Materials and Structures
DOI 10.1617/s11527-007-9296-z

ORIGINAL ARTICLE

Improving strength, drying shrinkage, and pore structure of concrete using metakaolin

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Received: 23 March 2007 / Accepted: 1 August 2007

Abstract This paper presents the results of an investigation on the use of metakaolin (MK) as a supplementary cementing material to improve the performance of concrete. Two MK replacement levels were employed in the study: 10% and 20% by weight of the Portland cement used. Plain and PC-MK concretes were designed at two water–cementitious materials (w/cm) ratios of 0.35 and 0.55. The performance characteristics of the concretes were evaluated by measuring compressive and splitting tensile strengths, water absorption, drying shrinkage, and weight loss due to the corresponding drying. The porosity and pore size distribution of the concretes were also examined by using mercury intrusion porosimetry (MIP). Tests were conducted at different ages up to 120 days. The results revealed that the inclusion of MK remarkably reduced the drying shrinkage strain, but increased the strengths of the concretes in varying magnitudes, depending mainly on the replacement level of MK, w/cm ratio, and age of testing. It was also found that the ultrafine MK enhanced substantially the pore structure of the concretes and reduced the content of the harmful large pores, hence made concrete more impervious, especially at a replacement level of 20%.

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Keywords Compressive strength · Concrete · Metakaolin · Pore structure · Portland cement · Shrinkage · Tensile strength

1 Introduction

Performance of concrete is determined by its mechanical and durability properties. There are so many studies in the literature focusing on the improvement of concrete performance by replacement of Portland cement to some extents of various mineral admixtures; such as, fly ash, silica fume, blast-furnace slag, etc. Due to pozzolanic and filling effects of these certain mineral admixtures, they are capable of enhancing the durability through the pore refinement and the reduction in the calcium hydroxide of the cement paste matrix [1]. Generally, the effects of mineral admixtures may be assessed as improvement in workability, durability to thermal cracking, durability to chemical attacks, and production of high performance concrete [2].

Recently, there has been a growing interest in the utilization of high-reactivity metakaolin (MK) as a supplementary cementitious material in concrete industry. MK is an ultrafine pozzolana, produced by calcining purified kaolinite clay at a temperature ranging from 700 to 900°C to drive off the chemically bound water and destroy the crystalline structure [3–5]. Unlike industrial by-products such as fly ash, silica fume, and blast-furnace slag, MK is refined carefully to lighten its color, remove inert impurity, and control particle size. The particle size of MK is generally less than 2 μm, which is significantly smaller than that of cement particles, though not as fine as silica fume [4, 6]. Moreover, the use of MK in concrete in its present form is relatively a new concept [7]. Recent works have shown that the inclusion of MK greatly influenced the mechanical and durability properties of concrete [4, 6–14]. It has also been demonstrated that concrete mixture incorporating high-reactivity MK gave comparable performance to silica fume mixtures in terms of strength, permeability, and chemical resistance [15–19]. The utilization of this material is also environmentally friendly since it helps in reducing the CO_2 emission to the atmosphere by the minimization of the Portland cement (PC) consumption.

The primary objective of this study was to investigate systematically the effectiveness of MK used at various replacement levels on the performance of the concretes in terms of compressive and splitting tensile strengths, water absorption, drying shrinkage, and pore structures. The normal and high strength concretes with and without MK were tested at different ages up to 120 days for aforementioned characteristics. Based on the test results, the influence of MK content, w/cm ratio, and age upon concrete properties were discussed.

2 Experimental procedures

2.1 Materials

Two different binding materials were used in the study, namely Portland cement and metakaolin (MK). Their chemical compositions and physical properties are presented in Table 1. Portland cement (CEM I 42.5R) was conforming to the Turkish standard TS EN 197-1 (which is mainly based on the European EN 197-1). The MK used in this study is a white powder with a Hunter L whiteness value greater than 90 (on a scale from “0-black” to “100-maximum whiteness”). It has a specific gravity of about 2.60, a specific surface area of 8600 m^2/kg, and an average particle size less than 2 μm. The fine aggregate was a mix of river sand and crushed sand whereas the coarse aggregate was a river gravel with a maximum particle size of 16 mm. Both aggregates were obtained from local sources. Properties of the fine and coarse aggregates are given in Table 2. A sulphonated naphthalene formaldehyde-based high range water-reducing admixture (HRWA) was used to give a consistent workability. The properties of the HRWA are shown in Table 3.

