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# Near surface characteristics of concrete containing supplementary cementing materials

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**Abstract**

This paper presents the results of an investigation on the use of metakaolin and silica fume as supplementary cementing materials in enhancing the near surface properties of concrete. Metakaolin and silica fume mixtures, each with 10% replacement, were prepared and tested for initial surface absorption, water absorption and sorptivity. Metakaolin and silica fume were found to enhance the overall near surface characteristics of the concrete. The inclusion of metakaolin and silica fume greatly reduced the initial surface absorption, water absorption and sorptivity of concrete in varying magnitudes. Generally, the curing method adopted had significant effects on the near surface properties of concrete incorporating metakaolin or silica fume.



*Keywords:* High-performance concrete; Metakaolin; Silica fume; Near surface characteristics

## 1. Introduction

It is an undeniable fact that concrete is the most widely used man-made construction material in the world today, and will remain so for decades to come. The popularity of concrete is largely due to the abundance of raw material, low manufacturing and maintenance cost, excellence in compression, durability to weathering and fire hazards, versatility in forming various shapes and its unlimited structural applications in combination with steel reinforcement. However, the cement industry is also highly energy intensive, and the emission of carbon dioxide during cement manufacturing has created enormous environmental concerns. There has also been an increase in the number of incidents where concrete structures experienced severe deterioration in extreme environments. All these factors have contributed pressures from various quarters to reduce cement consumption, and to intensify research in exploring the possibilities of enhancing strength and durability through the use of pozzolans as supplementary cementing materials. The utilization of calcined clay in the form of metakaolin (MK) as a pozzolan for concrete has received considerable interest in recent years. This interest has been focused on the consumption of calcium hydroxide (CH) produced by cement hydration which is associated with poor durability. Thus the use of metakaolin enhances long-term strength and durability. In addition, it is also possible to obtain early strength enhancement through the filler effect [1].

In this study, high reactivity metakaolin prepared by calcining refined local kaolin, is investigated for its viability as a pozzolanic microfiller for high-performance concrete in comparison with a trade silica fume. The study also investigates the effect of different curing regimes on the durability of concrete incorporating metakaolin or silica fume as supplementary cementing materials. Curing is essential for concrete to fully realize its potential properties [2]. The curing becomes more important for concrete incorporating pozzolan, in hot and dry environments [3]. The near surface durability performance, particularly the flow of water into metakaolin and silica fume concrete at various ages subjected to four different curing regimes are evaluated. These include air (no curing), plastic membrane, wet burlap and water.

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## 2. Experimental work

### 2.1. Materials

Ordinary Portland cement equivalent to ASTM C 150 Type 1, commercially available densified silica fume and metakaolin were used. Metakaolin was obtained by calcining refined kaolin at 700 °C for 7 h using a laboratory rotary furnace. Physical and chemical properties of the cementitious materials are presented in Tables 1 and 2 respectively. The specific surface (nitrogen adsorption) for silica fume is approximately 21.3 $m^2/g$, which is much higher than that for cement (4.2 $m^2/g$) and metakaolin (9.5 $m^2/g$). X-ray fluorescence analysis shows that its main chemical constituent is silica (92%) with 2.5% loss on ignition. Chemical analysis shows that the metakaolin is principally composed of silica (57%) and alumina (35%).

Siliceous sand and crushed granite stone were used as fine and coarse aggregates respectively. The physical properties of the aggregates used are summarised in Table 3. A polycarboxylic ether based superplasticizer was used as a chemical admixture. The dark brown liquid admixture had a 20% solids content and specific gravity of 1.05 at 20 °C. Mixing and curing water was taken directly from tap supply.

### 2.2. Mixture proportions

The mixture proportions are summarised in Table 4. The study covered three concrete mixtures that is control (C), 10% silica fume replacement (SF) and 10% metakaolin replacement (MK), which were designed in accordance to the Sherbrooke mix design method [4] for non-air entrained high-performance concrete. The as-received aggregates were not in saturated and surface dry condition and water corrections were made to the mixture proportions. Additional water contributed by the superplasticizer was also taken into account.

