

## Metakaolin Blended Cement Pastes

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**Abstract:** The free lime,  $\text{Ca}(\text{OH})_2$  resulting due to the hydration of the main calcium silicate phases ( $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$ ) of the cement (OPC) was found to decrease the resistance and durability of cement structures, but the pozzolanic properties of metakaolin (MK) with it can avoid this drawback. So, the kinetic reactions of MK in the OPC/ MK blended cement pastes were investigated. The consumption of  $\text{Ca}(\text{OH})_2$  was evaluated by IR and XRD techniques. Results revealed that water of consistency, WC, % and setting times (ST) gradually increased with the further addition of MK. Bounded water content also increased with MK content up to 21 wt. %, and then decreased, whereas the free  $\text{Ca}(\text{OH})_2$  content decreased. The same trend was displayed with bulk density, while the total porosity displayed the opposite. The compressive strength was positively affected due to the pozzolanic reaction effect of MK with the evolved  $\text{Ca}(\text{OH})_2$ . The results were confirmed by IR and XRD analyses which proved that the intensity of  $\text{Ca}(\text{OH})_2$  peaks continually increased up to 90 days, while those incorporating MK decreased with hydration ages. SEM images illustrated that the formed hydration products of MK cement pastes are the same as those of pure OPC pastes, but with modified crystals and morphologies.

**Keywords:** Metakaolin, blended cement, lime, pozzolanic activity, hydration, density, porosity, strength, IR, XRD, SEM.

**Abbreviations:** C :  $\text{CaO}$ , S :  $\text{SiO}_2$ , A :  $\text{Al}_2\text{O}_3$ , F :  $\text{Fe}_2\text{O}_3$ , H :  $\text{H}_2\text{O}$ , CH :  $\text{Ca}(\text{OH})_2$ , CSH: calcium silicate hydrate.

### 1. INTRODUCTION

#### 1.1. Scope of the Problem

Except water, the concrete is the most consumed material in the world although the cement is the most expensive and energy intensive ingredients of concrete, where for every one ton of cement production, about 0.5-1.0 ton of  $\text{CO}_2$  could be emitted into the atmosphere [1]. In order to reduce the unit cost of concrete and the required energy for its production, the reuse of waste materials and/or industrial byproducts is becoming very necessary. The use of waste materials at the expense of cement will minimize the quantities of materials sent to the landfill and the amount of cement used in concrete.

On the other side, the use of pozzolanic materials in cement and/or concrete is increasing worldwide due to its less energy consumption and lower cost. There are two main processes usually occur during hydration: the

first is the hydration of cement phases; and the second is the pozzolanic reactions between the pozzolanic materials and  $\text{Ca}(\text{OH})_2$  resulting from the first process to produce additional gels which improve strength and durability [2,3]. These materials are glass bottles [4-17] or liquids as black and/or white liquors [18,19], industrial by-products as GbFS, SF, FA [20-26] or natural materials [27]. Other materials such as calcined clays are also pozzolanic materials but require energy to produce as they are not either waste or industrial by-products [28,29]. However, the energy required for their production is much less than that used for cement.

Metakaolin (MK) is one of these calcined clays, where it arises from the calcination of kaolinitic clays [30]. Alternative pozzolanic materials are required to be used in order to improve the properties of concrete such as durability and reduce the amount of cement used in concrete production. This article explores the use of MK as a partial substitution of cement pastes, mortar or concrete. The physical, mechanical, and durability properties of cementitious systems will be reported based on the literature available. The use of MK as pozzolanic material in conjunction with cement was examined.

Clay is a fine-grained natural material (soil or rock) comprising one or more minerals with small amounts of organic materials and metal oxides. Geologic clay deposits are mostly composed of phyllosilicate minerals, depending on the composition of the original materials. Clay can have different colors, white, gray, brown, orange or red [31]. Clay minerals are formed by weathering of a variety of minerals. It is made through two main processes that may involve physical and chemical modifications or decomposition and recrystallization [31]. Khabit and Wild [32] as well as Frias and Cabrera [7] illustrated that the positive effect of metakaolin as a pozzolanic material, in modifying the pore size distribution, is closely related to the hydrated phases produced during the reaction as C-S-H,  $\text{C}_2\text{ASH}_8$  and  $\text{C}_4\text{AH}_{13}$ . Clays are often aluminosilicate materials which are often formed by the decomposition of igneous rocks such as granite. There are many varieties of clay minerals depending on the nature of their formation. The most important clay mineral is kaolin [33]. The calcination of kaolin can modify the reactivity of the formed metakaolin which is composed mainly of an amorphous mixture of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . The complete reactivity of this mixture can be obtained by the calcination of kaolin at the temperature range of 700-

900°C. Below 700°C, residual kaolin occurs, and above 900°C, the crystallization of metakaolin into  $\text{Al}_2\text{O}_3$  containing  $\text{SiO}_2$  in its spinel occurs. This greatly reduces the reactivity of the aluminosilicate mixture of metakaolin [34, 35]. It is well known that calcium hydroxide is one of the resulting products from the hydration of the silicate phases [ $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$ ] of Portland cement, which reduces its durability when exposed to aggressive media. The pozzolanic properties of metakaolin can avoid this drawback. So, a particular interest has been taken to the pozzolanic phenomenon between metakaolin and calcium hydroxide during the last two decades [36, 37].

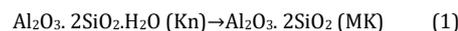
## 1.2. Objectives of The Study

On this basis, the main objective of this article is to study the influence of metakaolin on the hydration of Ordinary Portland cement pastes particularly on mechanical properties. The pozzolanic reaction of metakaolin with  $\text{Ca}(\text{OH})_2$  was investigated by Infrared spectrometry (FT-IR), Differential thermal analysis (DTA) and Scanning electron microscopy (SEM).

## 2. EXPERIMENTAL

### 2.1. Raw Materials

The used raw materials in the current research article are Ordinary Portland cement (OPC Type I- CEM I 42,5R) with the blaine surface area  $3450 \text{ cm}^2/\text{g}$ , and Kaolinitic clay (Kc) as a source of active nanosilica and nanoalumina with a fineness of  $62 \mu\text{m}$ . The OPC sample was supplied from Sakkara cement factory, Giza, Egypt, and its commercial name is known as "Asmant El-Momtaz". The clay sample (Kc) was taken from Toshka region, which is located on the latitude  $20^\circ 30' \text{ N}$  and longitude  $31^\circ 53' \text{ E}$  at 250 km south of Aswan and it was related to the Upper Cretaceous age. About 30 kg of Kc sample was collected from the 85<sup>th</sup> km north of Aswan/Abu-simple asphaltic road, which it is a dark yellowish grey. The Kc sample was first dried and then crushed, ground and quartered to have a representative sample which was fine ground to pass 200 mesh sieves ( $63 \mu\text{m}$ ). Metakaolin [Mkn] was produced by the calcination of clay (Kc) at  $800^\circ \text{C}$  for one hour as follows:



The MK particles are amorphous and crystalline and it is mainly composed of a large percentage of nano- $\text{SiO}_2$  and a lower percentage of nano- $\text{Al}_2\text{O}_3$ . The chemical analysis of the OPC, clay and MK samples is shown in Table 1. The mineralogical composition of the OPC sample was  $\text{C}_3\text{S}$ , 61.88 %,  $\beta\text{-C}_2\text{S}$ , 11.69 %,  $\text{C}_3\text{A}$ , 6.43 % and  $\text{C}_4\text{AF}$ , 12.07 % as supplied by the cement company. The mix composition is given in Table 2.

