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Effect of elevated temperature on physico-mechanical properties of metakaolin blended cement mortar

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Abstract. An experimental investigation was conducted to evaluate the performance of mortars with and without Metakaolin (MK) exposed to elevated temperatures 200°C, 400°C, 600°C and 800°C for two hours. The binder to sand ratio was kept constant (1:5.23). The ordinary Portland cement (OPC) was replaced with MK at 0%, 5%, 10% 20% and 30%. All mixtures were designed to have a flow of 94 ± 5%. The compressive strength of mortars before and after exposure to elevated temperature was determined. The formation of various decomposition phases were identified using X-ray diffractometry (XRD) and differential thermal analysis (DTA). The microstructure of the mortars was examined using scanning electron microscope (SEM). Test results indicated that MK improves the compressive strength before and after exposure to elevated temperature and that the 20% cement replacement of MK is the optimum percentage.

Keywords: elevated temperature resistance; metakaolin; mortar; microstructure; blended cement.

1. Introduction

The use of calcined clays as a pozzolanic additive for cement has been known since the Romans time. In recent years, there has been an increasing interest in the utilisation of metakaolin (MK) as a supplementary cementitious material in concrete (De Silva and Glasser 1990, Ambroise *et al*. 1994, Basheer *et al*. 1999, Palomo *et al*. 1999, Wild *et al*. 1996). In many countries around the world, kaolin and clay are used for producing active pozzolanic admixtures. These pozzolanic admixtures are used for reducing the Portland cement content in mortar and concrete production (Cook 1985, Ruiz 1965, Vu 1996). The positive effects exerted by such pozzolanic admixtures on properties of Portland cement mortar and concrete have been emphasized in many studies (Babu *et al*. 1993, Akkan and Mazlum 1993, Xu *et al*. 1995). In addition to strength gain, it was shown that such admixtures could improve the sulfate resistance of Portland cement mortar and concrete (Asbrudge *et al*. 1996, Akoz *et al*. 1995). Moreover, (MK) has enormous potential, as a pozzolanic material, in the production of mortar and concrete involving lower embodied energy, improved performance and enhanced durability of Portland cement (PC) mortar and concrete (West *et al*. 1994). MK is an ultra fine pozzolana, produced by calcining kaolin at temperatures between 700 and 900°C and consists

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predominantly of silica and alumina.

MK enhances the strength and durability of concrete through three primary actions which are the filler effect, the acceleration of ordinary Portland cement (OPC) hydration and the pozzolanic reaction with calcium hydroxide (CH). Wild *et al*. (1996) found that the filler effect was immediate, the acceleration of OPC hydration has its major impact within the first 24 h and the maximum effect of pozzolanic reaction occurs between 7 and 14 days. It was concluded that the optimum replacement level of OPC by MK to give maximum long term strength is about 20% by mass. Kostuch *et al*. (2000) discovered that a 10% replacement of cement with MK reduced the CH content in concrete by 70%, and a 20% replacement reduced it to almost zero at the age of 28 days. However, the amount of MK required for complete elimination of CH depends on a number of factors such as purity of MK, Portland cement composition, water/binder ratio and curing conditions (Oriel and Pera 1995). The reduction in CH content results in superior strength and durability performance, even at elevated temperatures (Lin *et al*. 1996).

According to the previous studies, the research work on MK is focused on two main areas. The first area refers to the kaolin structure, the kaolinite to metakaolinite transformation and the use of analytical techniques for the comprehensive examination of kaolin thermal treatment (Kristof *et al*. 1993, Sha and Pereira 2001, Kaloumenou *et al*. 1999, Kakali *et al*. 2001, Shvarzman *et al*. 2002). The second area regards the pozzolanic performance of metakaolin and its effect on cement and concrete properties (He *et al*. 1994, Dunster *et al*. 1993, Ramlochan *et al*. 2000, Gallias *et al*. 2000, Brooks *et al*. 2000, Kostuch *et al*. 1996, Sabir *et al*. 2001, Moulin *et al*. 2001, Vu *et al*. 2001, Gruber *et al*. 2001, Batis *et al*. 2002, Badogiannis *et al*. 2002). Recent works have shown that MK is effective as a supplementary cementitious material on improving the performance of mortar in relation to elevated temperature resistance.

