Particle size distribution was determined by Laser granulometry.

Specific surface of kaolins and metakaolins (obtained by kaolin heating at 750°C during 24 h), was measured by BET technique.

A JAF conduction calorimeter was used to follow metakaolin reaction with NaOH solutions. Mixes prepared for this purpose are given in Table II. Calorimetric data were obtained isothermally at 45°C with variable solution/solid ratio and different NaOH solution concentrations. Because mixes were done outside calorimeter, the fast heat evolution peak occuring when mixing MK with solution could not be registered.

Samples removed from the calorimeter at 50 hours, were treated with acetone-ethanol, dried in vacuum until constant weight and they were studied through XRD, FTIR. Their insoluble residue (I.R.) with diluted hydrochloric acid was determined at this time.

Identical samples as those used in the calorimeter runnings were synthesised to follow their hydration by other physical methods. These samples were placed in sealed plastic bags and submerged in a water bath at 45°C. At times determined by calorimetric studies (50 h), the reaction was stopped with acetone-ethanol treatment and the tests described earlier were carried out.

3. Results

3.1. Mineralogical characterization

In XRD difractograms of the two kaolins, kaolinite reflections can be seen (major phase) as well as quartz ones. Hinckley index has been calculated relating graphically the heights of kaolin reflections (020), (110), (11-1). In Table III, Hinckley indexes obtained for two kaolin samples are showed, likewise, quartz content of those samples determined by known addition method. Kaolin samples contain some quartz, but the amount present does not perturb the Hinckley index measurement. According to these results, C2 kaolin is less crystalline than C1 kaolin.

In the XRD difractogram of C2 kaolin, besides reflections corresponding to kaolinite, reflections corresponding to anatase, muscovite and pyrophyllite are observed (all of them of low intensity).

Fig. 1 shows the IR spectra of the two kaolins. Kaolinite absorption bands of of the C1 kaolin spectrum are more intense, sharp and they are shifted to lower frequencies than those showed in C2 kaolin spectrum.

The most significative case in kaolin spectra is the band at about 1100 cm^{-1}, less intense and broad in C2 kaolin. This band is assigned to partially polymerised amorphous silica [9] and it could indicate the lower crystallinity of this kaolin.-

With respect to H_2O vibrations in the 4000–3000 cm^{-1} region, some crystalline kaolins have strong and sharp absorption bands in 3630 and 3698 cm^{-1}, with others sharp but less intense at 3660 and 3670 cm^{-1}. The frequency at which these bands appear is determined by the distance of OH groups to the oxygen of neighbour groups. As this distance decreases, the vibration frequency is lower. In the two kaolins, these bands appear at almost the same frequency, but the band at 3670 cm^{-1} is much less intense in C2 kaolin; this could indicate, according to Murat [10] the lower crystallinity of this kaolin. Metakaolins are obtained by kaolin treatment at 750°C during 24 h.

Metakaolin difractograms present an amorphous halo that indicates the amorphous character of the product, likewise diffraction peaks corresponding to quartz. Besides, in metakaolin from C2 kaolin (MK2), the peaks corresponding to TiO_2 (anatase) and the reflections at 19°, 19,7°, 25,5°, 28,7°, 34,7° corresponding to dehydroxylated pyrophyllite appear. The structure of the pyrophillite present in metakaolin is a mix of tryclinic (1T) and monoclinic (2M) pyrophillite [11, 12].

In MK1 IR spectrum, bands at 460, 1080 and 1150 cm^{-1} appear, corresponding to Si-O vibrations from SiO_4. These bands are shifted to higher frequencies from those assigned in the literature [13]. At 800 cm^{-1}, a band appears corresponding to Al-O bending of tetrahedral Al.

