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# EFFECT OF FIRE ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF BLENDED CEMENT PASTES CONTAINING METAKAOLIN AND SILICA FUME

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## Abstract

The influence of high temperature on microstructure and mechanical properties of cement paste is vital to characterize fire resistance. Some experimental investigations on the microstructure and compressive strength of pre-heated metakaolin-silica fume blended cement pastes are presented in this paper. The aim of this investigation is to study the effect of substitution of metakaolin (MK) by silica fume (SF) on thermal stability of Portland cement-MK blended pastes. The kaolinte was thermally activated at 850°C for 2 hours. The cement pastes were prepared using standard water of consistency. The pastes were kept in moulds at 20°C and 100% relative humidity for 24 hours and then hydrated for 28 days under water. The hydrated pastes were exposed for 2 hours to temperature 200, 400, 600 and 800°C. The pre-heated specimens were tested for compressive strength, thermal stability, microstructure and phase composition. The thermal shock resistance were performed on cement pastes after hydration. The results of investigation showed that the compressive strength of pre-heated blended cement increases with temperature up to 400°C and then, it decreases as the pre-heated temperatures increase up to 800°C. The replacement of Portland cement, PC, by 15% MK and 15% SF in cement pastes increases the thermal shock resistance by about 20 times than control

**Keywords**: Metakaolin; silica fume; blended cement; microstructure; thermal shock resistance; compressive strength; DSC

## 1. Introduction

When reinforced concrete is subjected to high temperature as in fire, there is deterioration in

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its properties. The particular importance are loss in compressive strength, cracking and spalling of concrete, destruction of the bond between the cement paste and the aggregates and the gradual deterioration of the hardened cement paste. Assessment of fire-damaged concrete usually starts with visual observation of color change, cracking and spalling of the surface. The replacment of ordinary Portland cement by pozzolanic material improve mechanical properties and fire resistance [1-6].

The most common cementitious materials that are used as concrete constituents, in addition to Portland cement, are fly ash, FA, granulated blast furnace slag (BFS) and silica fume. They save energy, conserve resources and have many technical benefits [7]. Metakaolin, produced by controlled thermal treatment of kaolin, can also be used as a concrete constituent, since it has pozzolanic properties [8,9]. According to the literature, the research work on metakaolin is focused on two main areas. The first one refers to the kaolin structure, the kaolinite to metakaolinite conversion and the use of analytical techniques for the thorough examination of kaolin thermal treatment [10]. The second one concerns the pozzolanic behavior of metakaolin and its effect on cement and concrete properties [6,11–14]. Although there is a disagreement on specific issues, the knowledge level is satisfactory and is being continuously extended.

Pozzolanic high strength concretes (HSC) are used extensively throughout the world; the oil, gas, nuclear, and power industries are among the major users. The applications of such concretes are increasing day by day due to their superior structural performance, environmental friendliness, and energy conserving implications [15]. Apart from the usual risk of fire, these concretes are exposed to high temperatures and pressures for considerable periods of time in the above-mentioned industries. Although concrete is generally believed to be an excellent fireproofing material, many recent studies have shown extensive damage or even catastrophic failure at high temperatures. During the last decade, there has been extensive research on the fire performance of normal-strength concrete (NSC) as well as high strength concrete (HSC) incorporating FA, BFS and SF at elevated temperatures [16-18].

When fine pozzolana particles are dispersed in the paste, they generate a large number of nucleation sites for the precipitation of the hydration products. Therefore, this mechanism makes the paste more homogeneous and dense as for the distribution of the fine pores. This is due to the reaction between the amorphous silica of the pozzolanic and the calcium hydroxide produced by the cement hydration reactions [4-6]. In addition, the physical effect of the fine grains allows denser packing within the cement and reduces the wall effect in the transition zone between the paste and aggregate. This weaker zone is strengthened due to the higher bond developed between these two phases, improving the concrete microstructure and properties. In general, the pozzolanic effect depends not only on the pozzolanic reaction, but also on the physical or filler effect of the smaller particles in the mixture.

Durability of portland cement concrete is defined as its ability to resist weathering action, chemical attack, abrasion, fire or another process of deterioration. In other words, cement concrete will be termed durable, when it keeps its form and shape within the allowable limits, while exposed to different environmental conditions. Durability of concrete has been a major concern of civil engineering professionals.