2. Experimental work

The materials used in this investigation were OPC complying with ASTM C-150 requirements Type I of Blain surface area 3350 cm^2/g and metakaolin of Blaine surface area of 3600 cm^2/g and fine aggregate. Natural sand less than 5 mm with specific gravity of 2.65 and volumetric weight of 1.57 t/m^2. The gradation of fine aggregate satisfied ASTM C 33 requirements was employed for manufacturing the mortar. The chemical composition of cementitious materials is shown in Table 1.

The mortar was prepared using Portland cement that was partially substituted by MK as 0%, 5%, 10%, 20% and 30% by cement mass. The kaolin was heated at temperatures ranging from 700ºC to 900ºC for 2 hours to give active amorphous MK. The mix proportions of the mortar mixes are shown in Table 2. The pozzolan was introduced as cement replacement material and its proportions were determined on the basis of previous research works to achieve the optimum strength (Wild *et al.* 1996, Kostuch *et al.* 2000, Oriel and Pera 1995, Lin *et al.* 1996). As shown in Table 2, mix zero was the control mix (100% OPC, 0% MK) was also prepared for comparison purposes. All the mixtures were produced to achieve a flow of 94 ± 5% (ASTM C230/C230M-08) to obtain acceptable workability. The cement mortars were molded into 50 mm cubes for compressive strength determination. The moulds were vibrated for one minute to remove any air bubbles. The samples were kept in moulds at 100% relative humidity for 24 hours, and then were immersed in water for 28 days. The hardened mortars were then dried at a temperature of 105ºC for 24 hours in an electrical furnace. Then, they were kept for 2 hours at temperatures 200, 400, 600, and 800ºC.

Table 1 Chemical composition and physical properties of cementitious materials

Chemical composition (%)	OPC	MK
SiO_2	20.39	58.52
Al_2O_3	5.6	35.54
Fe_2O_3	3.43	1.15
CaO	63.07	1.24
MgO	2.91	0.19
Na_2O	0.38	0.25
K_2O	0.35	0.05
SO_3	0.7	0.06
C_3A	9.04	-
Phosphrous pentaoxide (P_2O_5)	-	0.09
Titanium (TiO_2)	-	0.04
Loss on ignition	2.06	2.74
Physical properties		
Specific gravity	3.15	2.34
Specific surface area (cm^2/g)	3350	3600

Table 2 Mix proportion of mortar mixtures

Mix	Blended cement		Batched quantities (kg/m^3)	
	MK %	OPC %	Blended cement	Sand
M0	0	100	300	1570
M5	5	95	285	1570
M10	10	90	270	1570
M20	20	80	240	1570
M30	30	70	210	1570

The specimens were maintained for 2 hours at each specified temperature to achieve the thermal steady state.

The specimens were allowed to cool in the furnace to room temperature. The compressive strength test was performed on dried and fired specimens. After carrying out the compressive strength test, the crushed samples were dried then grinded for thermal analyses. The kinetics of hydration was determined through phase change at the corresponding temperatures using a differential thermal analysis (DTA). During the DTA test, the sample was heated at a constant rate, 20°C/minute, in a nitrogen atmosphere. The crystalline phases present in the hydrated product were identified using the X-ray diffraction (XRD) technique. Nickle-filtered Cu-Kaaa radiation at 40 KV and 20 mA were used throughout in a Philips PW 1390 diffractometer. Scanning speed of 2°/min. were used. The scanning electron microscope (Philips – XL 30) was used for identification of the changes occurring in the microstructure of the formed and/or decomposed phases.

It is worth mentioning that the MK in this research was produced by incinerating kaolin (K) at 850°C for two hours in an electrical furnace. The kaolin powder was stored in the furnace before heating up, and after the incineration period MK was left to completely cool down. Figs. 1, 2 show the diffractograms of K and MK samples analyzed by X-ray diffraction.

