

Influence of the calcination temperature of kaolin on the mechanical properties of mortars and concretes containing metakaolin

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ABSTRACT. The effect of heating, to temperatures between 400 and 1200°C, on the dehydroxylation of kaolin and the pozzolanic activity of the resulting amorphous material were determined by a variety of analytical techniques. Mixtures of concrete containing variable amounts of kaolin calcined at 700°C were analysed and the results compared with those for concrete samples containing two different types of imported metakaolin. As shown in this work, Colombian kaolin can be used effectively as a raw material to obtain a highly active product (metakaolin). The optimum heating temperature for the kaolin is between 700 and 800°C.

KEYWORDS: calcined kaolinite clay, metakaolin, thermal process, pozzolanic activity, blended mortars and concretes, mechanical strength.

Heating kaolinite causes some structural changes that lead to the formation of metakaolin (2SiO₂.Al₂O₃) or mullite (3Al₂O₃.2SiO₂) (Sanz *et al.*, 1988; Kristof *et al.*, 1993; Moya, 1998). Metakaolin (MK), which is obtained by controlled thermal treatment of kaolin, is a highly-reactive amorphous aluminosilicate. Mixed with lime or cement, MK acts as a highly-reactive pozzolana (Kakali *et al.*, 2001; Shvarzman *et al.*, 2003), and endows mortar and concrete mixtures with improved strength-related mechanical properties (e.g. compressive and flexural strength), as well as reduced permeability (Frias & Cabrera, 2000; Malopesky & Pytel, 2000; Mejía de Gutiérrez *et al.*, 2000; Ramlochan & Thomas, 2000; Ramlochan *et*

al., 2000; Cabrera & Frías, 2001; Gruber *et al.*, 2001; Qian & Li, 2001; Sabir *et al.*, 2001; Vu *et al.*, 2001; Courard *et al.*, 2003; Frías & Sánchez de Rojas, 2003; Poon *et al.*, 2003; Bans *et al.*, 2005; Razak & Wong, 2005). As such, MK can be used to extend the service life of structures and architectural works in strongly aggressive environments, with some advantages over silica fume (e.g. its white colour, which improves the appearance of the end-products) (Caldarone, 1994; Balogh, 1995). Metakaolin has been marketed since 1994 by manufacturers such as Engelhard Corporation (MetamaxTM) and Advanced Cement Technologies (PowerpozzTM) in the USA (MKA), or the British company ECC International Europe (Metastar, Polestar) in Europe (MKE).

In this study, we obtained MK by thermal treatment of a Colombian kaolin and determined the strength-related mechanical properties of

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concretes containing it, with a view to comparing it with those of mixtures containing imported MK.

MATERIALS AND METHODS

Materials

The raw material used in this work was a sample of kaolin from La Unión (Antioquia, Colombia) which was pre-processed in order to obtain the following chemical composition: 45.5% SiO_2 , 1.30% Fe_2O_3 , 38.9% Al_2O_3 and 14.05% loss on ignition (LOI). Figure 1a shows the Fourier transform infrared (FTIR) spectrum for the kaolin as recorded on a Shimadzu FTIR 8400 spectrophotometer. As can be seen, the spectrum exhibits the typical bands for kaolinite at 3695, 3668, 3652 and 938 cm^{-1} , corresponding to the stretching vibrations of O-H bonds from the inner-surface hydroxyls in addition to the inner hydroxyl bands (3620 and 916 cm^{-1}) (Van der Marel & Beutelspaecher, 1976; Wilson, 1994; Gardolinski & Lagaly, 2005). Based on the X-ray diffraction

