Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 901–907

EFFECT OF THE KAOLIN PARTICLE SIZE ON THE POZZOLANIC BEHAVIOUR OF THE METAKAOLINITE PRODUCED

M. Kaloumenou, E. Badogiannis, S. Tsivilis and G. Kakali*

Inorganic and Analytical Chemistry Laboratories, Chemical Engineering Department
National Technical University of Athens, 9 Heroon Polytechniou St., 15773 Athens, Greece

Abstract

This paper reports an investigation of the effect of the particle size of kaolin on its transformation to metakaolinite. Kaolin from the island of Milos was either crushed or ground in order to produce four samples with different degrees of fineness (residue at 500 μm: 0–71.8%). The samples were treated thermally under different conditions in order to determine the optimum treatment conditions. The conversion of kaolinite to metakaolinite and the structural changes in the material during treatment were investigated by means of TG and XRD, respectively. Each sample was incorporated into a type I cement, at 20% by mass of cement, and the compressive strengths of the resulting blended cements were measured. It is concluded that the particle size of the raw kaolin does not affect the thermal conversion or the pozzolanic activity of the material. The use of crushed kaolin has many benefits since the furnace load can be increased, while the grinding process is needed only to reduce the size of the metakaolinite particles.

Keywords: kaolin, metakaolinite, particle size, pozzolanic behaviour, TG, thermal treatment, XRD

Introduction

The most common cementitious materials that are used as concrete constituents are fly ash, ggbs (ground granulated blastfurnace slag) and silica fume. They save energy, conserve resources and have many technical benefits [1]. Metakaolinite, produced by the controlled thermal treatment of kaolin, can be used as a concrete constituent, since it has pozzolanic properties [2, 3].

The literature indicates that research work on the transformation of kaolinite to metakaolinite is focused on three main areas. The first is the effect of the kaolin structure on the kaolinite-to-metakaolinite conversion [4–9]. The second deals with the use of thermoanalytical methods for investigation of the thermal treatment of kaolin [10–15], while the third concerns the pozzolanic behaviour of metakaolinite [2–3, 16–19]. Although there is disagreement in many partial topics, the level of

* Author to whom all correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

knowledge is satisfactory and is being continuously extended. It must be noted that the literature does not give answers to the effect of the kaolin particle size on the procedure, although this parameter affects mainly the economics of the processing.

The subject of this paper is the kaolin-to-metakaolinite conversion in relation to the duration and temperature of thermal treatment and the kaolin particle size. Additionally, the pozzolanic reactivity of the material produced is tested. This work comprises part of a project developed in our laboratory, aimed at an evaluation of poor-quality Greek kaolins.

Experimental

Results of the chemical analysis of the kaolin from the island of Milos are given in Table 1, while its XRD pattern is shown in Fig. 1. The main constituents of the kaolin are kaolinite and quartz. Alunite and cristobalite are also present as minor constituents. The kaolin was either crushed or ground in order to produce four samples with different degrees of fineness, referred as CR1, CR2, CR3 and GR, respectively. The particle size distributions of the samples, according to Rosin-Rammler, are shown in Fig. 2. The residue at 500 μm of the samples varies in the range 71.8–0.0%.

Table 1 Chemical analysis of the kaolin

Chemical analysis /%								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	*LOI*
64.58	20.49	0.72	0.50	0.12	0.20	0.00	2.00	8.10

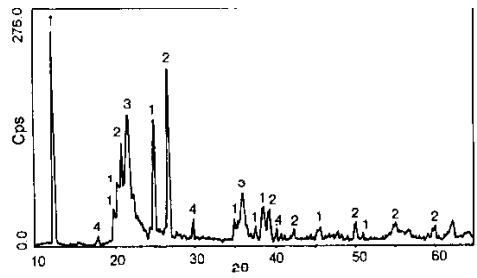

Fig. 1 XRD pattern of kaolin; 1 – kaolinite; 2 – quartz; 3 – cristobalite; 4 – alunite

The experimental procedure consists of the following stages.

Determination of the optimum treatment conditions

In order to define the optimum temperature, the sample GR (mass 140 g) was treated thermally at 550–950°C for a constant time of 3 h, using a laboratory pro-

rammable furnace. The temperature was raised at a constant rate (10°C min^{-1}) from mbient to the desired temperature.

In order to determine the optimum heating time, the sample GR was thermally reated at the previously established temperature for 1–8 h.

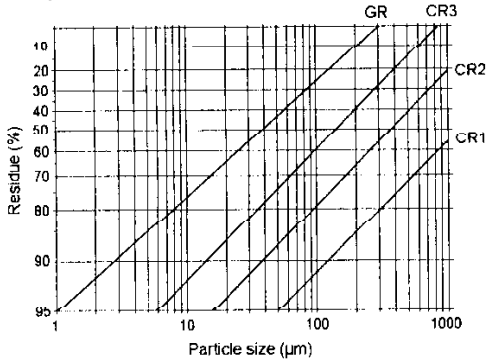

Fig. 2 Particle size distributions (Rosin-Rammler) of the crushed or ground kaolins

In both cases, thermogravimetric analysis (TG) was used to determine the losses n mass of the calcined kaolin samples, using a Netzsch STA409C instrument. The samples (~50 mg) were heated over the range 20 to 950°C at a constant rate of 20°C min^{-1} in an atmosphere of air.