Table 1 Properties of Portland cement and metakaolin

Item	Portland cement	Metakaolin
SiO_2 (%)	19.73	51.8
Al_2O_3 (%)	5.09	45.8
Fe_2O_3 (%)	3.99	0.35
CaO (%)	62.86	0.01
MgO (%)	1.61	0.03
SO_3 (%)	2.62	–
Na_2O (%)	0.18	0.13
K_2O (%)	0.80	0.06
Cl^- (%)	0.01	–
Insoluble residue (%)	0.24	–
Loss on ignition (%)	1.90	0.91
Free lime (%)	0.57	–
Specific gravity (g/cm^3)	3.14	2.60
Setting time, Vicat needle Initial/Final (h-min)	2–46/3–44	–
Expansion, Le Chatelier apparatus (mm)	1	–
Specific surface area (m^2/kg)	327	8600
Color	Gray	White

Table 2 Properties of aggregates

Sieve size (mm)	Fine aggregate		Coarse aggregate	
	River sand	Crushed sand	No I	No II
16.0	100	100	100	100
8.0	100	100	31.5	1.9
4.0	86.6	95.4	1.0	1.1
2.0	56.7	63.3	0.5	1.0
1.0	37.7	39.1	0.5	0.9
0.50	25.7	28.4	0.5	0.9
0.25	6.7	16.4	0.4	0.8
Fineness modulus	2.87	2.57	5.66	5.93
Specific gravity	2.66	2.45	2.72	2.73
Absorption, %	0.55	0.92	0.45	0.42

Table 3 Properties of the high-range water-reducing admixture (HRWA)

SG[a]	State	Freezing point	Color	Chloride content	Nitrate content	Main component
1.22	Liquid	−4°C	Dark brown	None	None	Sulphonated naphthalene

[a] SG: Specific gravity

2.2 Details of mixture proportions and casting of specimens

Two series of concrete mixtures were designed at low (0.35) and high (0.55) water–cementitious materials (w/cm) ratios. The control mixtures included only Portland cement with a content of 450 and 350 kg/m^3 for the low and high w/cm ratios, respectively. To develop the MK-modified concrete mixtures, however, the cement was partially replaced with 10% and 20% MK (by weight) for both series. Thus, totally six different mixtures were designed in this study. Details of the mixtures are presented in Table 4. Grading of the aggregate mixture was kept constant for all concrete mixtures. The mixtures given in Table 4 were designed to have slump values of 140 ± 20 mm and 180 ± 20 mm for the low and high w/cm ratios, respectively for the ease of handling, placing, and consolidation. The high range water-reducing admixture was added at the time of mixing to attain the specified slump at each w/cm ratio. All concretes were mixed in accordance with ASTM C192 in a power-driven revolving pan mixer. Specimens cast from each mixture consisted of eighteen 100 × 100 × 100 mm cubes for the compressive strength testing, eighteen 100 × 200 mm cylinders for the determination of splitting tensile strength, nine 100 × 100 × 100 mm cubes for the water absorption test, and three 70 × 70 × 280 mm prisms to monitor the drying shrinkage and weight loss. All specimens were poured into the steel moulds in two layers, each of which being vibrated for a couple of seconds.

2.3 Curing of the specimens

Drying shrinkage specimens were cured at 20°C and 100% relative humidity and demoulded after 24 h. After that, the specimens were exposed to drying in a humidity cabinet at 23 ± 2°C and 50 ± 5% relative humidity, as per ASTM C157 [20] for about 60 days. All the other specimens were maintained under a plastic sheet for 24 h, then demoulded and water cured until required for testing.

2.4 Test methods

To evaluate the strength characteristics of the plain and MK concretes, the compression test was carried out on the cube specimens by means of a 3000 kN capacity testing machine according to ASTM C39 [21] while the splitting tensile strength was conducted on the cylinder specimens according to ASTM C496 [22]. The strength measurements of concrete were performed at the ages of 1, 3, 7, 28, 90, and 120 days. Three specimens were used for each testing age.

