

## Hydration Behaviour and Characteristics of Binary Blended Metakaolin Cement Pastes

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Received: 14-12-2021

Accepted: 08-03-2022

**Abstract.** Cement production consumes large amount of energy to form clinker and carbon dioxide (CO<sub>2</sub>) emitted into the atmosphere causing global warming. To mitigate this challenge, the use of Metakaolin (MK) as supplementary cementitious material cannot be over emphasized. This study evaluated the use of Metakaolin (MK) on hydration development of MK-PC blended cements and strength of Mortars. The MK with a Blaine fineness of 7883 cm<sup>2</sup>/g was used to replace Portland Cement (PC) at a level of 0, 5, 10, 15, 20, 25 and 30 % by mass of PC at a constant w/b ratio of 0.50 to prepare blended cements. Hydration development of blended cement and compressive strength of Mortars were investigated using chemically bond water and free-lime contents and strength tests respectively. X – Ray diffraction (XRD) and scanning electron Microscopy (SEM) techniques were also utilised in the analysis of Pozzolanic reaction and hydration products. Test results indicates that Water of consistency, setting times for the mixes increased with increase in MK contents, influence of MK on the chemically bond water and free Lime contents of the blended cements were due to its filler and dilution effects and Pozzolanic reaction. The cumulative non-evaporable water and free-lime contents increased by partial replacement of PC with MK due to PC hydration and Pozzolanic reaction. The tested Mortar prepared with blended cements with 30 % PC replacement with MK shows a retardation of strength development with a low value at early ages (7 days) and increased in growth at later ages (28 days). The compressive strength of tested mortar for 90 days curing age for the blended mortar is 31 N/mm<sup>2</sup> close to that of control Mortar (35 N/mm<sup>2</sup>). The results obtained from XRD and SEM analysis indicated increase in Calcium Hydroxide (CH) consumption and Calcium Silicate hydrate (C-S-H) formation in blended cement pastes with curing time. The PC replacement with MK induced changes in Microstructures of blended cement paste and chemical composition of hydration products. These results are potentials for modelling the behaviour of MK-PC blended cements.

**Key words:** Metakaolin, compressive strength, Non-evaporable water, Hydration behaviour and Free lime content.

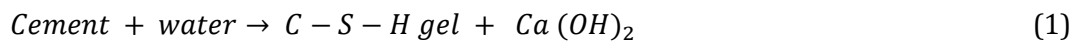
### 1. Introduction

Cement production consumes large amount of energy to form clinker and carbon dioxide (CO<sub>2</sub>) emitted into the atmosphere causing global warming. From the Cement industry alone, its contribution to global emission of green House gases especially CO<sub>2</sub> is 8 – 10 % (Mehta, 2002; Suhendro, 2014). It has been roughly estimated that one Ton of Portland Cement (PC) produced released one ton of CO<sub>2</sub> into the air. It is more worrisome being the third most energy-intensive industry (Shafiq *et al*, 2012) and this has raised serious environmental challenge in the built environment. To mitigate this, steps have been taken and the most effective is the reduction of clinker production by using supplementary cementitious materials (SCMs) during production or directly by replacement of cement at the building site. However, to make any meaningful impact in the reduction of CO<sub>2</sub> emission associated with cement production, maximum proportion of the admixture(s) should be used in cement, so as to lower the clinker content of the final product and the use of blended cements in general construction should be increased. The work of

(Ecosmart, 2008) has shown that globally, if just 30 % of cement used was replaced with SCMs, this will considerably reverse the rise of CO<sub>2</sub> emissions from cement production.

The works of (Li and Ding, 2003; Antoni et al., 2012; Moser *et al.*, 2010) have shown that SCMs such as Blast-furnace Slag (BFS), Fly-ash, (FA), Silica fume (SF), ground Limestone (GLS) and Metakaolin (MK) have been used in Binary blends of Portland cement (PC) used in civil and engineering constructions, thereby achieving energy cost savings, environmental protection and attaining special technical requirements such as durability. As a counter measure to reduce the amount of CO<sub>2</sub> generation and emission into the air, cement blended with MK is also required.

MK (Al<sub>2</sub>SiO<sub>2</sub>O<sub>2</sub>), is a highly amorphous dehydration product of Kaolinite, Al<sub>2</sub>(OH)<sub>4</sub>SiO<sub>2</sub>. Kaolinite is the mineralogical term that is applicable to kaolin Clays. Kaolin is a fine, white clay mineral that has been traditionally used in the manufacture of porcelains. When thermally activated between 600 to 850°C, a substantial loss of water occurs in its constituents which leads to a new arrangement of its crystal lattice structure giving birth to a phase transition called Metakaolin, Metakaolin has a highly disordered and amorphous character with high pozzolanicity. Its re-crystallization occurs forming Mullite leading to loss in pozzolanicity when activated beyond activation temperature range aforementioned (Badogiannis *et al.*, 2005). The Kaolin disintegrates maintaining a small part of AlO<sub>6</sub> octahedral, while the rest is transformed to more amorphous and reactive tetra- and penta- coordinated units (Abo-EL-Enein et al 2014). These units of Alumina on reaction with Calcium hydroxide (CH) produces additional alumina containing phases such as C<sub>4</sub>AH<sub>13</sub>, C<sub>2</sub>AH<sub>8</sub> and C<sub>3</sub>AH<sub>6</sub> (Saikia et al., 2006). MK, an SCM when it partially replaces cement in concrete reacts with Calcium hydroxide (Ca(OH)<sub>2</sub>), a by-product of hydration reaction of cement resulting to additional C-S-H gel which increase strength of concrete as shown in equation (1) and (2).



As seen from equation (1), when cement reacts with water, it becomes hydrated and that part of water becomes chemically bound. The degree of hydration, ( $\alpha$ ) is defined as the ratio of the hydrated cement to the original cement content. The work of (Powers and Brownyard, 1948) showed that the maximum amount of chemically bound water required for the system is about one quarter of the weight of cement. Hence the dire need for proper adoption of water – binder ratio that will not lead to excess water in the system. As the hydration process continues, there is growth of hydration products in form of crystals from the cement gels produced. The hydration of plain cement is in two phases; dissolution and precipitation. Cement dissolves into the mix water releasing ions forming aqueous solution or pore solution. Cement minerals, C<sub>3</sub>A and C<sub>3</sub>S being highly soluble forms higher concentration than other minerals. This increase in concentration continues until it becomes supersaturated. This means that the pore solution has a higher tendency to combine with other compounds to form new solid phases than to remain dissolved (Wild and Khatib, 1997). The C<sub>3</sub>A and C<sub>3</sub>S eventually combined with other compounds/ions and water to form new hydrated products different from the cement minerals which is precipitated. This is the precipitation stage of cement hydration. As new products are precipitated, the concentration of C<sub>3</sub>A and C<sub>3</sub>S in the solution are reduced and the solution is no longer supersaturated. Then more C<sub>3</sub>A and C<sub>3</sub>S get dissolved in the solution in an attempt to reach supersaturated state again, thus leading to another stage of formation of new precipitated products. This circle continues to repeat itself until the entire cement mix is fully hydrated. Similarly, from equation (2), Ca(OH)<sub>2</sub>, a by-product of cement hydration reacts with MK to form more C-S-H and thus improve strength of concrete. These two reactions form the basis for hydration behaviour of MK blended cement which requires more in depth study.

