

METAKAOLIN AS SUPPLEMENTARY CEMENTITIOUS MATERIAL Optimization of kaolin to metakaolin conversion

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In this paper the optimization of the kaolin calcination is studied, aiming at using the produced metakaolin as supplementary cementitious material. Representative samples of poor Greek kaolin (Milos island) and a high purity commercial kaolin were tested. Samples were heated at different temperatures during different times. The optimization of calcination conditions was studied by DTA-TG and XRD analysis of the raw and thermal treated kaolin samples, by pozzolanic activity analysis of metakaolins and finally by strength development analysis of cement-metakaolin mixtures. This approach showed that heating at 650°C for 3 h is efficient to convert poor kaolins with low alunite content to highly reactive metakaolins. However in the case of kaolin with a high alunite content, thermal treatment at 850°C for 3 h is required in order to remove undesirable SO₃. Evidence was found that poor kaolins can be efficiently used for the production of highly reactive metakaolins.

Keywords: cementitious materials, heat treatment, kaolin, metakaolin, minerals, pozzolanic activity

Introduction

Fired clays, ground and mixed with lime, are one of the first developed structural materials. Fired clays are at present still widely discussed in cement research literature for their technical properties.

It is well known that during calcination (450–600°C) kaolinite loses OH lattice water and is transformed to metakaolinite, a material with low degree of structural order. In metakaolinite the Si–O network largely remains intact and the Al–O network reorganizes itself. While kaolinite is crystalline, metakaolinite has a highly disordered structure and offers good properties as mineral additive [1–3].

Owing to its unstable atomic arrangement, particularly of its Al–O portions, metakaolin is much more reactive than kaolin. Although not cementitious itself, is a highly reactive pozzolana which reacts particularly well with lime and forms, in the presence of water, hydrated Ca and Al silicates compounds. Therefore, it is considered to be a good synthetic pozzolana. Its pozzolanic character and potential for use in concrete and cement-based composites have been reported in several papers [4, 5].

The development of pozzolanic properties in fired clays mainly depends, on the nature and abundance of clay minerals in the raw material, on the calcination conditions and on the fineness of the final product. The calcination temperature producing the reactive state is usually in the range of 600–800°C. On continued heating, recrystallization and formation

of mullite takes place resulting in a decline of material reactivity [6–15].

This work forms part of a research project, aiming at using poor Greek kaolins in concrete manufacture. The optimization of the kaolin to metakaolin conversion, the study of the CH-metakaolin system [16], the effect of the crystallinity of the original kaolinite on the pozzolanic activity of metakaolinite [17, 18] and the properties and behavior of metakaolin cement and concrete system [19, 20] are the main research topics of this project.

This paper is focused on the optimization of the thermal treatment conditions of kaolin and their effect on the reactivity of the produced metakaolin. The calcination process of kaolin was monitored using DTA and XRD techniques, while the pozzolanic activity of metakaolin was evaluated by means of the Chapelle test and the strength development of cement-metakaolin mortars.

Experimental

Four representative Greek kaolins (K1, K2, K3 and K4) from Milos Island, having varying chemical and mineralogical composition, were examined. In addition, commercial kaolin of high purity (KC) was also used as reference material. The chemical and mineralogical analysis of the materials is given in Table 1. K1 and K2 are typical samples with an average kaolinite

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Table 1 Chemical and mineralogical analysis of kaolins

	K1	K2	K3	K4	KC
Chemical analysis/%					
SiO ₂	73.45	72.47	38.92	65.92	47.85
Al ₂ O ₃	18.04	18.40	35.38	22.56	38.20
CaO	0.40	0.35	0.54	0.36	0.32
MgO	0.03	0.03	0.06	–	–
Fe ₂ O ₃	–	–	0.60	–	0.30
K ₂ O	0.80	0.80	2.51	0.57	0.27
L.O.I.	8.10	8.00	21.50	8.60	12.30
SO ₃	3.00	3.12	10.03	2.00	–
Mineralogical composition/%					
kaolinite	38	39	65	52	96
alunite	7	7	22	5	–
quartz*	55	54	8	41	–
illite	–	–	–	–	3

*quartz (mainly)+cristobalite

and low SO₃ content. K3 has an average kaolinite but high SO₃ content while K4 has the highest and the lowest content of kaolinite and alunite, respectively.