Table 2
Chemical properties of cement, metakaolin and silica fume

| | Cement | Metakaolin | Silica fume |
|---|---|---|---|
| *Chemical analysis (%)*[a] | | | |
| Silicon dioxide ($SiO_2$) | 20.99 | 57.4 | 92.06 |
| Aluminium oxide ($Al_2O_3$) | 6.19 | 35.26 | 0.48 |
| Calcium oxide (CaO) | 65.96 | 0.02 | 0.40 |
| Ferric oxide ($Fe_2O_3$) | 3.86 | 0.94 | 2.11 |
| Magnesium oxide (MgO) | 0.20 | 0.18 | 0.63 |
| Sodium oxide ($Na_2O$) | 0.17 | <0.01 | 0.28 |
| Potassium oxide ($K_2O$) | 0.60 | 3.17 | 1.24 |
| Phosphorous oxide ($P_2O_5$) | 0.05 | 0.09 | 0.02 |
| Titanium oxide ($TiO_2$) | 0.40 | 0.43 | <0.01 |
| Manganese oxide (MnO) | 0.06 | <0.01 | 0.23 |
| Loss on ignition, LOI | 1.53 | 2.52 | 2.54 |
| | 100.01 | 100.01 | 99.99 |
| *Bogue potential compounds (%)* | | | |
| Tricalcium silicate ($C_3S$) | 50.32 | | |
| Dicalcium silicate ($C_2S$) | 22.22 | | |
| Tricalcium aluminate ($C_3A$) | 11.06 | | |
| Tetracalcium aluminoferrite ($C_4AF$) | 11.75 | | |
| Equivalent alkalis | 0.56 | | |
| | 95.91 | | |

[a] Philips PW 1480 X-ray spectrometer.

### 2.3. Testing procedures

The durability was measured in terms of the initial surface absorption (ISAT), water absorption and sorptivity. The testing programme and types of specimen

Table 1
Physical properties of cement, metakaolin and silica fume

| Physical properties | Cement | Metakaolin | Silica fume |
|---|---|---|---|
| Colour | Greenish grey | Light creamy white | Greyish black |
| Specific gravity (ASTM D 854-92), % | 3.11 | 2.52 | 2.22 |
| Fineness,[a] % | | | |
| Passing 150 μm | 98 | 94 | 75 |
| Passing 75 μm | 91 | 88 | 36 |
| Passing 45 μm | 77 | 84 | 18 |
| Average particle size $D$ ($v$, 0.5)[a], μm | 23 | 9.5 | 99.4 |
| Specific surface, $m^2/kg$ | | | |
| Blaine (ASTM C 204-94a) | 343 | – | – |
| Nitrogen adsorption (BET)[b] | 4200 | 9500 | 21 300 |
| Standard consistency (ASTM C 187-86), % | 27.4 | – | – |
| Setting time (ASTM C 191-92), min | | | |
| Initial | 110 | – | – |
| Final | 300 | – | – |

[a] Obtained from laser particle size analysis, conducted using *Malvern Mastersizer X*.
[b] Brunauer–Emmett–Teller method, conducted using *Micromeritics ASAP 2000*.

Table 3
Physical properties of fine and coarse aggregates

| Physical properties | Fine aggregate (siliceous sand) | Coarse aggregate (granite stone) |
|---|---|---|
| Specific gravity (saturated surface dry) | 2.65 | 2.57 |
| Size | 75 μm–4.75 mm | 4.75–9.5 mm |
| Grading | Medium | Single-sized 10 mm |
| Moisture content (% of dry mass) | 0.05 | 0.25 |
| Water absorption (% of dry mass) | 0.40 | 1.67 |
| Fineness modulus | 2.5 | – |