Table 4 Mixture proportioning of the concrete

Concrete series	w/cm ratio	MK (%)	Cement (kg/m^3)	MK (kg/m^3)	Water (kg/m^3)	Fine aggregate		Coarse aggregate		HRWA[a] (kg/m^3)
						River sand (kg/m^3)	Crushed sand (kg/m^3)	No I (kg/m^3)	No II (kg/m^3)	
1	0.35	0	450	0	158	724	233	611	241	7.9
	0.35	10	405	45	158	720	232	608	240	10.1
	0.35	20	360	90	158	717	231	605	239	12.4
2	0.55	0	350	0	193	726	234	612	242	3.5
	0.55	10	315	35	193	723	233	610	241	4.4
	0.55	20	280	70	193	721	232	608	240	6.1

[a] HRWA: High-range water-reducing admixture

The water absorption test was conducted on concrete cubes (100 × 100 × 100 mm). The absorption test was carried out according to ASTM C642 [23]. Three specimens from each mixture were tested at the ages of 28, 90, and 120 days and the average values were reported. For the determination of water absorption by total immersion, the dry mass (M_d) for each sample was recorded and then totally immersed in water at 20°C until they achieved a constant mass (M_s). M_s was taken as the saturated mass. This took up to 48 h. The absorption percentage was then calculated by the following equation:

$$WA\ (\%) = 100 \times \frac{(M_s - M_d)}{M_d} \quad (1)$$

Drying shrinkage measurements were conducted in accordance with ASTM C157 [20]. The length change was measured by means of a dial gage extensometer with a 200 mm gage length. Measurements were carried out every 24 h for the first 3 weeks and then 3 times a week. At the same time, weight loss measurements were also performed on the same specimens. Variations in the drying shrinkage strain and the weight loss were monitored during the 60-day drying period (at 23 ± 2°C and 50 ± 5% relative humidity) and the average of three prism specimens were used for each property.

The tests of pore structure of the concrete samples were conducted at the age of 120 days using a mercury intrusion porosimetry (MIP). More specifically, the porosity of the specimen as well as its pore size distribution was measured. For this, the samples without coarse aggregate for microstructure testing were separated from the concrete cube specimens after the compressive strength testing due to the limitation of sample size for the porosimeter. The samples were dried at about 105°C before mercury intrusion porosimeter test. The samples were subjected to a maximum pressure of up to 227 MPa. A cylindrical pore geometry, a constant contact angle of 140°, and a constant surface tension of 483 dynes/cm were assumed [24, 25]. The mercury intruded pore diameter d at a pressure of P was calculated by using the following Eq. [25]:

$$d = -(1/P)4\gamma \cos\theta \quad (2)$$

where d is the pore diameter (µm), P is the applied pressure (MPa), γ is the surface tension of mercury (dynes/cm), and θ is the contact angle (degree).

3 Results and discussions

3.1 Compressive and splitting tensile strengths

Figure 1 shows the effect of MK on the 1, 3, 7, 28, 90, and 120-day compressive strengths of the concretes having different replacement levels of MK and w/cm ratios. As seen from the figure, there is an evident increase in the compressive strength owing to the increase in the MK content. The compressive strength values varied between 12.9–76.8 MPa and 13.8–98.5 MPa for plain and MK modified concretes, respectively. It was observed that the early (1–7 days) and long (up to 120 days) term compressive strength of the concretes incorporated with MK was about 5–23% and 10–30% greater than that of the plain concretes, respectively, depending mainly on replacement level of MK and w/cm ratio. As it is seen, the incorporation of MK enhanced not only the early-age strength but also provided higher strength at later ages. These results are in aggrement with results reported by Khatib and Hibbert [26] and Bai et al. [27]. In the work of Khatib and Hibbert [26], MK appeared to be very useful on the compressive strength development and the use of MK at 20% replacement level increased the compressive strength of the concretes by as high as 38, 54, and 43% at 7, 28, and 90 days, respectively. Furthermore, Bai et al. [27] found that MK contributed significantly to early strength development of concretes. They observed that in the early stages of curing, mixtures with 5% of MK exceeded the control mixture strength by up to 92%.