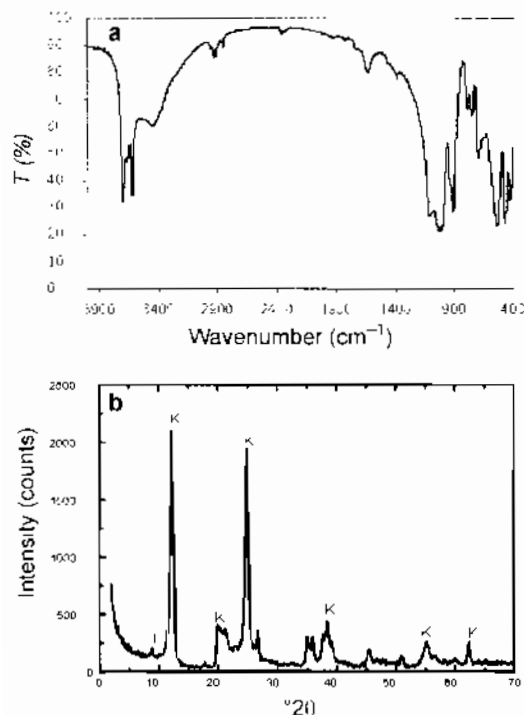


FIG. 1. (a) FTIR spectra, and (b) XRD patterns for La Unión kaolin.

(XRD) pattern for the material obtained with a Rigaku R-INT 2200 and on a semi-quantitative analysis of its constituent minerals using the disoriented powder technique (Fig. 1b), we found that the kaolin consisted of 97% kaolinite (K) and 3% mica. Also, as revealed by a transmission electron microscopy (TEM) study using a Zeiss EM910 microscope equipped with an Oxford Instruments Inca Energy EDX microanalytical system, the kaolin consisted of well defined heterometric crystals 2–2.5 μm or 0.2–0.3 μm in size in addition to micas at different stages of transformation into kaolinite as well as some halloysite (see Fig. 2). The presence of zircon and ilmenite crystals indicate that the kaolin was formed via a residual process.

The cement used in the mortar and concrete mixtures was type V Portland (OPC) and contained 20.27% SiO_2 , 3.91% Fe_2O_3 , 5.34% Al_2O_3 , 61.7% CaO , 1.44% MgO and 3.57% LOI. Its Blaine fineness was 420 m^2/kg .

Experimental procedure

The thermal treatment of the kaolin was conducted under controlled temperature and time conditions. The products obtained at different temperatures over the range 500–1200°C were characterized by XRD, FTIR, differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The DTA and TGA analyses were performed on Universal V2.5H equipment from TA Instruments (SDT 2960), using a heating rate of 2°C/min and an air-flow rate of 100 ml/min. Pozzolanic activity was determined chemically (NTC 1512), mechanically (ASTM C311) and from the proportion of calcium hydroxide combined with MK (DTG). The Colombian metakaolin (MKN) obtained was used in mixtures of mortar and concrete which were analysed for compressive strength. Finally, the results obtained for the concrete mixtures were compared with those of others containing an imported metakaolin (MKE or MKA) in identical proportions.

RESULTS AND DISCUSSION

Thermal treatment

Figure 3 displays the results of the DTA/TGA tests on the kaolin and clearly shows a peak at 516°C corresponding to its dehydroxylation (i.e. the



FIG. 2. TEM images showing (a) kaolin crystals.

conversion of kaolinite, $2\text{SiO}_2 \cdot \text{MK}$, $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) in addition to a small peak at 1000°C associated with the formation of the spinel phase that was subsequently converted to mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). Based on these results, the thermal treatment was conducted at different temperatures and times in order to conduct the thermal treatment of the kaolin (Table 1). The degree of dehydroxylation of the thermally-treated kaolin was calculated from the weight losses at each temperature. The degree of dehydroxylation was 0.90 at 600°C, 0.96 at 700°C

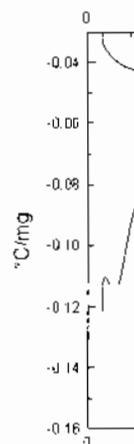


FIG. 3.