Table 4
Mixture proportions

| Mix | Cement ($kg/m^3$) | MK ($kg/m^3$) | SF ($kg/m^3$) | Water ($kg/m^3$) | W/CM | Granite stone ($kg/m^3$) | Siliceous sand ($kg/m^3$) | Superplasticizer ($L/m^3$) |
|---|---|---|---|---|---|---|---|---|
| C | 500 | – | – | 150 | 0.3 | 1050 | 695 | 19 |
| MK | 450 | 50 | – | 150 | 0.3 | 1050 | 685 | 19 |
| SF | 450 | – | 50 | 150 | 0.3 | 1050 | 680 | 19 |

Table 5
Testing programme

| Test | Specimen | Age at testing (days)[a] | Curing regime |
|---|---|---|---|
| Initial surface absorption | 150×150×150 mm cubes | 7, 28, 56 and 90 | Water, wet burlap, plastic sheet and air |
| Water absorption | 100×100×100 mm cubes | 7, 28, 56 and 90 | Water, wet burlap, plastic sheet and air |
| Sorptivity test | 100×200 mm cylinders | 7, 28, 56 and 90 | Water, wet burlap, plastic sheet and air |

[a] After 28 days of curing.

prepared are summarised in Table 5. For these tests, specimens were subjected to four different initial curing regimes that is water (W), burlap (B), plastic sheet (P) and air (A). The curing regimes and duration are described in Table 6. Durability tests were then conducted at ages 7, 28, 56 and 90 days after the initial curing of 28 days. Prior to testing, all specimens were dried in a laboratory oven until constant mass was achieved, taken as when the difference between two successive weights performed in an interval of 24 h was not more than 0.1% of the initial mass. The specimens were then taken out from the oven and left to cool overnight under laboratory conditions of 27 ± 2 °C and 85 ± 5% RH before conducting the tests.

ISAT was performed by measuring the absorption of water from a pressure head of 200 mm into the concrete from the top surface. The flow, in $ml/m^2/s$ was calculated at intervals of 10, 30, 60 and 120 min. The water absorption test was conducted by completely immersing dried cube specimens in water at 25 °C for 96 h. The sorptivity test was carried out by placing the cylindrical specimens on glass rods in a tray such that their bottom surface up to a height of 2 mm is in contact with water kept under laboratory conditions at 27 ± 2 °C and 85 ± 5% RH. This procedure was considered to allow free water movement through the bottom surface. The total surface area of water within the tray should not be less than 10 times that of the specimen cross-sectional area. Specimens were removed from the tray and weighed at intervals of 5, 10, 30, 60, 120 and 180 min. The volume of water absorbed per unit cross-sectional area at each time interval was evaluated and the sorptivity determined from the slope of the graph of the water absorbed against the square root of time. For each

Table 6
Curing regime

| Curing regime | Description |
|---|---|
| Air (A) | Specimens were exposed to air at 27 ± 2 °C and 85 ± 5% RH after demoulding until 28 days of age. |
| Plastic membrane (P) | Specimens were covered with one layer of polystyrene sheet for 72 h immediately after demoulding. Subsequently exposed to air at 27 ± 2 °C and 85 ± 5% RH until 28 days of age. |
| Wet burlap (B) | Specimens were covered with one layer of wet burlap for 72 h immediately after demoulding. The burlap was wetted twice a day. Specimens were then exposed to air 27 ± 2 °C and 85 ± 5% RH until 28 days of age. |
| Water (W) | Specimens were immersed in a water tank at 25 °C after demoulding until 28 days of age. |

test, measurements were obtained from three specimens and the average values reported with coefficient of variation ranging from 4% to 12%.

## 3. Results and discussion

### 3.1. Near surface properties

The ISAT was performed to obtain an indication of the durability of concrete subjected to external chemical attack. Concrete cover is the weakest, most permeable and absorptive part of the concrete matrix as compared to the internal microstructure. The near surface concrete is highly heterogeneous in nature, due to the relative movement of cement paste and aggregates during the compaction of fresh concrete and bleeding of mix water in the early stages of cement hydration. As a result, there is a porosity gradient in the near surface concrete, where the porosity of near surface is higher than that of internal part of concrete [5]. Therefore, the durability of the whole concrete can be characterised by simply determining the permeation characteristics of the concrete surface, which is considered as the most critical and vulnerable part towards external fluid ingress.

