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# Rate of pozzolanic reaction of metakaolin in high-performance cement pastes

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**Abstract**

This paper assesses the hydration progress in metakaolin (MK)-blended high-performance cement pastes with age from the measurements of compressive strength, porosity, and pore size distribution, the degree of pozzolanic reaction, and the $Ca(OH)_2$(CH) content of the MK-blended cement pastes at a water-to-binder ratio (w/b) of 0.3. Comparisons are also made with pastes containing silica fume (SF), fly ash (FA), and control Portland cement (PC). It is found that at early ages, the rates of pozzolanic reaction and CH consumption in the MK-blended cement pastes are higher than in the SF- or FA-blended cement pastes. The higher pozzolanic activity of MK results in a higher rate of strength development and pore structure refinement for the cement pastes at early ages. Although the rate of pozzolanic reaction of MK becomes slower after 28 days of curing, the pozzolanic reaction in the blended cement pastes with a w/b of 0.3 still continues at the age of 90 days. At this age, about half of the MK still are unreacted. 

*Keywords:* Metakaolin; High performance; Degree of pozzolanic reaction; Pore size distribution; Compressive strength

## 1. Introduction

The advances of concrete technology show that the use of mineral admixtures such as silica fume (SF) and fly ash (FA) is necessary and essential for producing high-performance concrete. In recent years, there has been a growing interest in the use of metakaolin (MK) for this purpose [1–5].

MK is a thermally activated aluminosilicate material obtained by calcining kaolin clay within the temperature range of 700–850°C [1,3,6]. It contains typically 50–55% $SiO_2$ and 40–45% $Al_2O_3$ and is highly reactive. It has been reported that the replacement of cement by 5–15% MK results in significant increases in compressive strength for high-performance concretes and mortars at ages of up to 28 days, particularly at early ages [2–5]. The replacement also results in improved concrete durability properties, including the resistance to chloride penetration, freezing and thawing, and deicing salting scaling [2,4].

While a number of studies have been conducted on high-performance MK concrete or mortars [2–5], there has been few studies concerning the hydration progress of MK in high-performance pastes at low water-to-binder (w/b) ratios. The only study involving the hydration of MK-blended cement pastes with low w/b ratios seems to have been carried out by Ambroise et al. [6]. In their study, the control paste was prepared at a water-to-cement ratio (w/c) of 0.25. The MK pastes were prepared at varied w/b ratios from 0.28 to 0.54 when the cement was replaced by 10–50% MK to achieve the same consistency as the control paste. Most of the studies on the hydration reactions of MK-blended cement pastes were carried out with a w/b ratio higher than 0.5 [7–11]. Khatib and Wild [8] and Wild and Khatib [9] found that at a w/b ratio of 0.55, there is a decrease in the porosity and the CH content of MK-blended pastes and mortars at ages between 7 and 14 days. Subsequently, beyond 28 days, the porosity and CH levels increase. These phenomena were attributed to a critical change in the reaction between MK and CH at around 14 days, which involves the phase transformation of the reaction products, that inhibits the reaction of MK with CH [8,9,12]. Consequently, the strength enhancement produced by MK reaches a maximum within the first 14 days and then declines [12].

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More recently, Frias and Cabrera [11] determined the pore size distribution and CH content of the MK-blended cement pastes with a w/b ratio of 0.55 at the ages of up to 365 days. They reported no increase in total porosity and CH content between the ages of 14 and 28 days, and suggested that the pozzolanic reactions in the pastes containing 10% and 15% MK completed at the ages of 56 and 90 days due to the total consumption of MK. It should, however, be noted that Murat [7], Khatib et al. [8], and Wild et al. [12] cured the samples in closed polythene containers, while Frias and Cabrera [11] cured the samples in airtight containers. Also, different types of cements were used for each study and the drying procedures varied widely.

The present study is concerned with the MK-blended cement pastes at lower w/b ratios. The hydration progress of MK-blended cement pastes at a w/b of 0.3 is assessed from measurements of compressive strength, porosity and pore size distribution, degree of pozzolanic reaction, and CH content. The degree of pozzolanic reaction of MK in these pastes was quantitatively determined using a selective dissolution method. This method has been developed for quantifying the degrees of pozzolanic reactions [13,14], which is different from traditional methods for assessing the degree of cement hydration through the determination of nonevaporable water and CH contents. Although a number of studies [13–17] on the degree of pozzolanic reactions for FA-, SF-, and zeolite-blended cement pastes have been presented using this method, no similar study has been presented for MK-blended cement pastes. The results are also compared with those obtained for MK-blended cement pastes prepared at higher w/b ratios and those for SF and FA-blended cement pastes.