TABLE III Crystallinity index and quarzt content in kaolins studied

KAOLIN	Crystallinity degree	Quartz content (% wt.)
C1	1.18	12.43
C2	0.7	7.04

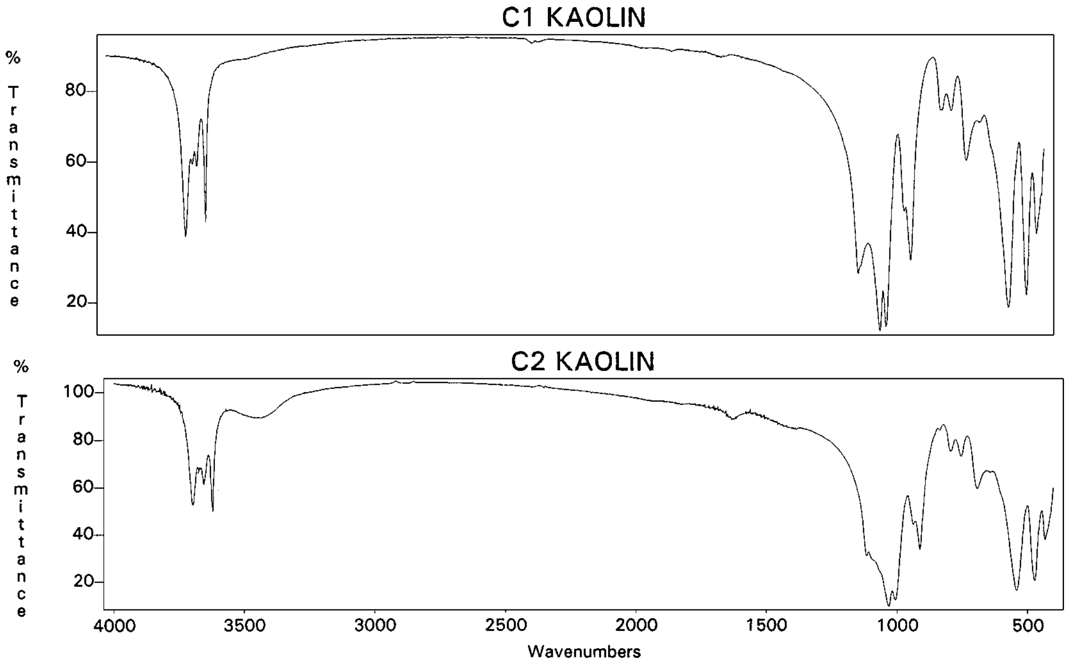


Figure 1 IR spectra of the two kaolins studied.

In MK2 IR spectrum, a series of weak bands at 415–440 cm^{-1}, one strong band at 490, other weaker band at 570 and a group of weak bands between 735–890 appear, that are interpreted as corresponding to dehydroxilated pyrophyllite. Bending vibration of Al-O of tetrahedral Al from metakaolin creates a band in 805 cm^{-1}.

In the 1000–1200 cm^{-1} region, the bands corresponding to Si-O of SiO_4 from the metakaolin appears, overlapped with those due to dehydroxilated pyrophyllite (1030 cm^{-1}, 1055 cm^{-1} , 1086 cm^{-1} y 1140 cm^{-1}). In Fig. 2, IR spectra of the two metakaolins is shown.

In Fig. 3a and b, DTA curves of kaolins are shown. Both the dehydroxilation endothermic peak of kaolinite and the exothermic related to Al coordination change from tetrahedral to octahedral occur at similar temperatures in both kaolins.

Some authors [14] relate the differences in the appearance temperature of the endothermic peak as well as its shape with different characteristics of the kaolin. Thus, the endothermic peak shape can be associated to kaolin crystallinity: the more sharp peak in C1 (Fig. 3a) and also more symmetrical indicates a higher crystallinity of this kaolin.

A kinetic study of the dehydroxylation of the two kaolins was carried out using their isothermal TG curves at three temperatures: 480°C, 520°C and 560°C.