The initial surface absorption test was performed to acquire the flow within the concrete surface at intervals of 10, 30, 60 and 120 min. The flow decreased exponentially with time. This was because the rate of absorption of water becomes less as time increases when the outer zone of the surface is saturated and it is more difficult for water to be absorbed by the inner pores. It was found that the flow data at interval of 10 min gave a more representative trend of the surface absorption characteristics. Flow rate of less than 10 min might not represent a stable and constant flow of water into the concrete, and the flow rates at 60 and 120 min intervals would not be suitable since the concrete surface would already be in a saturated state that the data obtained was not suitable for comparative purposes. The results of surface absorption for the 10 min duration (ISAT-10) up to age of 90 days are illustrated in the 3-D bar chart in Fig. 1. For the control mixtures, the air-dried specimens showed the greatest flow ranging from 0.255 ml/m$^2$/s for 7 days to 0.142 ml/m$^2$/s for 90 days, followed by the plastic sheet, wet burlap and water cured specimens. The same trend was noticeable for MK and SF mixtures, whereby air-dried specimens showed the highest absorption rates while water cured specimens were the least. It was apparent that both the SF and MK mixtures exhibited much lower flow results as compared to the control within the respective curing regimes. It was also observed that the SF mixtures were only significantly lower compared to the MK mixtures at later ages.

Sorptivity test differs from the ISAT as the former measures the rate of capillary suction as opposed to the

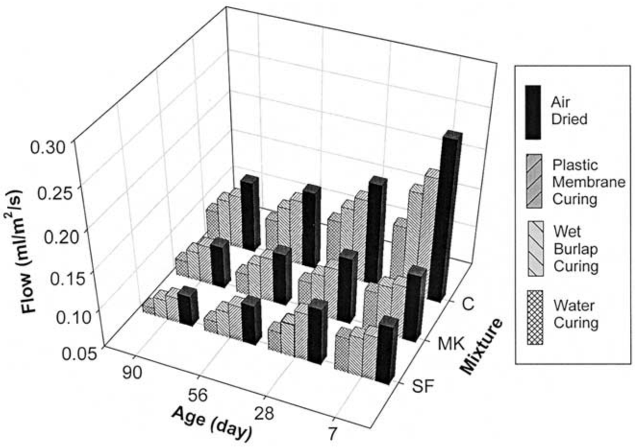


Fig. 1. 3-D bar chart for ISAT-10 (10 min).

bulk effect of capillary suction in the latter at a specified time. The value of sorptivity illustrates the water mass uptake by concrete from the bottom surface, in unit of mm$^3$/mm$^2$/min$^{1/2}$. The lower the sorptivity value, the higher the resistance of concrete towards water absorption. The decrease in sorptivity is due to several factors. Firstly, as the water invades the pores it encounters smaller pores hence slowing the rate of sorption. Secondly, even if the capillary pores form a strong interconnected network throughout the concrete, for example through the interfacial zone around the aggregates with larger capillary pores, the ingress of water particles may still be slow as the air–water interface rests at a stable configuration in the pore space. Any further absorption of water can only be transported through gel pores that are much smaller than capillary pores, or by moisture diffusion in both capillary and gel pores [6].