In the work of (Oriol and Pera, 1995), Mk was used as partial replacement of PC at 0, 5, 10 and 15 % and CH consumption, strength development were determined in MK-PC pastes and

mortars employing TGA analysis. Test results showed minimum value of CH at 14 days curing which was attributed to an apparent fact that more CH is being removed from the paste by reaction with MK than is being generated by the cement hydration which was due to a peak in pozzolanic activity of MK. However, after 365 days of curing, substantial amount of CH was still left, even in the paste with 15 % replacement of PC by MK. This shows that for total consumption of CH produced by PC, a higher level of PC replacement by MK in excess of 15 % is required which depend on purity of MK and quantity of CH produced by the PC which in turn, a function of PC composition and W/B ratio. The study further showed that compressive strength of MK-PC cement pastes was enhanced at all ages and for all substitution levels.

The work of (Wild et al., 1997) showed that for MK-PC paste with a W/B of 0.5 and cured in Lime-saturated water at room temperature between 30 to 40 % of MK is required to remove all the CH in MK-PC paste. The specific surface of MK can also enhance the strength of MK-PC cement paste. (Wild et al., 1996), established that when the specific surface area of Mk increased from 12,000 to 15,000 M<sup>2</sup>/kg, the age at which maximum strength enhancement occurs is reduced. Other reports in literature indicates the influence of MK on the strength of MK-PC concretes which exhibited strengths slightly greater than SF-PC mixtures at the same levels of cement replacements by pozzolans. In such works as (Wild et al., 1996), they established that three factors that influence the contribution of MK to concrete strength include filler effect (which is immediate), acceleration of PC hydration (which occurs within the first 24 hours) and the pozzolanic reaction (which occurs between the first 7 to 14 days) for all MK levels between 5 % and 30 % (Hamdy et al., 2018). The work of Dave et al. (2016) on hydration characteristics of Metakaolin pozzolanic cement pastes shows that when PC was replaced with 20 % MK content, there was increase in the standard water of consistency, acceleration in the initial setting time and high compressive strength at early ages. This may not be un-connected with the additional pozzolanic reaction coupled with PC hydration and the specific surface area of MK. The work of (Olubajo et al., 2020) also confirmed that the high specific surface area of MK due to its fineness increase the setting time of the MK-PC paste even at low replacement levels, hence its use as partial replacement of PC for better performance of advanced concrete. (Shafiq and Nurudin 2010), in their work on ternary blended cement reported that with increase of MK content from 5 to 25 % at constant RHA content, water consistency of the ternary cement paste experienced a variation as MK was increased up to 25 % at constant RHA up to 10 %. But at 10 % constant RHA, as MK content increases, water demand of the cement paste gradually increased. These changes could be attributed to pozzolanic reactions. The study further showed that a maximum compressive strength of 40.5 N/mm<sup>2</sup> was obtained at 60 days curing duration when PC was replaced by MK at 15 % at 5 % RHA constant. This was attributed to the high silica/alumina contribution to the matrix by MK inclusion, the calcium/silica (C/S) ratio in the matrix.

In the work of (El-Gamal et al., 2017), they investigated the degree of hydration of PC and PC/Fly-ash (FA) paste samples conditioned at different relative humidity. Test results showed that varying relative humidity affects compressive strength and degree of hydration considerably. At varying relative humidity, PC-FA pastes showed better compressive strength than PC pastes samples. The work of (Suprenant and Papadopoulos, 1991) investigated the hydration characteristics and compressive strength of hardened cement pastes containing Nano-Metakaolin and Nano-Metakaolin containing silica fume. Test results showed higher compressive strength values for PC- NMK blends compared with PC control values, but the values of free lime Content for all PC-NMK blended cement pastes are lower than those of PC control values especially at later ages showing that reactions still continued.

For the MK-PC composite cementitious system, because of the simultaneous presence of cement hydration and MK ash reaction, the amount of non-evaporated water and Calcium hydroxide (CH) which are cement water hydration products cannot be used to evaluate the degree of hydration of the individual components. To achieve this accurately, (Lam et al., 2000) used the selective dissolution by Hydrochloric acid (HCL) to test the degree of reaction of fly ash cement.

In the same vein, (Bentz, 2000) studied the hydration process of FA- cement composites and measured the degree of reaction of FA in composites materials by determining the chemically combined water and using selective dissolution by Hydrochloric acid. The work of (Wild et al., 1996) also showed that the same feat can be achieved for two different blended cement-FA systems using the same selective dissolution approach but with ethylene diamine Tetra acetic acid (EDTA) combined with Sodium hydroxide (NaOH), diluted NaOH solution and Portlandite content. From these studies, it showed that degree of hydration of blended cements can be determined from the values of its chemically bonded water and free lime content for both constituents of the composites employing the selective dissolution approach.

The influences of MK cement on hydration and microstructure development can be seen through its chemical and physical effects. Chemically by the pozzolanic reaction and physically by nucleation, dilution and filler effects as well as synergetic chemical interactions between MK and PC. The works of (Caldrone et al., 1994) and (El-Diadamony et al., 2018) showed that the main effects of MK on cement hydration is the immediate filler effect, the nucleation effect that accelerates the cement hydration occurs in the first 24 hours and the pozzolanic reaction which occurs in the first two to fourteen days. Nucleation and filler effects of MK on cement hydration is directly related to its surface area. This is because the finely divided particles promote surface adsorption and provide precipitation sites which results in improving the degree of hydration. It is strongly believed that the mechanism of nucleation of MK is derived when the hydrates adsorb on the surface of mineral grains of MK which catalyses the nucleation process by lowering the energy barrier for growth as opined by (El-Diadamony et al., 2018). The nucleation process is influenced by the high fineness (high surface area), rate of substitution of MK and its affinity for cement hydration (Naik et al., 2001). Since MK particles are finer than that of PC, it readily provides nucleation sites for cement hydration. This fact is strengthened by the work of (Clarridge, 2011) which showed that the use of MK at 10 to 15 % substitution of PC by mass first acts as a nucleating agent that accelerates the rate of PC hydration, secondly by providing a surface which enables the hydrating products to adsorb on the MK particle surface.