## 2. Materials and experimental details

### 2.1. Materials

The materials used in this study were Portland cement (PC) equivalent to ASTM Type I and low-calcium FA equivalent to ASTM Class F from local sources, MK named MetaStar 450 from ECC International, and condensed SF named Force 10,000D microsilica from W. Grace. The chemical and physical properties of these materials are given in Table 1, where the data for PC, MK, and FA were tested by the authors, while the data for SF were provided by the supplier. A naphthalene-based superplasticizer, which had a solids content of 38.6%, was used to produce an appropriate paste consistency.

Table 1
Chemical and physical properties of the PC, MK, SF, and FA

| Parameters | Cement | MK | SF | FA |
|---|---|---|---|---|
| $SiO_2$ (%) | 21.0 | 53.2 | 85–96 | 56.8 |
| $Al_2O_3$ (%) | 5.9 | 43.9 | – | 28.2 |
| $Fe_2O_3$ (%) | 3.4 | 0.38 | – | 5.3 |
| CaO (%) | 64.7 | 0.02 | – | < 3 |
| MgO (%) | 0.9 | 0.05 | – | 5.2 |
| $Na_2O$ (%) | – | 0.17 | – | – |
| $K_2O$ (%) | – | 0.10 | – | – |
| $TiO_2$ (%) | – | 1.68 | – | – |
| $SO_3$ (%) | 2.6 | – | 0.3–0.7 | 0.68 |
| Loss on ignition (%) | 1.2 | 0.50 | 3.5 | 3.90 |
| Specific gravity | 3.15 | 2.62 | 2.22 | 2.31 |
| Fineness (> 45 μm, %) | – | – | 3–5 | 6.3 |
| Specific surface ($cm^2/g$) | 3520 | 12,680 | – | 3960 |

### 2.2. Sample preparation and compression test

The cement pastes prepared in this study included: MK-blended pastes with MK contents of 5%, 10%, and 20%, SF-blended pastes with SF contents of 5% and 10%, an FA-blended paste with a FA content of 20%, and a control PC paste without any pozzolanic replacement. The w/b ratio for all the pastes was 0.3. The pastes were mixed in a mechanical mixer. Small amounts of superplasticizer (< 0.3% by weight of binder) were added to achieve an adequate consistency. Cube specimens of 70.7 × 70.7 × 70.7 mm in dimension were cast in steel moulds. They were removed from the moulds after 1 day and were then cured in water at 27°C. The compressive strengths of the pastes were determined at the ages of 3, 7, 28, and 90 days.

The fractured pieces of about 30 mm in sizes obtained from the compressive strength test were immediately soaked in acetone for 7 days to stop the hydration of the cementitious materials. They were then placed in a vacuum oven at 60°C to remove the acetone and to be dried for 48 h. The dried samples were placed into sealed plastic bags and reserved for other determinations. For the determination of porosity and pore size distribution, the sizes of the sample were further reduced to about 5 mm in diameter and 5 mm depth. For the determination of degree of hydration and CH contents, the samples were ground to pass a 150-μm sieve.

### 2.3. Determination of porosity, pore size distribution, degree of pozzolanic reactions, and CH content

The pore size distribution and porosity of the paste samples were determined by using a "Pore Sizer 9320" mercury intrusion porosimeter (MIP) supplied by Micromeritics [18], with a maximum mercury intrusion pressure of 210 MPa.

The determination of the degree of pozzolanic reactions of MK, SF, and FA was based on a selective dissolution procedure developed by Ohsawa et al. [13] and Li et al. [14]. The principle of the procedure is based on the assumption that the majority of the unreacted pozzolan is acid insoluble. In a blended cement paste, the pozzolan reacts with calcium hydroxide to form acid soluble hydration products. Thus, it is possible to dissolve the hydration products of cement and pozzolans, and the unreacted cement, leaving the unreacted pozzolan as insoluble residue [14]. Details of the test procedure can be found in our

Table 2
Compressive strength of control and blended cement pastes

| Mix | Compressive strength (MPa) | | | |
|---|---|---|---|---|
| | 3 days | 7 days | 28 days | 90 days |
| Control | 70.38 | 90.46 | 105.1 | 111.55 |
| 5% MK | 75.96 | 91.53 | 105.55 | 118.4 |
| 10% MK | 82.84 | 103.4 | 126.4 | 133.9 |
| 20% MK | 72.10 | 96.4 | 118.3 | 123.8 |
| 5% SF | 68.24 | 89.58 | 106.46 | 118.93 |
| 10% SF | 67.52 | 86.05 | 107.27 | 121.1 |
| 20% FA | 60.28 | 71.35 | 90.63 | 114.95 |

previous papers [15–17]. The degree of pozzolanic reaction of pozzolan (MK, SF, or FA) is defined as the percentage of reacted pozzolan relative to initial amount of the pozzolan in the cement paste.