In order to investigate the kaolinite to meta-kaolinite conversion as well as the alunite decomposition, DTA-TG analysis of the raw kaolins was performed using a Mettler Toledo TGA/SDTA 851 instrument. The samples (~50 mg) were heated from ambient to 950°C at a constant rate of 20 K min⁻¹ in air.

Samples of 140 g were heated at varying temperature (T: 550–950°C) during 1 to 8 h, using a programmable laboratory furnace. Mass loss during calcination was recorded for each kaolin sample. Before calcination, the kaolins were ground and their mean particle size (d₅₀) was 17.5, 14.0, 12.5 and 15.6 μm for K1, K2, K3 and K4, respectively. The mean particle size of the commercial kaolin KC was 6.0 μm.

In order to check the disappearance of the characteristic peaks of kaolinite, mineralogical analysis of the raw and thermally treated samples was carried out by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (CuK_α radiation, Ni Filter).

The pozzolanic activity of the calcined samples was evaluated according to Chapelle test [21]. 1 g metakaolin is mixed with 1 g Ca(OH)₂ and 100 mL boiled water. The suspension is subsequently boiled for 16 h and the free Ca(OH)₂ is determined by means of sucrose extraction and titration with HCl solution.

Each calcined sample was incorporated into a Type I cement, replacing 20% by mass of the cement with the produced metakaolin. The compressive strength after 28 days of the resulted mixtures was measured according to EN 196-1. The chemical anal-

Table 2 Chemical analysis of Portland cement and characteristics of clinker

Cement		Clinker	
Chemical analysis/%		Mineralogical composition/%	
SiO ₂	21.35	C ₃ S	60.1
Al ₂ O ₃	4.88	C ₂ S	15.9
Fe ₂ O ₃	3.82	C ₃ A	6.5
CaO	65.89	C ₄ AF	11.6
MgO	1.68	Moduli	
K ₂ O	0.60	Lime saturation factor (LSF)	0.959
Na ₂ O	0.07	Silica ratio (SR)	2.45
SO ₃	2.69	Alumina ratio (AR)	1.28
Cl ⁻	0.00	Hydraulic modulus (HM)	2.19

ysis of Portland Cement (PC-I/55) and the characteristics of clinker are given in Table 2.

Results and discussion

DTA-TG analysis

The main changes pointed out, by TG and DTA, during the heating of the samples are the following:

- T<100°C: low temperature release of water absorbed in pores, on the surfaces, etc.
- ~100–400°C: mass loss correlated with a pre-dehydration process, which takes place as a result of the reorganization in the octahedral layer, first occurring at the OH of the surface [10]
- ~400–650°C: dehydroxylation of kaolinite and formation of metakaolinite according to the reaction:

- $\text{Al}_2\text{SiO}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{SiO}_5(\text{OH})_x\text{O}_{2-x} + (2-x/2)\text{H}_2\text{O}$
- with a low value of x (about 10% of residual hydroxyl groups in metakaolinite)
- $\sim 500\text{--}900^\circ\text{C}$: decomposition of alunite in two stages according to the reactions:
- $2\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow 2\text{KAl}(\text{SO}_4)_2 + 2\text{Al}_2\text{O}_3 + 6\text{H}_2\text{O}$ ($480\text{--}620^\circ\text{C}$)
- $2\text{KAl}(\text{SO}_4)_2 \rightarrow \text{K}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 3\text{SO}_3$ ($770\text{--}900^\circ\text{C}$)

According to these reactions, alunite loses 13% of its mass during the first step and 29% during the second step, which corresponds to a 75% release of sulfates. According to the literature, 100% of sulfates are removed when alunite is mixed with kaolinite and quartz [9]. However, our study does not confirm this, since there was, still, detectable sulfate content in sample K3, after thermal treatment at 950°C .

- $\sim 1000^\circ\text{C}$: formation of mullite, as indicated by an exothermic peak.

According to the TG curves, the mass loss of samples K1, K2, K3, K4 and KC after calcination at 1000°C , is 9.26, 9.33, 10.84, 22.65 and 13.01 mass/mass%, respectively.