In addition, each sample was incorporated into a Type I cement, at 20% by mass of cement, and the compressive strengths of the resulting blended cements were measured after 1, 2, 7 and 28 days (EN 196-1).

Finally, powdered samples were measured on a Siemens D5000 diffractometer and the data were evaluated by means of Siemens 'Diffrac Eva' software in order to identify the conversion of kaolinite to metakaolinite.

Effect of the kaolin particle size on the result of thermal treatment

The samples CR1-CR3 and GR were thermally treated under the defined conditions. TG, XRD and compressive strength tests were carried out, as described above.

Results and discussion

Table 2 shows the losses in mass (TG) of the calcined samples. The untreated kaolin loses 8.1% of its mass in the range 20–950°C. The loss in mass up to 650°C is mostly due to combined water in the structure of the kaolinite mineral, while the rest of the loss up to 950°C is caused by the removal of SO_3 from alunite.

The XRD patterns of the above kaolin samples are shown in Fig. 3. The characteristic peaks of kaolinite are present in the raw kaolin, but disappear from the patterns of samples calcined over 650°C. Incomplete metakaolinization is indicated only in the kaolin treated at 550°C. Each sample, at 20% by mass of cement, was in-

Table 2 Loss in mass of calcined kaolin, treated at different temperatures for 3 h

Treatment temperature/°C	Untreated kaolin	550	650	750	850	950
Mass loss (TG)/%	8.10	2.44	1.61	0.65	0.19	0.08

Table 3 Compressive strength tests; the effect of the treatment temperature (t=3 h)

Sample	Temperature/ °C	Compressive strength/N mm^{-2}			
		1 day	2 d	7 d	28 d
OPC		21.0	30.1	43.5	55.7
GR	untreated	14.2	22.7	34.6	47.1
GR	550	11.1	19.8	35.0	53.1
GR	650	10.3	20.0	35.3	56.7
GR	750	10.8	20.8	36.2	56.2
GR	850	13.5	23.2	36.1	56.3
GR	950	14.7	23.5	35.4	50.0

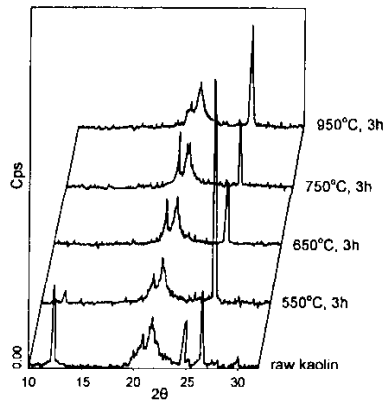

Fig. 3 XRD patterns of kaolin samples treated at different temperatures

corporated into a Type I cement and the compressive strengths of the resulting blended cements were measured (Table 3). The replacement of 20% of the cement lowers the early strength of a sample, as expected, due to the delay in the pozzolanic reaction. However, at 28 days, the samples containing metakaolinite after thermal treatment at 650–850°C yield the same strength as that of the mortar with pure OPC and a much higher strength than that of the mortar containing uncalcined kaolin. In Fig. 4, the pozzolanic behaviour of metakaolinite is clearly indicated. All the above results demonstrate that 650°C is the optimum temperature.

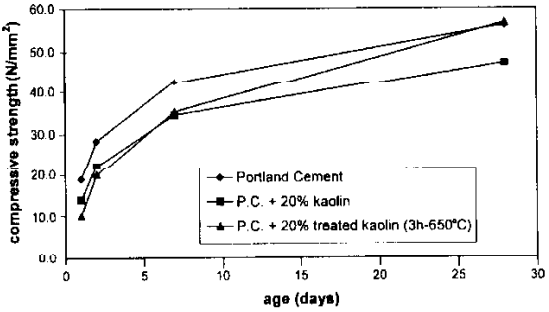

Fig. 4 Pozzolanic behaviour of thermally treated kaolin

The losses in mass (TG) of the calcined kaolins treated at 650°C for 1–8 h are given in Table 4. The samples treated for 3, 4, 6 or 8 h display negligible differences. The results of the compressive strength tests (Table 5) revealed that, after treatment at 650°C for 2–3 h, the mortars with 20% replacement of the OPC by calcined kaolin have higher 28-day compressive strengths as compared with the mortars containing kaolin heated at 650°C for more than 3 h.

Table 4 Loss in mass of calcined kaolin treated at 650°C for 1–8 h

Time/h	1	2	3	4	6	8
Mass loss (TG)/%	1.93	1.81	1.61	1.54	1.56	1.55

Table 5 Compressive strength tests; the effect of the duration of treatment (T=650°C)

Time/h	Compressive strength/N mm^{-2}			
	1 day	2 d	7 d	28 d
1	10.0	20.6	34.3	53.8
2	10.2	20.0	35.5	56.5
3	10.3	20.0	35.3	56.7
4	10.0	19.9	35.2	55.1
6	10.5	19.5	35.4	53.8
8	9.8	19.5	35.3	54.8

Table 6 Loss in mass of calcined kaolin (m=140 g, 650°C, 3 h); the effect of the kaolin particle size

Sample	CR1	CR2	CR3	GR
Mass loss (TG)/%	1.22	1.30	1.12	1.61

On the basis of the above results (Tables 2–5), a temperature of 650°C and a heating duration of 3 h were chosen for the investigation of the effect of the kaolin particle size on the kaolinite-to-metakaolinite transformation.