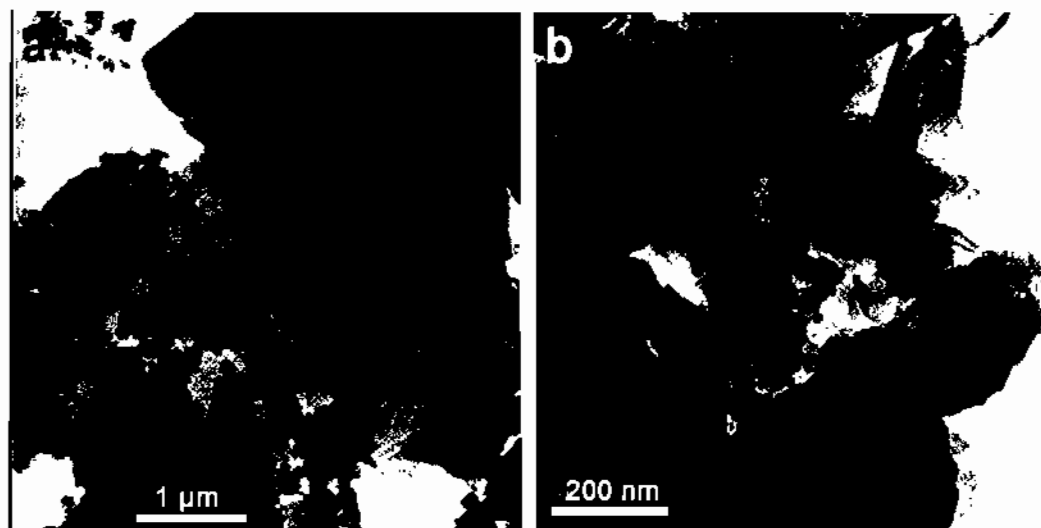


Fig. 2. TEM images showing (a) the transformation of mica into kaolinite; and (b) the formation of halloysites from kaolinite and nanometric kaolinite crystals.

conversion of kaolinite, $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, into MK, $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) in addition to an exothermic peak at 1000°C associated with the formation of a spinel phase that was subsequently transformed into mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). Based on the results obtained at different temperatures and times, we chose to conduct the thermal treatment at $500\text{--}1200^\circ\text{C}$ for 1 h. The degree of dehydroxylation of the thermally-treated kaolin was calculated (accounting for weight losses at each temperature) and found to be 0.90 at 600°C , 0.96 at 700°C and 0.97 at 800°C .

The XRD patterns for the original kaolin exhibited the typical peaks for kaolinite (K) at 12.4 , 20.1 and $24.9^\circ 2\theta$; as the kaolin dehydroxylated and MK formed, a broad band appeared in the 2θ region from 20 to 30° consistent with the presence of an amorphous material. Heating to temperatures $>900^\circ\text{C}$ caused the transformation into mullite, which exhibits typical peaks at 16.43 , 26.20 , 33.22 , 35.27 , 40.87 and $60.71^\circ 2\theta$.

Similarly, a comparison of the FTIR spectrum for the original kaolin with those for the thermally