Figure 1 presents the DTG curves of the studied samples. As can be seen, the kaolinite to metakaolinite conversion, in all samples, take place in the range $450\text{--}650^\circ\text{C}$. The peak area is proportional to the kaolinite content in the raw sample. In sample K3, the decomposition of alunite is also recorded. The first stage overlaps with the kaolinite decomposition and causes a clear increase of the peak area. Two more stages of mass loss are recorded in the range $700\text{--}900^\circ\text{C}$. As will be discussed further, the XRD

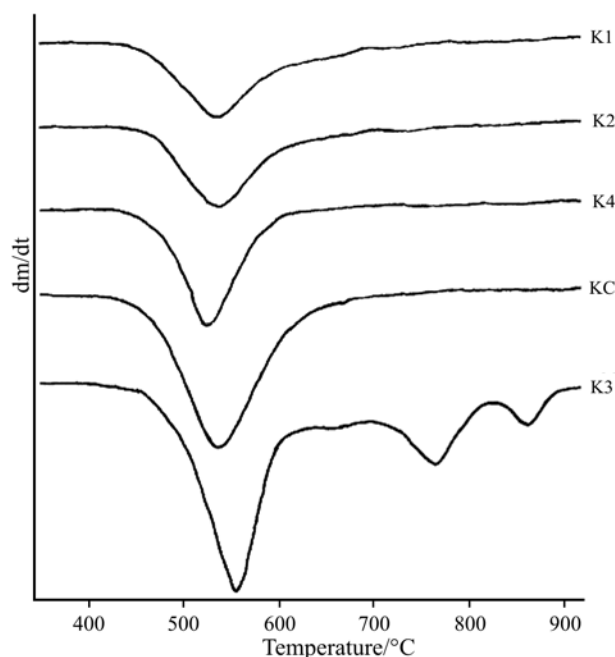


Fig. 1 DTG curves of kaolin samples

patterns of sample K3 (after thermal treatment at various temperatures) confirm that the alunite decomposition takes place in three stages.

Mass loss during calcination

Figure 2 shows the mass loss of kaolin samples in relation to the calcination temperature (calcination time: 3 h). As can be seen, the temperature increase above 650°C , does not cause any significant further mass loss in samples K1, K2, K4 and KC. This indicates that the kaolinite to metakaolinite conversion in these samples is almost complete, after thermal treatment at 650°C for 3 h. Sample K3 shows a continuous mass loss up to 850°C , due to the decomposition of alunite and the removal of sulfates. The SO_3 content of calcined kaolin K3 is related to the treatment temperature as follows: a) $T=650^\circ\text{C}$, $\text{SO}_3=10.56\%$, b) $T=750^\circ\text{C}$, $\text{SO}_3=6.90\%$, c) $T=850^\circ\text{C}$, $\text{SO}_3=2.37\%$, d) $T=950^\circ\text{C}$, $\text{SO}_3=2.23\%$. Since metakaolin is intended to be used as a supplementary cement material, K3 must be heated at 850°C in order to remove the excess SO_3 .

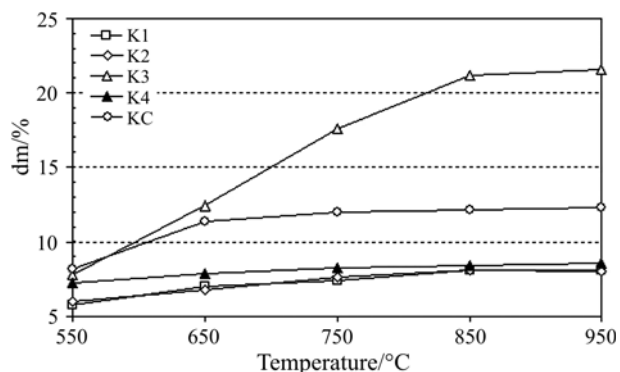


Fig. 2 Mass loss of kaolins in relation to the temperature of thermal treatment ($t=3$ h)

Figure 3 shows the mass loss of kaolin samples in relation to the calcination time. Based on the results mentioned above, the temperature of thermal treatment is 650°C , for the samples K1, K2, K4 and KC, and 850°C for the sample K3. As can be seen, the mass loss, in all samples, is stabilized after 2 or 3 h of thermal treatment.