The study aims to investegate the effect of high temperature treatment on the microstructure, mechanical and physical properties as well as the thermal shock resistance of cement-metakoline-silica fume blended pastes.

## 2. Expermental

The materials used in this investigation were Portland cement with a Blaine surface area of 3000 $cm^2/g$, metakaolin of Blaine surface area of 3600 $cm^2/g$ and silica fume of very high Blaine surface area 220000 $cm^2/g$. The chemical composition of starting materials is shown in Table 1.

The cement pastes were prepared using Portland cement that was partially substituted by metakaolin and silica fume as illustrated in Table 2. The kaolin was fired at 850 oC for 2 hours to give active amorphous metakaolin [8]. The starting materials were initially mixed with ethanol to attain ascertain homogenity. The pastes were prepared using the standard water of consistence. Table 3 illustrates the used water of consistence for different blended cement pastes.

The pastes were molded into 1 inch 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, then it was cured under water for 28 days.

Table 1**.** The chemical composition of starting material

| **Oxide composition** | **Portland cement (%)** | **Metakaolin (%)** | **Silica fume (%)** |
|---|---|---|---|
| CaO | 62.56 | 1.24 | 0.21 |
| $SiO_2$ | 20.85 | 58.52 | 96.10 |
| $Al_2O_3$ | 4.70 | 35.54 | 0.5 |
| $Fe_2O_3$ | 3.86 | 1.15 | 0.70 |
| MgO | 1.23 | 0.19 | 0.48 |
| $SO_3$ | 2.79 | 0.06 | 0.10 |
| $Na_2O$ | 0.49 | 0.25 | 0.31 |
| $K_2O$ | 0.12 | 0.05 | 0.49 |
| $Cl^-$ | --- | 0.05 | --- |
| Ignition loss | 2.82 | 2.74 | 1.14 |

Table 2. The dry mixes composition of blended cement (mass %)

| **Mixes** | **Portland cement** | **Metakaolin** | **Silica Fume** |
|---|---|---|---|
| M0 | 100 | 0 | 0 |
| M1 | 70 | 30 | 0 |
| M2 | 70 | 25 | 5 |
| M3 | 70 | 20 | 10 |
| M4 | 70 | 15 | 15 |

Table 3. The standard water of consistency for blended cement

| **Mixes** | **M0** | **M1** | **M2** | **M3** | **M4** |
|---|---|---|---|---|---|
| Water/ Bender | 0.25 | 0.2[illegible]69 | 0.2692 | 0.2885 | 0.2886 |

The hardened cement paste were dried at a temperature of 105 °C for 24 hours in an oven. Then, they were kept for 2 hours at temperatures 200, 400, 600, and 800 °C. Each tested temperature was maintained for 2 hours to achieve the thermal steady state. The specimens were allowed to be cool gradually inside the furnace to room temperature. The compressive strength was performed on dried and pre-heated specimens. The crushed samples (dried and fired) resulted from compressive strength tests were ground for thermal analyses and X-ray diffraction.

Differential scanning calorimetry run were conducted using a Shimadzu DSC-50 thermal analyzer at a heating rate of 20 °C/min. The sample chamber was purged with nitrogen at a flow of 30 ml/min. The thermal shock resistance were determined by heating the molded cement pastes after 28 days of curing under water (1" cubes) for 40 minutes at 800 °C followed by quenching in water for 5 minutes. Such cycles are repeated until the samples are broken, damaged or deteriorated.

The crystalline phases present in the hydrated product were identified using the X-ray diffraction technique. Nickle-filtered Cu-Kα radiation at 40 KV and 20 mA were used throughout in a Philips PW 1390 diffractometer. Scanning speed of 2°/min. was 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.