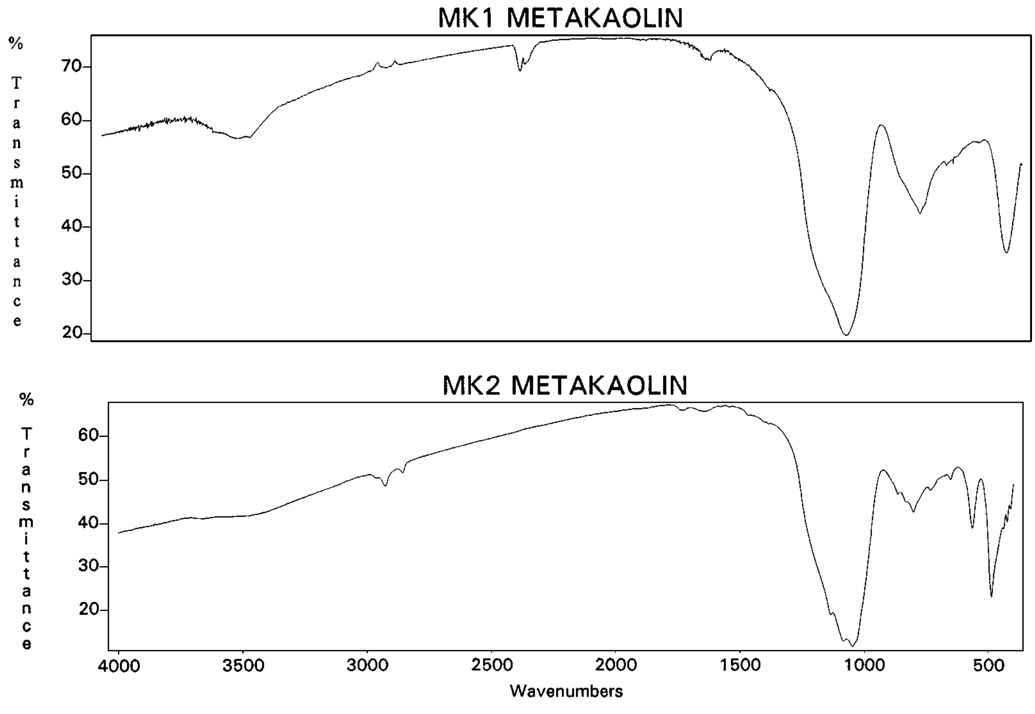


Figure 2 IR spectra of MK1 and MK2.

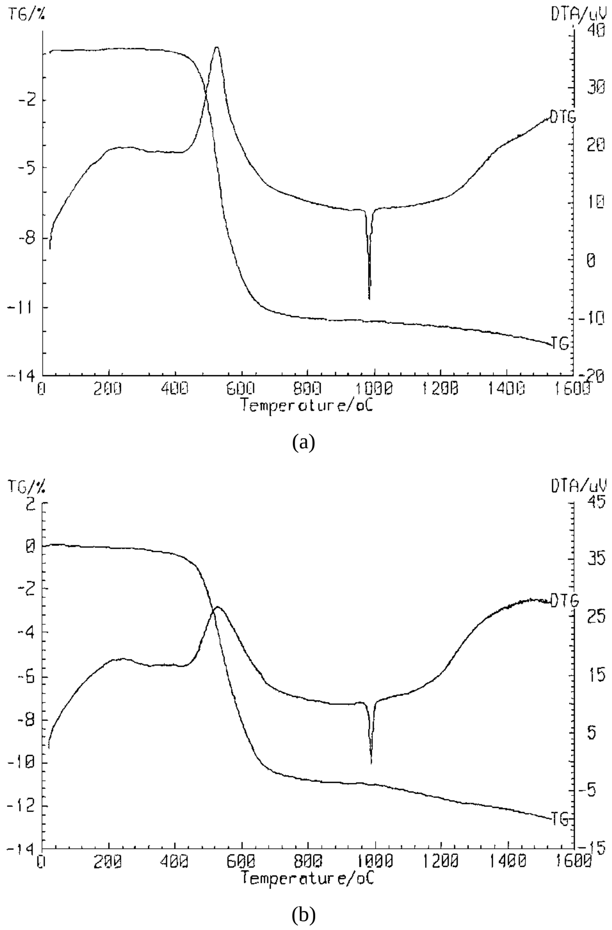


Figure 3 (a) DTA/TG curves for C1 kaolin; (b) For C2 kaolin.