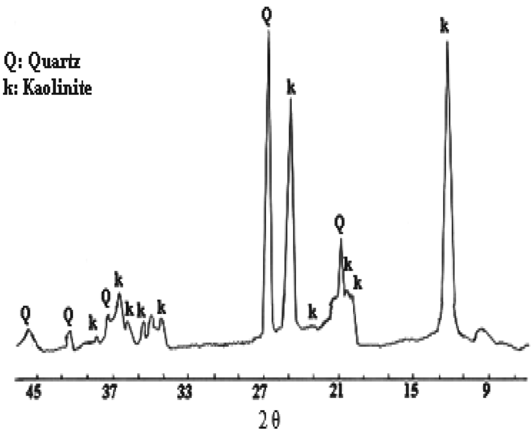


Fig. 1 X- Ray diffraction of kaolin

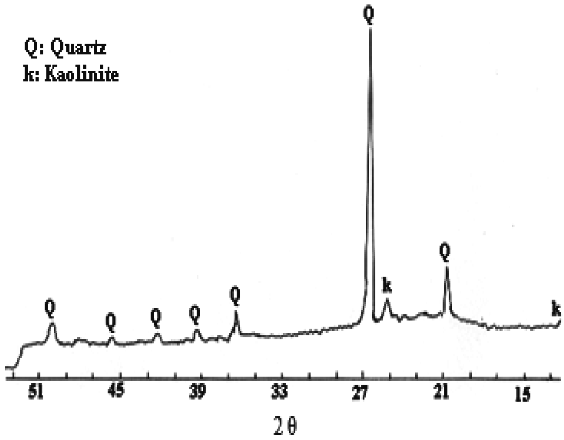


Fig. 2 X- Ray diffraction of metakaolin

3. Results and discussion

The test results reflect to what extend the blending percentage has affected the compressive strength and improvement of mortars performance. Blending increased the 28-day strength at all replacement levels as shown in Fig. 3. At a partial replacement level of 30%, the data reveal that the MK blended Portland cement mortars display lower strength than other replacement levels. On the other hand, at a partial replacement level of 20%, the results show that the MK blended Portland cement mortars display higher strength. The previous results obtained by Vu *et al*. (2001) indicated that the optimum Portland cement replacement level with MK is 20% at 28 days when water/binder ratio 0.53, 0.5, and 0.4 of the mortars. The previous study on mortar verifies and supports the present study. According to Wild (1996), concrete with MK shows maximum relative strength at 20% replacement. Also, Badogiannis *et al*. (2004) reported that the 20% cement replacement with

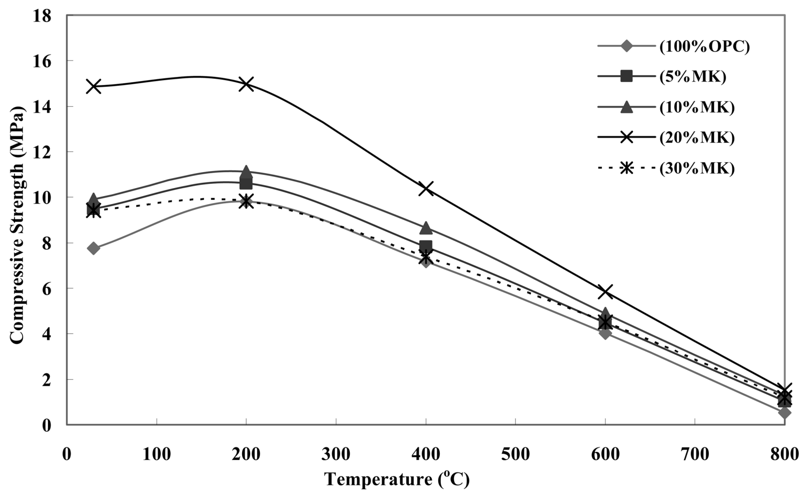


Fig. 3 Residual compressive strength of control and blended mortars exposed to elevated temperature

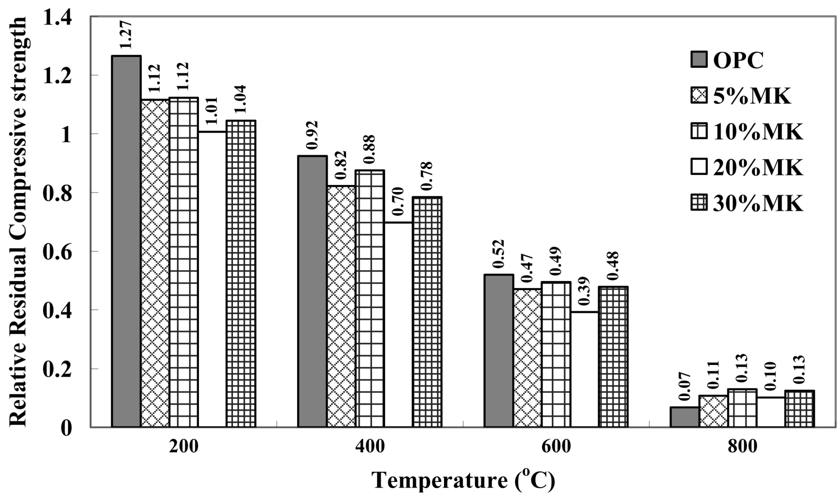


Fig. 4 Relative residual compressive strength of blended mortars exposed to elevated temperature

commercial metakaolin gave the maximum strength at 28-day. Moreover, other researchers reported that the optimum cement replacement level with MK is 20% by mass at age 28 days (Poon *et al.* 2003, Güneyisi and Mermerdas 2007). Present result on mortar therefore confirms and reinforces previous results on concrete.