### 2.2. Preparation and Methods

The OPC sample was replaced by 0, 7, 14, 21, 28 and 35 wt. % MK having the symbols M0, M1, M2, M3, M4 and M5, respectively. The blending process was

mechanically made in a porcelain ball mill (Lab.monomill, Puluerisette 6- FRITSCH, Germany) for one hour using four porcelain balls to assure the complete homogeneity of all batches. The standard water of consistency and setting times of the freshly prepared cement pastes were directly determined by Vicat Apparatus [38,39], where, water of consistency could be determined from the following relation:

$$\text{WC, \%} = A / C \times 100 \quad (2)$$

Where, A is the amount of water taken to produce a suitable paste, C is the amount of cement mix (300 g). Thereafter, the cement pastes were mixed using the predetermined water of consistency, then moulded into one inch cubic stainless steel moulds ( $2.5 \times 2.5 \times 2.5 \text{ cm}^3$ ), vibrated manually for two minutes and on a mechanical vibrator for another two minutes. The moulds were kept inside a humidity cabinet for 24 hours at  $23 \pm 1^\circ \text{C}$  and 100 % relative humidity, demoulded in the following day and soon cured under water till the time of testing for bulk density, total porosity and compressive strength at 1, 3, 7, 28 and 90 days. The bulk density (BD) of each specimen at any hydration age was determined [20,27,40,41] from the following equation:

$$\text{BD, g/cm}^3 = W_1 / W_1 - W_2 \quad (3)$$

Where,  $W_1$  is the saturated surface dry weight in air (g) and  $W_2$  is the submerged weight in water (g). The total porosity ( $\epsilon$ ) [42,43], was calculated from the following equation:

$$\epsilon = (0.99 \times W_e \times \text{BD}) / (1 + W_t) \quad (4)$$

Where, 0.99 is the specific volume of free water,  $W_e$  is the free or evaporable water content, BD is the bulk density,  $\text{g/cm}^3$  and  $W_t$  is the total water content which is equal to the sum of  $W_e$  and  $W_n$  contents, where  $W_n$  is the combined water. The compressive strength [44] was measured using the following equation:

$$\text{CS, MPa} = L (\text{KN}) / S_a (\text{cm}^2) \text{ KN/m}^2 \times 102 (\text{Kg/cm}^2) / 10.2 \quad (5)$$

The loading was applied perpendicular to the direction of the upper surface of the cubes. Three samples were tested for each mix at every hydration age and the mean value was considered. The broken specimens from the determination of compressive strength were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration [44,45]. The kinetics of hydration in terms of chemically bound water and free lime contents were also measured [27,46]. The bound water content (BW<sub>n</sub>) of the hydrated samples predried at  $105^\circ \text{C}$  for 24 hours was determined on the basis of ignition loss at  $900^\circ \text{C}$  for 30 minutes from the following relation:-

$$\text{BW}_n, \% = W_1 - W_2 / W_2 \times 100 \quad (6)$$

Where, BW<sub>n</sub>,  $W_1$  and  $W_2$  are combined water content, weight of sample before and after ignition, respectively. The free lime content (FL<sub>n</sub>) was measured by the modified extraction Franke method [47-49]. About 0.5g

sample + 40 ml ethylene glycol → heating to about 20 minutes without boiling. About 1–2 drops of pH indicator were added to the filtrate and then titrated against freshly prepared 0.1N HCl until the pink colour disappeared. The 0.1 N HCl was prepared using the following equation: Where,  $W_n$ ,  $W_1$  and  $W_2$  are combined water content, weight of sample before and after ignition, respectively. The free lime content of the hydrated samples pre-dried at 105°C for 24h was also determined. About 0.5 g sample + 40 ml ethylene glycol → heating to about 20 minutes without boiling. About 1–2 drops of pH indicator were added to the filtrate and then titrated against freshly prepared 0.1 N HCl until the pink colour disappeared. The 0.1 N HCl was prepared using the following equation:

$$V_1 = N \times V_2 \times W (7) \times 100 / D \times P \times 1000 \quad (7)$$

Where,  $V_1$  is the volume of HCl concentration,  $V_2$  is the volume required,  $N$  is the normality required,  $W$  is the equivalent weight,  $D$  is the density of HCl concentration and  $P$  is the purity (%). The heating and titration were repeated several times until the pink colour did not appear on heating. The free lime content [15,23,31,29] was calculated from the following relation:

$$FLn, \% = (V \times 0.0033/1) \times 100 \quad (8)$$

Where,  $FLn$  and  $V$  are the free lime content and the volume of 0.1 N HCl taken on titration, respectively.

The phase composition was investigated by infrared spectroscopy (IR), X-ray diffraction analysis (XRA) and scanning electron microscopy (SEM) for some selected samples. FT-IR analysis was carried out by Perkin Elmer FT-IR spectrometer in the range of 4000-400  $\text{cm}^{-1}$ , XRD method was employed by a Philips X-Ray Diffractometer of Mod. P.W. 1390 with Ni-filtered  $\text{Cu-K}\alpha$  radiation and SEM images were attained by JEOL-JXA-840 electron microprobe analyzer at accelerating voltage of 30 KV. The fractured surfaces were fixed on Cu-stubs by carbon paste and then mounted to be coated with a thin layer of gold. The SEM analysis was used to observe the crystal morphology of OPC/MK blended cement due to hydration.

### 3. RESULTS

#### 3.1. Water of Consistency and Setting Times

The results of water of consistency and setting times (Initial & final) of the pure OPC (M0) and the various OPC/MK blended cement pastes (M1-M5) are graphically represented in Figure 1. It is clear that the water of consistency of the pure OPC pastes (M0) was found to be 29 %. This ratio tends to increase linearly with the gradual replacing of MK (M1-M5).

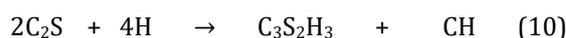
This is mainly attributed to the continual increase of the specific surface area of cement batches due to MK addition. Furthermore, the plasticity of the various cement pastes (M1-M5) increase little by little due to the high surface area of MK that required high quantities of water to form a suitable paste. In addition

to the pozzolanic reactions between MK and CH which required a high amount of mixing water [35,41,50]. These are the main factors responsible for the water demand of the OPC / MK cement pastes.

On the other side, the setting time (initial and final) of the pure OPC (M0) also increases with MK addition. This is essentially due to the gradual increase of mixing water of the various OPC/MK cement pastes (M1-M4). Therefore, both initial and final setting times are elongated [50,51].

#### 3.2. Chemically - Bounded Water Content

The chemically-bounded water contents of the various metakaolin blended cement pastes (M0-M5) are plotted as a function of hydration ages in Figure 2. As a general trend, the bounded water contents of all cement pastes increased with the increase of the hydration ages up to 90 days. This is essentially attributed to the normal hydration process of the main major phases of the cement, i.e.  $\text{C}_3\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  during the first 7 days of hydration, and  $\beta\text{-C}_2\text{S}$  after 28 days. The bounded water contents of M1, M2 and M3 containing 5, 10 and 15 wt. % MK are higher than those of the pure OPC pastes (M0) at all hydration ages. This is mainly contributed to the pozzolanic reactivity of MK towards the resulting  $\text{Ca}(\text{OH})_2$  or free lime from the hydration of calcium silicate phases of the cement ( $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$ ) to form CSH and/or CAH [8,17] as follows:-



Furthermore, the nanograin size particles or the high fineness of MK increased the water demand of the cement to make suitable pastes, which in turn increased the rate of pozzolanicity of MK to form additional hydration products. This was so reflected positively on the rate of hydration that it could enhance the quantity of hydration products, and hence the bound water contents increased [52,53]. In addition, the nanograin size particles of MK caused a segmentation of larger pores and increased the number of nucleating sites for the precipitation of hydration products of the cementitious paste. This will accelerate the reactions and form smaller  $\text{Ca}(\text{OH})_2$  crystals [53]. On contrast, the bounded water contents of M4 and M5 containing 20 and 25 wt. % MK are slightly lower than those of M0 at all hydration stages, i.e. with high content of MK, a part of MK only could be consumed by the evolved lime to form CSH and/or CAH, and the excess of MK nanoparticles could not be consumed due to the dilution effect of MK. So, the chemical reactions of the MK will enhance the physical effects due to the higher segmentation of pores and the refinement of  $\text{Ca}(\text{OH})_2$  grains as the hydration age proceeds [18,19,53]. On this basis, it could be concluded that the higher addition of MK more than 15 wt. % must be avoided.

