

# EFFECT OF SILICA FUME AND METAKAOLINE POZZOLANA ON THE PERFORMANCE OF BLENDED CEMENT PASTES AGAINST FIRE

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*The aim of this investigation is to study the effect of the substitution of metakaoline (MK) by silica fume (SF) upon the thermal stability of Portland cement -MK blended pastes. The kaoline was thermally activated at 850°C for 2 hours. The cement pastes were prepared with constant consistency. The pastes were kept in moulds at 20°C/100 % relative humidity for 24 hours and then hydrated for 28 days under water. The hydrated pastes were exposed for 2 hours to temperatures of 100, 200, 400, 600 and 800°C. The hydrated specimens were tested for compressive strength, thermal stability and phase composition after heat treatment. It was found that, after increase of compressive strength of control cement paste up to 200°C, the paste suffers a more loss of compressive strength with further increasing treatment temperatures. But, it was evidenced that the compressive strength of blended cements increases with temperature up to 400°C and then, it decreases as increase the treatment temperatures up to 800°C. The replacement of Portland cement (PC) by 15 % MK and 5 % SF in cement pastes increases the thermal shock resistance by about 10 times.*

## INTRODUCTION

Portland cement mainly consists of four clinker minerals (namely  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ ) and gypsum as setting additive regulator. When Portland cement is mixed with water, its phases start to hydrate. The reaction of tricalcium aluminate ( $C_3A$ ) and ferrite phase ( $C_4AF$ ) predominates at early ages of hydration. Ettringite is the usual product in the early ages of the hydration of Portland cement. The reaction of calcium silicate phases ( $C_3S$  and  $\beta$ - $C_2S$ ) predominates from about the time of initial set onward forming calcium silicate hydrates and  $Ca(OH)_2$ .

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. Also, it has been of considerable scientific and technological interest over the last few decades [1,2].

Pozzolans are incorporated as active addition or substitutions to the ordinary Portland cement and concrete due to their capacity for reacting with lime which that, principally originated during the hydration of Portland cement [3].

The result of this reaction is the formation of cementitious compounds. This pozzolanic reaction modifies some properties of the cement and the resulting concrete.

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.

Therefore, the addition of pozzolans to Portland cement increases its mechanical strength and durability when compared to the blank paste, because of the interface reinforcement. The physical action of the pozzolans provides a denser, more homogeneous and uniform paste.

Natural pozzolans have been used since antiquity with excellent results for production of durable concrete

[7]. By-products as pozzolanic additives are now used for the production of high-performance concrete. Fly ash and silica fume are used to improve the resistance of concrete in aggressive environments. Recently, some activated materials, such as metakaolin, which is produced by heating kaolinite, have been shown to be an excellent pozzolanic material.

In the present study, the utilisation of calcined clay in the form of metakaoline and silica fume as a pozzolanic addition for cement paste has been taken considerable interest. Much of this interest has focused on removal of the calcium hydroxide, which is produced by the hydration of cement and which is associated with poor durability, specially in case of elevated temperature (from 100 to 800°C). Calcium hydroxide removal has a major influence on resistance to fire, which is derived from the additional cementitious phases generated by reaction of calcium hydroxide and metakaoline and also due to the filler effect in the poor system [8-13].

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

Table 1. The chemical composition of starting material.

Oxide composition	Portland cement (%)	Kaoline (%)	Silica fume (%)
CaO	62.56	0.67	0.21
SiO <sub>2</sub>	20.85	53.03	96.10
Al <sub>2</sub> O <sub>3</sub>	4.70	33.47	0.5
Fe <sub>2</sub> O <sub>3</sub>	3.86	1.86	0.70
MgO	1.23	2.0	0.48
SO <sub>3</sub>	2.79	0.21	0.10
Na <sub>2</sub> O	0.49	---	0.31
K <sub>2</sub> O	0.12	---	0.49
Cl	---	0.05	---
Ignition loss	2.82	8.39	1.14

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

Mixes	Portland cement	Metakaoline	Silica Fume
M0	100	0	0
M1	80	20	0
M2	80	15	5
M3	80	10	10
M4	80	5	15
M5	80	0	20

Table 3. The standard water of consistence for blended cement.

Mixes	M0	M1	M2	M3	M4	M5
Water/Cement ratio (%)	0.26	0.278	0.279	0.303	0.334	0.35

## EXPERIMENTAL

The materials used in this investigation were Portland cement with a Blaine surface area of 3000 cm<sup>2</sup>/g, metakaolin of Blaine surface area of 3600 cm<sup>2</sup>/g and silica fume of very high Blaine surface area 220000 cm<sup>2</sup>/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°C for 2 hours to give active amorphous metakaolin [5]. The starting materials were initially mixed with ethanol to attain ascertain homogeneity. 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 2 cm 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. The hardened cement pastes were dried at a temperature of 105°C for 24 hours in an oven. Then, they were kept for 2 hours at temperatures of 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 cool in the furnace to room temperature. The compressive strength was performed on dried and fired specimens. The crushed samples (dried and fired) result from compressive strength tests were ground for thermal analyses.

