

Hydration Kinetics and Fire Resistance of Recycled Low Grade Alumino-Silicate Refractory Bricks Waste-Metakaolin Composite Cement Pastes

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Abstract— The aim of the present work is to study the effect of low grade aluminosilicate refractory bricks (ASRBs) with metakaolin (MK) on the hydration properties and the fire resistance of composite cement pastes at elevated temperature up to 800 °C. The composite cement are composed of constant proportion of ordinary Portland cement (OPC) (80 wt%) with variable amounts of ASRBs and MK. The substitution of 20% ASRBs with MK increases the water of consistency and retarded the initial as well as the final setting times, whereas the free lime contents and the bulk density decreases with MK. The compressive strength increases with MK content which enhanced the early and long term strength. It acts also as micro-filler that accelerates initial cement hydration. The fire resistance of composite cement pastes was evaluated up to 800 °C with rate of firing 5 °C/min. and soaking time for 2 h. The physico-mechanical properties such as, weight loss, bulk density and compressive strength were determined at each firing temperature. Moreover, some selected samples were investigated by using XRD, DTA/TG and SEM techniques analyses. Cement pastes containing 20 wt% ASRBs (PC-A) is the optimum composite cement paste which gives high bulk density and compressive strength. It can be concluded the cement paste PC-A has a good fire resistance paste.

Keywords— MK, ASRBs, DTA, XRD, Hydration, Fire resistance cement.

I. INTRODUCTION

Pozzolanas are naturally or artificial siliceous and aluminous materials, which possesses little or non-cementitious properties. But, in a finally divided form in the presence of water, they react with lime (CH) at room temperature to form calcium silicate and calcium aluminosilicate hydrates (C-S-H and C-A-S-H, respectively) [1,2]. Presently, the use of pozzolan incorporated in mortar and concrete has become much common throughout the world. The application of such material is increasing due to their superior structural performance, environmental friendliness and energy conservation implications [3]. Pozzolanas such as Fly ash, silica fume, Rice husk ash, ground granulated blast furnace slag and Metakaolin are commonly used for partial replacement of cement. Each of the pozzolanic materials induces various characteristics which have been explored by the researchers throughout the world [4].

Metakaolin, (MK) $\text{Al}_2\text{Si}_2\text{O}_7$, is a largely amorphous product of kaolinite $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$, after calcination at a temperatures between 500 and 850 °C. It contains silica and alumina in an active form which will react with CH, in the presence of water, forming cementitious C-S-H gel, together with crystalline products, which include calcium aluminate and aluminosilicate hydrate (C_3AH_6 , C_4AH_{13} and C_2ASH_8) [5,6]. Many researchers have a lot of interest in MK as it has been found to possess both pozzolanic and microfiller characteristics [7-10].

Fired low grad aluminosilicate refractory bricks (ASRBs) are commonly found in furnace as well as fire places. ASRBs are usually composed of a combination of clay minerals with silica, alumina or kaolin. There are few tries recorded for use aluminosilicate refractory bricks fired at temperature above 1500 °C as supplementary cementitious materials (SCM's). In a previous work [11], the pozzolanic activity of ASRBs with CH up to 30 wt% has somewhat potential to be used as a pozzolanic and filling material in cement based system. The substitution of 5-10 wt% of OPC by ASRBs gives higher compressive strength than that of OPC up to 90 days.

Concrete generally provides adequate fire resistance for most applications. It is well known for its capacity to endure high temperatures and fires owing to its low thermal conductivity and high specific heat [12]. However, it does not mean that fire, or high temperatures do not affect concrete at all. The durability properties of concrete are significantly affected at elevated temperatures [13-19]. At temperatures above 300 °C, evaporation of the bound water increases the deterioration of concrete and thereby the compressive strength decreases [20]. When temperature exceeds 400 °C, C-S-H disintegrates [13]. Thus, the

critical exposure temperature range is 400-800 °C in terms of compressive strength loss. The effect of elevated temperatures on the mechanical durability properties of concrete has been investigated in order to produce fire resistant materials [21-23]. The aim of the present work is to study the effect of substitution of ASRBs with MK on the hydration properties and the fire resistance of composite cement pastes at temperature up to 800°C. Moreover, some selected pastes were investigated by using XRD, DTA/TG and SEM technique analyses.

II. MATERIALS AND METHODS

The materials used in this work were ordinary Portland cement (OPC) and fired clay refractory bricks (ASRBs) as waste product supplied from Suez Cement Company, Suez. Kaolinite clay was supplied from Abu Zneima zone, South of Sinai, Egypt. The physico-chemical analysis of starting materials is shown in Table 1.

TABLE 1
PHYSICO-CHEMICAL ANALYSIS OF OPC, ASRBs AND MK

a) Oxide composition, %	OPC	ASRBs	MK
CaO	62.72	1.45	0.28
SiO ₂	20.68	50.12	55.10
Al ₂ O ₃	4.90	41.04	34.10
Fe ₂ O ₃	3.35	2.56	5.24
MgO	2.64	0.31	0.25
SO ₃	2.65	1.50	0.01
Na ₂ O	0.11	0.19	0.10
K ₂ O	0.14	1.20	0.02
TiO ₂	0.12	0.50	2.00
P ₂ O ₅	0.10	0.20	1.00
L.O.I	2.73	0.54	1.50
b) Blaine surface area/ cm ² g ⁻¹	3400	7100	11000
c) Residue on sieve/ %			
90 micron	0.00	1.50	1.00
45 micron	12.00	13.60	12.80
d) Specific gravity/ g cm ⁻³	3.15	2.95	2.65
e) Insoluble residue/ %, HCl/Na ₂ CO ₃	0.45	75.71	63.45

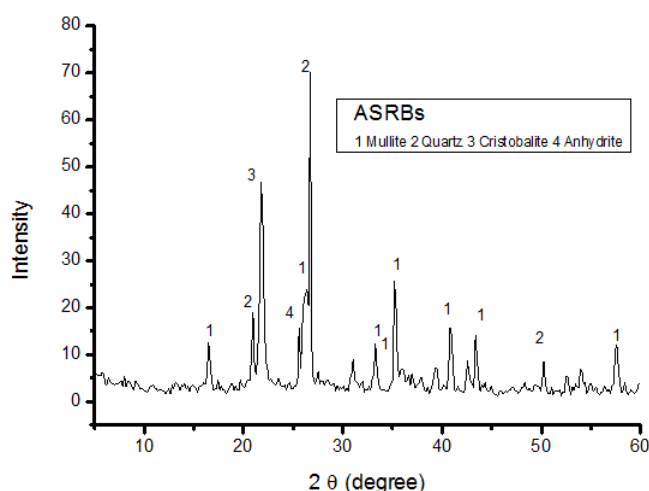


FIG.1A XRD PATTERN OF ASRBs [11]