The results of the sorptivity test are shown in Fig. 2. Generally, all mixtures have a low sorptivity value that is below 0.1 mm$^3$/mm$^2$/min$^{1/2}$, which is to be expected of

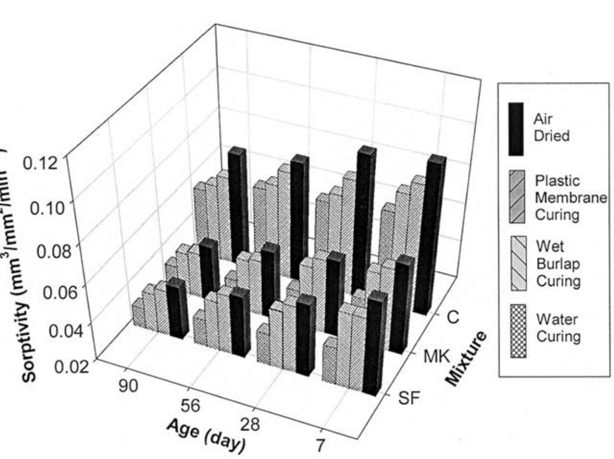


Fig. 2. 3-D bar chart for sorptivity test.

concrete cast using low water/binder ratio. Specimens which underwent water curing, particularly SF and MK showed marked decrease in sorptivity values indicating dense concrete with finer pores and lesser interconnected network of capillary pores. The sorptivity values for all the water cured control, metakaolin and silica fume specimens drop by 29%, 34% and 39% respectively, compared with the corresponding air cured specimens. Furthermore it can be observed from the 3-D plot that the effect of curing method is more dominant in the mixtures containing the pozzolan since the values of the water cured specimens are much lower than the other specimens within each respective mixture. For the specimens cured with plastic sheet, wet burlap or air-dried, there is insufficient water to promote complete pozzolanic reaction, thus accounting for higher sorptivity values. This demonstrates the importance for good curing in the MK and SF concretes.

The volume of pore space in concrete, as distinct from the ease with which fluid can penetrate it, is measured by absorption. The percentages of water absorbed by all mixtures under different curing regimes are illustrated in Fig. 3. It is noticeable that all mixtures despite their curing regimes, have low absorption characteristic that is less than 10%. It can be seen that the trend between mixtures is similar to that of initial surface absorption and sorptivity whereby mixtures containing silica fume and metakaolin have much lower values. For the control mixtures the decrease in absorption values becomes insignificant from 28 days onwards implying that there is no marked decrease in volume of pore space within the concrete irrespective of the curing method adopted. However, for the SF and MK mixtures especially the water cured specimens, there is a marked decrease in absorption values with age presumably as a result of pozzolanic reaction which effectively reduces the volume of pore space.

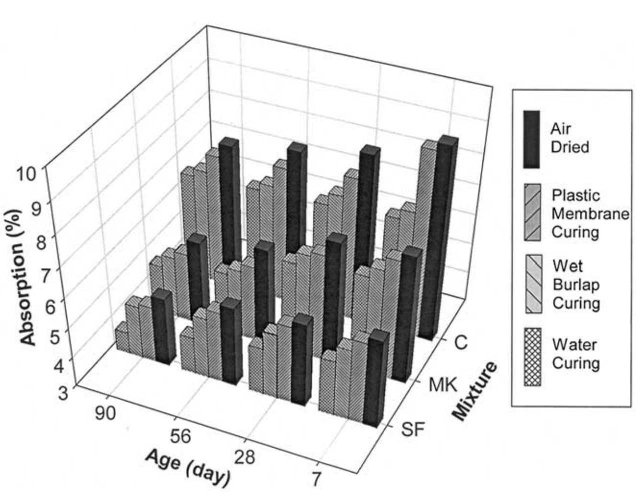


Fig. 3. 3-D bar chart for water absorption test.

The presence of metakaolin and silica fume acting as pozzolanic microfillers helped to reduce the size of capillary pores of cement paste, causing the pore system to become segmented through partial blocking. In this case, the capillary pores were only interconnected by gel pores, which are much smaller and almost impermeable [7]. Besides promoting pozzolanic reaction to form secondary hydration products, it is presumed that metakaolin and silica fume filled up some of the voids, making the pore network discontinuous. This deduction is in agreement with the conclusion made by Sabir et al. [8] in that the presence of pozzolans alters the pore structure in concrete, which greatly improves the resistance of the transportation of water and diffusion of harmful ions that lead to deterioration of the matrix.