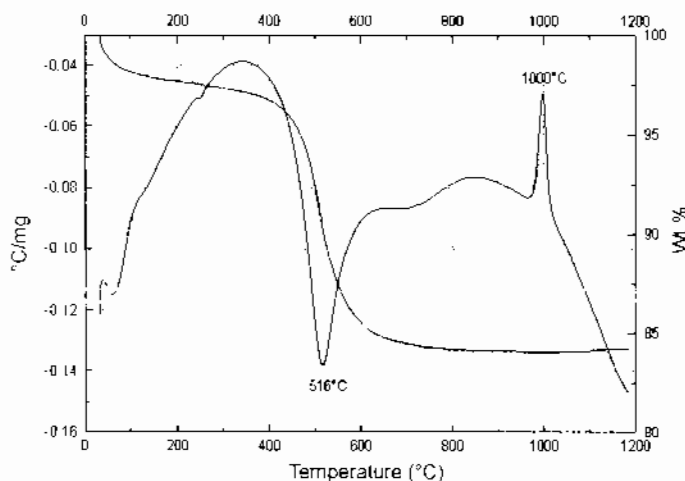


Fig. 3. DTA and TGA results for La Unión kaolin

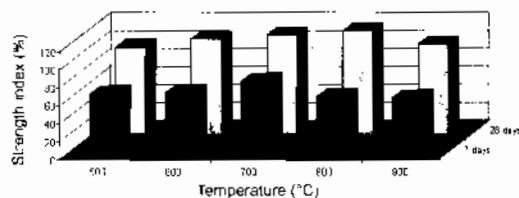


Fig. 4. Percent increase in compressive strength after 7 and 28 days of curing.

treated kaolin samples revealed a decrease in the bands corresponding to vibrations of the O–H bond (i.e. 3695, 3620 and 911 cm^{-1}) at temperatures $>500^\circ\text{C}$, in addition to broadening in others (particularly those in the 1000 cm^{-1} region). The band at 536 cm^{-1} , associated with the ^{11}Al –O bond (octahedral), disappeared gradually as a new one associated with the $^{1\text{A}}\text{Al}$ –O bond emerged at 820 cm^{-1} ; this confirms the transformation into MK. These results are consistent with those reported by other authors (Van der Marel & Beutelspacher, 1976; Rahier, 2000; Kakali *et al.*, 2001).

Pozzolanic activity

For a cement to be considered pozzolanic as per ASTM C618, it must exhibit a strength index $>75\%$

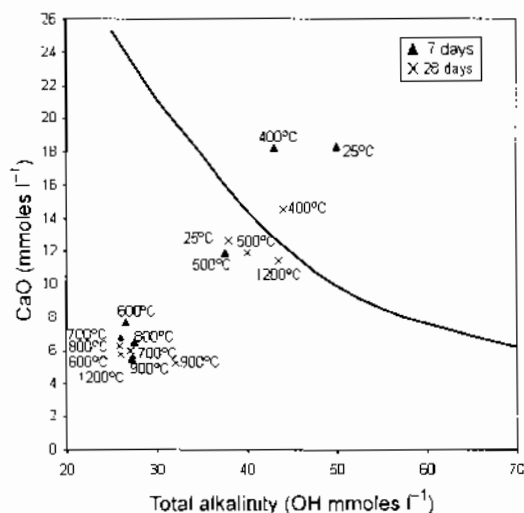
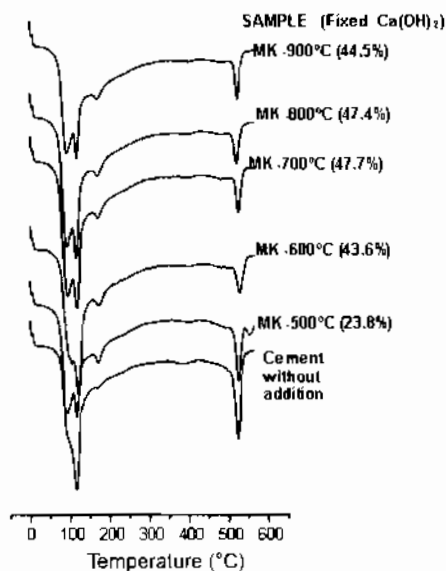


Fig. 5. Results of the Frattini and fixed calcium hydroxide (DTG) tests.

after 28 days. This index is calculated as the ratio of the compressive strength of a mortar with 20% added MK to that of a reference mortar with no additional MK (ASTM C311). As can be seen in Fig. 4, the kaolin samples heated at temperatures of 600 to 800°C exhibit a strength index $>100\%$ (e.g. the sample heated to 800°C exhibited an index of 115% after 28 days of curing).