### 3.3. Free Lime Content

The free lime contents of the OPC (M0) and the various MK blended cement pastes (M1-M5) are plotted as a function of hydration ages in Figure 3. The free lime content of the OPC pastes [M0] gradually increased with hydration ages up to 90 days due to the continuous hydration of calcium silicate phases of the cement with water to form CSH (C<sub>3</sub>S in early ages and β-C<sub>2</sub>S in later ages). This is usually followed by the release of Ca (OH)<sub>2</sub> as shown in equations 9 and 10 [8]. The increase of free Ca (OH)<sub>2</sub> contents of cement blends M1 and M2 up to 7 days is mainly contributed to the normal hydration process of silicate phases of the cement, whereas its decrease up to 28 days is essentially attributed to the consumption of the released Ca (OH)<sub>2</sub> due to the pozzolanic reaction of MK with it to form CSH-gel [11] as follows:



The reincreased of Ca (OH)<sub>2</sub> is principally due the full consumption of MK added, i.e. there is no further MK to react with the excess Ca(OH)<sub>2</sub>. The free Ca (OH)<sub>2</sub> content of M3, M4 and M5 incorporated 15, 20 and 25 wt. % MK, respectively, decreased bit by bit up to 90 days, i.e. there are enough MK to react with further Ca (OH)<sub>2</sub>. MK can easily react and combine with a significantly large amount of free Ca (OH)<sub>2</sub> due to the presence of active amorphous silica and alumina [17,20]. So, it can be concluded that the amount of combined Ca (OH)<sub>2</sub> increased with both MK content and W/C- ratio.

### 3.4. Bulk Density And Total Porosity

The bulk density and apparent porosity of the OPC (M0) and the various MK blended cement pastes (M1-M5) are graphically represented as a function of hydration ages in Figures 4 and 5, respectively. As the hydration age progressed, the bulk density slightly increased up to 90 days, whereas the total porosity decreased. This is mainly contributed to the gradual and continual formation of hydration products from the hydration of cement phases, and the pozzolanic reactions of MK with the released Ca(OH)<sub>2</sub> from the first process, which in turn deposited into the pore structure of the hardened cement pastes. The total porosity accordingly decreases and the bulk density improved and enhanced [9,21]. The bulk density of M1, M2 and M3 with 5, 10 and 15 wt. % MK are higher than that of the control mix (M0), while their total porosities are lower at all hydration stages. This is due to the additional hydration products from the pozzolanic reactions of MK with the released Ca(OH)<sub>2</sub>, in addition to the filling effect of the unreacted MK nanoparticles [21,22]. Furthermore, the fine particles of MK cause a high segmentation of large pores and increase the number of nucleating sites for the precipitation of hydration products. This will accelerate the hydration reaction and form smaller Ca(OH)<sub>2</sub> crystals because of the refinement of the Ca(OH)<sub>2</sub> grains with hydration

ages [22,23,57]. At early ages of hydration up to 3 days, the bulk density of M<sub>3</sub> with 15 mass% Mkn is lower and the apparent porosity is higher than those of the OPC pastes (M<sub>0</sub>). While at later ages of hydration, the bulk density becomes higher and the apparent porosity becomes lower up to 90 days. This is due to the increase of mixing water and the decrease of cement content. In M4 and M5 containing 20 and 25 wt. % MK, the bulk density values are lower and those of the total porosity are higher than those of the OPC pastes (M0) at all hydration periods up to 90 days. The decrease of bulk density and the increase of the total porosity are mainly due to the decrease of the main cementing material responsible for the hydration process, and also the high content of mixing water. So, as the mixing water increases the total porosity increases and the bulk density accordingly decreases [20,21,53].

### 3.5. Compressive Strength

The compressive strength of the OPC (M0) and various MK blended cement pastes (M1-M5) is graphically represented as a function of hydration time in Figure 6. The compressive strength values of the hardened cement pastes sharply increased during the early ages of hydration up to 7 days, and then slightly increased onward. This is essentially attributed to the continual formation of hydration products which soon deposited into the pore volume of the hardened cement pastes. This in turn decreased the total porosity and increased the bulk density. As a result, the compressive strength improved and enhanced [9,23]. The slight increase of compressive strength from 28 up to 90 days is due to the slow rate of hydration of cement phases at later ages and the fast pozzolanic reactions of MK at early ages due to the full consumption of MK nanoparticles by the formed lime. So, the rate of hydration process and also the pozzolanic activity of MK decreased largely. This evidently reflected on the compressive strength values [51-53].

The pozzolanic cement pastes of M1, M2 and M3 incorporating 5, 10 and 15 wt. % MK exhibited higher compressive strength values when compared to those of the blank (M0) at all hydration times. This is due to the high level of pozzolanic reactivity of MK. This increases the amount of combined Ca (OH)<sub>2</sub> and also the cementing materials as CSH and/or CASH. This reflected positively on the compressive strength. Furthermore, the addition of MK causes a high segmentation of large pores and increases the number of nucleating sites for the precipitation of the hydration products. This accelerates the reactions and forms smaller Ca (OH)<sub>2</sub> crystals [19,21].

The compressive strength of the hardened cement pastes of M4 and M5 containing 20 and 25 wt. % MK is slightly lower than those of the blank (M0) at all hydration times. This may be due to the large deficiency of the main cementing material of cement and the higher amounts of MK reacted so rapidly with

the evolved  $\text{Ca}(\text{OH})_2$  that the excess MK behaves as an inert material [20,27]. Moreover, the high content of MK increases the W/C ratio, which in turn creates a more porous structure. So, the bulk density and the compressive strength diminished [28,29]. Accordingly, i.e. the increase of w/c ratio and reduced cement content are two factors affecting the compressive strength. Moreover, the high amounts of MK at the expense of the OPC decrease the main binding properties of the whole mix. So, the hardening properties are reduced and accordingly the compressive strength is adversely affected [9]. Although the high MK content could consume a high amount of the evolved  $\text{Ca}(\text{OH})_2$  from hydration process, the residual MK particles which are not completely reacted only act in this case as a filler or an inert material, i.e. there is not enough  $\text{Ca}(\text{OH})_2$  to react with [25,29,54]. Accordingly, these are the main factors affecting the compressive strength. Consequently, the addition of higher amounts of MK more than 15 wt. % is undesirable.

### 3.6. IR Spectroscopy

Figure 7 shows the FT-IR spectra of control cement pastes (M0) hydrated for 1, 3, 7, 28 and 90 days to show the rate of hydration, while Figure 8 indicates the FT-IR spectra of M0, M3 and M5 cement pastes hydrated up to 90 days to show the pozzolanic reactions of MK with the released free lime. It is good mention that the sharp absorption band at wave number  $3644\text{ cm}^{-1}$  is related to the free  $\text{OH}^{-1}$  group coordinated to  $\text{Ca}^{2+}$ , i.e. free lime,  $\text{Ca}(\text{OH})_2$ . The intensity of the  $3644\text{ cm}^{-1}$  absorption band of the blank (M0) characterizing the free  $\text{Ca}(\text{OH})_2$  increased with hydration ages up to days 90 days due to the continual and rapid hydration of  $\text{C}_3\text{S}$  at early ages and  $\beta\text{-C}_2\text{S}$  at later ages (Fig.7). In contrast, the intensity of the same absorption band of M3 and M5 slightly decreased due to the pozzolanic reactions of MK with a part of the evolved  $\text{Ca}(\text{OH})_2$  to form CSH and /or CAH (Fig.8). Moreover, the intensity of  $\text{Ca}(\text{OH})_2$  absorption band highly decreased with the increase of MK content (Fig. 8). The intensity of the broad absorption band at wave number  $3800\text{-}2900\text{ cm}^{-1}$  which is due to the  $\text{OH}^{-1}$  group associated to  $\text{H}^+$  bond, i.e. related to the symmetrical stretching frequency of water, increased with hydration time due to the consumption of large amount of water molecules to form the hydration products. The two absorption bands at  $1660\text{-}1500$  and  $1480\text{-}1240\text{ cm}^{-1}$  are related to the main silicate band involve Si-O stretching vibration bands of CSH. The band at  $874\text{-}876\text{ cm}^{-1}$  may be due to CAH. The intensity of the three absorption bands at  $1210\text{-}760\text{ cm}^{-1}$  characterizing  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  is irregular due to the rate of carbonation and sulphonation of CSH and /or CAH, respectively, whereas the vibrations of  $\text{CO}_3^{2-}$  are smaller than those of  $\text{SO}_4^{2-}$  [55,56].