## 3. Results and Discussion

Figure 1 illustrates the development of compressive strength for control and blended cement pastes thermally treated at 200, 400, 600 and 800°C for 2 hours. It is evident that, the compressive strengths of control, M0, M1 and M2 cement pastes increase with temperature up to 200 °C then decrease up to 800 °C. It also, shows that, the compressive strengths of blended cement pastes, M3 and M4 increase as the treatment temperature increases up to 400 °C then decrease as the treatment temperature increases up to 800 °C. Evidently, the increase of compressive strength up to 200 °C may be due to the additional hydration of unhydrated cement grains as a result of steam effect under the condition of the so-called internal autoclaving effect. The increase of compressive strength of blended cement pastes may be due to the pozzolanic reaction of metakaolin and silica fume with free lime to produce more CSH and CAH phases that deposit in the pore system. The compressive strengths of control, M0, M1 and M2 cement pastes start to decline at 200 °C whereas those of other blended; M3 and M4 cement pastes even at 400 °C. This phenomenon is contributed to higher volumes of CSH and CAH phases formed in the blended cement pastes on the one hand and reduction in $Ca(OH)_2$ contents on the other hand relative to those developed in control, M1 and M2 cement pastes. Cement matrix with higher volumes of gel-like hydration products, and lower crystallic $Ca(OH)_2$ contents has improved fire resistance. The decrease in compressive strength with temperature may be due to the dehydration of the calcium hydroxide at about 500 °C producing CaO and $H_2O$. Over 600 °C strength losses are mainly caused by calcium carbonate dissociation and subsequent $CO_2$ escape from $CaCO_3$. Strength losses of M3 and M4 blended cement pastes are less significant than that of control M0, M1 and M2 cement paste.

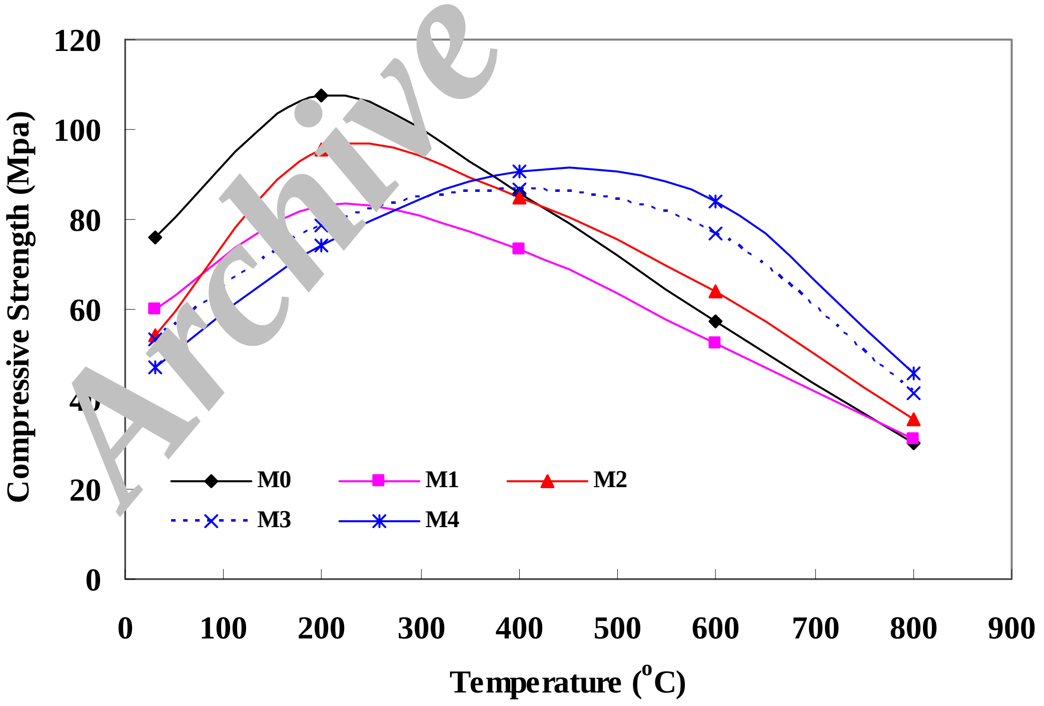


Figure 1. Variation of compressive strength of cement pastes with temperature for different admixtures blended cements

The formation of CSH as a results of pozzolanic reaction is deposited in porous as well as the fillar effect of fine MK and SF. Evidently, this leads to bridge the porous as well as redusing the internal thermal stress. Therefore, the increase of compressive strength can be partially due to the strengthened hydrated cement pastes during the evaporation of free water, which leads to greater Van der Waal's forces as a result of the cement gel layers moving closer to each other [19]. Because transportation of moisture in concrete is rather gradual, residual moisture in concrete allowed accelerated hydration at the early stage of heating concretes to high temperatures. Further hydration of cementitious materials is another important cause of the hardening of hydrated cement pastes. The compressive strength of blended cement pastes M3 and M4 has higher values than other control and blended cement pastes up to 800 °C. This may be due to the principal reaction between the metakaolin ($Al_2O_3.2SiO_2$) and the calcium hydroxide derived from cement additional, cementitious aluminum containing CSH gel, together with crystalline products, which include calcium aluminate hydrates and alumino-silicate hydrates (i.e., $C_2ASH_8$, $C_4AH_{13}$ and $C_3AH_6$). The decrease in compressive strength after 400 °C, may be due to the propagation of microcracks. The crystalline products formed depend principally on the metakaoline/calcium hydroxide ratio and reaction temperature. The formation of CAH and CASH phases, increase the compressive strength.