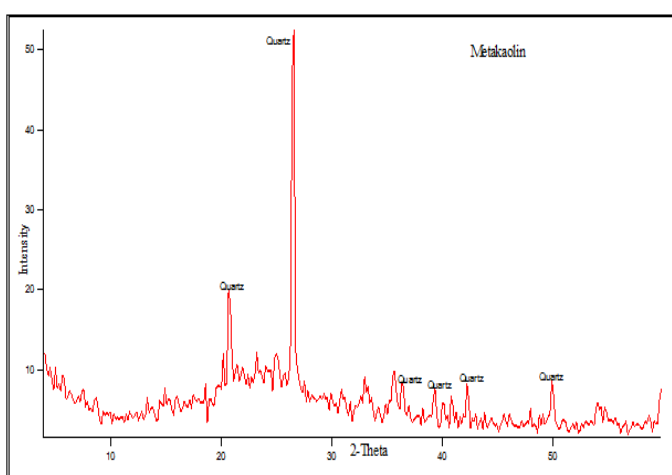


FIG. 1B XRD PATTERN OF MK [10]

TABLE 2
THE MIX COMPOSITION OF THE INVESTIGATED MIXES, %

Mix. No.	OPC	ASRBs	MK
OPC	100	00	00
PC-A	80	20	00
PC-AM	80	10	10
PC-M	80	00	20

Thermally heated pastes were prepared using the standard water of consistency. The samples were demoulded after 24 h, cured for 28 days under tap water, dried for 24 h at 105 °C, then subjected to thermal treatment for 2 h at 250, 450, 600 and 800 °C with 5 °C/min rate of heating, then cooled to room temperature in the furnace. Bulk density and compressive strength of treated cement pastes were determined after immersing the pastes overnight under kerosene [2]

The XRD technique was carried out using BRUXER, Axs D8 ADVANCE A8 and GERMANY Diffractometer as described in a previous work [10]. The differential thermal analyzer of the type Simultaneous TGA/DSC MODEL SDTQ600 (USA) was also used. A sample of 50-mg (- 53 μ m) was used at 20 °C/min heating rate. The interpretation of the thermal charts was based on the data given by Plummer & Mackenzie [29]. The microstructure of the heat treated samples was studied by using SEM of freshly fractured specimens, coated with a 300-400 Å layer of gold, using JEOL apparatus with high resolution SEM [30].

III. RESULTS AND DISCUSSION

3.1 Hydration kinetics of recycled aluminosilicate refractory bricks-metakaolin composite cement pastes

3.1.1 Water of consistency and setting time

The water of consistency, initial and final setting times of the composite cement pastes are represented in Fig. 2. Mix PC-A (20 wt., % ASRBs) filled cement paste gives the lower water of consistency in comparison with OPC as well as other composite cement pastes. This is due to that ASRBs has some crystalline phases such as quartz, cristobalite and mullite which have low pozzolanic activity substitution of 20 wt % ASRBs with MK increases the water of consistency due to the high reactivity of MK which has high specific surface area (11,000 cm²/g) resulting high water adsorption/absorption as well as the presence of the amorphous structure in MK [31]. It is clear that substitution of more than 10 wt % of ASRBs with MK somewhat retards the initial and final setting times. This is due to the pozzolanic activity of MK and ASRBs as well as the increase of water/cement (w/c) ratio which favors the formation of ettringite [32]. As ASRBs content decreases up to complete substitution the initial and final setting times are accelerated due to the high pozzolanic activity of MK [33].

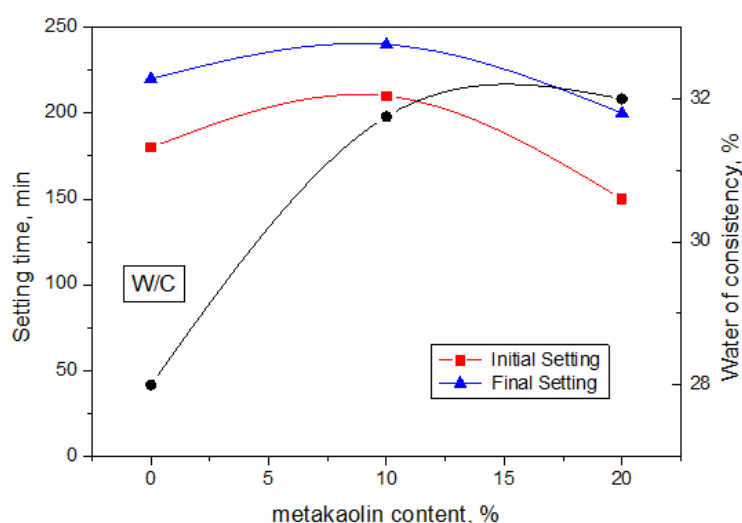


FIG. 2. WATER OF CONSISTENCY, INITIAL AND FINAL SETTING TIME OF COMPOSITE CEMENT PASTE OF ASRBs AND MK

3.1.2 Combined water content

The combined water contents of composite cement pastes are represented up to 90 days in Fig. 3. The combined water content increases gradually with curing time for all cement pastes due to the progress of hydration. It is clear that the combined water increases with MK content which is attributed to increase the amount of water of consistency as well as its high specific area ($11000 \text{ cm}^2/\text{g}$) and amorphous material. Mix PC-AM gives higher combined water than all cement pastes. This is mainly due to the presence of two Pozzolanic materials which act as nucleating agent [33], that increases the rate of hydration of OPC and Pozzolanic reaction between ASRBs and MK with liberated lime to form more hydration products.

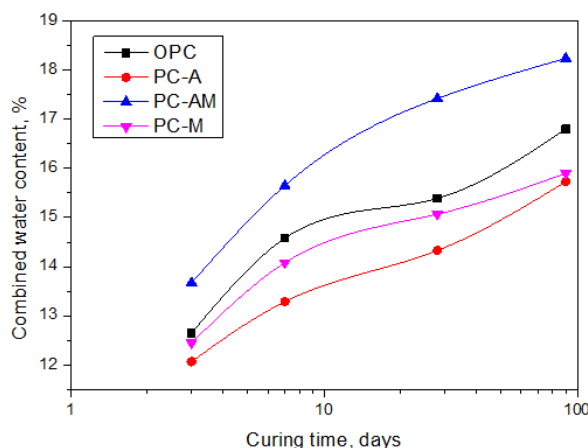


FIG. 3. CHEMICALLY COMBINED WATER OF HYDRATED OPC AND COMPOSITE CEMENT PASTES UP TO 90 DAYS

3.1.3 Free lime contents

The free lime contents of OPC as well as composite cement pastes are plotted up to 90 days in Fig. 4. The free lime content of the OPC paste increases up to 90 days; due to the continuous hydration of the C_3S and C_2S , liberating free lime (CH). The free lime contents of all composite cement pastes increase with curing time up to 7 days, then decrease up to 90 days. This is due to the liberation of free lime during hydration of Portland cement pastes exceeds the rate of consumption by pozzolanic reaction of ASEBs as well as MK. On the other hand, the substitution of ASRBs with 20 wt., % MK decreases the free lime up to 90 days due to the higher pozzolanic activity of MK than ASRBs to react with liberated lime.