The CH content was determined by using a differential scanning calorimeter. One hundred milligrams of ground sample and 20 mg of $Al_2O_3$ of analytical reagent grade were mixed and heated at the rate of 10°C/min in an air atmosphere. The CH content is calculated from the weight loss between 425°C and 550°C and expressed both as a percentage by weight of ignited sample and a percentage by weight of the cement in the sample.

## 3. Results and discussion

### 3.1. Compressive strength

The results of the compressive strength tests are shown in Table 2, where each value is the average of three measurements. It can be seen that the cement pastes containing 5% to 20% MK had higher compressive strengths than the control at all tested ages from 3 to 90 days, with the paste containing 10% MK performing the best. The cement pastes containing SF or FA had lower compressive strength than the control at early ages. The SF replacements resulted in higher compressive strengths than the control at 28 and 90 days, while the FA replacement resulted in a higher compressive strength than the control only at 90 days.

The above results indicate that at early ages, the MK used in this study contributed better to the compressive strength development of high-performance cement pastes than the SF. This observation is similar to those observed by Zhang and Malhotra [4] for concrete with a w/b of 0.4 and by Curcio et al. [5] for mortars with a w/b of 0.33. The lower rate of strength development for SF pastes at early ages can be related to the state of SF used in this study, which was supplied in a densified form [19].

### 3.2. Porosity and pore size distribution

The results of MIP are summarized in Table 3, where each value is the average of two measurements. The results show that for all the pastes, the porosity and average pore size decreased as the curing age increased. The pastes containing MK had lower porosity and smaller average pore diameters than the control paste and the SF pastes with the same percentages of replacement at all the tested ages. This indicates that the MK used in this study is more effective than the SF in the refinement of the pore structure of the blended cement system, although they both reduce the porosity and pore sizes of the cement pastes at the studied replacement levels. In comparison, the cement paste containing 20% FA showed higher total porosity than the control until the age of 28 days, indicating the lower pozzolanic activity of this type of material.

The effects of pozzolans and curing age on the pore size distributions of cement pastes are shown in Fig. 1. It can be seen that at all studied ages, the cumulative mercury intrusion curves for the all the pastes containing MK lie on the finer side when compared with those for the control and for the pastes containing SF or FA and the difference becomes more significant after 7 days of curing. This indicates a higher rate of pore structure refinement for the MK pastes.

It is noted that Khatib and Wild [8] and Frias and Cabrera [11] reported higher porosity values for the MK pastes than for the control paste when prepared with a w/b of 0.55, while the present results show lower porosity values for the MK pastes when the pastes were prepared with a w/b of 0.3. The present results are however similar to those obtained by Ambroise et al. [6], who reported that a 20% MK-blended paste with a w/b of 0.34 had nearly the same porosity as a control PC paste with a w/b of 0.25. Although Ambroise et

Table 3
Average pore diameter and porosity of control and blended cement pastes

| Mix | Average pore diameter[a] (μm) | | | | Total porosity (% v/v) | | | |
|---|---|---|---|---|---|---|---|---|
| | 3 days | 7 days | 28 days | 90 days | 3 days | 7 days | 28 days | 90 days |
| Control | 0.0380 | 0.0371 | 0.0362 | 0.0348 | 20.11 | 17.99 | 15.58 | 14.04 |
| 5% MK | 0.0357 | 0.0279 | 0.0257 | 0.0243 | 18.17 | 15.36 | 13.82 | 12.51 |
| 10% MK | 0.0287 | 0.0251 | 0.0197 | 0.0186 | 16.84 | 15.18 | 12.37 | 11.68 |
| 20% MK | 0.0204 | 0.0143 | 0.0122 | 0.0114 | 16.30 | 12.85 | 10.73 | 9.21 |
| 5% SF | 0.0366 | 0.0370 | 0.0367 | 0.0349 | 18.72 | 16.83 | 14.53 | 13.84 |
| 10% SF | 0.0353 | 0.0341 | 0.0325 | 0.0306 | 16.97 | 15.49 | 14.23 | 13.42 |
| 20% FA | 0.0368 | 0.0356 | 0.0347 | 0.0339 | 22.35 | 18.59 | 15.62 | 13.82 |

[a] Average pore diameter = $4I_{tot}/A_{tot}$, where $I_{tot}$ is the total mercury intrusion volume and $A_{tot}$ is the total mercury-intruded pore surface [18].