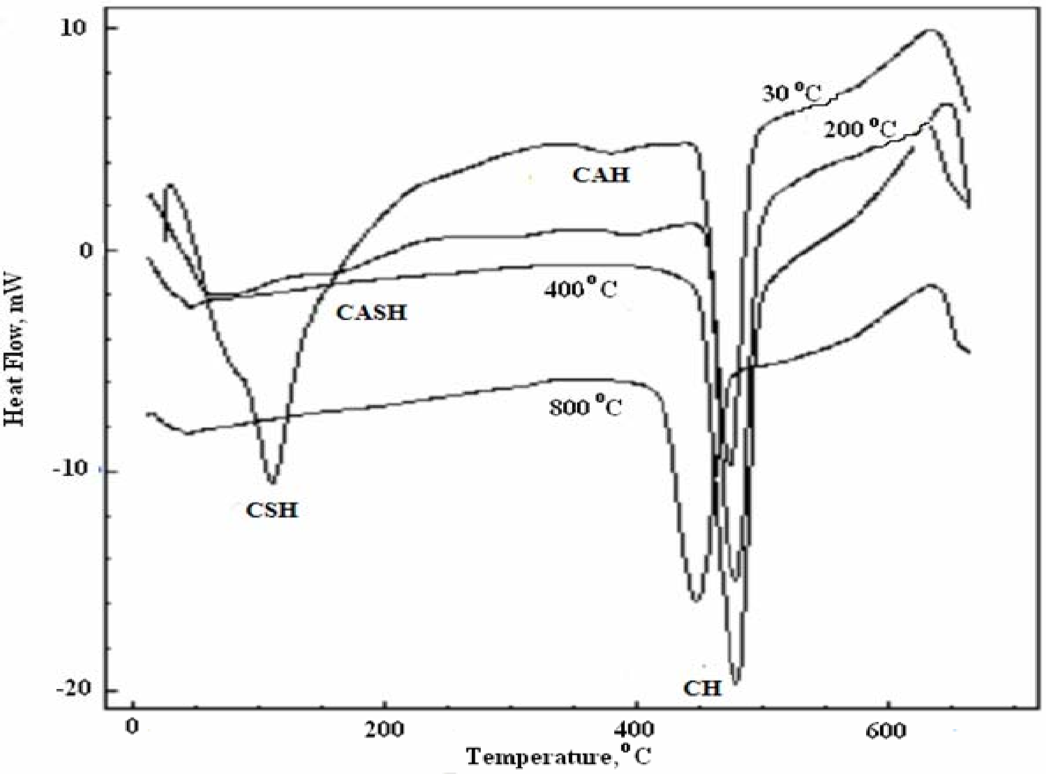


Figure 2. DSC thermograms of the Portland cement paste thermally treated at different temperatures

The variations of the DSC thermograms of control, M0, and blended cement pastes, M4 at ambient temperature, pre-heated at200, 400 and 800 $^{o}$C are shown in (Figures. 2 and 3). Evidently, there are almost four endothermic peaks. The first peak located at about 110-120$^{o}$C, is mainly due to the decomposition of calcium silicate hydrates; CSH. The second endothermic peak observed at about 160$^{o}$C represents the decomposition of the calcium sulpho-aluminate. The third endothermic peak at about 350$^{o}$C is due to the dissociation of $C_2SH$. The forth endothermic peak was observed at around at 470$^{o}$C represents the decomposition of $Ca(OH)_2$. As the pre-heated temperature increases the peak area of calsuim hydroxide increases up to 600 oC and shefted to word lower temperature at 800$^{o}$C pre-heated control cement paste, M0, as shown in Figure 2. This is due to the formation of ill-crystals of $Ca(OH)_2$. Also it is clear that the thermograms of the blended cement paste M4 that pre-heated at 200, 400 and 800 oC show very weak endothermic peaks Figure 3. It is clear that the calcium hydroxide peak area decreases as pre-heated temperature increases. Evidently, this is due to further reaction between metakaolin, silica fume and CaO at high temperature up to 800 $^{o}$C. It is obvious that the enthalpy of calcium hydroxide phases in control cement paste, M0, (Figure 2) decreases from 60.22 J/g to 48.58 J/g as the treatment temperature increases up to 800$^{o}$C. On the other hand, the enthalpy of calcium hydroxide phase in the blended cement paste M4 (Figure 3) decreases from 13.06 J/g to 1.9 J/g as the pre-heated temperature increases up to 800$^{o}$C. This is due to the formation of ill-crystals (this is indicated by the decrease in enthalpy) of free lime as a result of further reaction of pozzolana at elevated temperatures.