### 3.2. Durability performance

The durability performances for the mixtures under different curing regimes for surface absorption, sorptivity and absorption are expressed in the form of relative indices. The index is computed as a ratio of the measured parameter of a reference specimen and the corresponding measured parameter of a specimen under one of the aforementioned curing regimes. In this study, the reference specimen always refers to the control specimen (C-W) subjected to full water curing. A value of 1.0 is thus obtained for the relative indices of C-W for all the tests at different ages.

Fig. 4 plots the relative flow indices for ISAT-10 of all three concrete mixtures under different curing regimes. Generally all the MK and SF specimens have lesser flow rates resulting in higher index values than C-W, with the exception of MK-A, MK-P and SF-A at the later ages. The pozzolan mixtures also tend to have much lesser improvements with time of the surface impermeability compared to the water cured control specimens. In contrast, there are marked improvements in the resistance towards transport of water at the surface of the air, plastic sheet and wet burlap cured control specimens from 7 to 28 days. No further improvement in performance over the water cured control specimens was apparent after 28 days for these specimens.

The plot of relative sorptivity indices shown in Fig. 5, clearly distinguishes the prevailing effect of water curing on the metakaolin and silica fume specimens. This reinforces the earlier remarks regarding the effect of curing method on sorptivity values for concrete incorporating pozzolan. Generally all the pozzolan concrete performed better than the water cured control and marked improvements in terms of lower rate of water penetration through capillary suction were apparent up to 56 days. This trend was however not evident for the control specimens subjected to air, plastic sheet and wet burlap curing.

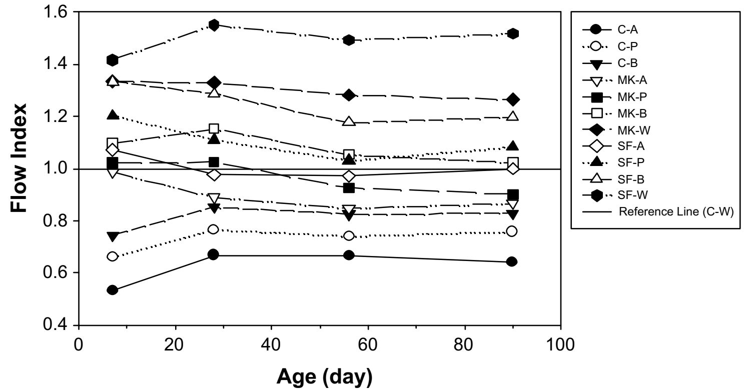


Fig. 4. Relative indices for ISAT-10.

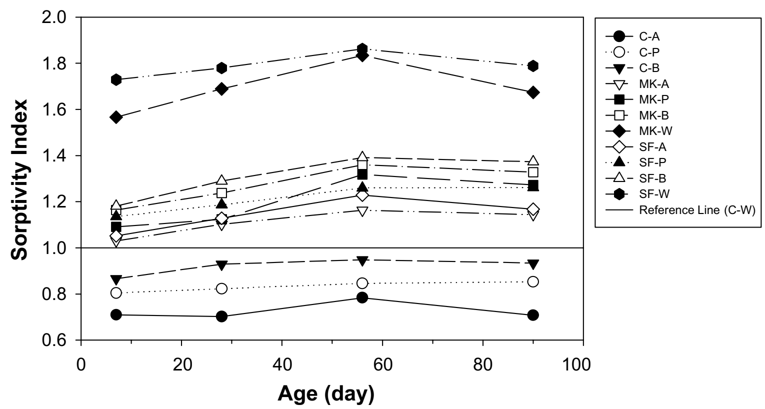


Fig. 5. Relative indices for soprtivity test.