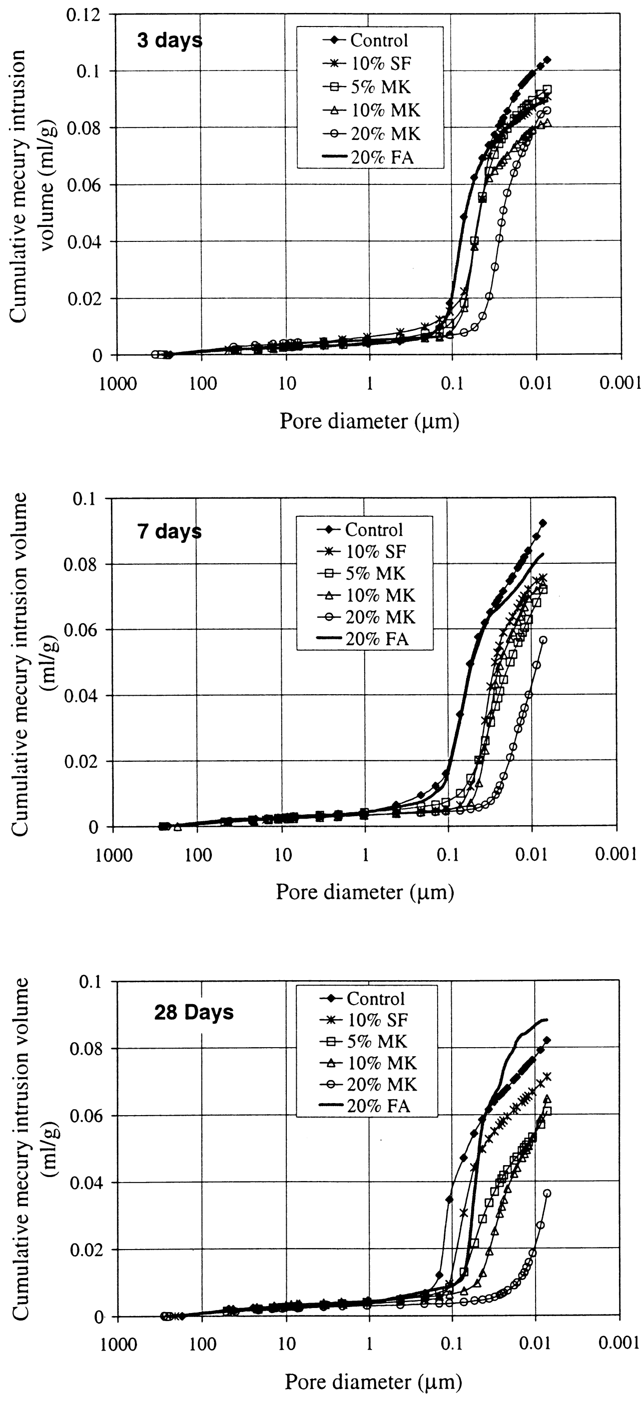


Fig. 1. Pore size distribution of control and blended cement pastes at (a) 3, (b) 7, and (c) 28 days.

al. [6] did not compare the porosity of MK and PC pastes with the same w/b ratio, their results inferred that the porosity of the paste with a w/b of 0.34 and 20% MK should be lower than a PC paste with the same w/b ratio. This is because, in general, the porosity of a PC paste increases as the w/b increases. Thus, it can be believed that MK contributes better to the pore structure refinement of cement pastes at a lower w/b ratio than at higher w/b ratio.

### *3.3. Degree of pozzolanic reactions*

The results of the pozzolanic reaction of the pastes at different ages are shown in Table 4, which are presented as the percentage values of the reacted pozzolan relative to the initial amount of the pozzolan in the paste, and each value is the average of two measurements.

The results show that the degree of pozzolanic reaction of MK at each age is higher at a replacement level of 5% than at the replacement levels of 10% and 20%. Similar results are also observed for the degree of pozzolanic reaction of SF. This observation agrees with our previous results, which showed higher degree of pozzolanic reaction of FA in blended cement pastes with a lower replacement level than with higher replacement levels [16,17]. The higher rate of pozzolanic reaction in cement pastes with a lower replacement level can be attributed to the higher concentration of CH available for the pozzolan to react with.