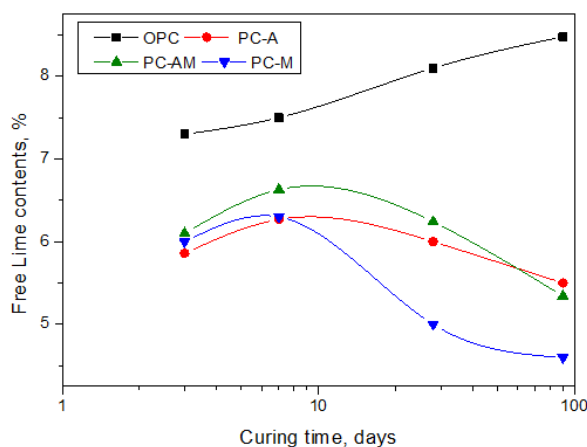


FIG. 4. FREE LIME CONTENTS OF HYDRATED OPC AS WELL AS COMPOSITE CEMENT PASTES UP TO 90 DAYS

3.1.4 XRD Analysis

Figure 5 illustrates the XRD patterns of hydrated cement pastes cured up to 28 days. The figure shows the presence of portlandite in all cement pastes but decreases with the substitution of ASRBs with MK. Mix PC-M cement paste shows the lower CH than the other composite mixes (PC-A and PC-AM), and lastly OPC. The anhydrous phases of C_2S and C_3S are still present. The quartz peaks are also still present in PC-M cement pastes due to its unhydraulic properties. On the other hand, the CaCO_3 peaks decrease with MK content due to the effect of CO_2 in the presence of H_2O to form $\text{Ca}(\text{HCO}_3)_2$. The

OPC paste gives the higher rate of carbonation due to its higher content of $\text{Ca}(\text{OH})_2$. ASRBs have somewhat pozzolanic activity and filler effects [11]. The C-S-H gel is overlapped with CaCO_3 peak.

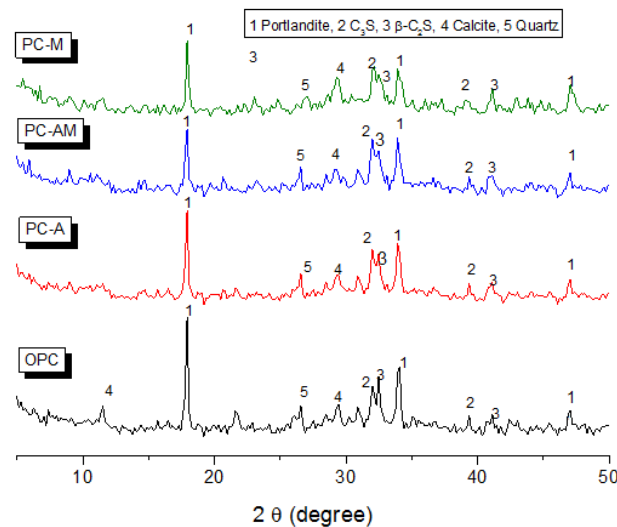


FIG. 5. XRD PATTERNS OF HYDRATED OPC AND COMPOSITE CEMENT PASTES CURED UP TO 28 DAYS

3.1.5 Thermal Analysis

Figure 6 illustrates the DTA/TG thermograms of the hydrated mix PC-A pastes cured at 3 and 90 days. The DTA curves show the occurrence of four endothermic peaks. The first endothermic peak located below 100°C is due to the removal of free water and the decomposition of the amorphous part of C-S-H. The second endotherm $130\text{--}160^\circ\text{C}$ represents the decomposition of small amount of crystalline part of C-S-H, C-A-H, C-A-S-H as well as C_2ASH_8 [2, 34], with a mass loss of 6.66 and 8.57 % for 3 and 90 days, respectively. The endothermic peak located at about 160°C increases with curing time due to the formation of excessive amounts of C-A-H and C-A-S-H as well as C-S-H. The third endotherm in range $410\text{--}490^\circ\text{C}$ is due to the dehydroxylation of CH [35, 36], with a mass loss of 3.96 and 5.18 % for 3 and 90 days, respectively. These values indicate that the ASRBs have little pozzolanic activity with CH. The fourth endotherm with the range $685\text{--}760^\circ\text{C}$ due to the decomposition of amorphous and crystalline CaCO_3 [35, 37], with a mass loss of 6.50 and 10.13 % for 3 and 90 days, respectively. These phases are formed as a result of the pozzolanic activity of ASRBs with CH [11]. The main features of the curves are characterized by the relative increase of C-S-H, C-A-H and C-A-S-H peaks with ASRBs. The CaCO_3 is still present, due to the carbonation of CH which has a highly amorphous character, and readily attacked by the atmospheric CO_2 . This is in an agreement with that of DTA.

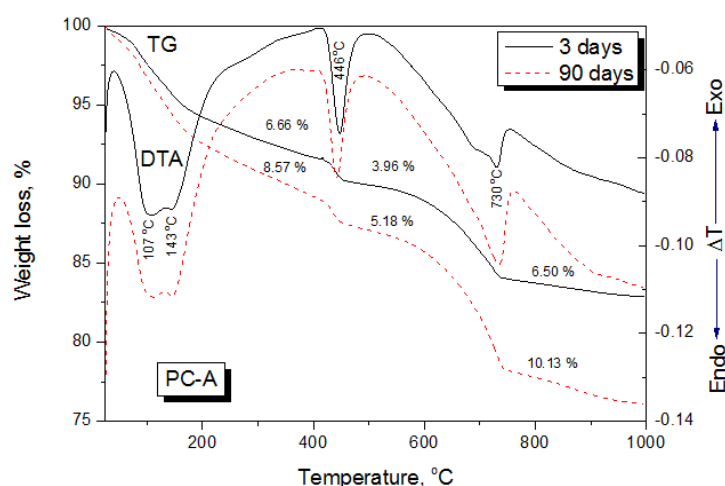


FIG. 6. DTA/TG CURVES OF HYDRATED MIX PC-A CURED AT 3 AND 90 DAYS

Figure 7 shows the DTA/TG curves of PC-AM hydrated cement pastes cured at 3 and 90 days. The first two endothermic peaks within temperature range of $90\text{--}220^\circ\text{C}$ are mainly due to the dehydration of interlayer water of C-S-H and C-A-H or C-A-S-H as well as the presence of carboaluminate [36], with a mass loss of 6.63 and 9.02 % for 3 and 90 days, respectively.