The conclusion extracted from this study is that dehydroxylation rate at a fitted temperature is lower for C2 kaolin (Fig. 3b).

In Fig. 4, dehydroxilation degree (α) is represented versus $t/t_{0.5}$, where $t_{0.5}$ is the time at which 50% of the dehydroxilation has been produced. For a given kaolin, it is observed that α vs. $t/t_{0.5}$ curves are the same at the three temperatures, indicating that activation enthalpy is constant through the dehydroxilation process [15].

Dehydroxilation curves have been fitted to various reaction mechanisms, but only a good result is obtained when data is adjusted to the following equation:

TABLE IV Activation energy and Arrhenius preexponential factor

	Ea(Kcal/mol)	A(min^{-1})
C1	41.02	1.72×10^{10}
C2	40.58	4.98×10^{9}

TABLE V B.E.T. specific surface and particle sizes for the kaolins and their corresponding metakaolins

	BET (m^2/g)	10%wt. Under (μm)	50%wt. Under (μm)	90%wt. Under (μm)
C1	8.4	2.41	7.65	19.11
C2	9.5	1.40	6.44	49.43
MKC1	7.7	3.12	12.12	45.71
MKC2	6.7	1.65	7.66	48.41

$$\frac{d\alpha}{dt} = k(1-\alpha)^2 \quad \text{(second order reaction).}$$

Integrated equation is: $1/(1-\alpha) = kt$.

α vs. t curves are fitted to second order until high α values (0.9) in the two kaolins. Representing $1/(1-\alpha)$ versus t for each temperature, it is possible to obtain the rate constants for dehydroxilation reaction. From rate constants values, the activation energy for the process, according to Arrhenius law can be obtained, representing $\ln K$ versus $1/T$ (Fig. 5).

The activation energies obtained, as well as the values for the Arrhenius preexponential factor (Table IV) are of the same order than those found by Johnsson and Kessler [15].

The Arrhenius preexponential factor is directly proportional to the kaolin specific surface.

In Table V, grain size (in μm) for which 10%, 50% and 90% of the sample weight is inferior, as well as specific surface measured by B.E.T..

In Fig. 6a and b, particle size distribution of the two kaolins is shown. C1 kaolin curve is (Fig. 6a) a Gaussian, whereas the one of C2 kaolin (Fig. 6b) presents two modes, centred at 3.7 μm y 43 μm.

These results show that C1 kaolin has lower particle size and higher specific surface than C2 kaolin. Metakaolin formation involves specific surface decrease.