The dilution effect of MK particles on PC pastes occurs when PC is substituted with MK leading to its decrease in the system. This is related to an increase in the effective water-to-cement ratio of the system binder. The presence of MK particles consequently enhanced PC hydration early by providing more nucleation sites for more hydration to take place and at later stages, more hydration by pozzolanic reactions with CH from PC hydration. (BS EN 196-3, 1995) showed that the dilution effect of MK is more pronounced when it is used at 15 – 20 % replacement level of PC. At this level of substitution, there is more MK particles in the system and with its high surface area, higher rate of reaction is prompted and sustained only if there is more water but with w/b ratio being constant, no additional water is available to lubricate and sustain the rate of reaction which then stalls the reaction leading to decrease in strength.

Microstructure of cement paste consists of the capillary and gel pores. Capillary pores are long continuous pores that exist within the un-hydrated cement paste and the gel pores are very small dimension and occurs within the reacted products. As hydration reaction progresses, this decrease the volume of the capillary pores because of the increase in PC gels or crystals. The capillary pores in the system consequently diminishes in size, gradually shortens until the connection between them is ceased. This means that the microstructure of the pastes changes as the degree of hydration changes or progresses which requires investigation. Other factors also affect the setting and hardening of PC and blended cement pastes such as consistency, setting time, compressive strength and the nature of the cement mix (Kakali et al, 2001).

Generally, degree of hydration of PC pastes can be determined by calculating the amount of Ca (OH)<sub>2</sub> in the paste, quantity of chemically bound water, fraction of un hydrated cement, liberated heat of hydration and strength of the hydrated cement. Among these methods, estimation of the amount of Ca (OH)<sub>2</sub> content is mostly used. This can be achieved by using solvents to extract the

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Ca (OH)<sub>2</sub> from the paste, by quantitative X – ray diffraction method and by thermal analysis. When cement and other pozzolanic materials react with water for initiation of hydration reactions, they form hydration products that chemically bind water. Evaporable or free water remains dispersed throughout the pore structure and allows for further hydration of cementing materials. The DOH of any cement paste,  $\alpha$  is a function of the non-evaporable water,  $W_n$ , initial mass of cement present in the sample and  $k$  which represents the mass of chemically combined water needed to fully hydrate one grain of cement as shown in equation (3):

$$\alpha = W_n / ck \quad (3)$$

(ASTM C 191, 2008), developed an expression in relation to equation (3) for DOH of a binary, ternary or quaternary mix. This was adopted and used for the study. The study evaluated the hydration behaviour and characteristics of PC paste, PC blended pastes with varying amounts of MK in terms of compressive strength, chemically combined water and free lime content at varying ages of hydration. The study also investigated the effect(s) of MK content on the fresh properties of the cement pastes, the use of XRD and SEM to investigate the hydration products of some selected samples.

## 2. Materials and method

### 2.1. Materials

Portland Cement (PC) used for the study was obtained from a local dealer of Dangote Cement Company, Nigeria, of grade CEM 1-42.5N. MK used for the study is a product from de-hydroxylation of Kaolin obtained from Madagali, Yobe state, Nigeria and thermally activated at 750°C at 10° C/min for 2 hours at the central services laboratory, National Cereals research institute, Badeggi, Niger state, Nigeria. It was cooled to room temperature in a desiccator ground with a local mill and sieved through a 75µm sieve. Choice for the calcination temperature was based on the work of (Ambrose et al., 1985). Calcination below 700° C results in poor reactive MK while calcination above 850° C leads to crystallization which reduce its reactivity (Abo-El-Enein et al., 2014). Preliminary tests were conducted on the materials and the physical and chemical properties are shown in Table 1. The mineralogical composition of MK is as shown in Figure 1. The main mineral and amorphous Alumino-silicate phase is quartz. The amorphous phase is formed due to reactions between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

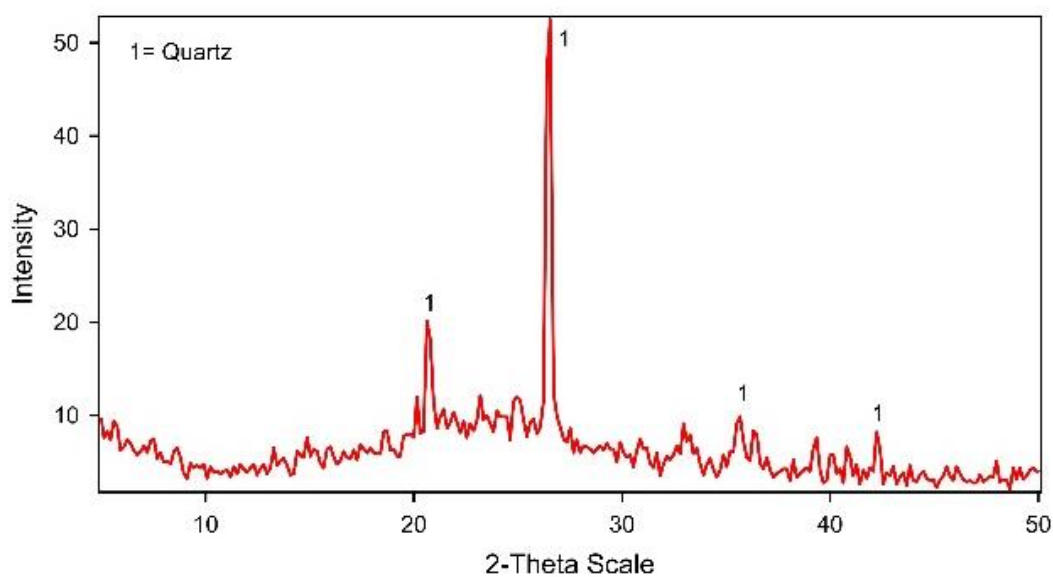


Fig. 1. XRD pattern of MK

## 2.2. Preparation of Samples

Six different blended cement Mortar mixes were prepared with a mix ratio of 1:3. The Sample mixes were prepared, substituting PC with 5 % stepwise increase up to 30 % of MK. Mixing of the dry constituents mechanically was attained with a local mill for one hour so as to attain homogeneity, then kept in air tight plastic containers for further investigation. The Mortar specimens were then mixed in standard mixer for about 5 minutes continuously, poured into 25 mm cubic steel Moulds, left to set at ambient temperature and at about 86 % relative humidity for 24 Hours, de-moulded and cured for 90 days immersed in water. Maximum replacement of PC with MK was 30 % by weight for all mixtures. Composition of binders is shown in Table 2.