XRD analysis

The XRD patterns of the produced metakaolins show that the characteristic peaks of kaolinite disappear after the thermal treatment of samples over 650°C . Incomplete metakaolinitization is indicated only in samples burnt at 550°C . At higher temperatures (above 800°C), crystallization occurs and γ -alumina and

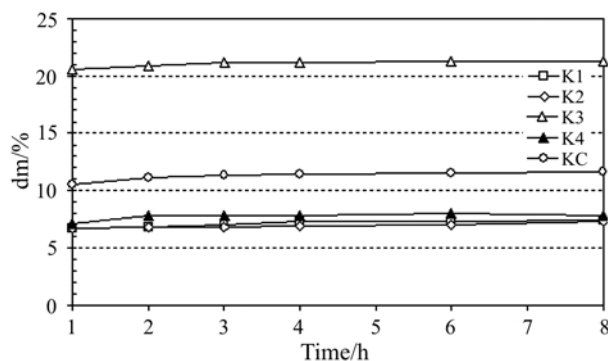


Fig. 3 Mass loss of kaolins in relation to the duration of thermal treatment (K1, K2, K4, KC: $T=650^{\circ}\text{C}$, K3: $T=850^{\circ}\text{C}$)

transition phases of metakaolinite are formed. At even higher temperatures, formation of mullite occurs.

Figure 4 presents the XRD background in the range $2\theta=20-30^{\circ}$ in relation to the temperature of the calcination ($t=3$ h). The XRD background in this area is considered to be proportional to the degree of disorder in the calcined samples. As can be observed, the background generally increases as the temperature of the thermal treatment increases up to 650°C . At higher temperature, a gradual decrease of the background is recorded. This indicates that the kaolinite decomposition has been completed at 650°C and disordered metakaolinite which has been formed at 650°C is gradually converted to more ordered forms at higher temperature.

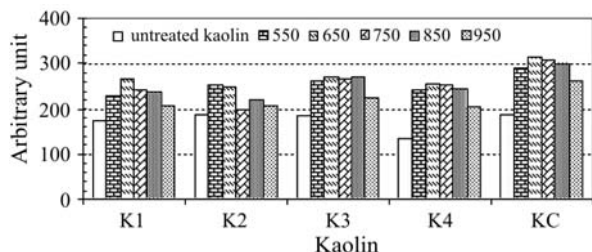


Fig. 4 XRD background ($2\theta:20-30^{\circ}$) of thermal treated kaolins in relation to the temperature of treatment ($t=3$ h)

XRD patterns of the sample K3 (Fig. 5) after thermal treatment for 3 h, at $550, 650, 750, 850$ and 950°C show step by step the decomposition of the alunite. Since metakaolins are intended to be used as supplementary cement materials, the removal of the SO_3 is essential. Alunite and kaolinite are still present at 550°C but they almost disappeared at 650°C . The identified products of the alunite decomposition are: $\text{KAl}(\text{SO}_4)_2$ and little $\text{Al}_2(\text{SO}_4)_3$ at 650°C , $\text{KAl}(\text{SO}_4)_2$, $\text{Al}_2(\text{SO}_4)_3$ and K_2SO_4 at 750°C , mullite, $\gamma\text{-Al}_2\text{O}_3$ and K_2SO_4 at 950°C . This indicates that alunite is firstly decomposed into $\text{KAl}(\text{SO}_4)_2$, and then into K- and Al-sulfates. $\text{KAl}(\text{SO}_4)_2$ is decomposed above 850°C and