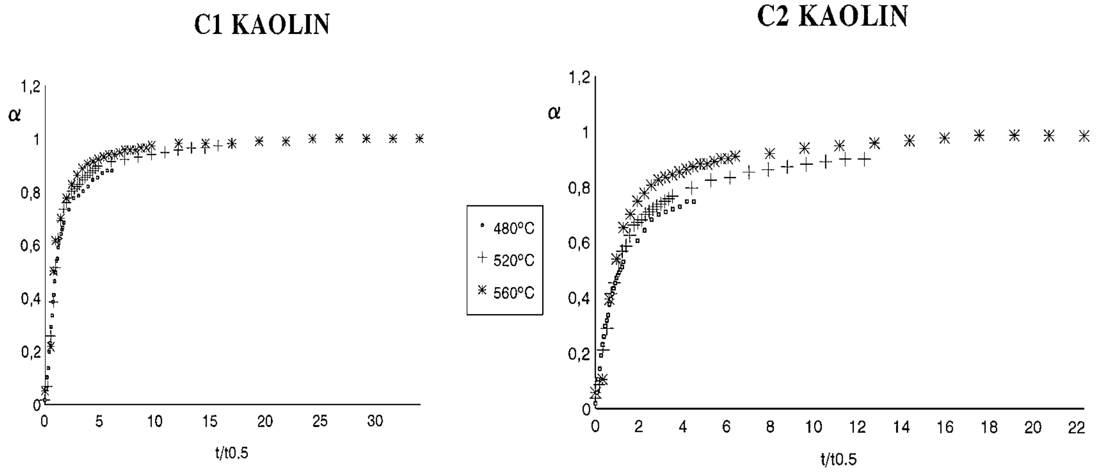


Figure 4 Dehydroxilation degree vs. $t/t0.5$ for the two kaolins at the three temperatures studied.

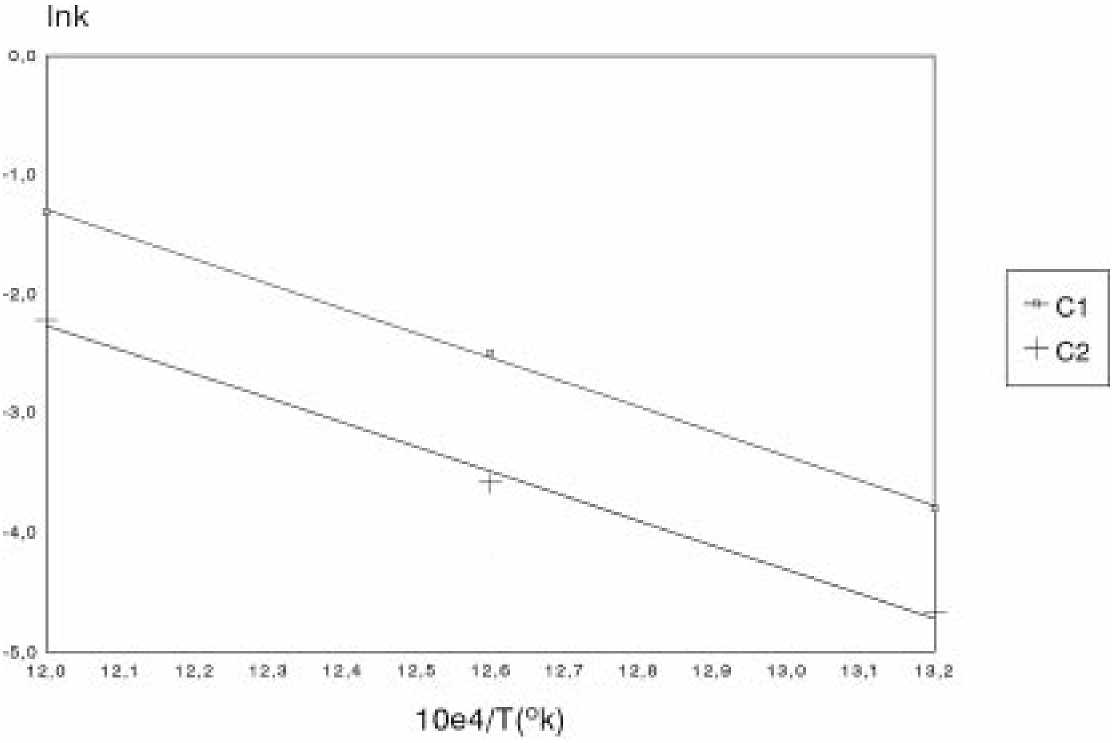
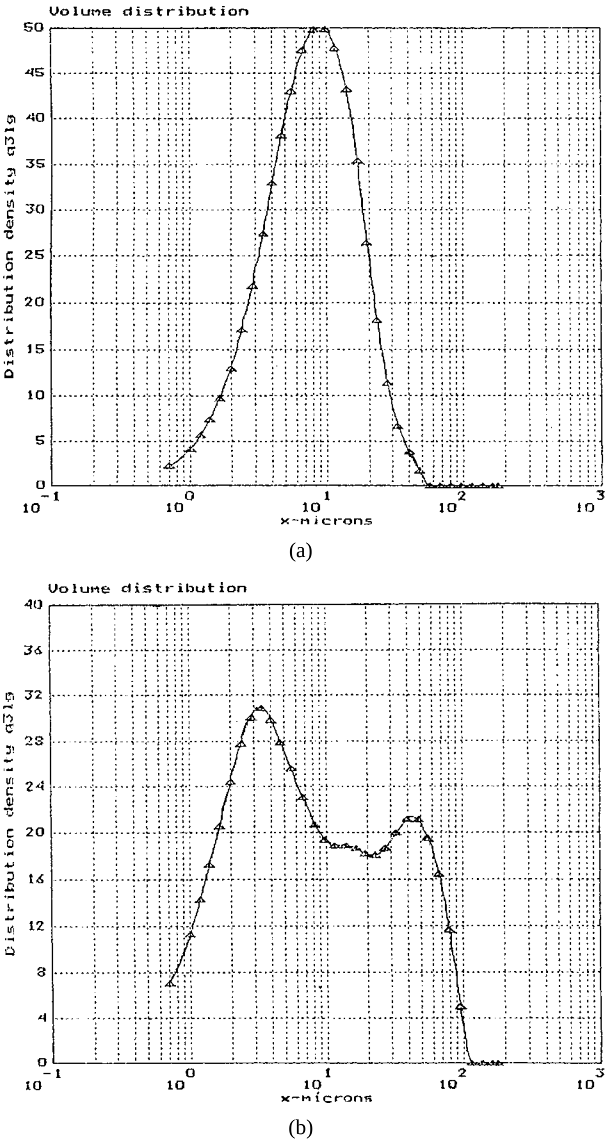