When the level of the compressive strength is compared at 28 days onwards, the highest strengths of 50 and 75 MPa measured at 28 days were achieved at 10% replacement of cement by MK for the high and low w/cm ratios, respectively. When the replacement level further increased to 20%, the increase in the strength values lessened gradually. However, a marked difference in strength value between plain and MK-modified concretes was observed at later ages, particularly at 120 days. It was also evident from Fig. 1 that MK had a remarkable effect on strength development characteristic of concretes for both w/cm ratios. With respect to the 28-day compressive strength, the strength gain of plain concretes at 120 days was in the range of 12–20% while that of MK modified

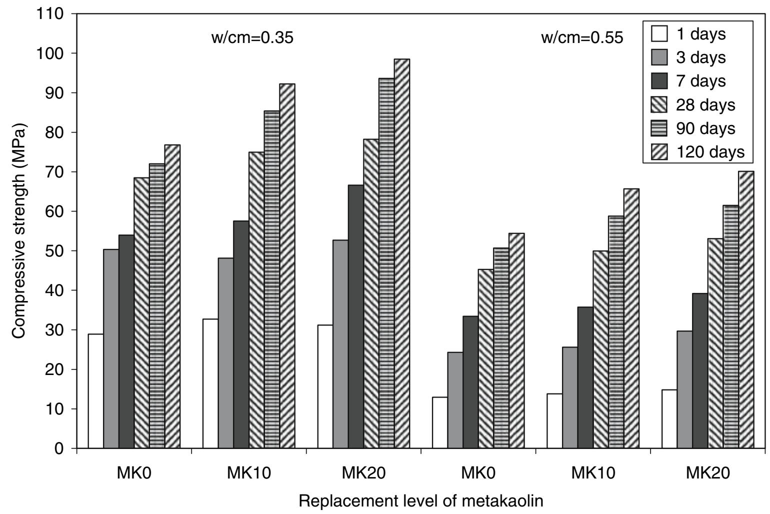

Fig. 1 Effect of metakaolin (MK) on the compressive strength development of concretes having different w/cm ratios

concretes ranged from 23 to 32%. In MK concretes, metakaolin contributes to the strength of concrete at later ages mainly by the fast pozzolanic reaction [12]. The addition of MK into the matrix improves the bond between the cement paste and the aggregate particles as well as increasing the density of the cement paste, which in turn significantly improves the compressive strength of the concretes. According to the literature, the main factors that affect the contribution of MK in the strength are (a) the filling effect, (b) the dilution effect, and (c) the pozzolanic reaction of MK with CH [28].

The strength development pattern for splitting tensile strength is similar to that of compressive strength, as can be seen in Fig. 2. The highest tensile strength value was obtained for the concrete with 20% MK for both w/cm ratios. In general, the splitting tensile strength increased with the increase in MK content at all ages. However, the increase in the splitting tensile strength was smaller compared to that obtained in the compressive strength. For example, at the high w/cm ratio, the compressive strengths of concretes containing 20% MK were approximately 14, 22, 17, 17, 21, and 30% higher than that of the plain concretes at 1, 3, 7, 28, 90, and 120 days, respectively. However, the companion strength increments in the splitting tensile test were about 6, 28, 7, 8, 18, and 22% at 1, 3, 7, 28, 90, and 120 days, respectively.

Neville [29] reported that the splitting tensile strength of concrete has a close relationship with compressive strength. However the ratio of the two strengths depends on the general level of the strength of concrete. In other words, as the compressive strength increases, the tensile strength also increases but at a decreasing rate. There are several empirical formulations for evaluating splitting tensile strength f_{sp} and compressive strength f'_c, and most researchers achieved the expression of the type:

$$f_{sp} = k(f'_c)^n \tag{3}$$

where f_{sp} and f'_c are splitting tensile and compressive strengths measured on 150×300-mm cylinders at 28 days (MPa), respectively, k and n are coefficient that can be obtained from the regression analysis. The n value is generally within the range of 0.50–0.75. The existing expressions for estimating splitting tensile strength, as suggested by ACI [30], CEB-FIB [31], and TS 500 [32], are given below, respectively.