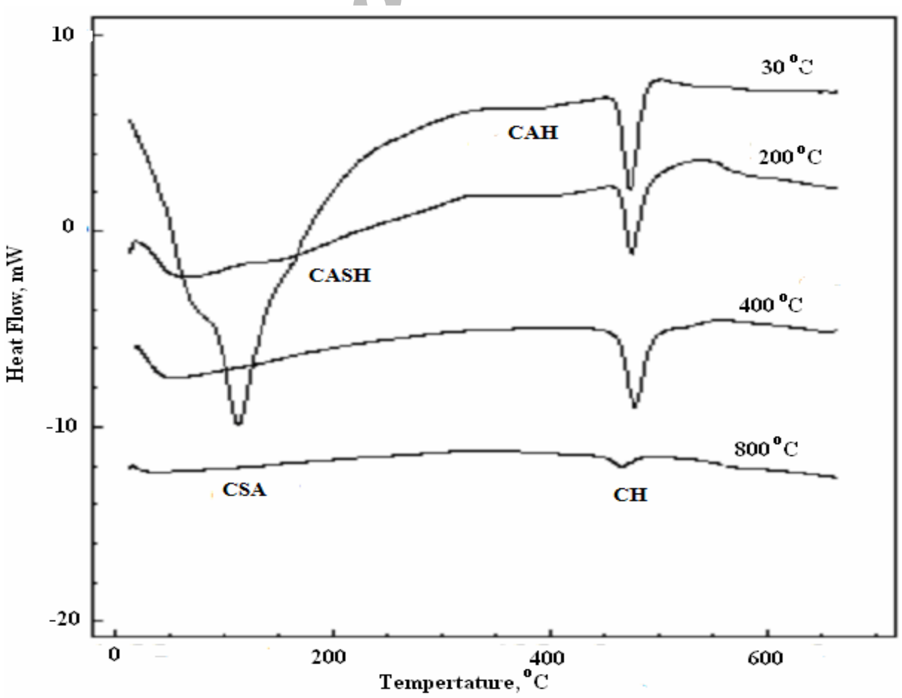


Figure 3. DSC thermograms of the blended cement pastesM4 (70% Portland cement, 15% MK, and 15% SF) thermally treated at different temperatures

The effects of admixtures on thermal shock resistance of hydrated blended cement pastes are shown in Figure 4. Evidently, the thermal shock resistance increases as the silica fume ratio increases in blended cement pastes. Therefore, the higher replacement of metakaolin by silica fume in investigation blended cement pastes leads to higher thermal shock resistance. This may be due to consumption of free lime released during hydration. During heating, the outer layers of the test specimen tend to expand more than inner layers. Subsequent sudden cooling will unbalance the internal equilibrium, with significant internal stresses developed as the outer layers attempt to contract relative to the inner [1]. The differential deformation between the different layers leads to further crack activities. Evidently, the hardened Portland cement paste, M0, can resist only 3 cycle's thermal shock. This is due to the free lime released during hydration of Portland cement. The $Ca(OH)_2$ crystals transform into CaO crystals during heating. Since CaO is often rehydrates in the humid environment and forms $Ca(OH)_2$ again with increase in volume leading to complete failure of the hardened cement paste [1].