**Table 1. Mix Proportion for Mortar**

Table 2: Mix Proportion for Mortar						
Materials (Kg/m <sup>3</sup> )						
S/no	Mix ID	PC	MK	Sand	Water	W/C
1	PC	186.00				
2	5MK – PC	176.70	9.30			
13	10MK – PC	167.40	18.60			
4	15MK – PC	158.10	27.90	114	93	0.5
5	20MK – PC	148.80	37.20			
6	25MK – PC	139.50	46.50			
7	30MK – PC	130.20	55.80			

## 2.3. Method

### 2.3.1. Consistency and setting times

Tests for consistency and setting times of PC and PC-MK pastes were conducted in accordance with BS EN 196- 3 provisions. The values of consistency, setting times (initial and final) of the pastes were determined using the Vicat apparatus in accordance with (Kondo et al. 1975) and (ASTM C 618-00, 2000) provisions. The water of consistency as well as setting times of the prepared pastes were directly determined using equation (4).

$$W_c (\%) = \frac{L}{W} \times 100 \quad (4)$$

Where  $W_c$  is the water of consistency,  $L$  is the amount of water required to produce a suitable paste and  $W$  is the mass of binder sample. The initial setting time is the time taken to reach the initial set while the final setting time is the time taken to attain final setting of paste.

### 2.3.2. Compressive strength

The required water of consistency was used to mix the PC and PC-MK blended dry mixtures to obtain fresh mortar pastes and then cast in 50 x 50 x 50 mm moulds, vibrated and then kept under room temperature and relative humidity of about 86 % for 24 hours. Thereafter, the specimens were de-moulded and cured for 7, 14, 28, 56 and 90 days respectively. The specimens were tested for compressive strength for the aforementioned cured ages. Three cubes of the hardened pastes were tested for compressive strength and average value recorded for each age.

### 2.3.3. Degree of Hydration of PC and PC- MK

Fragments from the crushed specimens of the hardened cement pastes were ground, dried for 30 minutes and sieved through a 75 $\mu$ m sieve. The hydration reaction was stopped by immersion in a mixture of (1:1) Methanol to Acetone for about 30 minutes. With the aid of the ground dried sample, kinetics of hydration was evaluated on the basis of chemically combined water, ( $W_n$ ), at different ages of hydration. using the Ignition Loss test at 1100°C for two hours, the chemically

combined water content was determined using equation (5). The test was repeated twice for each sample and the mean value recorded.

$$W_n (\%) = W_o - W_i / (W_i - PCLoI) \times 100 \quad (5)$$

Where  $W_o$  is dried sample mass at 110°C and  $W_i$  is ignited sample mass at 1100°C,  $PC_{LoI}$  is loss on ignition of PC. With known value of  $W_n$  % and inserted in equation (3), DOH for PC paste was determined for all ages. However, for PC-Mk blended pastes, equation (6) (ASTM C 191, 2008) was used as thus stated.

$$W_n / b_{tot} = M_{110oC} / M_{1100oC} \left[ \frac{G_u}{b_{tot}} \{1 - LOI_{GU}\} + \frac{M_k}{b_{tot}} \{1 - LOI_{MK}\} \right] - \frac{G_U}{b_{tot}} - \frac{M_k}{b_{tot}} \quad (6)$$

Where,  $b_{tot}$  is total mass of cementing binders,  $G_U / b_{tot}$  is ratio of GU to total binder used,  $M_k / b_{tot}$  is ratio of MK to total binder used,  $LOI_{GU}$  and  $LOI_{MK}$  is the loss - on - ignition values of GU and MK,  $G_U$  is initial mass of general use cement (PC), binder,  $M_{110oC}$  is mass of binder when oven dried,  $M_{1100oC}$  is mass of binder when ignited. Similarly, using the glycerol/ethanol extraction approach the free lime content, (%), was determined and the mean value for two repeated test values for each sample was recorded. (Said-Mansour, et al., 2011; Amin et al., 2012).

The fragments of the end products were prepared and the phase compositions of the formed hydrates was investigated with an X-Ray diffraction (XRD) analysis technique using a Philips PW 1050 Diffractometer. Data from the analysis was obtained with the aid of an XRD software (pdf-21 data base on CD-Release, 2005). Microstructure of the hardened blended cement Mortar was studied with the aid of SEM Inspect S equipped with an EDX analyser.

### 3. Results and discussion

#### 3.1. Physical and chemical properties of constituent materials

##### 3.1.1. Physical Properties

Table 2 showed the physical and chemical properties of PC and MK.

**Table 2. Physical and Chemical Properties of Materials**

Materials	PC (wt %)	MK (wt %)
Physical Properties		
Specific gravity (g/cm <sup>3</sup> )	3.15	2.52
Blaine Fineness (cm <sup>2</sup> /g)	3045	7483
Loss on ignition (LOI)	2.98	1.22
Chemical composition		
Calcium Oxide, CaO %	64.19	0.39
Silicon dioxide, SiO <sub>2</sub> %	19.57	54.30
Aluminum Oxide, Al <sub>2</sub> O <sub>3</sub> %	5.47	38.30
Ferric Oxide, Fe <sub>2</sub> O <sub>3</sub> %	3.24	4.28
Magnesium Oxide, MgO %	2.01	0.08
Manganese Oxide, MnO %	1.25	
Sodium Oxide, Na <sub>2</sub> O %	0.26	0.12
Potassium Oxide, K <sub>2</sub> O %	0.45	0.50
SO <sub>3</sub>	2.74	0.22

The results of the average specific gravities indicated that PC has a value of 3.15 and MK has a value of 2.52. The specific surface area of PC is 3045 cm<sup>2</sup>/g and that of MK is 7483, more than twice that of PC. This means that MK particles is much finer than PC particles, thus occupy more space than Pc and more volume of it is obtained when used to replace PC in mortar or concrete.

### 3.1.2. Chemical Properties

From Table 2, sum of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  (SAF) = 96.88 % which exceeds 70 % for MK thus satisfied (Abo-El-Enein et al., 2014) provisions value for MK is more than twice that for PC indicating high specific surface area which enhances MK reactivity. Specific gravity of MK (2.52) less than that for PC (3.15) makes it a filler which also aids reaction.

## 3.2. Standard consistency and setting times

### 3.2.1. Standard consistency of PC and Mk-PC Pastes

Water of consistency ( $W_c$ ), and setting times for PC and MK- PC pastes containing MK at varying proportions is shown in Figure 2a and 2b. For neat PC paste, it is 33 %. The water of consistency of MK-PC pastes is higher than that for PC paste. Addition of MK increased the water for normal consistency. This may be attributed to the high reactivity of MK, amorphous structure and higher specific surface area of MK particles which required more water of hydration compared with that for PC which does not require such quantity of water. From Figure 2a, the standard water of consistency,  $W_c$ , increases with increase in MK content. This is fruitful as it facilitates more reactions between MK particles and primary hydrates of PC. The increase of MK content by 10 % increase the water of consistency by 1.52 % and by 30 % MK content, increases  $W_c$  by 9.01 %. The increase in  $W_c$  by 9.01 % when MK replaced PC up to 30 % is due to the aforementioned factors.

### 3.2.2. Setting time

Initial and final setting times for the Mk-PC pastes is shown in figure 1b as prolonged compared with PC value.