The residual compressive strength after cooling was determined by an unstressed compression test (Phan 1996). This method gives lower values of compressive strength as compared to stressed tests and hence is thought to be suitable for obtaining the limiting results (Phan 1996). The test results are shown in Figs. 3, 4. Fig. 3 shows the residual compressive strength of each group at different elevated temperatures while Fig. 4 depicts the relative increase or decrease in the compressive strength of each group as compared to its original compressive strength before heating. From the perspective of residual compressive strength of MK mortar, the heating regime can be divided into two regions as room temperature up to 400°C and 400–800°C. A distinct pattern of strength gain and then loss was observed in each region. Initially MK mortars of mixes M5, M10 and M30 showed an increase in compressive strength at 200°C. This increase may probably be due to the hydration of unhydrated MK particles which were activated as a result of temperature rise. Since the hydration in MK mortars is slowed down after 14 days due to the blocking of capillaries (Wild *et al.* 1996), such an increase in strength at elevated temperatures can be anticipated. A similar increase in strength was observed in pure OPC mortar. This increase may probably be due to additional hydration of unhydrated cement grains as a result of steam effect under the condition of the so-called internal autoclaving formed in cement paste (Nimityongskul and Daladar 1995). In this temperature range the compressive strength of OPC mortar was lower than those of MK mortars and the optimum partial replacement of cement with MK was 20%. At a temperature higher than 400°C, the OPC and MK mortars showed a sharp reduction in compressive strength followed by severe cracking. Also, in this temperature range the compressive strength of OPC mortar was lower than those of MK mortars and the optimum partial replacement of cement with MK was 20%.

Fig. 5 shows DTA thermograms of control and blended mortars exposed to elevated temperatures. These curves illustrate that the hydrates present in a Portland cement mortar are calcium silicate hydrate (CSH), calcium hydroxide (CH), Quartz and calcium carbonate. In MK blended mortar, a