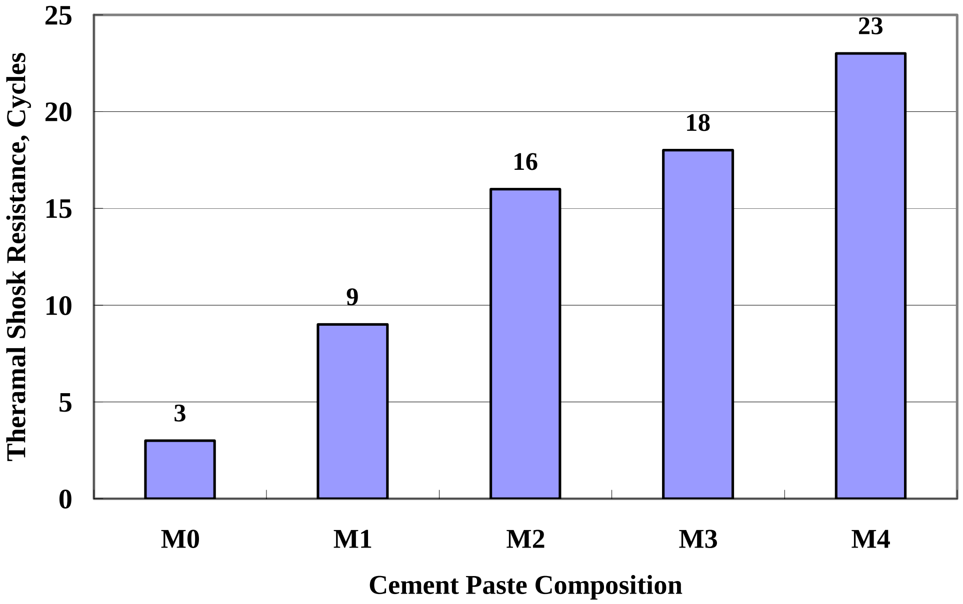


Figure 4**.** Thermal shock resistance of control and blended cement pastes

The replacement of Portland cement by 30% metakaolin in blended cement paste, M1, leads to increase the thermal shock resistance up to 9 cycle's. This is due to the pozzolanic activity of metakaolin during hydration and at 800$^o$C, the $SiO_2$ and $Al_2O_3$ of metakaolin react with CaO. It also clear that, the replacement of metakaolin by 5% in the blended system, M2; leads to thermal shock resistance of 16 cycle's. The results show that the 30 % wt. replacement of Portland cement by pozzolanic admixture consisting of 15 % wt. of metakaolin and 15 % wt. of silica fume creates the most durable hydrate phase to thermal shocks. Evidently, the thermal shock resistance of blended cement pastes is considerably higher when highly effective microfiller-microsilica is added.

Figures 5-6 illustrate the XRD patterns of pre-heated control and blended cement pastes. It is clear that, the XRD patterns of the OPC cement pastes pre-heated at ambient temperature, 200, 400 and 800$^{o}$C are presented in Figure 5. Evidently, the crystalline phase of CH (portlandite) was decreases as the pre-heated temperature increases up to 800°C. This is due to thermal decomposition of calcium hydroxide phase at 570°C. The replacement of OPC by metakaolin and silica fume is shown in Figure 6. Basically, the calcium hydroxide phase decreases as the ratio of MK and SF increase, while the weak peaks of CAH and CASH in pastes replaced by SF and MK, slightly increase. The XRD patterns of the hydrate products are plotted in Figure 6, the MK were replaced by 15% SF. It can be observed that the crystalline peak of CH decreases as the replacement rate increases while the weak peak of CSH and gehlenite hydrate ($C_2ASH_8$) increases. In Figure 6, the decrease of the CH peak is related with the consumption by pozzolanic reaction of MK and SF [9].

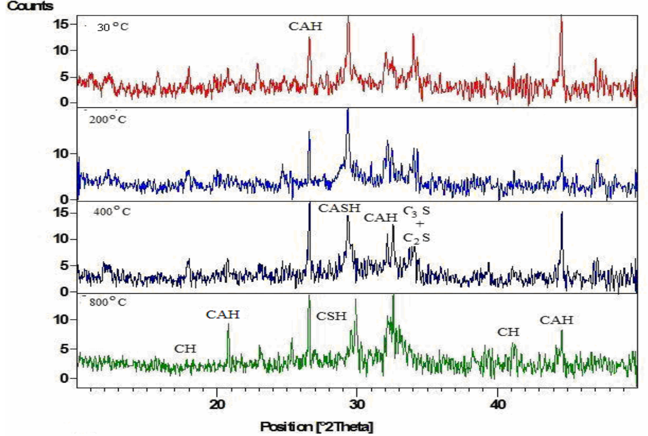


Figure 5. X-ray pattern of pre-heating hydrated cement pastes (M0)