Differential scanning calorimetry runs 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 (2 cm 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.

## RESULTS AND DISCUSSION

Figure 1 illustrates the typical development of compressive strength for control and blended cement pastes thermally treated at 100, 200, 400, 600 and 800°C for 2 hours. It is evident that, the compressive strength of control cement paste increases with temperature up to 200°C then decreases up to 800°C. It also, shows that, the compressive strength of blended cement pastes increases 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 metakaoline and silica fume with free lime to produce more CSH and CAH phases which deposit in the pore system. The compressive strength of control cement paste starts to decline at 200°C whereas those of blended 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  $\text{Ca(OH)}_2$  contents on the other hand relative to those developed in control cement paste. Cement matrix with higher volumes of gel-like hydration products, and lower crystalline  $\text{Ca(OH)}_2$  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  $\text{CaO}$  and  $\text{H}_2\text{O}$ . Over 600°C strength losses are mainly caused by calcium carbonate dissociation and subsequent  $\text{CO}_2$  escape from  $\text{CaCO}_3$ . Strength losses of blended cement pastes are least significant than that of control cement paste. This is contributed to lesser  $\text{Ca(OH)}_2$  contents found in blended cement pastes because of pozzolanic reaction consuming free lime disposable for  $\text{Ca(OH)}_2$  formation, and hence for easy carbonation to  $\text{CaCO}_3$ .

Both produce a reduction in the solid skeleton mass of the cement paste. However, the release of chemically bound water contributes vapour pressure that becomes significant in low porosity structure. Therefore, the outer surfaces of the test specimen tend to expand more than the inner during heating, depending on the magnitude of the thermal gradient. Consequently cracks develop until the internal stresses are held in equilibrium by the strength of the microstructure. As the specimen reaches the point of uniformity, the temperature

gradient diminishes. The compressive strength of blended cement paste M2 (80 % PC, 15 % MK & 5 % SF) has a higher value than other control and blended cement pastes increases up to 800°C. This is due to the pozzolanic reaction of metakaoline and silica fume particles which were activated as a result of temperature rise with the free lime released during hydration of Portland cement. The decrease in compressive strength after 400°C, may be due to the propagation of microcracks. It is also obvious that the compressive strength of blended cement paste M2 has a higher value at 100°C; but the blended paste M5 (80 % Portland cement & 20 % SF) possess a lower value. This may be due to the principal reaction between the metakaoline ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) 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.,  $\text{C}_2\text{ASH}_8$ ,  $\text{C}_4\text{AH}_{13}$  and  $\text{C}_3\text{AH}_6$ ). The crystalline products formed depend principally on the metakaoline/calcium hydroxide ratio and reaction temperature [14]. The formation of CAH and CASH phases, increase the compressive strength. Therefore, the blended cement paste M2 that thermally treated at 800°C conserves a 85 % of its original compressive strength but the control cement paste maintains only 33 % of its original compressive strength.

The variations of the DSC thermograms of control (M0) and blended cement pastes (M2) treated at 100, 200, 400, 600 and 800°C are shown in (Figures 2 and 3). Evidently, there are almost four endothermic peaks. The first peak located at about 110-120°C, is mainly due to the decomposition of calcium silicate hydrates; CSH. The second endothermic peak observed at about 160°C represents the decomposition of the calcium sulpho-aluminate. The third endothermic peak at about 350°C is due to the dissociation of  $\text{C}_2\text{SH}$ . As the treatment temperature increases the peak area of calcium hydroxide increases up to 600°C. It is clear that the thermograms of the blended cement paste M2 that thermally treated at 800°C show very weak endothermic peaks, but the control cement paste have a weak crystals of calcium hydroxide. Evidently, this is due to further reaction between metakaoline, silica fume and  $\text{CaO}$  at high temperature (800°C). It is obvious that the enthalpy of calcium hydroxide phases in control cement paste (Figure 2) decreases from 73.72 J/g to 67.77 J/g as the treatment temperature increases up to 800°C. On the other hand, the enthalpy of calcium hydroxide phase in the blended cement decreases from 22.13 J/g to 1.6 J/g as the treatment temperature increases up to 800°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 Evidently, the products of further reaction and