Figure 5 Ln K vs. $1/T$ for the two kaolins studied.



(a)

(b)

Figure 6 (a) Particle size distribution for C1 kaolin; (b) For C2 kaolin.

4. Metakaolin reactivity in alkaline solutions

In order to study the transformations taking place during metakaolin reaction in alkaline media of different concentration and to compare differences existing among these transformations depending on the raw kaolin and the different dosages, isothermal conduction calorimetry studies were carried out.

Results obtained in calorimetry studies are shown in Table VI where Insoluble Residue in hydrochloric acid of the samples after 50 hours of alkaline treatment are also shown. From these results, the following can be extracted:

- The induction period increases as NaOH solution concentration increases.
- The induction period increases as liquid percentage increases (except for compositions with 12 M and MK2 metakaolin in which there is little variation).
- Total heat increases as liquid percentage and NaOH concentration increases.

TABLE VI Results of the calorimetric tests

COMP.	INSOLUBLE RESIDUE	TOTAL HEAT (KJ/Kg)	MAX.RATE (W/Kg)	Tmax. (h)
T1220	49.97	231.75	16.02	3.6
T1230	30.62	365.73	16.50	3.4
T1250	20.39	434.76	16.90	3.8
G1250	11.26	568.76	14.72	3.5
T1520	41.81	314.35	15.15	5.8
T1530	23.93	441.82	14.86	7.9
T1550	18.45	442.69	15.16	8.4
G1550	8.96	602.10	43.65	10.7
T1820	34.67	398.94	13.05	19.4
T1830	20.80	418.04	9.41	32.8
T1850	15.95	471.23	8.21	45
G1850	8.26	647.97	27.04	24.5

- Total heat released is higher when MK1 is used.
- In the case of MK2, insoluble residue decreases as both NaOH concentration and liquid percentage (% Na_2O increase) increase. When MK1 is used, insoluble residue variation is very little when solution concentration increases because this metakaolin has already reacted with 12 M concentration.