The kaolins with different particle sizes were treated at 650°C for 3 h and the losses in mass of the calcined samples were determined by means of TG (Table 6). It was found that the coarser kaolins (CR1–CR3) undergo lower losses in mass than that of the ground one (GR) (a low loss in mass of the calcined kaolin corresponds to a greater degree of conversion during heating). The above phenomenon may be attributed to the lesser depth of the material bed in the case of the coarse kaolin as the bulk density of the coarse kaolin (d_{CR1}=1186 kg m^{-3}) is greater than that of the ground one (d_{GR}=826 kg m^{-3}). Experiments on samples with the same bed depth, but with modification of the sample mass, indicated a similar mass loss for all the samples (Table 7).

Table 7 Losses in mass of calcined samples with different particle sizes and the same bed depth (650°C, 3 h)

Sample	CR1	CR2	CR3	GR
Bulk density/kg m^{-3}	1186	1157	1108	826
Mass/g	201	196	188	140
Mass loss (TG)/%	1.56	1.65	1.63	1.61

Table 8 Compressive strength tests; effect of the kaolin particle size (Treatment conditions: t=3 h, T=650°C)

Sample	Compressive strength/N mm^{-2}			
	1 day	2 d	7 d	28 d
CR1	11.0	19.4	35.5	52.2
CR2	9.4	20.5	35.3	52.8
CR3	10.1	20.1	35.5	53.2
GR	11.3	19.5	35.9	53.1

The XRD patterns of the above kaolin samples demonstrated the disappearance of the characteristic peaks of kaolinite. After grinding of the coarse kaolins (CR1–CR3), the compressive strength tests revealed (Table 8) that the mortars with 20% replacement of OPC by calcined kaolin have the same 28-day strengths, independently of the initial kaolin particle size. The above results are of great interest, as the use of crushed kaolin instead of ground kaolin has many benefits since the furnace load can be increased, while the grinding process is needed only to reduce the size of the metakaolinite particles.

Conclusions

The following conclusions can be drawn from the present study:

The particle size of the initial kaolin (for the studied range of fineness) does not affect the kaolinite transformation nor the pozzolanic behaviour of the material produced.

The used of crushed kaolin has many benefits since the furnace load can be increased, while the grinding process is needed only to reduce the size of the metakaolinite particles.

* * *

The authors wish to acknowledge the help of the Titan Cement Company S.A. for research collaboration on the evaluation of poor-quality Greek kaolins.

References

1 A. M. Neville, Porperties of concrete, Addison Wesley Longman Ltd., 4th and final edition. England 1996.
2 C. He, E. Makavicky and B. Osback, Applied Clay Science, 9 (1994) 165.
3 A. M. Dunster, J. R. Personage and M. J. K. Thomas, J. Materials Science, 28 (1993) 1345.
4 I. Lapides, N. Lahav, K. H. Michaelian and S. Yarin, J. Thermal Anal., 49 (1997) 1423.
5 G. B. Mitra and S. Bhattacherjee, The American Mineralogist, 54 (1969) 1409.
6 J. Dubois, M. Murat, A. Amroune, X. Carbonneau and R. Garbon, Applied Clay Science, 10 (1995) 187.
7 S. Chandrasekhar, Clay Minerals, 31 (1996) 253.
8 A. J. Leonard, J. American Ceramic Society, 60 (1977) 37.
9 E. Kristóf, A. Z. Juhász and I. Vassányi, Clays and Clay Minerals, 41 (1993) 608.
10 L. Piga, Thermochim. Acta, 265 (1995) 177.
11 Gensai Cai, J. Thermal Anal., 45 (1995) 167.
12 F. Földvári, J. Thermal Anal., 48 (1997) 107.
13 V. Balec and M. Murat, Thermochim. Acta, 282 (1996) 385.
14 J. Kristóf, M. Tóth, M. Gábor, P. Szabó and R. L. Frost, J. Thermal Anal., 49 (1997) 1441.
15 M. Gábor, M. Tóth and G. Komáromi-Hillier, Clays and Clay Minerals, 43 (1995) 223.
16 C. He, B. Osback and E. Makavicky, Cem. Conc. Res., 25 (1995) 1691.
17 M. S. Surana and S. N. Joshi, Advances in Cement Research, 3 (1990) 81.
18 K. A. Gruber and S. L. Sarkar, World Cement, 27 (1996) 78.
19 E. Badogiannis, M. Kaloumenou, G. Kakali and S. Tsivilis, 1st Int. Conf. on the Chemical Sciences and Industry, Halikidiki, Greece, 1998, 1, p. 456.