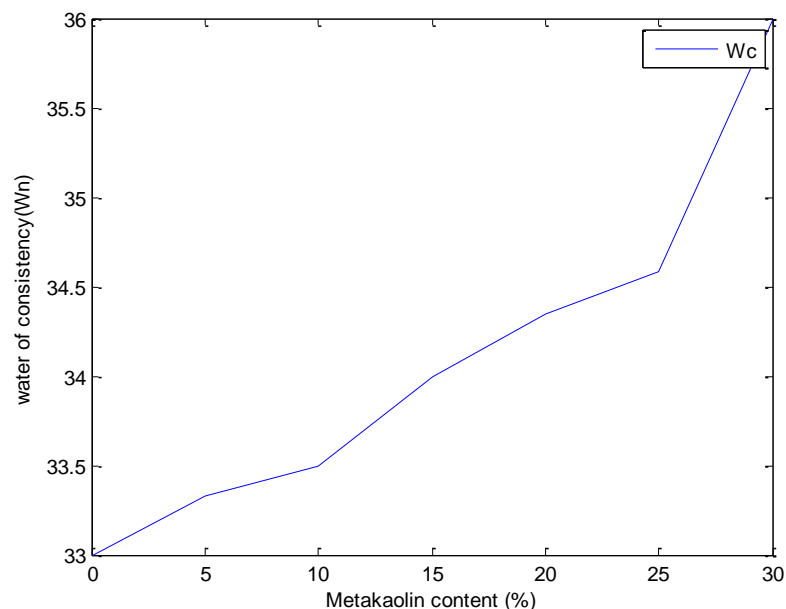


Fig. 2a. Normal consistency,  $W_c$  for varying Metakaolin content.

The Initial setting times (IS) and final setting times (FS) increased steadily with increase in replacement level of PC with MK. This is due to reduction of  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  in PC which is responsible for acceleration of the chemical reaction which in turn determines the initial and final setting times of the paste. This is also due to the coating effect of the particles on the cement grains as well as the formation of ettringite (end product due to reaction between CH and



$C_3AH_6$ ). Generally, the setting of Mk-PC blended pastes is not consistent with increase in MK content as can be seen in figure 2b. At an increase of 5 % Mk content, Wc increased by 1.5 % and at 30 % increase of MK content, Wc increased by 9.01 %. Hence, the increase of Mk content levels as a replacement of PC in MK-PC cements is not proportional to increase in Wc of the blended cements. This is in consonance with the work of (Badogiannis et al., 2005).

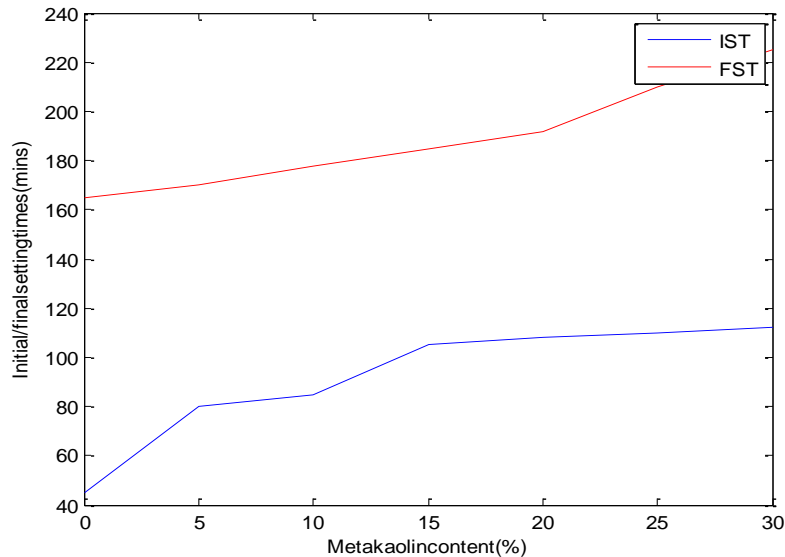


Fig. 2b. IST and FST of PC/MK-PC pastes; NB. IST is Initial setting time, FST is final setting time.

### 3.3. Compressive strength

Figure 2 showed the compressive strength test results for PC and Mk-PC hardened Mortar pastes. It is observed that compressive strength of PC paste increased steadily with increase in hydration period, but for MK-PC pastes, it is less up to 21 days. This is due to the fact that it is the hydration of PC due to its  $C_3S$  and  $C_2S$  contents which mainly contributed to hydration products (C-S-H) which are responsible for strength increase at this stage. This is more in PC pastes than in MK-PC pastes due to reduction in PC content. Also, the MK particles becomes the precipitation sites for the early hydration of C-S-H and CH which hinders pozzolanic reaction, furthermore, the strong dependency of the breaking down of glass phase on the alkalinity of the pore water which could only attain the high pH of 12 after some days of hydration. But at 28 days and beyond, increase in strength of MK-PC pastes improved, equalled and even surpassed that of PC values. This is because, in addition to the strength from PC hydration, in MK-PC pastes, MK reacted with calcium hydroxide (CH), by-product of PC hydration to form more C-S-H which increased the strength of the MK-PC pastes (Amin et al., 2012). It is further observed that strength in MK- PC pastes is maximum in mix 15MK- PC paste for all ages as compared with other mixes. This can be attributed to PC hydration and pozzolanic reactions between MK and CH, Silica and Alumina ( $SiO_2$  and  $Al_2O_3$ ) ions from MK which dissolved readily in solution to react with  $C_3S$  and  $C_3A$  ions from PC to form more C-S-H and C-S-A-H as precipitations when solution saturation is attained (Abo-El- Enein et al., 2013). The strength decreased at 20MK- PC paste up to 30MK-PC paste at all ages. This is due to dilution effect; More  $Ca^{++}$  ions from addition of MK and less  $SiO_2$ , due to reduction in PC content resulting in unbalanced  $C^{++}/Si$  ratio in the solution which led to reduction in strength for both 20MK-PC and 30MK-PC Pastes.