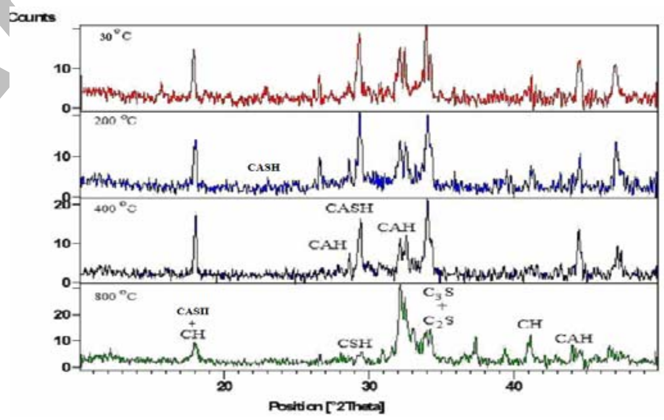
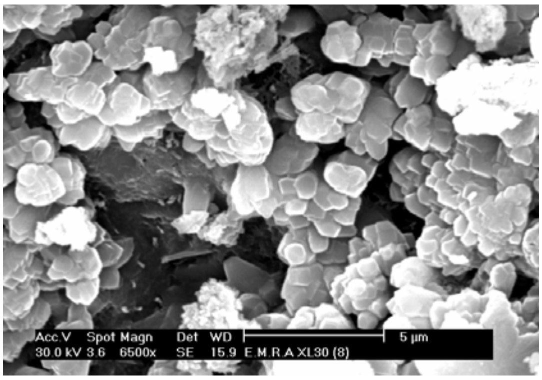
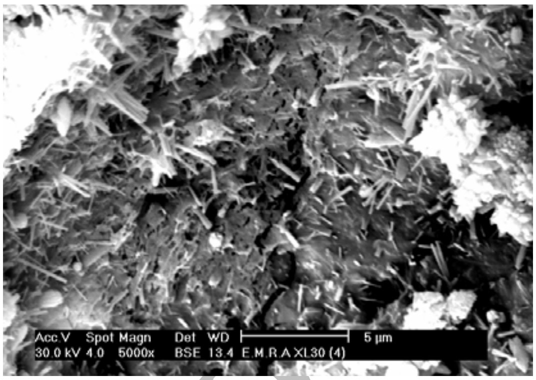


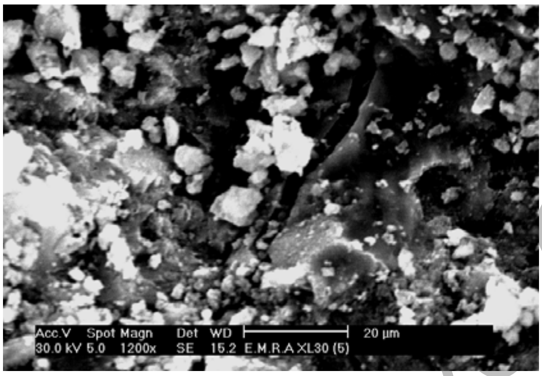
Figure 6. X-ray pattern of pre-heating hydrated blended cement pastes (M4)



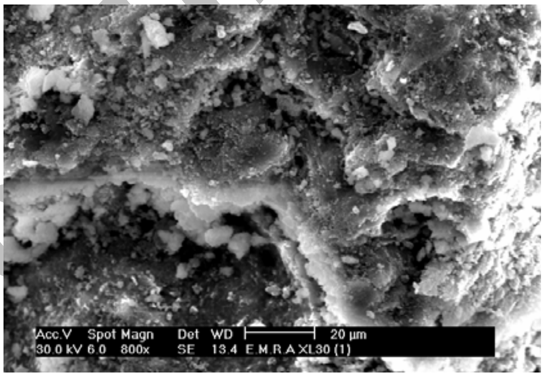
a) SEM micrograph of OPC cement paste at 30°C