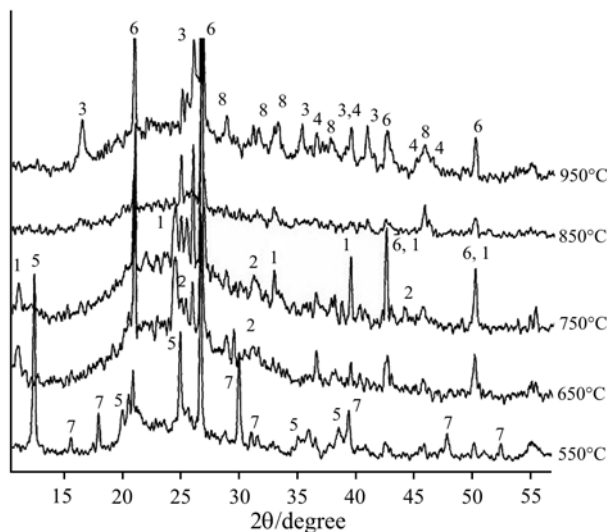


Fig. 5 XRD patterns of kaolin K3 treated at different temperatures for 3 h (1 – $\text{KAl}(\text{SO}_4)_2$, 2 – $\text{Al}_2(\text{SO}_4)_3$, 3 – mullite, 4 – $\gamma\text{-Al}_2\text{O}_3$, 5 – kaolinite, 6 – quartz, 7 – K-alunite and 8 – K_2SO_4)

the released Al_2O_3 , in the form of $\gamma\text{-Al}_2\text{O}_3$, is gradually incorporated in mullite. The DTA/TG curves of the sample also confirm the three-stage decomposition of alunite.

XRD patterns of kaolins K1, K2, K4 and KC treated at 650°C for varying time (1 to 8 h) show that characteristic peaks of kaolinite are disappeared after 2 h.

Pozzolanic activity

According to Chapelle test, the pozzolanic reactivity is evaluated on the basis of the amount of $\text{Ca}(\text{OH})_2$ consumed per gram of metakaolin during the pozzolanic reaction. Figure 6 presents the results of the Chapelle test for the studied kaolins, in relation to the temperature of their thermal treatment ($t=3$ h). As can be seen, the highest reactivity, in the case of K1, K2 and K4,

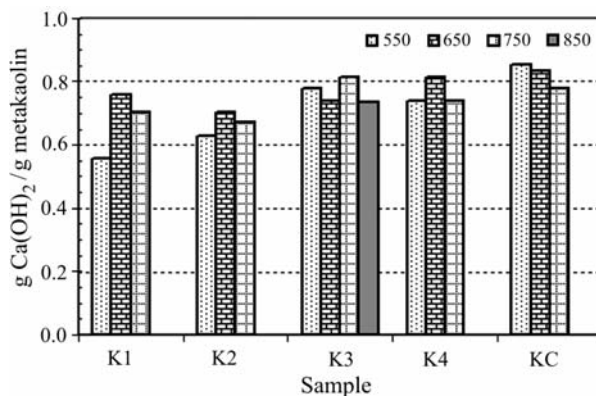


Fig. 6 Reacted $\text{Ca}(\text{OH})_2$ per g of metakaolin in relation to the calcination temperature ($t=3$ h)

was recorded after thermal treatment at 650°C, confirming the previous results. The thermal treatment at higher temperature lowers the pozzolanic activity, since the re-crystallization of metakaolinite reduces the availability of Al and Si that can react with Ca(OH)₂.

The reactivity of the metakaolin K3 differs from the other samples due to the high alunite content in the original sample. This sample shows the higher reactivity at 550 and 750°C, because the soluble sulfate salts, formed during the decomposition of alunite, also consume Ca(OH)₂. However, taking into account that SO₃ must be removed, the temperature of 850°C is the most appropriate.

As expected, the commercial product KC is the most reactive sample, since it has a considerably higher kaolinite content and lower mean particle size. Concerning the poor kaolins, the recorded differences of the metakaolinite reactivity are attributed to the varying kaolinite content and crystallinity of the original kaolin. As it was established elsewhere, well-ordered kaolinite is transformed in less reactive metakaolinite [5, 9, 18].

Compressive strength of cement-metakaolin mixtures

Figure 7 presents the 28 days compressive strength of the cement-metakaolin mixtures in relation to the temperature of the thermal treatment of kaolins. In cement mixtures with the calcined kaolins K1, K2 and K4 the best results were recorded when kaolins were treated at temperatures 650–750°C. In the sample with the kaolin K3, the best result was recorded when the kaolin was thermally treated at 850°C. In this case, the pozzolanic reactivity of metakaolin cannot be fully exploited because at lower temperatures, the negative effect of high SO₃ prevails, while at higher temperature the recrystallization of metakaolin has already started.