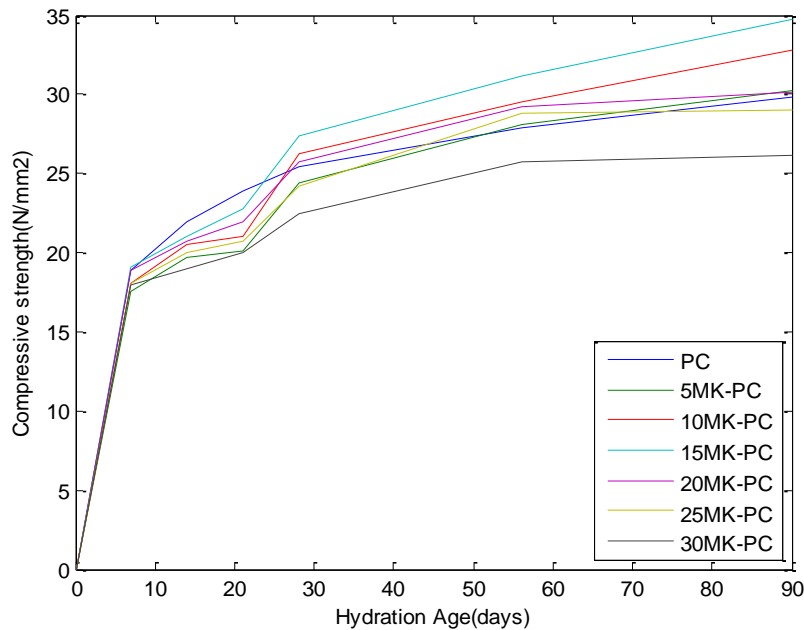


Fig. 3. Compressive strength versus Age for PC /PC-MK Pastes

### 3.4. Chemically combined water ( $W_n$ ) and Free Lime content (%)

Figure 4 showed the results of chemically combined water for PC and MK-PC pastes studied. It has been observed that for PC paste,  $W_n$ , steadily increased for all hydration ages which can be attributed to progressive hydration reaction of PC. It also showed that hydration rate is high from point of mixing to a few days, slowed down due to shielding from cement grains by initially formed hydration products and the rate of hydration gradually picked up again and steadily increased to 90 days as can be seen from the fairly flat shape of the graph between 28 to 90 days. The  $W_n$  content for most MK-PC pastes are high compared with that for PC paste and the highest value obtained was for 15MK-PC paste as from 28 to 90 days. Similarly (Figure 4), the values of the free lime content (%) obtained from the PC paste studied increased continuously with increase in hydration age while for MK-PC pastes increased and then decreased at later ages. For the PC paste, the continuous increase in free lime content (%) with increase in hydration age is due to continuous release of CH from the PC hydration even up to later ages. However, for MK-PC pastes, it increased up to about 60 days of hydration and then decreased. This is due to increase in CH content from PC hydration which is more than its consumption by the pozzolanic reaction (MK + CH) at ages up to 60 days. But at later ages, the consumption of CH through pozzolanic reaction becomes higher than that obtained from hydration reaction which led to decrease in free lime (%) content for MK - PC pastes compared with values of PC paste. The work of Gupta and Vyas (2018) has shown that increase in the percentage of pozzolanic material used to replace PC in PC blended pastes is shown by a marked decrease in the values of free lime (%) content.

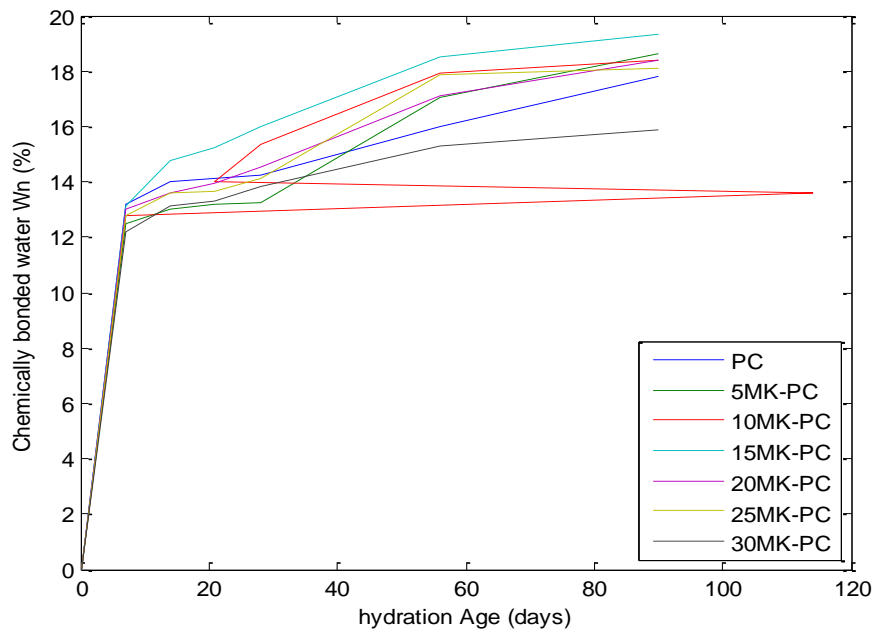


Fig. 4. Chemically combined water ( $W_n$ ) versus hydration age for all pastes

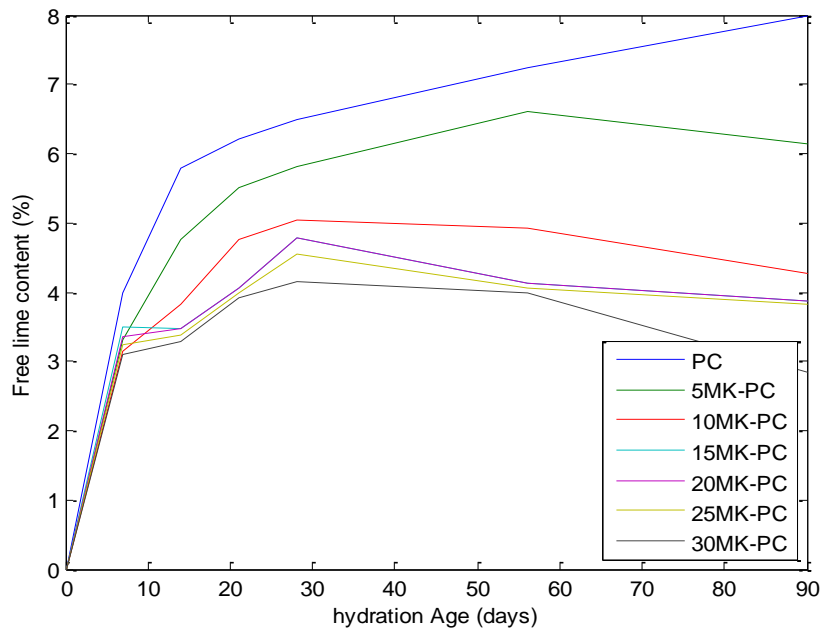


Fig. 5. Free Lime content versus hydration ages for all pastes

### 3.5. Mineralogical Analysis

Figures 6 – 7 presents the XRD patterns of neat PC and MK-PC blended cement pastes with 0, 10, 20 and 30 % MK content after 28 and 90 days of curing. The spectra in the region of  $2\theta$  between  $10^\circ$  and  $60^\circ$  were used to investigate the change in hydration products of neat PC and blended cements with curing age. The diffraction peaks of PC and the blended cements at different ages show similar collections. From the figures, it can be shown that the main minerals are Alite, A, which is  $C_3S$ , Belite, B,  $C_2S$ , Quartz, Q which is  $SiO_2$ , calcium Silicate Hydrates (C-S-H), Calcium

Hydroxide (CH) and calcium Aluminate silicate hydrate (CASH). Alite ( $C_3S$ ) and Belite ( $C_2S$ ) are primary minerals found in PC. Calcium hydroxide or Portlandite (CH) is generated during hydration of PC and present in solution with the primary Minerals,  $C_3S$  and  $C_2S$  in the pastes. During hydration of PC,  $C_3S$  and  $C_2S$  reacts with water, producing Calcium silicate hydrate (C-S-H) and Calcium hydroxide (CH). In Figure 6, the hydration of PC produced CH whose intensity peaks can be observed around 2 theta of  $18.00^\circ$ ,  $34.10^\circ$ ,  $47.17^\circ$  and  $50.81^\circ$  respectively. For the PC-MK mixes, it exhibits lower intensity peaks at 90 days curing (Figure 7) due to additional pozzolanic reactions which consumes CH to form more C-S-H and also due to replacement of PC by MK which in turn leads to reduction of the clinker phase ( $C_3S$  and  $C_2S$ ), resulting to lower generation of CH. As curing or hydration age increases up to 180 days or more, CH intensity peaks reduces drastically or disappears completely because they are used to produce more C-S-H.