### 3.7. SEM Microscopy

The SEM microscopy of the hydrated interfacial layers of M0 and M3 cement pastes hydrated 1, 28 and 90 days are shown in Figure 9. The main phase of hydration of the OPC pastes (M0) after one day is the needle-like crystals of ettringite which are clearly observed besides  $\text{CaCO}_3$  globules. The crystals of M0 after 28 days are very dense and exhibited a very low crystallinity, where the main hydration products are clusters or formless CSH and/or CAH, large amounts of crystalline  $\text{Ca}(\text{OH})_2$  which occurs as relatively crystalline aggregates and monosulphate hydrate. The crystals of MK blended cement pastes of M3 demonstrated that a large quantity of well crystallized hydration products are developed due to the normal hydration and pozzolanic phenomenon of MK with the released free  $\text{Ca}(\text{OH})_2$  from the hydration process. These products are the same as those occurring in the OPC pastes but with well developed crystals.

### 3.8. XRD Analysis

Figure 10 indicates the XRD patterns of the pure cement pastes (M0) and MK blended cement pastes of M2 and M3 incorporated 10 and 15 wt. % MK, respectively. As it is clear, the free lime content of M0 at two theta degree 18 is the highest, while of M3 is the lowest, i.e. the free lime content decreased due to the presence of MK pozzolanic material which reacted with it to form hydration products (CSH and/or CAH). This is clearly seen with M3 at two theta degrees of 26.5, 29.5, 32.5 and 34.2, where the intensity of peaks of hydration product increased.

## 4. CONCLUSIONS

Use of pozzolanic materials in cementitious systems improve and enhance strength development and durability of the resulting product. Calcined clay or MK is viable alternatives for other serious pozzolanic materials. MK is an excellent pozzolana because it reduces the level of  $\text{CO}_2$  emitted into the atmosphere and it can also improve the performance of cementitious composites. In OPC/MK blended cement pastes, each of these materials operates in a different but cooperative way according to their particle size, physical and chemical activities. The addition of MK at the expense of OPC by 21 wt. % increased their water of consistency, setting time either initial or final, bounded water content, bulk density and compressive strength, but decreased the free  $\text{Ca}(\text{OH})_2$  content and total porosity due to the pozzolanic and filler effects of MK and therefore, it is considered as the optimum level addition to the mix. With any further addition of MK, the hydration rate of the OPC decreased due to the dilution effect of the main binding material and MK. So, the MK particles only act as a filler and seem to be as a pore-reducing or filling material, in addition to the pozzolanic action with the released  $\text{Ca}(\text{OH})_2$ . The IR

and XRD analyses illustrated that the intensity of free Ca (OH)<sub>2</sub> peaks decreased with the hydration age and MK content. The SEM images demonstrated that the formed hydration products of the OPC/MK blended cements are the same as those formed in pure OPC pastes, but with different rates, modified or developed crystals and morphologies.

## 5. DECLARATIONS

### 5.1. Availability of Data and Materials

The data used or analyzed during the present study are available from the corresponding author on reasonable request.

### 5.2. Competing Interests

I confirm that I have read Springer Open's guidance on competing interests, and there are no competing interests in the manuscript.

### 5.3. Author's Contribution

The author did all the analysis and testes mentioned in the current study.

## REFERENCES

- [1] M. Rubenstein, Earth Institute, Emission from the cement industry, earth Institute, Columbia University, 2012. <http://blogs.ei.columbia.edu/2012/05/09/emissions-from-the-cement-industry/>
- [2] H. El-Didamony, I. M. Helmy, A. A. Amer and M. Heikal, M., Utilization of some Egyptian byproducts in the preparation of blended cements, Zement-Kalk-Gips, 9 (1995) 502-507.
- [3] M. Kuroda, T. Watanabe and N. Terashi, N, Increase of bond strength at interfacial transition zone by the use of fly ash, Cem.Concr.Res., 30, 2000, 253-258.
- [4] Y. Shao, T. Lefort, S. Moras and D. Rodriguez, Studies on concrete containing ground waste glass. Cem. Conc. Res., 30, 1, 2000, 91-100.
- [5] I. B. Topcu and M. Canbaz, Properties of Concrete containing waste glass, Cem.Concr.Res., 34, 2004, 267-274.
- [6] C. Shi, Y. Wu, C. Riefler and H. Wang, H, Characteristics and pozzolanic reactivity of glass powders, Cem. Concr. Res.; 35, 5, 2005, 987-93.
- [7] A. Shayan and A. Xu, Performance of GP as a pozzolana material in concrete: A field trial on concrete slabs, Cem. Concr. Res., 36, 2006, 547-468.
- [8] Shayan A, Xu A. (2006), "Performance of glass powder as a pozzolanic material in concrete: a field trial on concrete slabs". Cem. Concr. Res., 36, 3, 457-68.
- [9] C. H. Chen, R. Huang. J. K. Wu, C. C. Yang, Waste E-glass Particles used in cementitious mixtures, Cem Concr Res, 36, 2006, 449-56
- [10] B. Taha and G. Nounu, Properties of concrete contains mixed colour waste recycled glass as sand and cement Replacement, Constr. Build. Mater., 22, 5, 2008, 713-20.
- [11] O. Ozkand and I. Yuksel, Studies on mortars containing waste bottle glass and industrial by-products, Constr. Build. Mater., 22, 2008, 1288-1298.
- [12] B. Taha and G. Nounu, Utilizing waste Recycled Glass as sand/ Cement replacement in concrete, Journ. of materials in civil Engineering, 2009, 709-721.
- [13] I. Kourti and C. R. Cheeseman, Properties and microstructure of lightweight aggregate produced from lignite coal fly ash and recycled glass, Resour. Conserv. Recycl., 54, 2010, 769-775.
- [14] L. M. Mageswari and B. Vidivelli, The use of sheet glass powder as fine aggregate replacement in concrete", Civil Engin. Jour., 4, 2010, 65-71.
- [15] D. Patel, R. K. Yadav and R. Chandak R., Strength characteristics of pre cast concrete blocks incorporating waste glass powder,"ISCA J. Engineering Sci.,Vol.1(1), 2012, 68-70.
- [16] N. Tamanna, M. Sutan, I. Yakub, D. T. C. Lee, Strength Characteristics of Mortar Containing Different Sizes Glass Powder, 5, 1, 2014 . DOI: <https://doi.org/10.33736/jcest.127.2014>
- [17] M. V. Hussain and R. Chandak, Use of waste glass powder as partial replacement of cement in concrete, Intern. Jour. Emerg. Trends in Engin. & Develop., Issue 5, Vol. 2, 2015. [http://www.rpublication.com/ijeted/ijeted\\_index](http://www.rpublication.com/ijeted/ijeted_index)
- [18] H. H. M. Darweesh, A. H. Abdel and M. G. El-Meligy, Utilization of pulp black liquor waste as a cement admixture", Intern. Journ. Basic and Applied Sciences, 2, 3, 2013, 230-238.
- [19] H. H. M. Darweesh and M. G. El-Meligy, Utilization of Pulp White Liquor waste as a cement admixture", Amer. J. Mining and Metallurgy, Vol. 2, No. 4, 2014, 88-93.
- [20] H. H. M. Darweesh, Effect of the combination of some pozzolanic wastes on the properties of Portland cement pastes. iiCL'industria italiana del Cemento, 808, 2005, 298-311.
- [21] H. El-Didamony, H. H. M. Darweesh and R. M. Mostafa, Characteristics of pozzolanic cement pastes Part I: Physico-mechanical properties" Sil. Ind. (Cer. Sci. & Techn.), 73 (11-12), 2008, 193-200.
- [22] I. Kourti, and C> R. Cheeseman, Properties and microstructure of lightweight aggregate produced from lignite coal fly ash and recycled glass, Resour. Conserv. Recycl., 54, 2010, 769-775.
- [23] J. M. Khatib, Performance of self-compacting concrete containing fly ash, Construction and