With respect to XRD and FTIR of these samples activated during 50 hours and treated as described in the experimental part:

In XRD of these compositions, a big amorphous halo and some zeolite diffraction lines can be observed. In compositions with MK2 (T1220-T1850), diffraction lines of a sodalite type zeolite $Na_8(AlSiO_4)_6(OH)_2 \cdot xH_2O$ are observed; lines corresponding to the zeolite, becomes more intense as volume of activator increases, however this effect is not seen when NaOH concentration increases. In compositions with MK1 (G1250-G1850), besides sodalite type zeolite, the crystallization of $AlNaSiO_4 \cdot 1{,}03H_2O$ and faujasite is observed. The intensity of zeolite diffraction lines is low and similar to those observed in the treatment of MK2 with the same liquid percentage.

In IR spectra of alkaline activated MK2, as the aggresivity of the treatment increases (higher concentration or liquid percentage), a progressive shift of metakaolin band at 1100 cm^{-1} towards lower frequencies ($\gg$990 cm^{-1}), the progressive decrease of 800 cm^{-1} band until its disappearance and the formation of a new band at about 720 cm^{-1} characteristic of the formed polymer can be observed. In these spectra, the bands corresponding to dehydroxylated pyrophyllite and the zeolites identified by XRD remain.

IR spectra of alkali treated MK1 show the same bands displacements as those described former for MK2, but a total metakaolin reaction can be here observed at the lowest solution concentrations. Zeolite bands are also observable.

5. Discussion

Kaolin used for this study have a similar chemical composition, both containing some quartz as secondary specie. C2 kaolin has also small proportion of anatase and pyrophyllite.

The crystallinity of C1 kaolin is higher than that of C2, according to crystallinity degree indicators as Hinckley index, the more sharp and intense IR bands at 1100 cm^{-1} and 3670 cm^{-1} and the more sharp and symmetric shape of DTA dehydroxilation peak. Both kaolins dehydroxilate at similar temperatures and with very similar activation energies. The dehydroxilation rate at one given temperature is higher in C1 kaolin than in C2. Preexponential factor in Arrhenius equation, directly proportional to kaolin specific surface, is higher in C1 kaolin. B.E.T data confirm this.

Laser ray diffraction granulometry shows a particle size distribution very different in both samples, gaussian in the case of C1 kaolin and bimodal in C1 kaolin.

Thermal treatment of both kaolins at 750°C during 24 h, produces their dehydroxilation and, subsequently, the destruction of the crystalline structure, as well as a reduction in specific surface of the material. Their particle size distribution do not differ essentially. C2 kaolin contains dehidroxilated pyrophyllite and anatase in small proportion.

Alkaline activation of metakaolins until production of cementitious material is an exothermic process having three steps, an initial and very fast step of dissolution, strongly exothermic followed by an induction period in which heat exchange rate decreases and finally, a last exothermic step of reaction reactivation in which precipitation of cementitious materials occurs and after which, heat exchange rate decreases as reaction goes through.

During first and second steps, material is in plastic state and after third step, material harden has been produced.

Mechanism governing the induction period, as well as kinetic in each process step are unknown, however, the enlargement of this period when water/solid ratio increases, suggests that a critical concentration (oversaturation) of ionic species must be reached before cementitious material precipitation occurs. On the other hand, concentration of ionic species necessary for precipitation, would be higher when medium ionic force increases. This would justify the increase in the induction period when Na concentration of activator solution increases. Later studies in this way must be carried out.

The material obtained after metakaolins alkaline activation is mainly an amorphous sodium aluminosilicate and it can be characterized through FTIR, by its bands at 990 y 720 cm^{-1} [2].