The maximum intensity peaks for C-S-H at 28 days of curing were observed at around 2 theta of  $29.09^\circ$  for all the mixtures. The formation of C-S-H gel generally dominates the mechanical performance of concrete matrix. From the study, it can be observed that the PC-MK blended mixtures exhibited higher intensity peaks of C-S-H gel than that for PC mix. This is due to the C-S-H production from PC hydration in addition to C-S-H produced due to pozzolanic reaction between MK and CH.

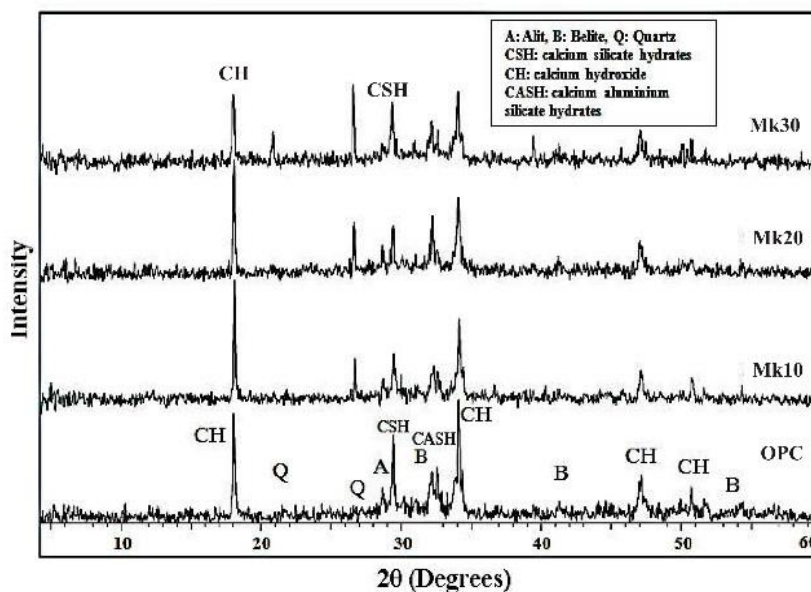


Fig. 6. XRD Pattern for mixes PC, 10PC-MK, 20PC-MK and 30PC-MK for 28 days

Similarly, the calcium Aluminate in the MK reacts with water producing calcium aluminate Silicate hydrate ( $C_3AH_6$ ). The Mineral phase of CASH was found in the form of Gismondine at around 2 theta  $33.15^\circ$ . Their intensity peaks were found to be significantly lower at 28 days of curing than at 90 days (figure 7).

The peaks of Gismondine were found to be higher for PC-MK blended mixtures than for PC mix, which might be due to the presence of high aluminate phases in the Mk Ash. The work of Gupta and Vyas (2018) show that the presence of high aluminate phases of the Mullite (aluminium Silicon oxide) phase in MK ash reacts with CH to form CASH or Gismondine. Also, its formation along with CSH gel partially enhance the densification of cement paste (Tang et al, 2016).

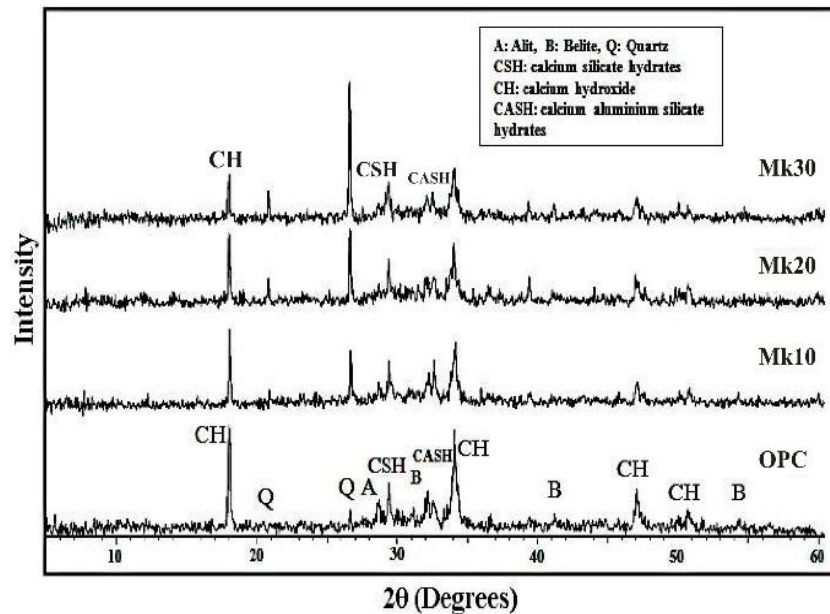


Fig. 7. XRD Pattern for mixes PC, 10PC-MK, 20PC-MK and 30PC-MK for 90 days.