- Building Materials 2 Journal, 22, 9: 2008, 1963-1971. DOI: 10.1016/j.conbuildmat.2007.07.011.
- [24] H. H. M. Darweesh, Geopolymer cements from slag, fly ash and silica fume activated with sodium hydroxide and water glass", *Interceram International*, 6, 1, 2017, 226-231.
- [25] H. H. M. Darweesh, Mortar composites based on industrial wastes, *International Journal of Materials and Lifetime*, Vol. 3 (1), 2017, 1-8. DOI: 10.12691/ijml-3-1-1.
- [26] A. Machowsk , Z. Kedynskil, I. Wilinska and B. Pacewska,, A study of the early hydration processes and properties of fly ash-slag binders, *Bull. Mater. Sci.*, 42: 2019, 213. <https://doi.org/10.1007/s12034-019-1886-1>.
- [27] H. H. M. Darweesh, Utilization of Perlite Rock in Blended Cement-Part I: Physicomechanical properties, *Direct Res. Journ. Chem. Mate. Sci.*, 2014, 2354-4163.
- [28] J. M. Khatib and J. J. Hibbert, Selected engineering properties of concrete incorporating slag and metakaolin, *Construction and Building Materials Journal*, 19 (6): 2005, 460-472. DOI: 10.1016/j.conbuildmat.2004.07.017.
- [29] J. M. Khatib, Metakaolin concrete at a low water to binder ratio, *Construction and Building Materials Journal*, 22(8): 2008, 1691-1700. DOI: 10.1016/j.conbuildmat.2007.06.003.
- [30] R. Siddique and J. Klaus, Influence of MK on the properties of mortar and concrete: A review, *Applied Clay Science* 43, 2009, 392-400.
- [31] G. Sposito, *The chemistry of soil*, 3rd Edition, OxfordUniversity Press, New York. 255, 2016.
- [32] J. M. Khatib and S. Wild, Pore size distribution of MK paste, *Cem. Concr. Res.* 26, 10, 1996, 1545-1553.
- [33] M. Mura and C. Comel, Hydration reaction and hardening of calcined clays and related minerals. III-Influence of calcinations process of kaolinite on mechanical strengths of hardened metakaolinite, *Cem. Concr.Res.*,13, 5, 1983, 631-637.
- [34] J. Ambroise, S. Martin-Calle and J. Pera, Pozzolanic behavior of thermally- activated Kaolin, *Proc. 4th Intern. Congr. Fly ash, silica fume, slag and natural pozzolans in concrete*, Amer. Concr. Inst., Istanbul, 1, 132, 1992, 731-748.
- [35] S. Johansson and P. J. Andrsen, Pozzolanic activity of calcined molar clay, *Cem. Concr. Res.* 20, 1990, 447-452.
- [36] J. G. Cabrera and S. O. Nwaubari, Strength and Chloride permeability of concrete containing red tropical soils, *Mag. Concr. Res.*, 145, 164, 1993, 169-178.
- [37] J. Ambroise, S. Maximilien and J. Pera, Properties of metakaolin blended cement, *Adv. Cem. Based Mater.*, 1, 1994, 161-168.
- [38] B. B. Sabir, S. Wild and J. Bai, Metakaolin and calcined clays as pozzolana for concrete, a review, *Cem. Concr. Compos.* 23, 2001, 441-454.
- [39] ASTM-Standards, Standard Test Method for Normal water of Consistency of Hydraulic Cement, C187-86: 1993, 148-150. Reapproved in ASTM Annual Book of ASTM Standards, 2008.
- [40] ASTM -Standards, Standard Test Method for Setting Time of Hydraulic Cement. C191-92: 1993, 866-868. Reapproved in ASTM Annual Book of ASTM Standards, 2008.
- [41] P. C. Hewlett, *Lea's chemistry of cement and concrete*, 5<sup>th</sup> edn, Oxford: Elsevier Science & Technology Books, 2004. ISBN : 0470 24416 X (Wiley).
- [42] H. H. M. Darweesh and A. Nagieb, Hydration and micro-structure of Portland/Calcined Bentonite Blended Cement Pastes, *Indian Journal of Chemical Technology*, 14, 2007, 301-307.
- [43] H. El-Didamony, M. Y. Haggag and S. A. Abo-El-Enein, Studies on Expansive cement : II. Hydration kinetics, surface properties and microstructure, *Cem. Concr. Res.*, 8, 1978, 351-358.
- [44] R. Kondo, S. A. Abo-El-Enein and M. Diamon, Kinetics and mechanism of hydrothermal reaction of granulated blast furnace slag, *Bull. Chem. Soc. Japan*, 48, 1975, 222-226.
- [45] ASTM-Standards, C 170-90, Standard test method for compressive strength of dimension stone, 1993, 828-830.
- [46] H. H. M. Darweesh and, M. R. Abo El-Suoud, Saw Dust Ash Substitution for Cement Pastes-Part I, *American Journal of Construction and Building Materials*, 2, 1, 2017, 1-9. doi: 10.11648/j.ajcbm.20170201.11
- [47] B. Franke, Determination of calcium oxide and calcium hydroxide in water free and water containing calcium silicates, *Zeitschrift fur Anorganischen allgemeine Chemie*, 247, 1941, 180-184.
- [48] E. E. Pressler, S. Brunauer and D. L. Kantro, Investigation of the Franke method of determining free calcium hydroxide and free calcium oxide, *Analytical Chemistry*, 28, 1956,1957, 896-902.
- [49] M. P. Javellana and I. Jawed, Extraction of the free lime in Portland cement and clinker by Ethylene glycol, *Cem. Concr. Res.* 12, 3, 1982, 399-403.
- [50] M. Frias and J. G. Cabrera, Pore size distribution and degree of hydration of MK- cement pastes, *Cem. Concr. Res.*, 30, 2000, 561-569.
- [51] N.B. Singh and B. Middendorf, Chemistry of blended cements part-II: silica fume, metakaolin, reactive ashes from agricultural wastes, inert materials and non-Portland blended cements, *Cem. Inter.* 6, 2009, 78-93.

- [52] K. Mukesh, S. K. Singh, N. P. Singh and N. B. Singh, Hydration of multicomponent composite cement: OPC-FA-SF-MK, *Constr. Build. Mater.* 36, 2012, 681-686.
- [53] L. Senff, J. A. Labrincha, V. M. Ferreira, D. Hotza and W.L. Repette, Effect of nano-silica on rheology and fresh properties of cement pastes and mortars, *Constr. Build. Mater.* 23, 2009, 2487-2491.
- [54] R. L. Day and C. Shi, Influence of the fineness of pozzolan on the strength of lime / natural pozzolan cement paste, *Cem. Concr. Res.* 24, 1994, 1485-1491.
- [55] J. Bensted, Applications of Infrared Spectroscopy to cement hydration. Construction materials group and institute of materials meeting on techniques for characterization of cement hydration, London; Society of Chemical Industry, 1994.
- [56] A. H. Delgado, R. M. Paroli and J. J. Beaudoin, Comparison of IR techniques for the characterization of construction cement minerals and hydrated products, *Appl. Spectrosc.* 50, 8, 1996, 970-976.