Comparing the different pozzolanic materials, the results show that, initially, the rate of pozzolanic reaction of MK is greater than that of SF. At 3 days, the degree of pozzolanic reaction of MK in the pastes at the MK replacement levels of 5% and 10% was 20.6% and 15.3%, which were 30% and 49% higher than that of SF in corresponding blended cement pastes. For longer curing times, the reaction rate was reduced for both MK and SF, but the reduction was greater for the MK. Thus, the differences between the degrees of pozzolanic reaction of MK and SF became small at 28 days, and the latter exceeded the former at 90 days. The higher initial reactivity of MK can be attributed to its $Al_2O_3$ phases [5], which are involved in the formation of $C_2ASH_8$ (gehlenite) and a small amount of crystalline $C_4AH_{13}$ phase [7]. The higher initial reactivity of MK used compared to SF may also be related to its fineness, although the data on the specific surface of the condensed form of SF used in this study were unavailable due to the difficulty in obtaining reliable test results. In comparison, FA in a paste with a 20% replacement level showed lower degrees of pozzolanic reaction than the MK and the SF at all ages tested.

It is important to note that, although the rate of MK reaction becomes slower after prolonged curing, there was still a considerable increase in the degree of pozzolanic reaction of MK from 28 to 90 days. For example, for a cement paste with 10% MK, the degree of pozzolanic

Table 4
Degree of reaction of MK, SF, and FA in blended cement pastes

| | Degree of reaction of pozzolans (%) | | | |
|---|---|---|---|---|
| Paste | 3 days | 7 days | 28 days | 90 days |
| 5% MK | 20.56 | 29.52 | 39.44 | 56.28 |
| 10% MK | 15.34 | 26.98 | 36.28 | 50.96 |
| 20% MK | 9.38 | 18.64 | 30.82 | 41.29 |
| 5% SF | 15.86 | 24.64 | 38.53 | 54.85 |
| 10% SF | 10.32 | 21.25 | 35.38 | 52.06 |
| 20% FA | 3.98 | 7.29 | 17.54 | 28.69 |

reaction of MK was 36.3% at 28 days and 51.0% at 90 days. The reaction of MK was still not completed at the ages of 90 days and about half of the MK are still unreacted.

### 3.4. CH content

The CH contents of the pastes at different ages are given in Table 5 (based on the ignited weight of the sample) and Fig. 2 (based on the weight of cement in the pastes), where each value is the average of two measurements. It can be seen that when calculated based on the weight of the ignited sample, all blended cement pastes show lower CH contents than the control paste. However, when calculated based on the weight of cement in the paste (Fig. 2), the pastes containing MK and SF still show lower CH contents relative to the control paste, but the paste containing 20% FA shows higher CH content until the age of 7 days. The latter is consistent with the results of other researchers [20–22].

It is interesting to note that initially the difference in the CH content between the MK and SF pastes with the same replacement levels is small. This difference increases with curing age and reaches a maximum at 28 days and decreases afterward. At 90 days, the CH contents in SF pastes are reduced to the same levels of the MK pastes at the same replacement levels. This phenomenon is somewhat similar to that observed for the degree of pozzolanic reaction, except that the MK pastes and SF pastes reach nearly the same degree of pozzolanic reaction at an earlier age of 28 days. A longer period of curing is required for the CH content of SF pastes to be reduced to the level of MK paste.

Comparing with the results reported by others [9,11], when calculated based on the weight of cement, the CH levels observed in the present study with a w/b ratio of 0.3 are lower than that of a w/b ratio of 0.55 for both the control pastes and the blended pastes with the same MK replacement levels. For example, Frias and Cabrera [11] reported CH contents of about 24%, 15%, and 10% for the control paste, and the pastes with 10% and 20% MK, respectively, at the age of 90 days. But in the present studied, the observed CH contents were only 12.88%, 3.47%, and 0.74%, respectively, for the equivalent pastes. Furthermore, the amounts of CH consumed by the reaction of MK in cement pastes with different percentages of MK replacements and w/b ratios can be roughly estimated by subtracting the CH contents of the MK pastes from that of the control paste. It is found that the CH consumption in the pastes with 10% MK is similar at a w/b of 0.55 and at a lower w/b of 0.3 (9% vs. 9.41%), but in the pastes with 20% MK it is slightly higher at a w/b of 0.55 than at a w/b of 0.3 (14% vs. 12.14%). It is known that the CH content in a PC paste indicates the degree of hydration of the cement, while the CH consumption in a blended cement paste is related to the degree of pozzolanic reaction. The above comparison seems to show that while a lower w/b ratio significantly reduces the degree of cement hydration, it has little effect on the degree of pozzolanic reaction of MK at a 10% replacement level. It may reduce the degree of pozzolanic reaction of MK at higher replacement levels.