The third endothermic peak located at range 410-475 °C is due to the decomposition of CH [35], with a mass loss of 3.50 and 4.34 % for 3 and 90 days, respectively. The last endothermic peak located with temperature range 700-780 °C is due to the decomposition of CaCO_3 [35, 37], with mass loss of 6.50 and 10.27 % for 3 and 90 days, respectively. It is clear that the second endothermic peak located at about 150 °C increases with curing time due to the formation of excessive amounts of C-A-H and C-A-S-H as well as C-S-H. These phases are formed as a result of the pozzolanic reaction of both ASRBs and MK with CH. The main features of the curves are characterized by the relative decrease of the peak area of CH and increase of C-S-H, C-A-H and C-A-S-H peaks with both ASRBs and MK. The decrease of the CH endothermic peak is due to the consumption of the residual lime by pozzolanic reaction with active silica and alumina containing ASRBs as well as MK. Also, the CaCO_3 is still present, due to the carbonation of CH by atmospheric CO_2 . This is in an agreement with the results of DTA.

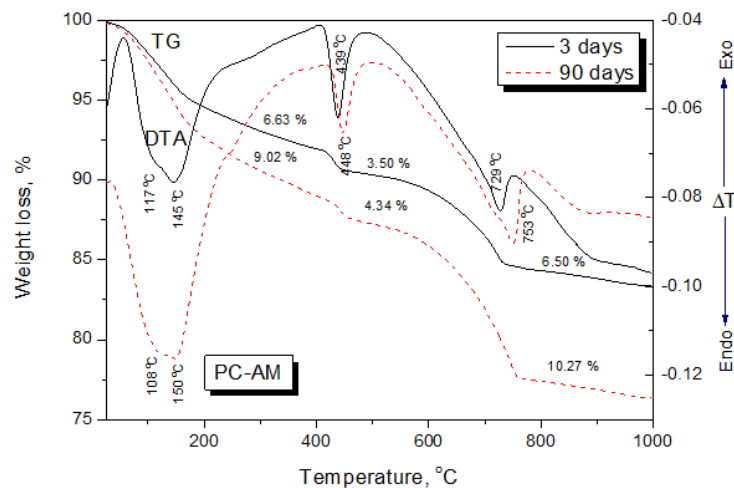


FIG. 7. DTA/TG CURVES OF HYDRATED MIX PC-AM CURED AT 3 AND 90 DAYS

Figure 8 illustrates the DTA/TG thermograms of hydrated cement pastes PC-M cured at 3 and 90 days. There are four endothermic peaks located within temperature range 25-1000 °C. The first two endothermic peaks at range 85-160 °C are mainly due to the dehydration of interlayer water of C-S-H and C-A-H or C-A-S-H as well as carboaluminate [36], with a mass loss of 7.85 and 11.84 % for 3 and 90 days, respectively. This means that MK acts as micro-filler and nucleating agent which accelerates the rate of hydration and then the combined water increases. This is in an agreement with the results of DTA. The third endotherm at 448-443 °C is due to the dehydroxylation of CH [35], with a mass loss of 3.02 and 4.09 % for 3 and 90 days, respectively. The last endothermic peak located at 730-738 °C is due to the decomposition of CaCO_3 [35, 37], with mass loss of 5.89 and 7.48 % for 3 and 90 days, respectively. Also, the CaCO_3 is still present, due to the carbonation of CH by atmospheric CO_2 .

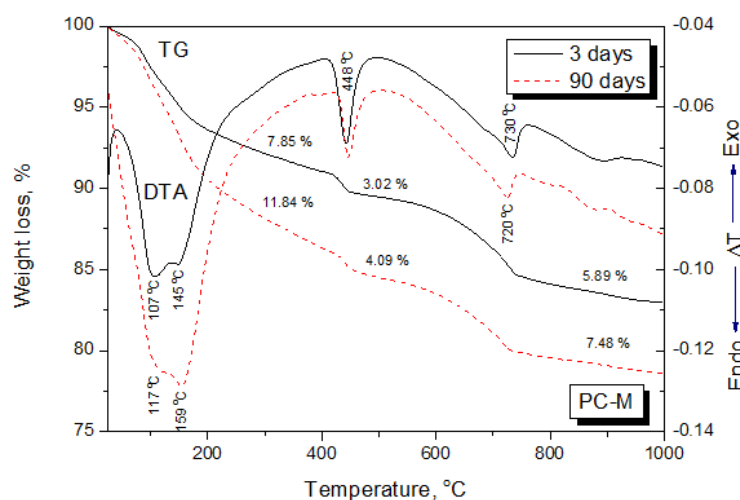


FIG. 8. DTA/TG CURVES OF HYDRATED MIX PC-M CURED AT 3 AND 90 DAYS

Figure 9 represents the DTA/TG thermograms of the hydrated OPC and composite cement pastes at 90 days. The first thermal degradation stage in the temperature range 77-192 °C with the maximum decomposition peak DTG_{max} at 98, 150, 150 and 156 °C corresponding to the dehydration of C-S-H, C-A-H and C-A-S-H with a weight loss of 9.67, 8.57, 9.02 and 11.84 % for OPC, PC-A, PC-Am and PC-M, respectively. The third thermal stage in the temperature range 409-483 °C with the maximum decomposition peak DTG_{max} at ≈ 441 °C corresponding to the dehydroxylation of $Ca(OH)_2$ with a weight loss of 6.804, 5.18, 4.34 and 4.09 % for OPC, PC-A, PC-Am and PC-M, respectively. The fourth thermal decomposition step proceeds at 695-790 °C with the maximum decomposition peak DTG_{max} at 714, 728, 748 and 728 °C corresponding to the decomposition of $CaCO_3$ with a weight loss of 5.68, 10.13, 10.27 and 7.48 % for OPC, PC-A, PC-Am and PC-M, respectively. It is clear that intensities of the endothermic peaks characteristic for hydrated products is large with PC-M due to the pozzolanic activity of MK.