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Tables and Figures:

TABLES

Table 1- Chemical composition of the raw materials, mass%

Material Oxide	OPC	Kaolin (Kn)	Metakaolin (MK)
L.O.I	0.85	11.05	0.11
SiO <sub>2</sub>	20.33	44.89	53.82
Al <sub>2</sub> O <sub>3</sub>	4.96	37.73	42.39
Fe <sub>2</sub> O <sub>3</sub>	3.97	0.85	0.95
CaO	62.75	0.26	0.29
MgO	2.23	0.12	0.13
TiO <sub>2</sub>	-----	1.90	2.13
SO <sub>3</sub>	2.40	-----	-----
Na <sub>2</sub> O	0.35	0.09	0.11
K <sub>2</sub> O	0.21	0.06	0.07
Blaine	3300 cm <sup>2</sup> /g	73 μ	73 μ

Table 2-Composition of the defferent OPC/MK blended cement batches, wt. %

Cement batches	OPC	MK
M0	100	-----
M1	93	7
M2	86	14
M3	79	21
M4	72	28

FIGURES

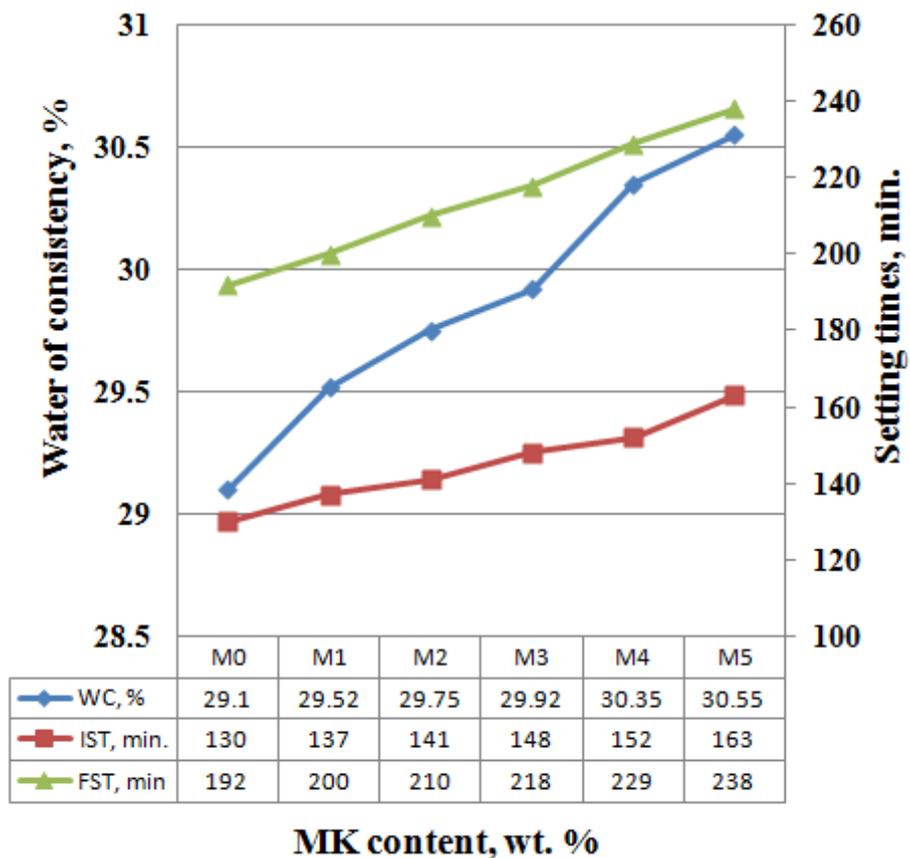


Figure 1-Water of consistency and setting times of metakaolin blended cement pastes.

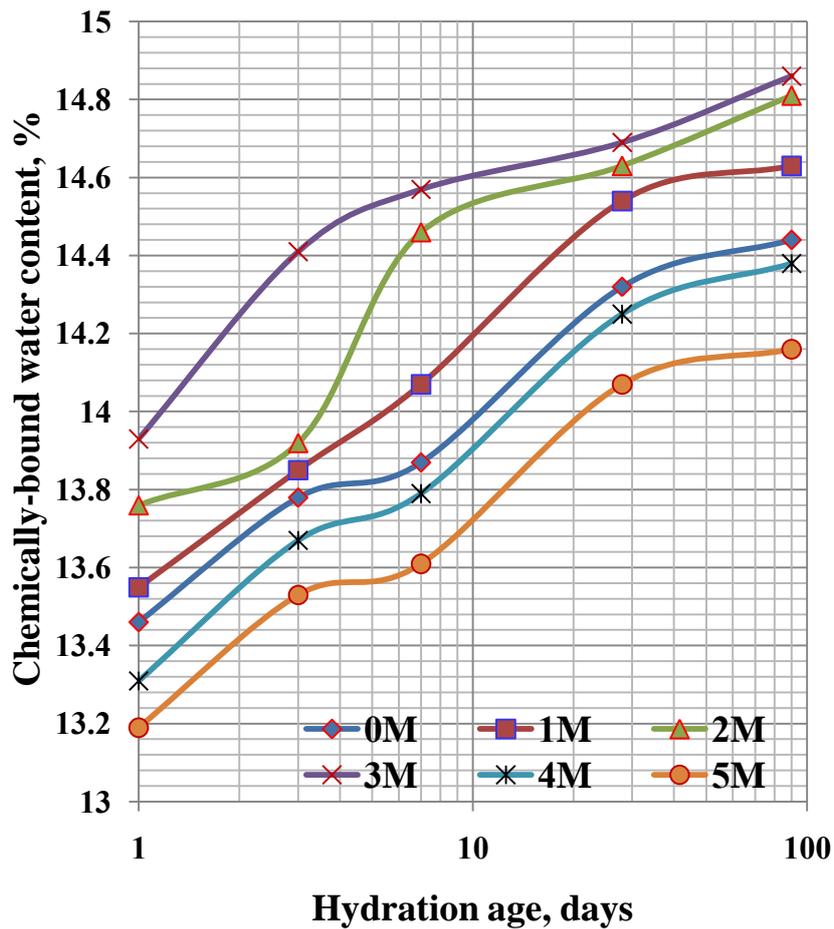


Figure 2-Chemically-bound water content of metakaolin blended cement pastes hydrated up to 90 days.

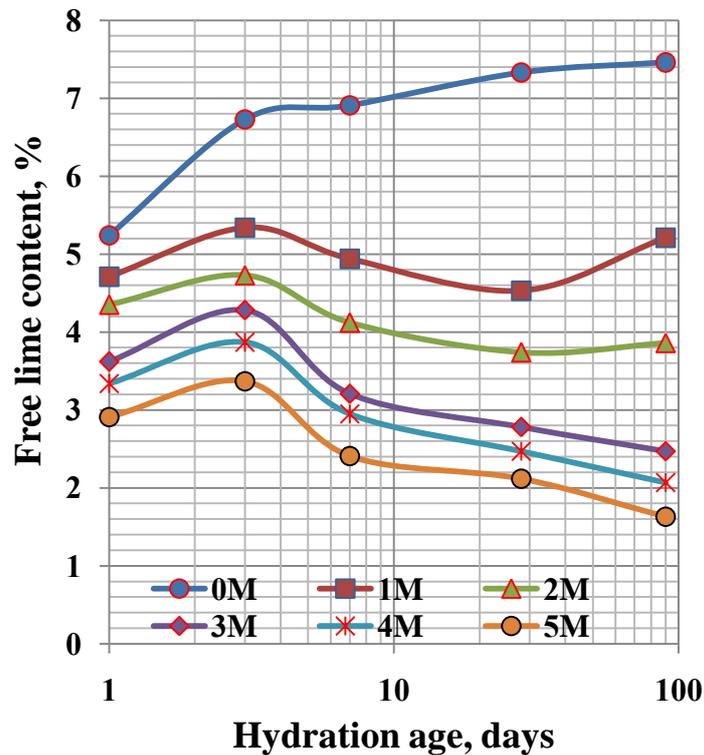


Figure 3-Free lime content of metakaolin blended cement pastes hydrated up to 90 days.