b) SEM micrograph of blended cement paste at 30°C

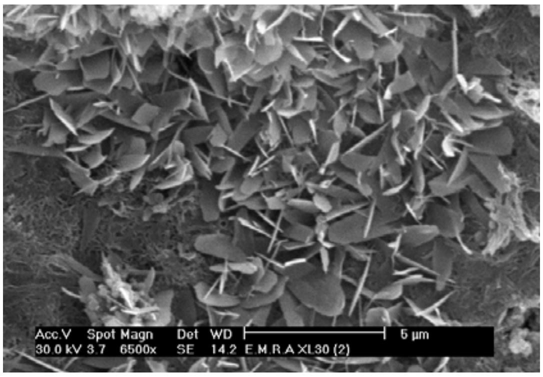


c) SEM micrograph of OPC cement paste at 200°C

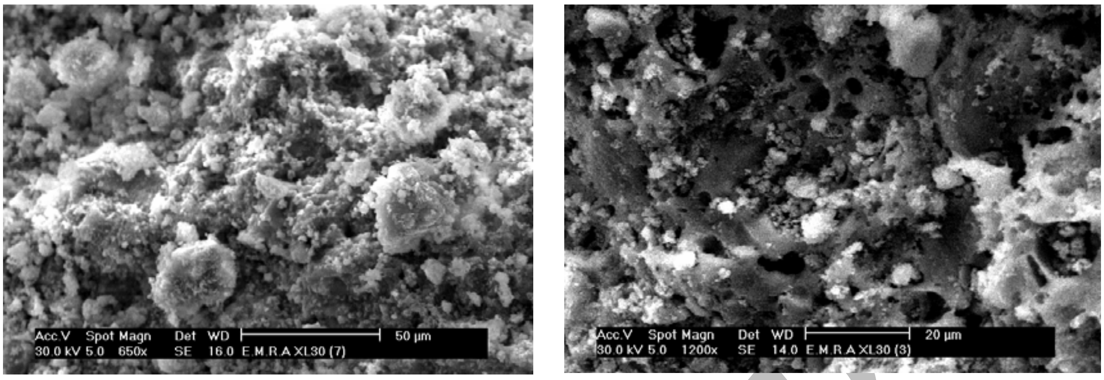


d) SEM micrograph of blended cement paste at 200°C

e) SEM micrograph of OPC cement paste at 400°C



f) SEM micrograph of blended cement paste at 400°C



g) SEM micrograph of OPC cement paste at $800^oC$

h) SEM micrograph of blended cement paste at $800^oC$

Figure 7. SEM micrograph of OPC (M0) and blended cement pastes (M4) pre-heated at different temperature

Figure 7 illustrates the SEM micrograph of pre-heated control and blended cement pastes. Figure (7-a, c, e and g) shows the SEM micrograph of OPC pastes hydrated at ambient temperature and pre-heated at 200, 400 and $800^oC$ for 2 hours respectively. It is clear that the hydration products formed up to $200^oC$ having a massive structure of well crystalline C-S-H and sheets of $Ca(OH)_2$ representing the microstructure; Fig (7-a and c). Evidently, the micrograph of sample pre-heated at $400^oC$ safer partial decomposition in formed phases. The micrograph of the pre-heated OPC pastes at 800°C Figure (7-g); shows a week structure with appearance of micro cracks and pores. However, these leading to a destruction of binding forces as represented by the low compressive strength. On the other hand, the $800^oC$ pre-heating was already identified as a critical temperature for the water saturation moisture content of the material and thus for the open porosity as well as the significant increase in porosity due to the $CaCO_3$ decomposition was accompanied by the micro-structural damage of the Portland cement matrix that was also documented in the SEM analysis. Figure (7-b, d, f and h) illustrates the SEM micrographs of blended cement pastes M4, 15% metakaolin and 15% silica fume, after pre-heated at 200, 400 and $800^oC$. Clearly, the microstructure was relatively compact; the cement binder exhibited a low porosity. Evidently, the microstructure of blended cement paste pre heated at $800^oC$ Figure (7-h); displayed the formation of dense masses of hydration products having micro-and narrow pores. However, these to relatively high compressive strength values as compared with those of OPC paste at $800^oC$.

## 4. Conclusions

The main conclusion derived from this study may be summarized as follows:

1. The residual compressive strength of the above cement blend paste heated to $800^oC$ is

higher than the residual compressive strength of the Portland cement. In addition, the microstructure of blended cement pastes, M4, pre-heated at 800 $^{o}$C is dense than OPC pastes at the same condition.

2. The replacement of OPC by 15% wt. of metakaolin and 15% wt. of silica fume increase the thermal shock resistance by 20 times than control.
3. The blended M4 can be applied as a fire resistance bonding materials.

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