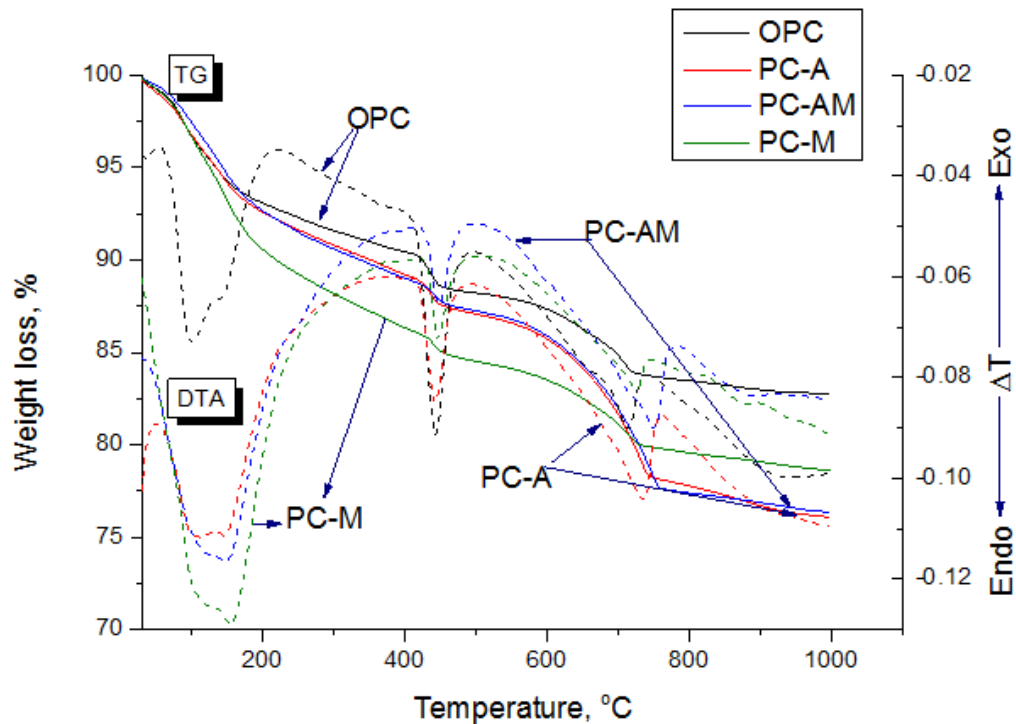


FIG. 9 DTA/TG THERMOGRAMS OF THE HYDRATED OPC AND CEMENT PASTES AT 90 DAYS

3.1.6 Insoluble residue

The insoluble residue (unreacted part) contents of hydrated OPC and composite cement pastes are graphically represented up to 90 days in Fig. 10. It is clear that the insoluble residue content decreases with curing time as well as MK content, due to the decrease of ASRBs content and the high reactivity of MK with glassy phase which reacts with CH. Mix PC-M pozzolanic cement paste shows the lower insoluble residue contents than other composite cement pastes. The increase of insoluble residue of composite cement PC-A is mainly due to the high amount of crystalline phases in ASRBs such as quartz, cristobalite and mullite which are unhydraulic in comparison to MK. OPC pastes show very small amount of insoluble residue due to the absence of ASRBs and MK.

3.1.7 Bulk density

The bulk density of hydrated OPC and composite (ASRBs – MK) cement pastes are represented up to 90 days in Fig. 11. The bulk density increases with curing time for all cement pastes due to the progress of hydration giving more hydration products that fill some of pores of cement pastes which increase the bulk density of cement paste. The bulk density decreases with MK content due to its lower specific gravity (2.65 g/cm^3) in comparison with ASRBs (2.95 g/cm^3) and the increase of the water of consistency with MK content. So, PC-A paste shows the higher bulk density than OPC as well as other composite cement pastes. The higher bulk density of PC-M than PC-AM at 3 – 7 days is mainly due to the more hydraulic property of MK than ASRBs.

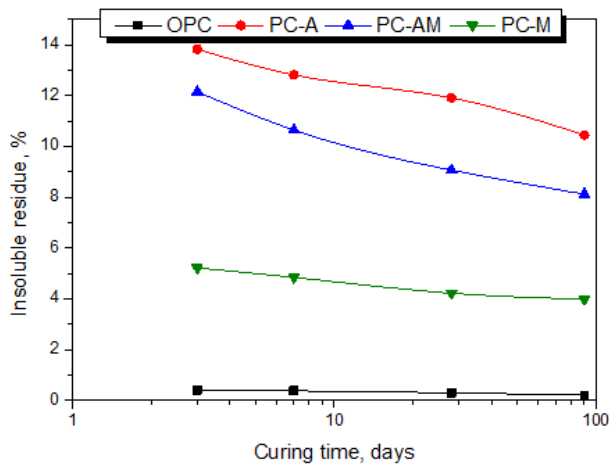


FIG. 10. INSOLUBLE RESIDUE CONTENTS OF HYDRATED OPC AND COMPOSITE CEMENT PASTES UP TO 90 DAYS

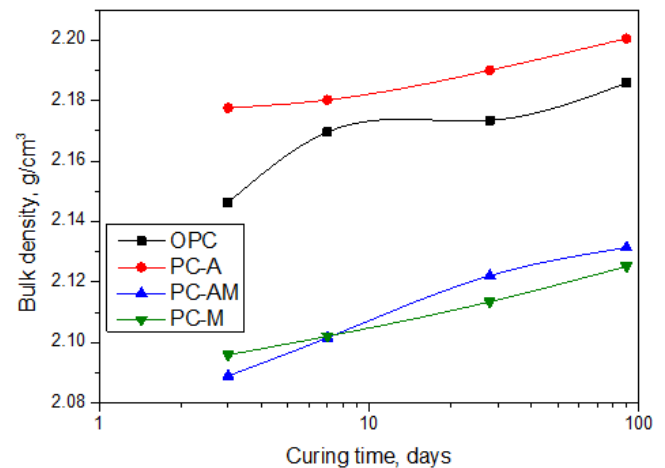


FIG. 11. THE BULK DENSITY OF OPC AS WELL AS COMPOSITE CEMENT PASTES CURED UP TO 90 DAYS

3.1.8 Compressive strength

The compressive strength of OPC and composite cement pastes is plotted in Fig. 12. The compressive strength increases with curing time for all cement pastes up to 90 days. This is mainly due to the increase of the hydration products, especially C-S-H which accumulates within the available pores giving high strength [38]. The C-S-H phase is the most cementitious or binding phase and hence contributes to the strength of cement paste. The compressive strength increases with MK content due to its pozzolanic activity which is higher than ASRBs as well as MK gives enhanced early and long term strength [6]. It acts also as micro-filler that accelerates initial cement hydration and rapidly consumes the portlandite liberated from OPC to give additional hydration products [39]. Mix PC-M cement paste gives compressive strength nearly equal to the neat cement paste.

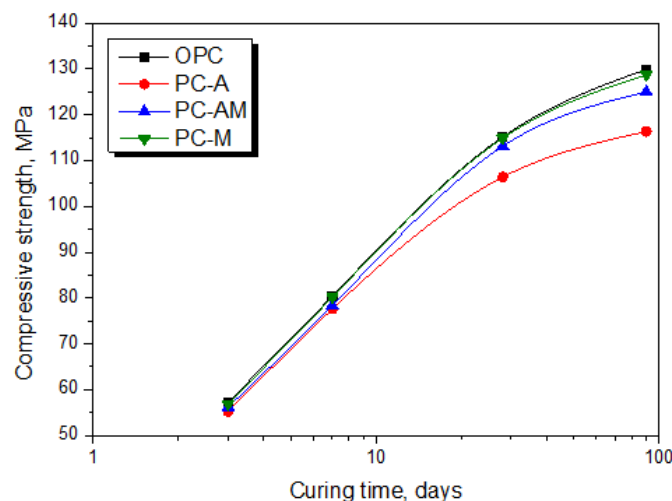


FIG. 12. COMPRESSIVE STRENGTH OF HYDRATED OPC AND COMPOSITE CEMENT PASTES UP TO 90 DAYS

3.2 Effect of fire on the physico-mechanical properties of cement pastes

When hardened Portland cement paste is exposed to high temperatures, complex physico-chemical transformation takes place. The main components of cement paste, C-S-H and CH, dehydrated at high temperature ($> 105^{\circ}\text{C}$). This leads to irreversible changes of the structure of cement paste [40] and the structure of cement paste undergoes substantial changes. The phases present in cement paste exhibit different heat-induced deformations. The hydration products C-S-H and CH, shrink due to dehydration. The un-hydrated clinker, however, expands due to thermal dilation. The micro-cracks in heated cement paste are caused by the strain mismatch of the shrinking hydration products and expanding clinker particles [40]. As a result of the shrinking microstructure, the porosity of the cement paste increases with temperature.