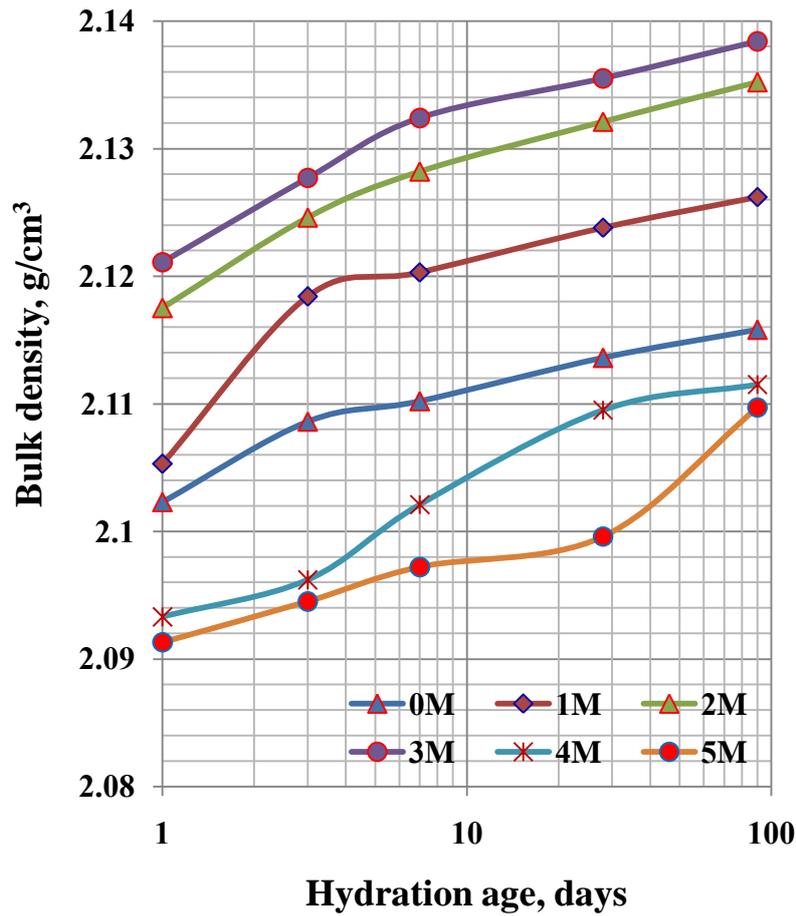


Figure 4-Bulk density of metakaolin blended cement pastes hydrated up to 90 days.

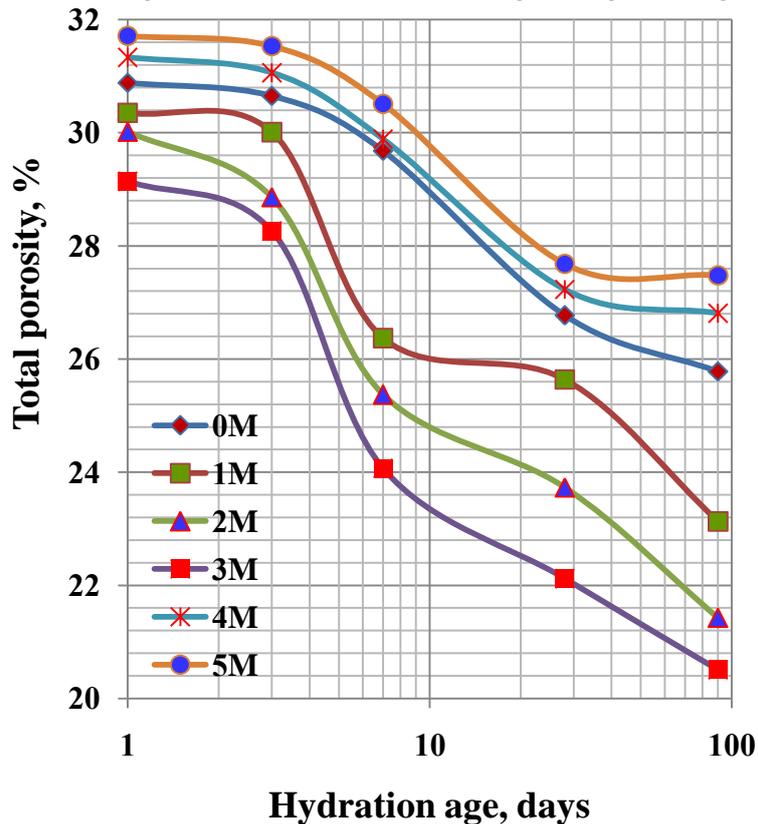


Figure 5-Total porosity of metakaolin blended cement pastes hydrated up to 90 days.

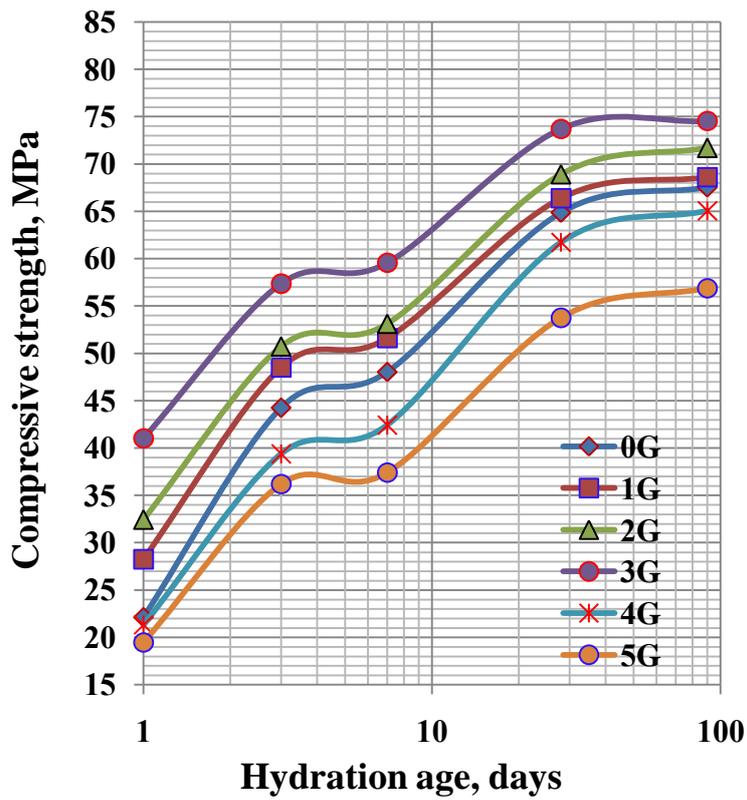


Figure 6-Compressive strength of metakaolin blended cement pastes hydrated up to 90 days.