$$f_{sp} = 0.59(f'_c)^{0.5} \tag{4}$$

$$f_{sp} = 0.301(f'_c)^{0.67} \tag{5}$$

$$f_{sp} = 0.35(f'_c)^{0.5} \tag{6}$$

Figure 3 shows the observed relationship between the splitting tensile and compressive strengths of the concretes tested at 28 days. For comparison, the Eqs. 4 through 6 are also included in the diagram. To make use of them, 100-mm cube compressive strengths (used in the current study) were converted

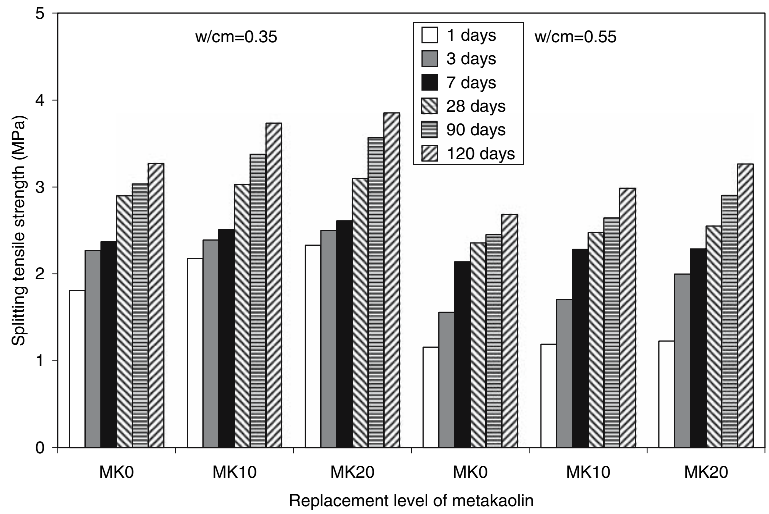

Fig. 2 Effect of metakaolin (MK) on the splitting tensile strength development of concretes having different w/cm ratios

to 150 × 300-mm cylinder strengths by multiplying by a factor of 0.83, assuming that the conversion factors from a 100-mm cube to 100 × 200-mm cylinder and from a 100 × 200-mm cylinder to 150 × 300-mm cylinder are 0.91, respectively [33]. From Fig. 3, it was observed that there was a considerably high relationship between the splitting tensile and compressive strengths of the concrete so that a regression analysis provided correlation coefficient (R^2) of 0.98. Within the strength range of this study, both ACI and CEB-FIB models appeared to be well close to each other but provided relatively higher predictions. However, TS 500 model provided lower values compared to the experimental data. Furthermore, the proposed equation of this study fell within the range of TS 500 and ACI and/or CEM-FIB models.

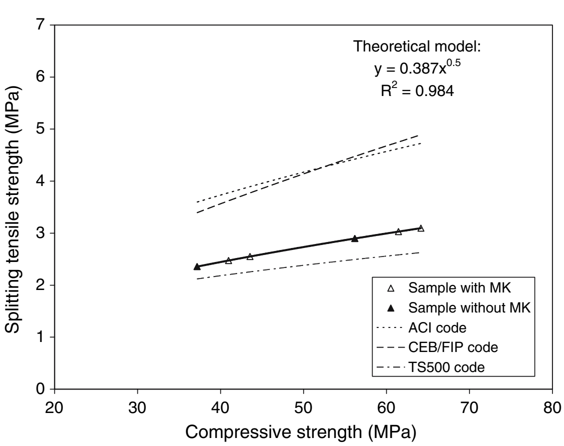

Fig. 3 Relationship between compressive and splitting tensile strengths

3.2 Water absorption

Figure 4 shows the variation in water absorption of the concrete with different replacement levels of MK, w/cm ratio, and testing age. It was observed that the water absorption characteristics of the concrete specimens decreased with increasing MK content, irrespective of w/cm ratio and testing age. As can be expected, the water absorption of both the plain and especially MK concretes have a decreasing tendency with the increase in the curing period. At 28 days of curing, the beneficial effect of MK in reducing the water absorption was noticeable due to the filling effect of ultrafine MK as well as its pozzolanic reaction. Wild et al. [16] reported that in the presence of MK, the filling effect is immediate, the acceleration of OPC hydration has its major within the first 24 h, and the level of pozzolanic reaction is considerably high within first 7–14 days for all MK levels between 5 and 30%. However, the differences in the water absorption characteristics of the plain and MK concretes became more significant at later ages (90 and 120 days) and were remarkably lower for MK concrete compared to the plain concrete, especially at high w/cm ratio. Furthermore, the reduction in the water absorption with increasing the test age was about 12 and 21% for the plain concretes of the low and high w/cm ratios, respectively, while it was about