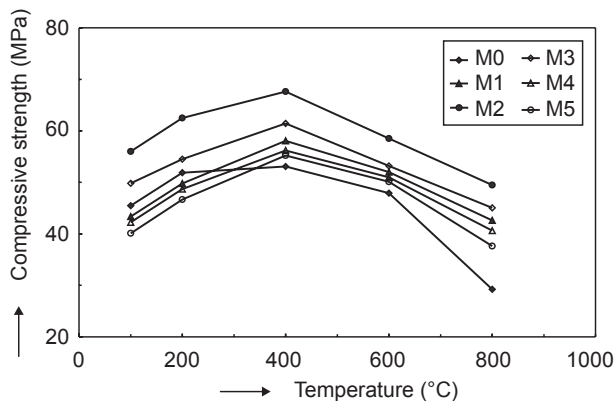


Figure 1. Variation of compressive strength of cement pastes with temperature for different admixtures blended cements.

physical filler of pozzolana deposit in the porous system lead to cross link inside it; which lower the temperature gradient across this system. Therefore, the thermal stresses induced by heat flow may be considered a singular at the tip of cracks, which is similar to the isothermal condition [7].

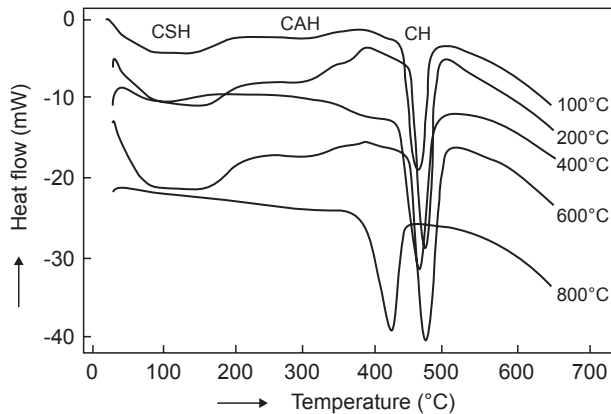


Figure 2. DSC thermograms of the Portland cement paste thermally treated at different temperatures.

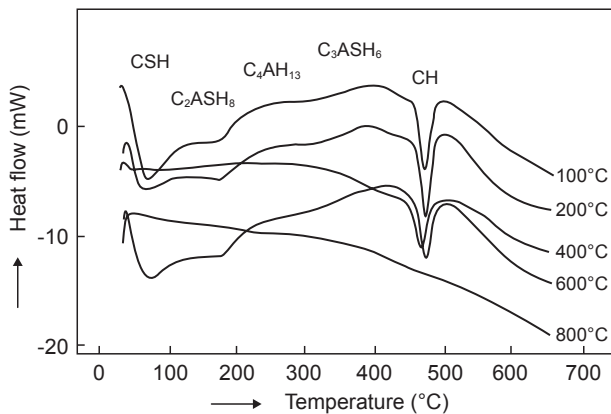


Figure 3. DSC thermograms of the blended cement pastes (80 % Portland cement, 15 % MK, and 5 % SF) thermally treated at different temperatures.

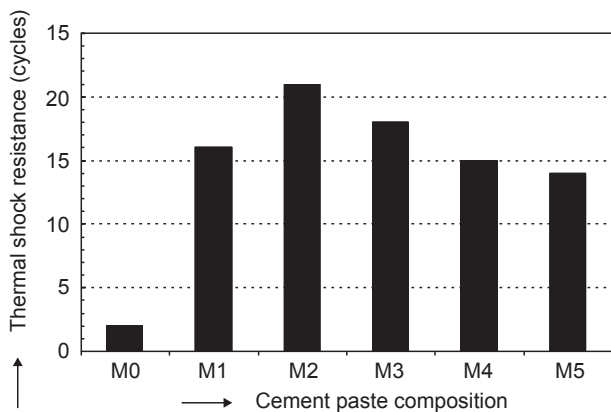


Figure 4. Thermal shock resistance of cement pastes.

The effect of admixtures on thermal shock resistance of hydrated blended cement pastes is shown in Figure 4. During heating, the outer layer of the test specimen tends 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 [15]. The differential deformation between the different layers leads to further crack activities. Evidently, the hardened Portland cement paste (M0) can resist only 2 cycles thermal shock. This is due to the free lime released during hydration of Portland cement. The  $\text{Ca}(\text{OH})_2$  crystals transform into  $\text{CaO}$  crystals during heating. Since the surface area of  $\text{CaO}$  is very large, it often re-hydrates in the humid environment and forms  $\text{Ca}(\text{OH})_2$  again with volume expands by 44 % leading to complete failure of the hardened cement paste [12].