3.2.1 Weight loss

The weight loss of cement pastes heated treated up to 800 °C is represented in Fig. 13. The weight loss increases with temperature due to the removal of free water at 105 °C, a partially decomposition of C-S-H, C-A-H and C-A-S-H. Moreover, the decomposition of gehlenite hydrate (C_2ASH_8) takes place above 200 °C and dehydroxylation of CH at 450-550 °C [41]. Also, the decomposition of $CaCO_3$ occurred at 600-800 °C [42]. The substitution of ASRBs with MK increases the weight loss due to the higher water of consistency of MK cement pastes. Mix PC-A and PC-AM give the lowest weight loss values at 800 °C. This may be due to the pozzolanic activity of MK which consumes portlandite forming additional thermally stable minerals and decreases the micro-cracks as well as the high thermal stability of ASRBs.

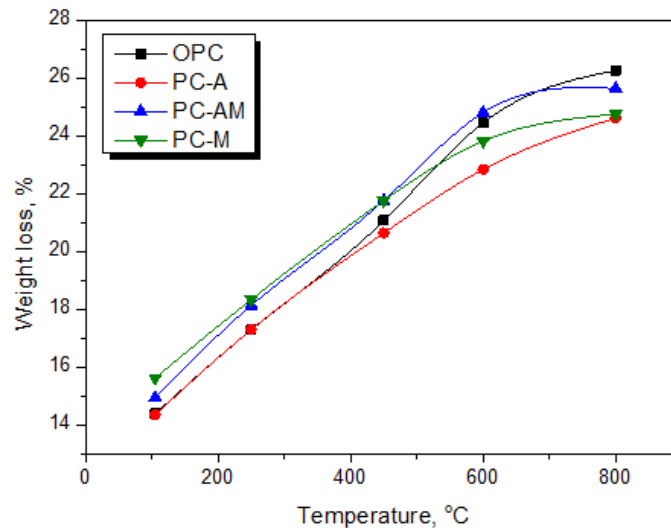


FIG. 13. WEIGHT LOSS OF HYDRATED OPC AND COMPOSITE CEMENT PASTES HEAT TREATED UP TO 800°C

3.2.2 Bulk density

The bulk density of cement pastes heated treated up to 800 °C is represented in Fig. 14. The bulk density of all cement pastes decreases from 105 to 250 °C, due to the removal of free, adsorbed and some of combined water which leads to micro-cracks as well as increases the opening of the pore system of cement pastes. From 250 up to 800 °C the bulk density increases due to the additional hydration products as well as a result of the so-called internal autoclaving [42]; it is also due to the associated shrinkage from the removal of H_2O and CO_2 to give a dense structure [43]. Evidently, the bulk density decreases with MK content, due to the relatively higher water of consistency of MK cement pastes. MK has more pozzolanic property which acts as nucleating agent that increases the rate of hydration of cement to form more cementitious materials that fill some pores producing closed compact structure [33]. Mix PC-A gives higher bulk density up to 800 °C. This is due to the higher specific gravity of ASRBs than MK. The specific gravity of ASRBs and MK is 2.96 and 2.65 g/cm³, respectively.

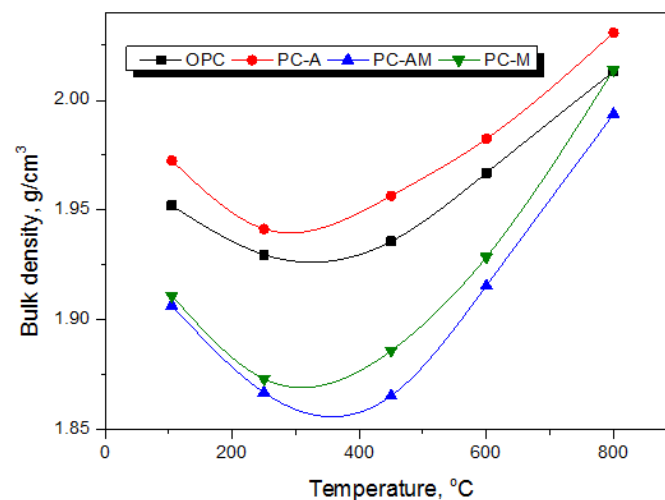


FIG. 14. BULK DENSITY OF OPC AND COMPOSITE CEMENT PASTES FIRED UP TO 800 °C

3.2.3 Compressive strength

Figure 15 shows the compressive strength of cement pastes with thermal treatment. It is clear that the compressive strength of heat treated of OPC pastes is lower than ASRBs/MK composite cement pastes. The compressive strength increases up to 250 °C. This may be due to the additional hydraulic reaction of ASRBs and MK with portlandite to produce more hydraulic products such as C-S-H, C-A-H and C-A-S-H phases deposited in the pore system and also as a result of internal autoclaving effect [44]. The compressive strength of composite cement pastes start to decline at 450 °C, which may be due to the dehydroxylation of the Ca(OH)_2 producing CaO and H_2O . Over 450 up to 600 °C, the relatively sharp reduction is mainly caused by dissociation of portlandite (CH) giving CaO and water vapour. The compressive strength of all cement pastes decreases with lower rate up to 600 °C. This is mainly due to, physical filler of pozzolana deposits in the porous system that leads to cross link which lowers the temperature gradient across this system. Therefore, the thermal stresses induced by heat flow may be considered a singular at the tip of cracks [45]. Up to 800 °C the compressive strength decreases for all cement pastes, this due to that the amorphous C-S-H starts to recrystallize into $\beta\text{-C}_2\text{S}$ or CS (wollastonite), when the temperature exceeds 700 °C the recrystallization of C-S-H causes shrinkage and changes the microstructure of compressive strength [46]. The PC-A is the optimum composite cement paste, which gives higher bulk density and compressive strength. It is found also that OPC pastes give the lower compressive strength up to 800 °C. Therefore, the pozzolanic materials enhance the fire resistance of OPC pastes.