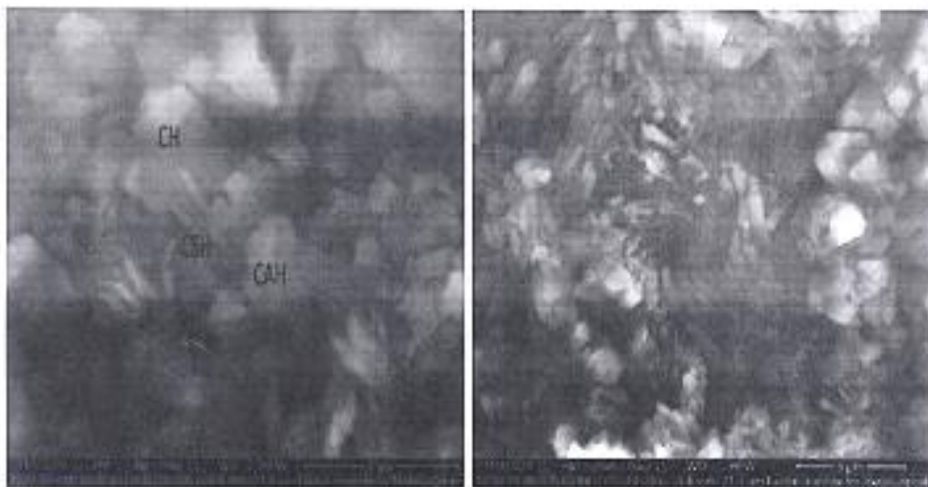
It is an established fact that the amorphous silica, which is the reactive component in pozzolanic materials like MK reacts with CH to produce additional hydrate products. From the study, the diffraction peaks of Alite ( $C_3S$ ) as A and Belite ( $C_2S$ ) as B can be seen in the OPC Mix only around  $2\theta$   $29.5^\circ$  and  $54^\circ$  respectively while Q ( $SiO_2$ ) which is quartz appeared mainly at  $23^\circ$  and  $28^\circ$  which increases with increase in MK content (highest in MK30 mix) for all the mixes labelled; OPC, MK10, MK20, and MK30, representing control PC, 10 %MK, 20 % MK and 30 %MK at 28 and 90 days curing duration as shown in figures 6 – 7 respectively. In each Figure, CH intensity decreases gradually as aforementioned with both curing age and percentage replacement level of MK. This indicates that the incorporation of MK yields the pozzolanic reaction which proceeded even after 90 days curing duration, producing C-S-H and CASH which further increase the strength of the Mortar. This accounts for the diminishing of the CH intensity peaks.

### 3.6. Microstructural Analysis

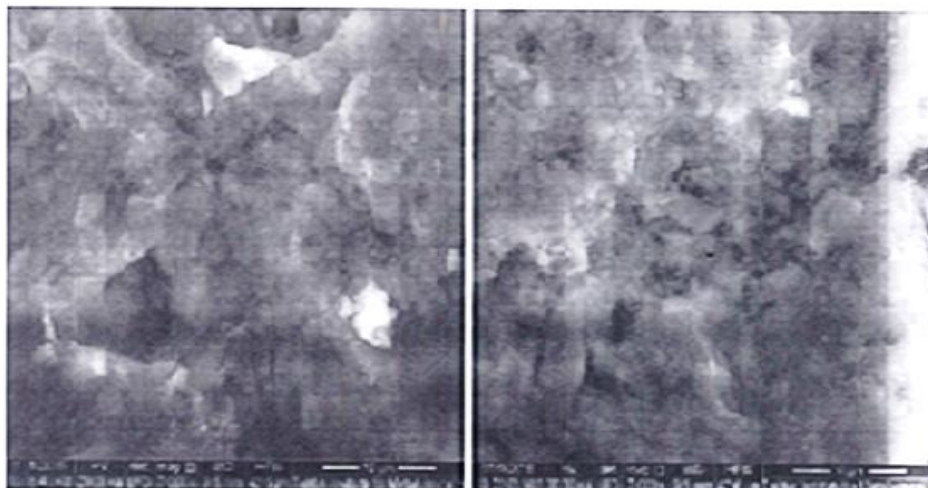
The chemical compound that affects the HCP of PC and PC-MK pastes performance and the changes in the microstructure due to the presence of MK were investigated by SEM. After compressive strength test and hydration behaviour in terms of non-evaporable water, Free Lime water content, the core of the cross section areas of the test specimen was prepared and coated with Gold for 30 seconds, then observed under aforementioned SEM equipment so as to study the evolution of the microstructure due to the presence of MK in the blended cement and PC control. Test results are produced images of the distribution and volume of pores and the morphology of Particles in the HCP for the specimens. SEM Micrographs of PC and blended cement at 28 and 90 days hydration age are shown in Figures 8 and 9. Test result for PC specimen (Figure 8) shows that PC particles have an irregular polygonal shape with sizes ranged from less than  $5\ \mu m$  to  $15\ \mu m$ . On the other hand (Figure 9), MK particles are elongated like-microfibers and some like flakes with a rough surface. The PC-MK HCP image is finer than that for the PC. The image shows PC Mix at 28 days curing as a matrix with a crystallized CH and poorly crystallized C-S-H Gel and pores occupying considerable volume in the matrix, though forming a compact microstructure. However, with partial replacement of PC with MK as shown in Figure 8b at 90 days, the paste showed more dense and compact though in homogeneous microstructure. With development of more cement hydration and pozzolanic reaction, the

microstructure of blended cement becomes denser with further formation of more C-S-H and  $C_3A \cdot H_6$  Gels. Also, only a few CH with irregular shapes have been detected in the blended cement pastes instead of the CH crystal with Hexagonal plate structure as in PC paste. This is attributed to the consumption of CH by MK during the pozzolanic reaction.

The result indicates that the characteristics of the PC-MK blended cement has the potential to enhance the properties of PC while in service. This is because MK is a pozzolan with a specific surface area of about 12,000  $M^2/Kg$ , specific gravity of 2.50  $g/cm^3$  compared with PC with a specific surface area of 373  $M^2/Kg$ , specific gravity of 3.15 $g/cm^3$  for PC. This shows that MK has very small particles and hence can enhance PC in two fundamental mechanisms: (a) by filling of interstitial pores inside the skeleton mesh of PC matrix, thereby improving the density and strength as well, and (b) by contribution to more strength through pozzolanic reaction with CH liberated during PC hydration.



**Fig. 8. SEM Micrograph for the hardened neat PC after 28 days of hydration**



**Fig. 9. SEM micrograph for the hardened PC-MK30% Paste after 90 days of hydration**

#### **4. Conclusion**

Hydration and strength development of blended cement with MK were investigated using chemically combined water, Free-Lime content and compressive strength Tests,. XRD, SEM

techniques were applied in the analysis of pozzolanic reaction and hydration products. From the results of compressive strength tests, and that obtained from analysis of the hydration products using aforementioned techniques, the following conclusions were drawn:

1. Test results on the mechanical characteristics showed that for all curing ages the PC strength were higher up to 21 days compared with blended strength values, but at 28 days upward, strength of blended cements equal and even surpassed control values due to additional strengths from pozzolanic reactions.
2. Standard consistency in MK- PC binders increased with increase in replacement level of the PC with MK due to its high water requirement, its high specific surface area and its degree of reactivity.
3. There is a remarkable modification observed in the hydration product of CH, CSH gel and CASH on the cement matrix containing the blended cement as shown in the XRD test results.
4. The incorporation of MK improves the densification of the blended cement matrix as shown in the SEM analysis test results. It further showed a remarkable impart of MK on the formation of the hydration products, its ability to form better bonding with paste content which leads to improvement in the mechanical performance of MK blended cement mixture.
5. The chemical and morphological changes observed in the developed binders was achieved through microstructural analysis.

Based on the mechanical and microstructural characteristics, MK content up to 25 % as a replacement of PC can be utilized in the production of mortar of concrete for construction.

**Conflicts of interest:** The author declares no conflict of interest.

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