The results of the Frattini tests for paste mixtures containing 20% of thermally treated kaolin were fairly consistent with the mechanical-strength values. In fact, the samples heated at temperatures of 500 to 900°C shifted to the lower-left zone as the temperature increased: this was especially apparent after 28 days and reflects an increased pozzolanic character in the resulting material. Conversely, the original sample (25°C), and those heated at 400 and 1200°C, plot above the solubility curve (see Fig. 5a) (Mejía de Gutiérrez *et al.*, 2004).

The pozzolanic activity was confirmed by analysing for calcium hydroxide fixed in paste with 20% of MK. Following curing for 60 days, the weight loss corresponding to the DTG peak at 440–580°C was evaluated (Bhatti, 1991). Such a peak is associated with the dehydroxylation of calcium hydroxide, $\text{Ca}(\text{OH})_2$. The largest proportion of lime fixed by the MK, 47.7%, corresponded to the sample heated at 700°C, followed by that heated at 800°C (see Fig. 5b).



Mortar and concrete mixture strength tests

As shown in Fig. 6, the best results were obtained with 20% kaolin heated at 600 or 800°C. The 20% kaolin heated at 600 or 800°C exhibited an increased compressive strength compared to the reference mortar (no kaolin added). The increase in strength at short curing times was similar irrespective of the heating temperature of the kaolin ($\sim 10\%$). After 28 days of curing, the heating temperature had a minor influence as it caused increased decomposition of kaolinite (0.97 at 800°C) and, therefore, an increased MK content in the resulting material. In all of these tests were considered pozzolanicity tests.

Based on this information, the best results were obtained by heating at 700°C. The pozzolanicity tests mixtures. The amounts, per m³ of concrete, were 475 kg of binder (O.C. 42.5) and 1743 kg of siliceous aggregate (O.C. 1.25 sand), the water-binder ratio was 0.40. The maximum nominal aggregate used in the mixture was 1.25. The fineness module (a single test) to describe the grading curve of the aggregate was 2.8. Metak

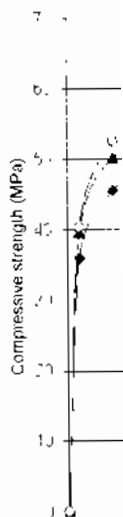


Fig. 6.

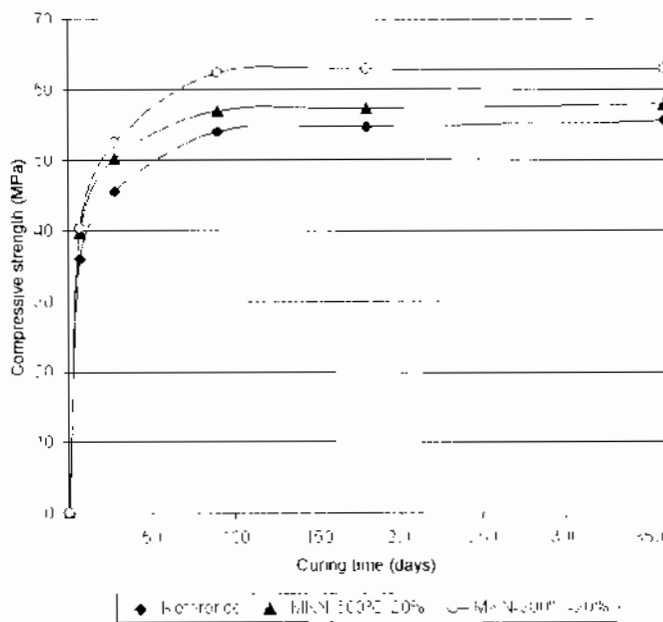


FIG. 6. Compressive strength of blended mortars (20% MK).

Mortar and concrete mixtures: compressive strength tests

As shown in Fig. 6, the blended mortars with 20% kaolin heated at 600 or 800°C exhibited an increased compressive strength relative to the reference mortar (no kaolin added). As a rule, the increase in strength at short curing times was similar irrespective of the heating temperature of the kaolin (~10%). After 28 days, however, the heating temperature had a more significant influence as it caused increased dehydroxylation of the kaolinite (0.97 at 800°C) and thus also resulted in an increased MK content in the mixture. The results of these tests were consistent with those of the pozzolanicity tests.