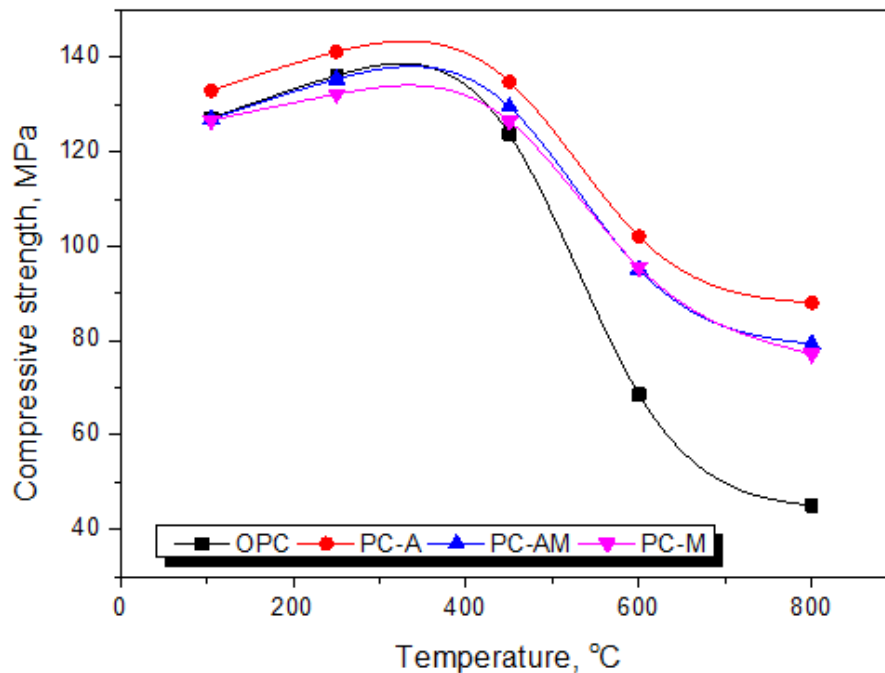
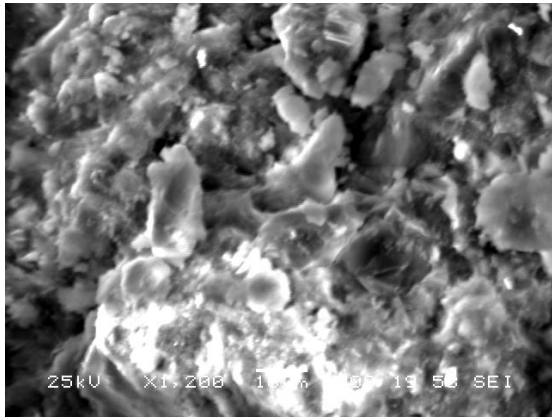
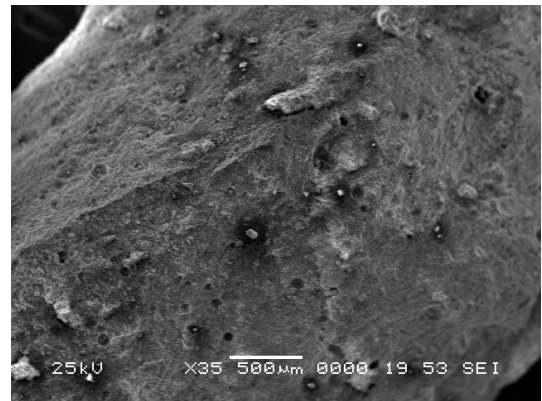
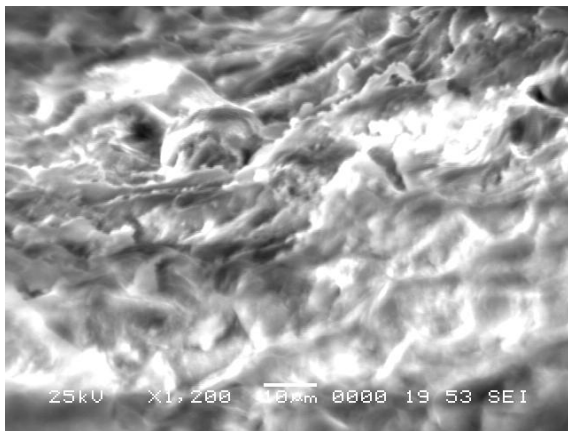
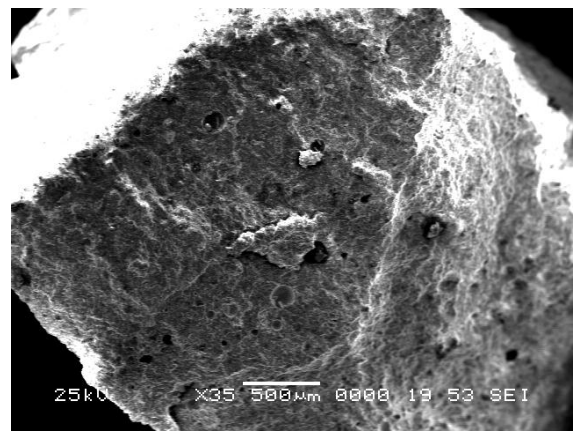
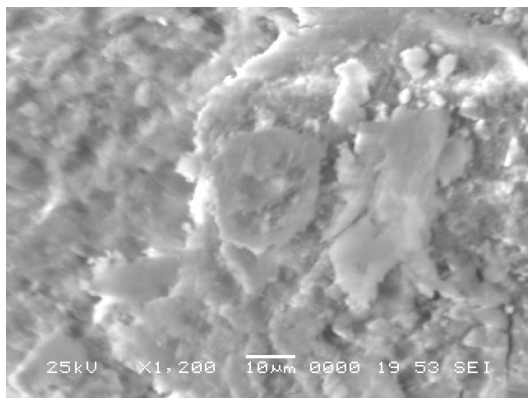
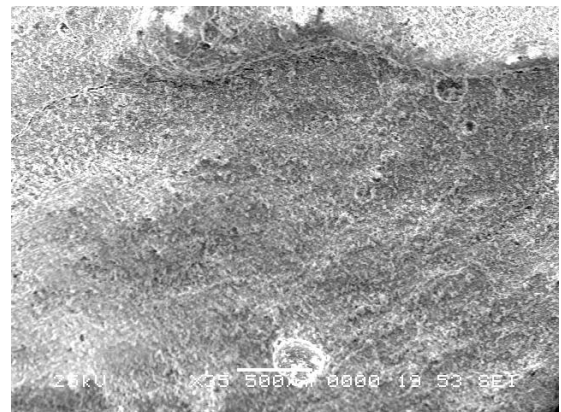