Figure 8 presents the 28 days compressive strength of the cement-metakaolin mixtures in relation to the time of the thermal treatment of kaolins

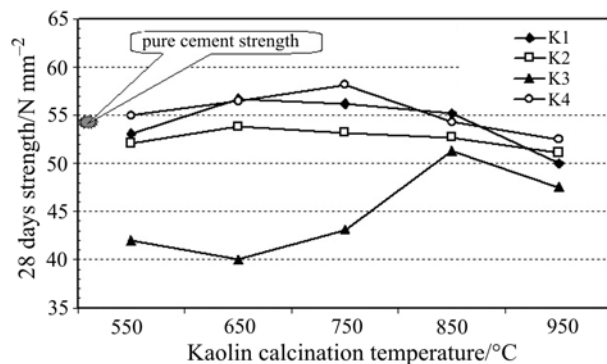


Fig. 7 28 days compressive strength of cement-metakaolin mixtures in relation to the calcination temperature (*t*=3 h)

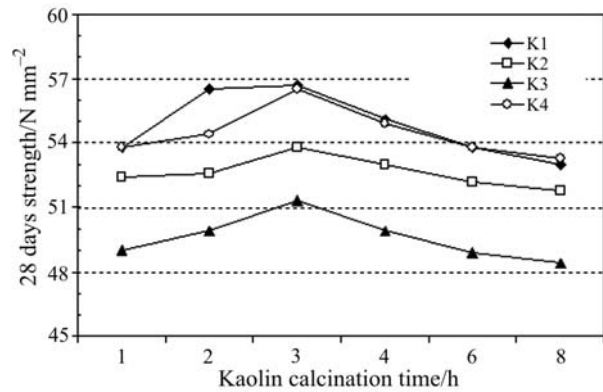


Fig. 8 28 days compressive strength of cement-metakaolin mixtures in relation to the duration of kaolin thermal treatment (K1, K2, K4: *T*=650°C, K3: *T*=850°C)

(K1, K2, K4: *T*=650°C, K3: *T*=850°C). In all cases, the best results were recorded when the thermal treatment lasted for 3 h.

The metakaolin cements, containing kaolins treated at 550–850°C (K1, K2, K4) and 850°C (K3), have a similar compressive strength as the pure cement (Fig. 7). These results are very promising, since in our tests the mean particle size of metakaolins was as high as about 15 μm. In practice, when metakaolin is used as cement or concrete constituent, its mean particle size is less than 5 μm. In this case, the 'filler effect' improves the early strength of the cement, while the completion of the pozzolanic reaction is accelerated, leading to improved 28 days compressive strength.

Final remarks

Tables 3 and 4 summarize the optimum thermal treatment conditions for the samples K1, K2 and K4, as they were evaluated on the basis of the above mea-

Table 3 Suggested thermal treatment temperature of kaolins K1, K2 and K4

Criterion	Temperature range/°C
TG (Fig. 1)	450–650
Mass loss during calcination (Fig. 2)	650
XRD (Fig. 4)	650
Chapelle test (Fig. 6)	650
Compressive strength (Fig. 7)	650–750

Table 4 Suggested thermal treatment time (650°C) of kaolins K1, K2 and K4

Criterion	Heating time/h
Mass loss during calcination (Fig. 3)	2–3
XRD (XRD analysis)	>2
Compressive strength (Fig. 8)	3

surements. As it is shown, thermal treatment at 650°C for 3 h meets all the criteria.

In the case of kaolin with high alunite content (K3), thermal treatment at higher temperature (850°C) for 3 h is required in order to remove most of the undesirable sulfates.

Conclusions

The following conclusions can be drawn from the study of kaolin to metakaolin conversion:

- Thermal treatment at 650°C for 3 h is efficient for poor kaolins with a low alunite content. At these conditions the produced metakaolin exhibits the highest pozzolanic reactivity.
- In the case of kaolin with high alunite content, thermal treatment at 850°C for 3 h is required in order to remove the undesirable SO₃.
- Poor kaolins can be efficiently used for the production of highly reactive metakaolins.

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