Based on this information, we chose the material obtained by heating at 700°C to add to concrete mixtures. The amounts, per m³ of concrete used, were 475 kg of binder (OPC + addition) and 1743 kg of siliceous aggregate (60% gravel + 40% sand), the water/binder ratio was kept constant at 0.40. The maximum nominal size of the coarse aggregate used in the mixtures was 19.1 mm and the fineness module (a single parameter used to describe the grading curve of fine aggregate) of the fine aggregate was 2.8. Metakaolin was added as a

10% partial replacement of cement (OPC) in the concrete mix. In addition, we studied similar concrete mixtures containing two types of imported MK (MKF and MKA). Accomplishing the desired slump in the mixtures (e.g. 95+10 mm) required using an additive (Sikament NS). The amount of additive used in the blended concretes with MKN, MKA and MKF was 1.7%, 0.6% and 0.9%, respectively, relative to the cement.

Figure 7 shows the results of the compressive strength tests for the concrete samples. The mixtures containing MKN exhibited greater strength

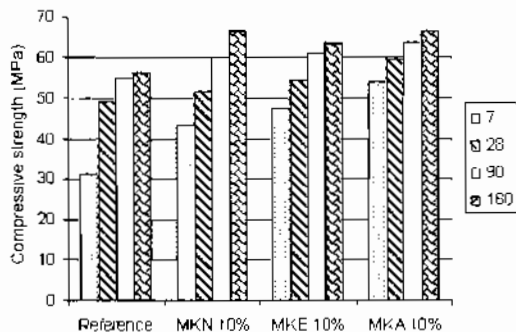


FIG. 7. Compressive strength of concrete mixtures containing a 10% proportion of various metakaolins.

than the reference samples, but were initially weaker than the samples containing MKE and MKA. After 90 and 180 days of curing, however, the results were comparable (e.g. the strength of the MKN-containing samples after 180 days was 18% greater than those of the reference mixture); this can be ascribed to differences in particle size distribution between the materials (see Fig. 8).

The average particle size for MKN, MKE and MKA was 11.15, 2.87 and 7.35 μm , respectively, and the proportion of particles sized 10–100 μm was 51, 11 and 40%, respectively.

CONCLUSIONS

The results obtained in this study allow us to draw the following conclusions:

(1) The optimum temperature for heating a kaolin in order to obtain MK with a high pozzolanic index is 600–800°C, where the degree of kaolinite dehydroxylation is 0.90–0.97. Based on our results, this temperature range also results in the smallest degree of crystallinity in the treated material.

(2) Heating the studied kaolin at 700–800°C produces a MK of increased pozzolanic activity (specifically, 115% after 28 days for the samples heated at 800°C).

(3) Concrete supplied with the MKN prepared in this work was initially found to exhibit less compressive strength than concrete supplied with two imported kaolins (MKA and MKE) in the same proportion (10%). However, after 90 days these were comparable.

(4) Further testing will be required in order to investigate the effect of MK particle-size distribution on the concrete strength.

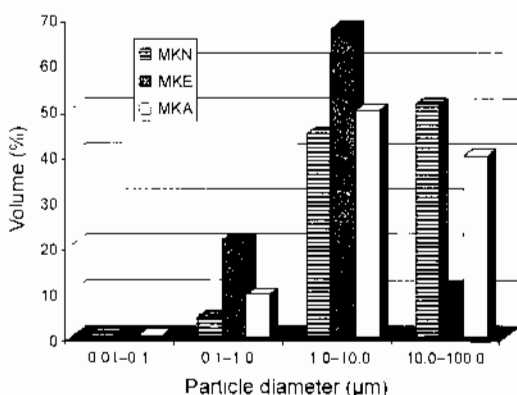


FIG. 8 Particle-size distribution for the metakaolins.

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