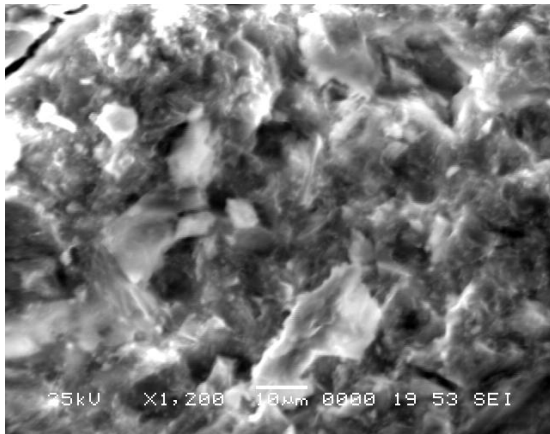
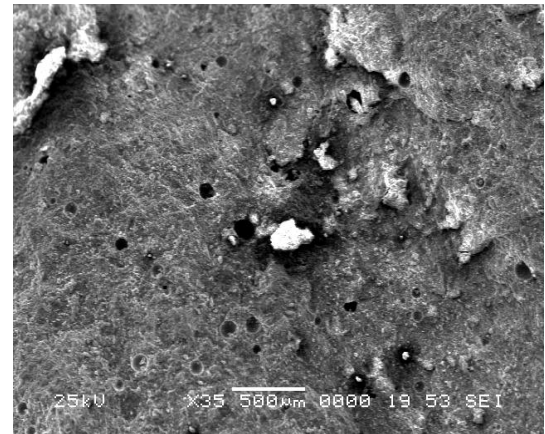
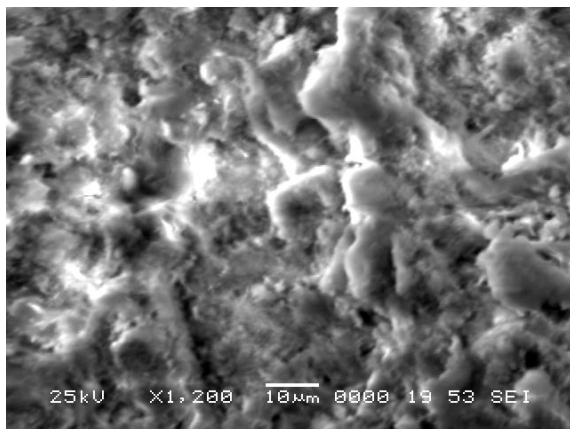
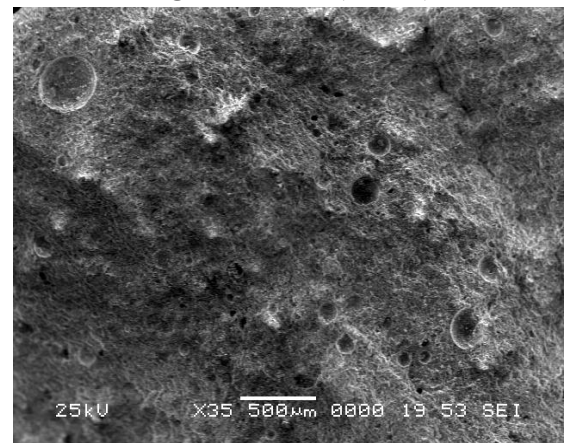
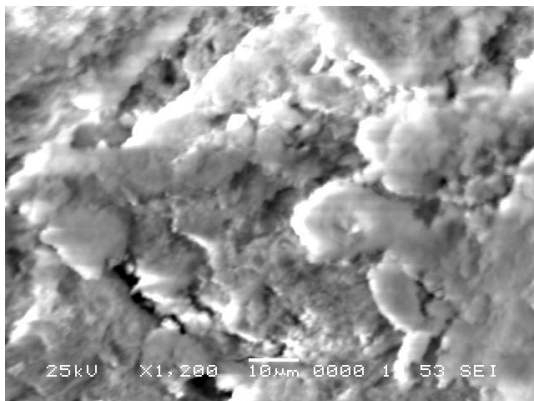
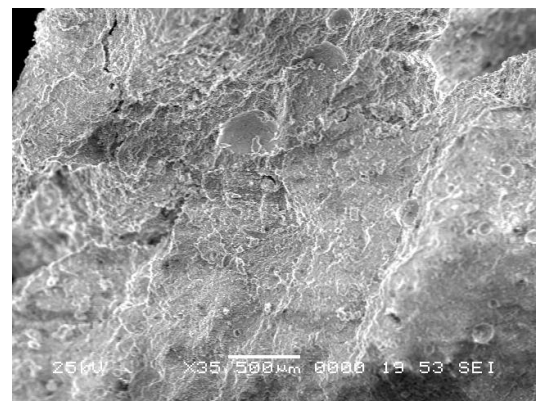
FIG. 15. COMPRESSIVE STRENGTH OF OPC AND COMPOSITE CEMENT PASTES FIRED UP TO 800 °C

3.2.4 SEM micrographs

SEM micrographs of cement pastes thermally treated up to 800 °C are seen in Fig. 16a-c. The micrograph of PC-A displayed the presence of a nearly amorphous C-S-H and dense microstructure as shown in Fig. 16a. It was clear that, the microstructure of mix PC-A thermally treated at 250 °C was perfectly stable for thermal treatment and illustrates a dense structure of hydrated products as shown. Therefore, the replacement of OPC by 20 wt% of ASRBs resulted in an improvement of thermal stability of the hardened composite cement. At 450 °C, the pores appear to increase in size and some micro-cracks also appear (Fig. 16b). Fig. 16c illustrates the SEM micrograph of treated at 800 °C, it represents the formation of unhydrated phases such as $\text{b-C}_2\text{S}$, C_3S and wollastonite due to the decomposition of C-S-H at higher temperature as well as the presence of some micro-cracks [19]. These micro-cracks tend to decrease the compressive strength.

**Fig. 16a PC-A (250 °C)****Fig. 16a PC-A (250 °C)****Fig. 16b PC-A (450 °C)****Fig. 16b PC-A (450 °C)****Fig. 16c PC-A (800 °C)****Fig. 16c PC-A (800 °C)**

The micrograph of PC-M pastes thermally treated up to 800 °C is seen in Fig. 17a-c. At 250°C, it was clear that, the presence of pores nearly connected and adjusted to some large particles affected negatively on the strength (Fig. 17a). At 400 °C, some micro-cracks start appearing and pores are slightly bigger than at 250 °C (Fig. 17b). Thermal treatment of mix PC-M at 800 °C showed a decomposition of the hydration products with the formation of micro-cracks in the structure as shown in Fig. 17c.

**Fig. 17a PC-M (250 °C)****Fig. 17a PC-M (250 °C)****Fig. 17b PC-M (450 °C)****Fig. 17b PC-M (450 °C)****Fig. 17c PC-M (800 °C)****Fig. 17c PC-M (800 °C)**

IV. CONCLUSION

When MK is substituted instead of ASRBs the water of consistency increases with MK, the initial and final setting times are retarded. The combined water increases due to the high water of consistency of cement pastes. The free lime content of cement pastes increases up to 7 days then decreases up to 90 days. The substitution of ASRBs to 20 wt% MK decreases the free lime up to 90 days due to its high pozzolanic activity than ASRBs. PC-M cement paste gives compressive strength nearly equal to the neat cement paste. The effect of fire on the mechanical properties of cement pastes was carried out by the determination of weight loss, bulk density and compressive strength of heat treated hardened cement pastes treated up to 800°C. Cement pastes containing 20 wt, % ASRBs (PC-A) is the optimum composite cement paste which gives high bulk density and compressive strength. PC-A mix has a good fire resistance paste.

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