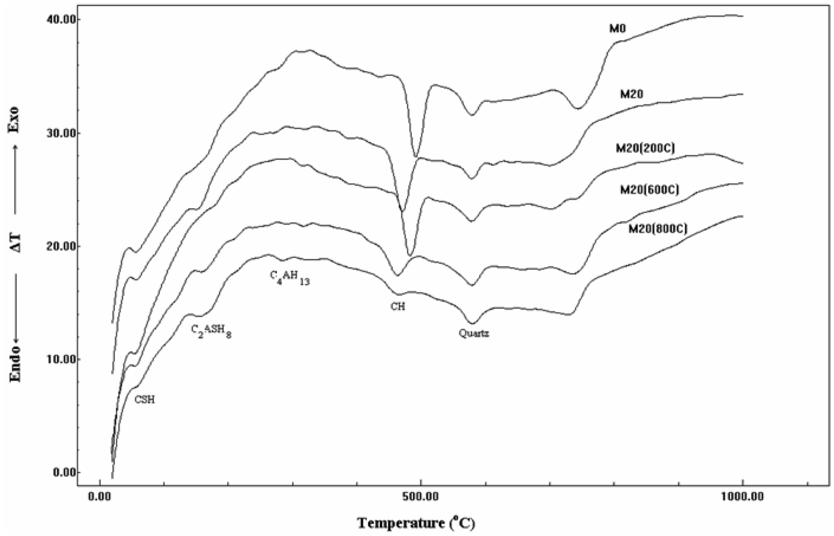


Fig. 5 DTA thermograms of blended mortars exposed to elevated temperature

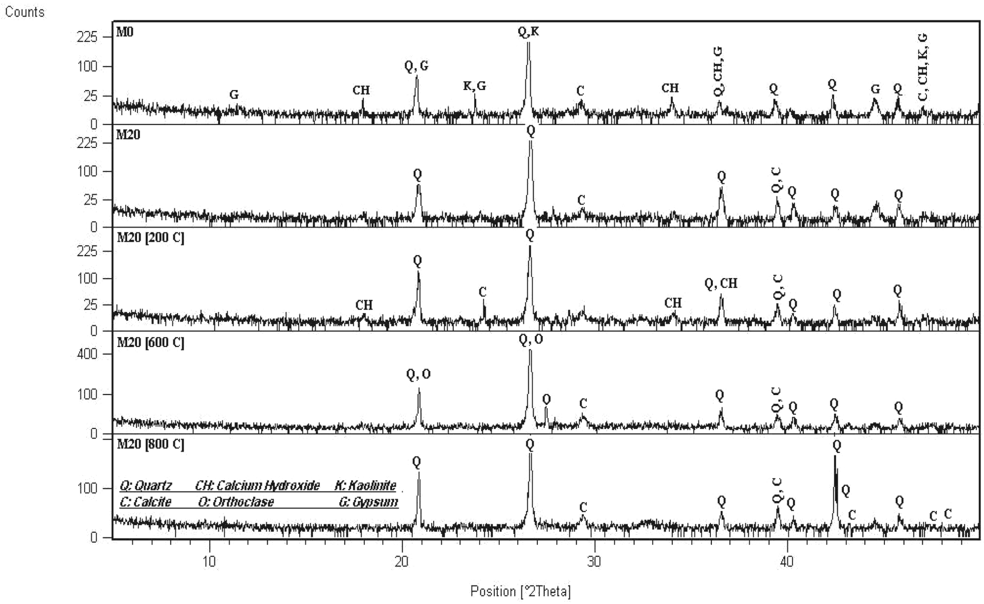
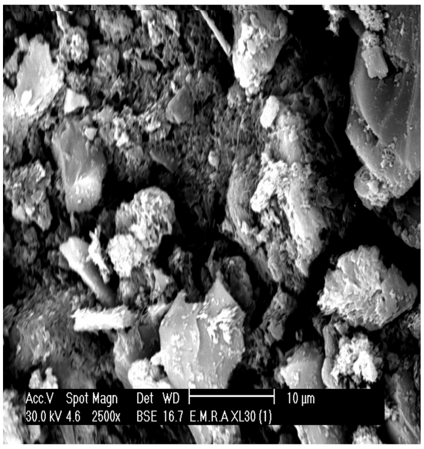


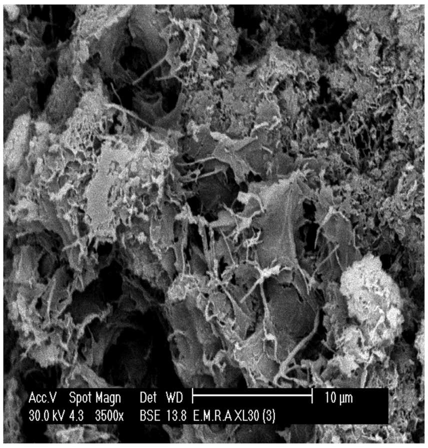
Fig. 6 X-ray patterns of control and blended mortars exposed to elevated temperature

peak also appear at about 170°C, which is attributed to the C_2ASH_8 phase. The C_2ASH_8 phase appeared as the predominant phase of the pozzolanic reaction between Mk and calcium hydroxide. The amount of this phase increases with the decrease of the lime contents. Another important aspect obtained from DTA curves is the appearance of a weak endothermic band at 220°C. This band is assigned to the C_4AH_{13} phase.

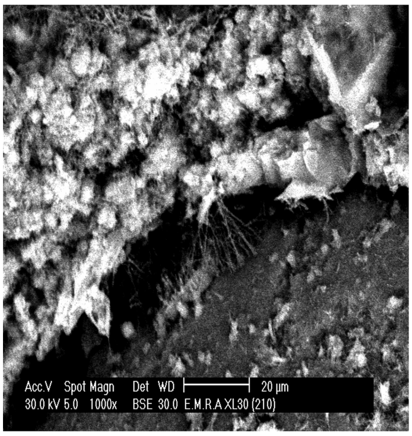
Fig. 6 illustrates the X-ray patterns of control and blended mortars exposed to elevated temperature. The exact identification of hydration products in cement mortars, by means of X-ray