There is a gradual improvement of the relative water absorption indices with time for the pozzolan concrete over the control as illustrated in Fig. 6. A similar conclusion can be drawn regarding the effect of curing method on pozzolan concrete. However, the differences in the water absorption characteristics due to the curing method becomes more significant after 28 days and is greater for the silica fume compared to metakaolin concrete.

The effect of curing method on the durability performance is apparent from the results. Water curing regime has produced the least permeable concrete since there was continuous supply of water for hydration and pozzolanic reaction to take place for the first crucial 28

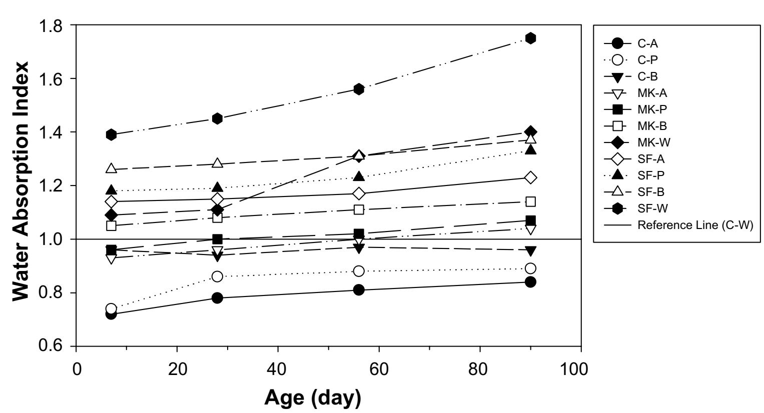


Fig. 6. Relative indices for water absorption test.

days. The reactions continued even after the specimens were exposed to air. This is primarily due to sufficient entrapped water within the microstructure of the concrete, which promotes the development of the hydration products. Wet burlap curing for 72 h provided extra source of water externally and prevented moisture depletion within the concrete, whereas the plastic membrane only functioned to prevent or minimise evaporation of water from the concrete within the curing period. This explains why concrete which underwent wet burlap curing performed much better than concrete subjected to plastic membrane curing since there will be more water available for continued hydration and pozzolanic reaction. Curing regime has greater influence on concrete incorporating metakaolin and silica fume than that of OPC concrete. Generally the pozzolan concretes irrespective of the curing method adopted, exhibited comparable or better near surface characteristics compared to OPC concrete with full water curing.

## 4. Conclusions

The following conclusions are drawn based on results of the present study:

1. This study found that the addition of metakaolin and silica fume into concrete significantly decreased the initial surface absorption, water absorption and sorptivity of concrete, when compared to plain OPC control mixture.
2. Curing played a critical role in realising the full potential of concrete. Full water curing gave the least permeable concrete, followed by wet burlap curing and plastic membrane curing. Air-dried concrete exhibited inferior near surface durability characteristics.
3. Generally there is a gradual improvement with time of the measured characteristics. However, this is only applicable to the OPC control mixture. For mixtures with metakaolin or silica fume subjected to the same curing regime, it is apparent that the improvement is only marginal. This seems to indicate that the level of pozzolanic reaction is almost complete during the initial 28 days curing period.
4. It was also observed that large differences in values between air and water curing were obtained for the pozzolan mixtures. This illustrates and reinforces the importance of good curing for concrete containing supplementary cementing materials.
5. Based on the relative indices computed, there is no evidence of a general and common trend for the enhancement of the near surface properties for the pozzolan mixtures. It is very much dependant on the properties measured.
6. Silica fume mixture exhibited marginally lower absorption characteristics than metakaolin mixture subjected to the same curing regime suggesting that silica fume is a much better pozzolan. However, it is more susceptible to differences in curing method compared to metakaolin.
7. Based on the results of the tests of near surface properties it is proposed that for low permeability concrete the value of sorptivity should be less than 0.1 $mm^3/mm^2/min^{1/2}$, which relates well with the ISAT 10 min value of less than 0.25 $ml/m^2/s$, as suggested by other researchers.

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