Total heat released in the different reactions studied increases as Na_2O concentration increases and has higher values, in the same conditions, for MK1 (with higher specific surface), than for MK2. Also, Insoluble residues (Ins. Res.) of samples made from MK1 are lower than those of MK2 and all these data indicate that their reaction degree has been higher.

Ins.Res. could be a good way to measure the reaction degree reached, understanding this as metakaolin amount that remains unreacted. However, this parameter is not a direct measurement of the formed polymer because it contains also the amount of formed zeolites. The induced error when I.R. is considered as reaction degree is very small in those samples in which the lower liquid proportion is used (and even for the intermediate proportion), for whatever NaOH concentration, because they only contain traces of zeolites.

Reaction degree depends on activator solution concentration and on liquid/solid ratio. So, considering I.R. as the reaction degree, when representing it versus % Na_2O, a non lineal dependence can be observed, obeying the following equation:

$$\mathrm{RI} = 124.75 - 12.006\%\ \mathrm{Na_2O} + 0.3319\ (\%\mathrm{Na_2O})^2 \quad \text{with } R^2 = 0.937$$

Insoluble residue decreases exponentially as Na_2O in solution increases. This evolution is clearer for MK2, whereas reaction is almost complete for G1250 sample (synthesised with the lower Na_2O concentration in the activator solution).

So, reaction degree increases as NaOH concentration increases as it does reaction heat, for both MK2 and MK1. Reaction degree is superior in the same conditions for compositions with MK1. This result would be justified by its higher specific surface.

Besides, total reaction heat of C2 samples has a lineal variation with the insoluble residue according to the following equation:

$$\text{Total Heat} = 568.796 - 6.2348\,\text{RI}, \quad \text{with } R^2 = 0.9116$$

and, in this case, RI and total heat could be used as a measurement of reaction degree.

References

1. J. SANZ, A. MADANI, J. M. SERRATOSA, A. MOYA and S. AZA, *J. Am. Ceram. Soc.* **71**(10) (1988) 418.
2. A. PALOMO and F. P. GLASSER, *Br. Ceram. Trans. J.* **91** (1992) 107.
3. A. PALOMO, A. MACÍAS and E. MENÉNDEZ, in Proceedings of the Fourteenth Int. Conf. on Cement Microscopy, Costa Mesa, California, 1992.
4. M. L. GRANIZO, M. T. BLANCO-VARELA, F. PUERTAS and A. PALOMO, in X Int. Congress on the Chem. of Cement, Gothenburg, Vol. 3, p. 8.
5. A. MADANI, A. ANZAR, J. SANZ and J. M. SERRATOSA, *J. Phys. Chem.* **94** (1990) 760.
6. D. ROLLMANN, “Synthesis of Zeolites: An Overview” (1984). NATO ASI Series, No. 80. p. 109.
7. J. DAVIDOVITS, U.S. Patent 45009985 (1985).
8. D. N. HINCKLEY, in Eleventh Nat. Conf. on Clays and Clay Minerals.
9. M. P. DE LUXÁN and T. VÁZQUEZ, *Il Cemento.* **71**(3) (1974) 113.
10. M. MURAT, *Cem. and Concr. Research* **13** (1983) 511.
11. G. W. BRINDLEY and R. WARDLE, *Am. Mineralogist.* **55** (1970) 1259.
12. R. WARDLE and G. W. BRINDLEY, *ibid.* **57** (1972) 732.
13. H. J. PERCIVAL, J. F. DUNCAN and P. K. FOSTER, *J. Am. Ceram. Soc.* **57**(2) (1972) 57.
14. L. BRAMAO, J. G. CADY, S. B. HENDRICKS and M. SWERDLOW, *Soil Sci.* **73** (1952) 273.
15. H. B. JOHNSON and F. KESSLER, *J. Am. Ceram. Soc.* **52**(4) (1968) 199.
16. M. L. GRANIZO and M. T. BLANCO-VARELA, *J. Thermal Analysis* **52** (1998) 957.

Received 27 January 1997
and accepted 19 April 1999