Table 5
$Ca(OH)_2$ content of control and blended cement pastes (based on percentage of ignited weight)

| Paste | $Ca(OH)_2$ content (%) 3 days | 7 days | 28 days | 90 days |
|---|---|---|---|---|
| Control | 10.36 | 11.68 | 12.65 | 12.88 |
| 5% MK | 8.76 | 7.93 | 6.83 | 5.92 |
| 10% MK | 6.77 | 5.94 | 3.92 | 3.12 |
| 20% MK | 5.76 | 3.12 | 1.53 | 0.59 |
| 5% SF | 9.28 | 8.87 | 7.85 | 6.25 |
| 10% SF | 7.76 | 7.26 | 6.54 | 3.21 |
| 20% FA | 9.85 | 9.48 | 8.76 | 6.87 |

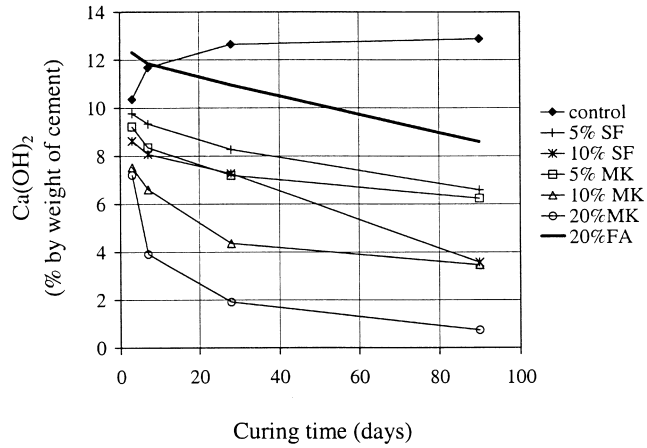


Fig. 2. $Ca(OH)_2$ content calculated based on the weight of cement content.

On the other hand, it is noted that Frias and Cabrera [11] found that for the cement pastes prepared with a w/b of 0.55 and with 10% and 15% MK replacements, there were inflexion points in the patterns of CH content at 56 and 90 days, respectively. They considered that these points represented the end of pozzolanic reaction, and concluded that the complete consumption of MK occurred at about 90 days. It seems that this conclusion cannot be applied to MK pastes with lower w/b ratios. Although the present study did not determine the CH content at the ages of 56 and after 90 days, the results of the degree of hydration have shown that the consumption of MK has not been completed within the studied ages.

## 4. Conclusions

The aim of this paper is to assess the progress of the pozzolanic reaction of MK-blended cement pastes prepared with a w/b ratio of 0.3. A series of tests on the compressive strength, porosity and pore size distribution, degree of pozzolanic reaction, and $Ca(OH)_2$ content of MK-blended cement pastes has been carried out. Comparisons have been made with the results obtained from SF- and FA-blended cement pastes, and with those obtained by other researchers for MK pastes with higher w/b ratios. Based on the results and discussion, the following conclusions can be drawn.

1. At early ages, the rates of pozzolanic reaction and CH consumption in MK-blended cement pastes were higher than in SF- or FA-blended cement pastes. This indicates that the MK used in this study had a higher initial reactivity than the SF and the FA when used in cement pastes with a w/b ratio of 0.3.
2. Due to its high initial reactivity, MK resulted in a higher rate of compressive strength development and pore structure refinement for the high-performance cement pastes when compared with SF. It also resulted in lower mercury-intruded porosity than the control.
3. The rate of pozzolanic reaction in MK pastes became slower after 28 days of curing. After that, the pore size distribution of MK pastes was slightly coarsened. This coarsening happened at a later age in a cement paste with a lower w/b ratio than in a paste with a higher w/b ratio. However, the pozzolanic reaction of MK was still not completed at the age of 90 days with about half of the MK unreacted. The degree of pozzolanic reaction and CH consumption level of the SF pastes may reach or exceed those of MK pastes at the ages of 28–90 days.

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