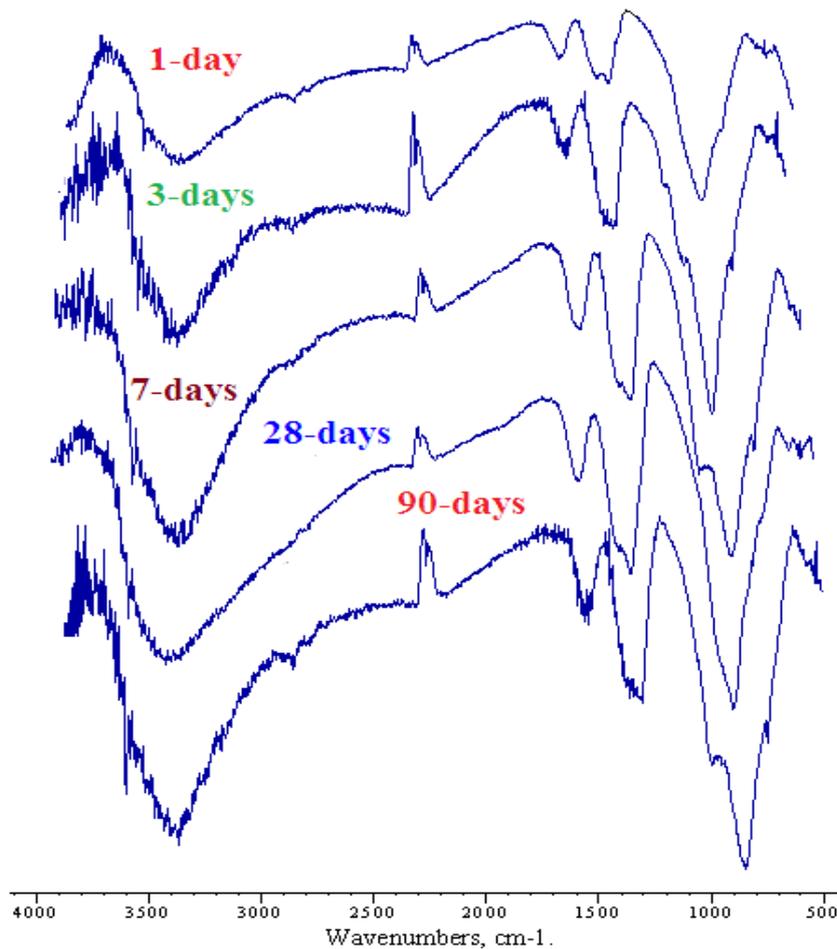
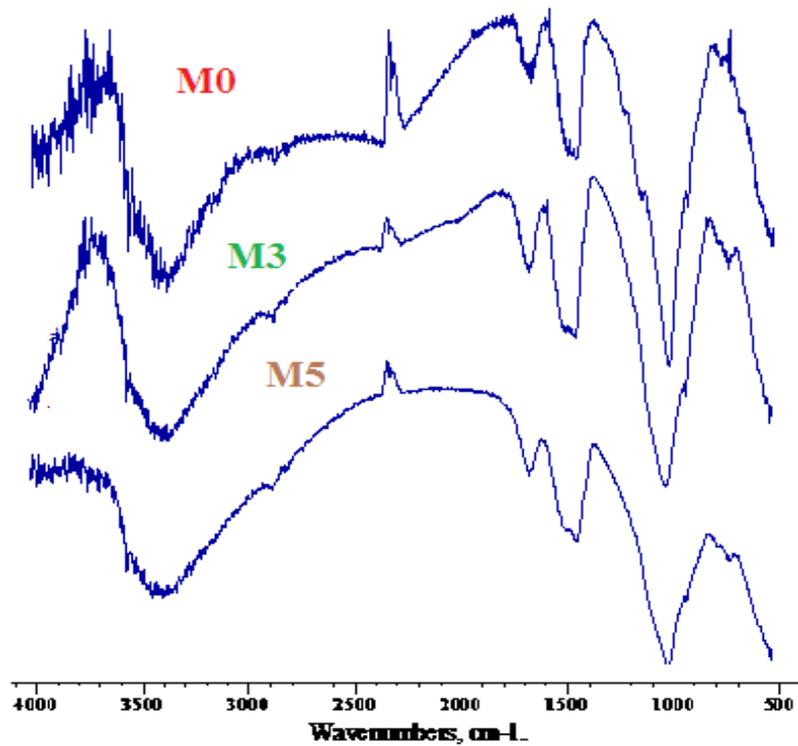
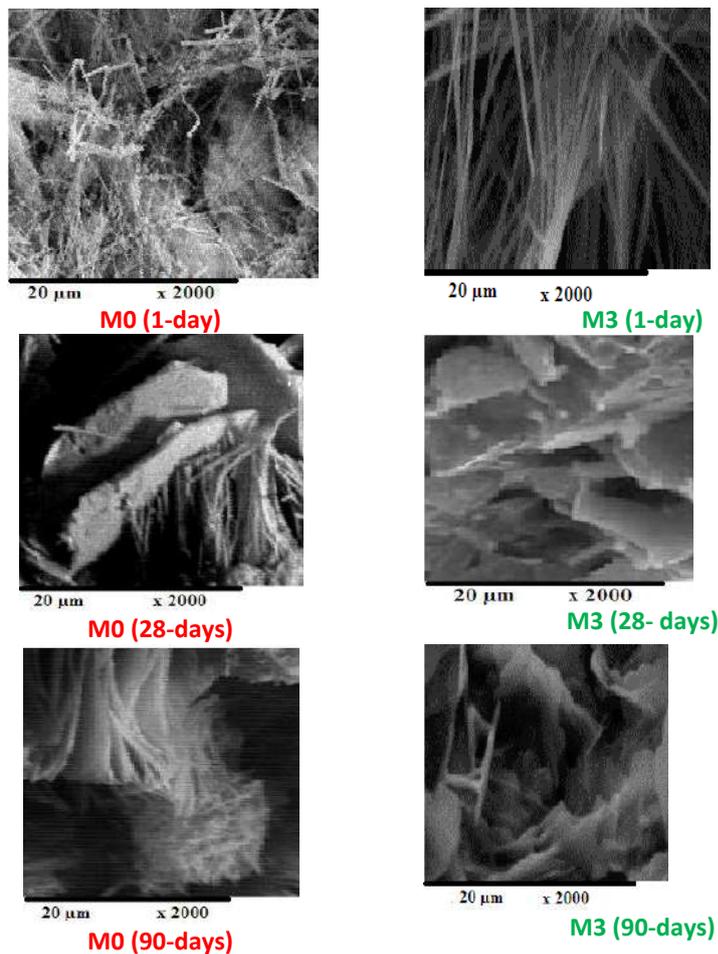


Figure 7- FTIR spectra of M0 cement pastes hydrated up to 90 days showing the hydration of the OPC pastes.



**Figure 8-** FTIR spectra of M0, M3 and M5 cement pastes hydrated up to 90 days showing the pozzolanic reactions of MK with  $\text{Ca}(\text{OH})_2$ .



**Figure 9-** SEM microscopy of M0 and M3 hydrated at 1, 28 and 90 days.

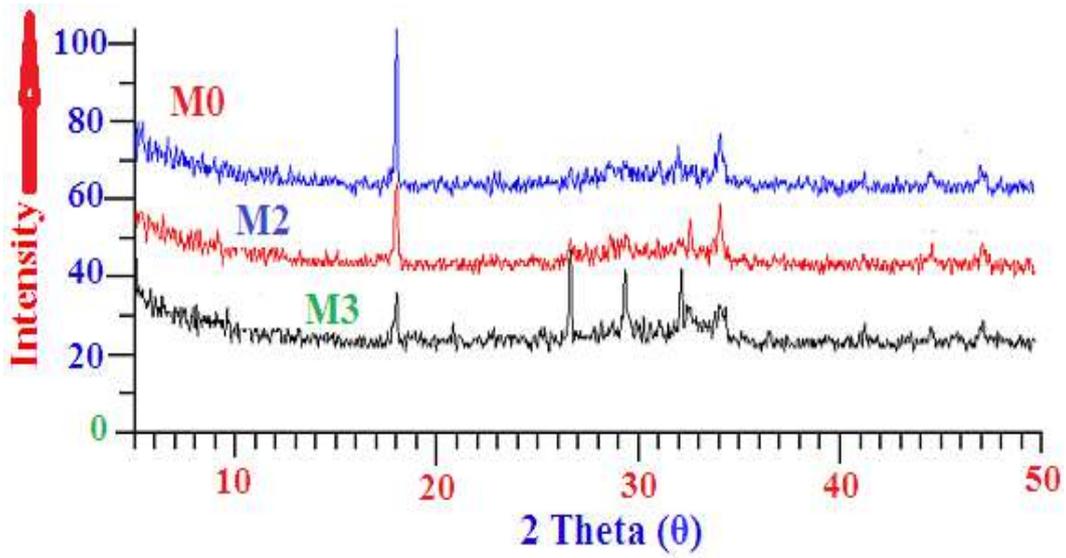


Figure 10- XRD patterns of M0, M2 and M3 hydrated at 28 days.