The replacement of Portland cement by 20 % metakaoline in blended cement paste (M1) leads to increase the thermal shock resistance up to 16 cycles. This is due to the pozzolanic activity of metakaoline during hydration and at 800°C, the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  of metakaoline react with  $\text{CaO}$ . It also clear that, the replacement of metakaoline by 5 % in the blended system (M2); leads to thermal shock resistance of 21 cycles. The results show that the 20 wt.% replacement of Portland cement by pozzolanic admixture consisting of 15 % wt. of metakaoline and 5 wt.% of silica fume creates the most durable hydrate phase to thermal shocks. However, the increase of  $\text{SiO}_2$  ratios with high surface area in silica fume and decrease of metakaoline (i.e.  $\text{Al}_2\text{O}_3$  phase); leads to re- decrease in thermal shock resistance from 18 to 14 cycles in the blended M3-M5 pastes respectively. Evidently, the thermal shock resistance of blended cement pastes is considerably higher when highly effective microfiller-microsilica is added. It can be assumed that this admixture partially reacts with  $\text{Ca}(\text{OH})_2$  during curing. At the temperature of 800°C it together effectively binds  $\text{CaO}$ .

## CONCLUSIONS

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

1. The resistance to thermal shock of the cement paste at 800°C followed by immediate water quenching is significantly increased when Portland cement (100 wt.%) is replaced by cement blend consisting of 80 % wt. of Portland cement, 15 wt.% of metakaoline and 5 wt.% of silica fume..
2. This is confirmed by the fact that residual compressive strength of the above cement blend paste heated to 800°C is 85 % of that at 20°C. In contrast with it,

residual compressive strength of the Portland cement paste is 33 % at the same curing regime only.

3. It is noteworthy to devote further attention to studying 80 wt.% Portland cement + 15 wt.% metakaoline + + 5 wt.% silica fume binding system with expectations of the improved fire resistance using concrete for the test.

#### References

1. Park Y.S., Suh J.K., Lee J.H., Shin Y.S.: *Cem.Concr.Res.* 29, 1397 (1999).
2. Nehdi M., Hayek M.: *Cem.Concr.Res.* 35, 731 (2005).
3. Zelig J., Rusie D., Veza D., Krestulovic R.: *Cem.Concr.Res.* 30, 1655 (2000).
4. Sabir B.B., Wild S., Bai J.: *Cem.Concr.Composites* 23, 441 (2001).
5. Rojas M.F., Cabrera J.: *Cem.Concr.Res.* 32, 133 (2002).
6. Antonovich V., Goberis S.: *Mater.Sci.* 9, 379 (2003).
7. Morsy M.S.: Ph.D. Thesis, Ain Shams University, 1996.
8. Morsy M.S., Galal A.F., Abo-El-Enein S.A.: *Cem.Concr. Res.* 28, 1157 (1998).
9. Morsy M.S., Abo-El-Enein S.A., Hanna G.B.: *Cem.Concr. Res.* 27, 1307 (1997).
10. Gu P., Fu Y., Xie P., Beaudoin J.J.: *Cem.Concr.Res.* 24, 682 (1994).
11. Vydra V., Vodak F., Kapickova O., Hoskova S.: *Cem.Concr.Res.* 31, 1023 (2001).
12. Hung Y., Wong Y., Poon C., Anson M.: *Cem.Concr.Res.* 31, 1065 (2001).

13. Nassif A.Y.: *Magazine of Concr.Res.* 52, 287 (2000).

14. Murat M.: *Cem.Concr.Res.* 13, 259 (1983).

15. Nassif A.Y., Rigden S., Burley E.: *Magazine of Concr. Res.* 51, 255 (1999).

#### VLIV KŘEMIČITÉHO ÚLETU A PUCOLÁNOVÉHO METAKAOLINU NA OHNIVZDORNOST SMĚSNÉ CEMENTOVÉ PASTY

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Cílem výzkumu je studovat efekt náhrady metakaolinu (MK) křemičitým úletem (SF) na teplotní stabilitu směsných past portlandského cementu s metakaolinem. Kaolin byl teplotně aktivován při 850°C po dobu 2 hodin. Byly připraveny cementové pasty o stejné konzistenci. Pasty byly po dobu 24 hodin uloženy ve formách při 20°C a 100 % relativní vlhkosti a poté 28 dnů hydratovány pod vodou. Hydratované pasty byly vystaveny po dobu 2 hodin teplotě 100, 200, 400, 600 a 800°C. Poté byly hydratované vzorky zkoušeny na pevnost v tlaku, teplotní stabilitu a fázové složení. Bylo zjištěno, že po zvýšení tlaku na kontrolních cementových pastách ohřivaných do 200°C trpí pasta s dalším zvýšením zkušební teploty více ztrátou odolnosti v tlaku. Prokázalo se ale, že do 400°C se pevnost v tlaku směsných cementů zvyšuje s rostoucí teplotou, a poté s teplotou zvyšující se až k 800°C klesá. Náhrada portlandského cementu (PC) 15 % MK a 5 % SF v cementové pastě zvyšuje odolnost vůči teplotnímu šoku přibližně 10krát.