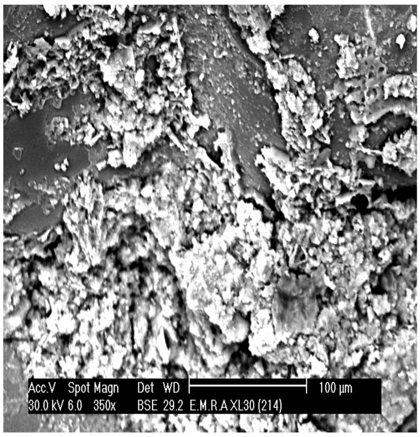
(a) SEM micrograph of control sample



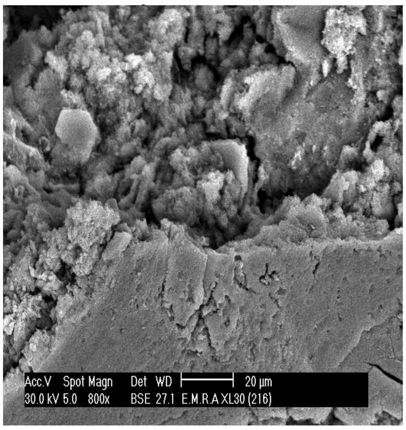
(b) SEM micrograph of control sample thermally treated at 800 ^{o}C for 2 hr.



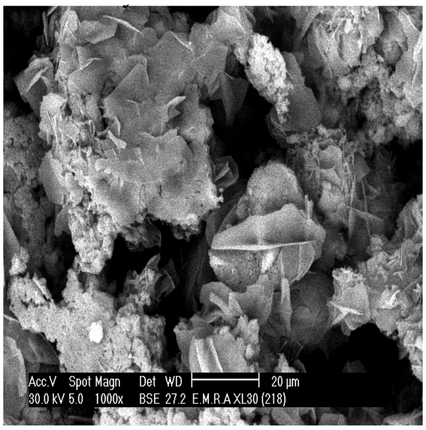
(c) SEM micrograph of blended mortar Thermally treated at 200 ^{o}C for 2 hr.



(d) SEM micrograph of blended mortar thermally treated at 400 ^{o}C for 2 hr.



(e) SEM micrograph of blended mortar thermally treated at 600 ^{o}C for 2 hr.



(f) SEM micrograph of blended mortar thermally treated at 800^{o}C for 2 hr.

Fig. 7 SEM micrographs of control and blended mortars exposed to elevated temperature diffraction (XRD), is difficult due to their low degree of crystallinity and/or their small amounts. In all MK–cement mortar, XRD patterns indicate a decrease of $Ca(OH)_2$ content, in comparison with control sample due to the pozzolanic reaction. Our measurements showed that the main peaks in the XRD patterns of MK–cement mortars correspond to $Ca(OH)_2$ and the anhydrous clinker phases. XRD patterns of MK–cement mortars showed some indications of Ca–Al–Si hydrates.

The variations of the SEM micrograph for the control M0 and blended mortars M20 thermally treated at 200, 400, 600 and 800°C are shown in Fig. 7. Evidently, the microstructure of the control OPC mortar displayed the existence of microcrystalline and nearly amorphous, mainly as calcium silicate hydrates (CSH). In addition to large crystals of calcium hydroxide Fig. 7(a), after firing at 800°C, the scanning electron micrograph displayed the formation of large-and microcracks with the decomposition of the hydration products Fig. 7(b). The SEM micrographs obtained for the pozzolanic mortars for mix M20 indicated that the hydration products obtained after 28 days of hydration are perfectly stable for thermal treatment at temperatures up to 200°C. This is can be clearly understood from the microstructure of the hardened blended mortar M20 after thermal treatment at 200°C, 400°C and 600°C, where the microstructure displayed the existence of calcium silicate hydrates (CSH), calcium hydroxide (CH). Therefore, the replacement of OPC by 20% MK blended mortar resulted in an improvement of the thermal stability of mix M20 as indicated from the SEM micrographs shown in Figs. 7(c), 7(d) and 7(e). Upon firing of M20 mortars at 800°C, however, a decomposition of the hydration products was observed with the formation of microcracks in the structure (Fig. 7(f)).

5. Conclusions

On the basis of the results obtained in this study the following conclusions can be drawn:

1. Based on the mechanical and physical properties of metakaolin blended mortar, a 20% metakaolin content seems to be, generally, more favorable than other investigated ratios.
2. The pozzolanic reaction of metakaolins is accelerated as the exposure temperature increased, accompanied by a steep decrease of calcium hydroxide content.
3. Metakaolin has a positive effect on the mortar strength at the age of 28 days, and after exposure to elevated temperatures up to 800°C.

6. Suggestion for future research

Based on the results obtained from this study, it is suggested that further research is conducted on cmentitious systems incorporating metakoalin using higher temperature ranges (e.g., up to 1000°C) for longer durations of exposure (e.g., 3 hours). It is recommended that other cmentitious composites (ternary or quaternary binders), comprising limestone filler, silica fume, fly ash, etc. be investigated under such severe conditions.

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