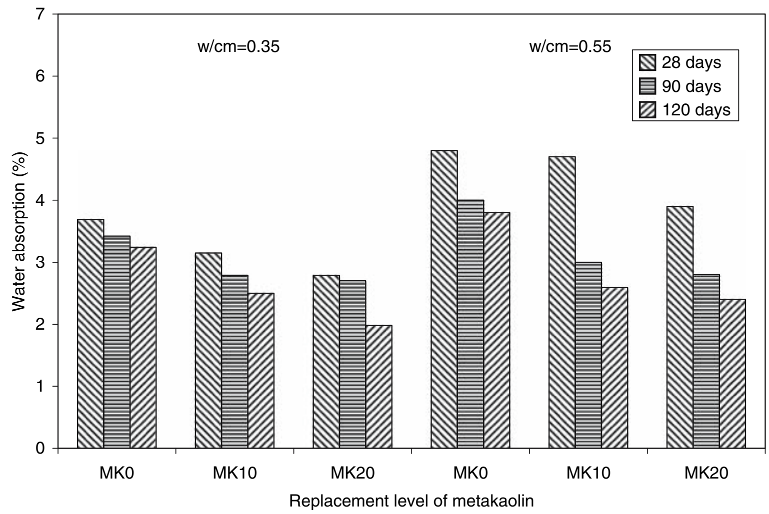

Fig. 4 Effect of metakaolin (MK) on the 28, 90, and 180 day water absorptions of concretes having different w/cm ratios

20–29% and 38–45% for the MK concretes, respectively. This reduction in the water absorption with age indicates superior performance of the MK blended cement concretes over the conventional concrete. This may be explained by the pozzolanic activity of MK during the prolong curing. It is well known that the pozzolanic reactions contribute to the refinement of the binder capillary porosity, with its direct consequences on the improvement of the durability characteristics of the concrete [13].

3.3 Drying shrinkage and weight loss

Drying shrinkage tests alone cannot offer sufficient information on the behavior of concrete structures since virtually all concretes are restrained in some way, either by reinforcement or by the structure. However, drying shrinkage tests can provide necessary information on how the drying shrinkage stresses develop [34].

The strain developments versus time of the drying shrinkage specimens at two w/cm ratios are presented in Fig. 5. It was observed from the figure that the drying shrinkage of the concretes having 0.35 and 0.55 w/cm had decreasing tendency with little fluctuations with the drying period. At early test ages, the shrinkage of all the specimens exhibited a very steep development. The difference between amount of the drying shrinkage of plain and MK modified concretes was small, especially for the low w/cm ratio. But after about 2 weeks the difference became much

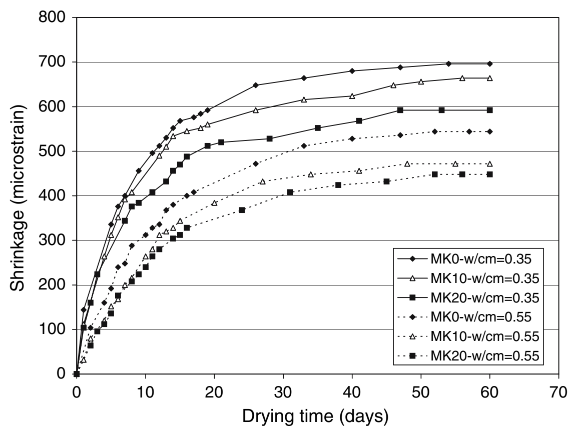

Fig. 5 Drying shrinkage vs. drying time graphs of plain and MK concretes having w/cm ratios of 0.35 and 0.55

clear and the shrinkage of concrete with MK decreased with increasing replacement levels of MK. When the shrinkage strain at 60 days of drying was considered, the MK concrete had remarkably lower shrinkage strain in comparison to the plain concrete. It was pointed out that the higher the replacement of MK, the higher the reduction in the shrinkage, irrespective of w/cm ratio. For example, at low w/cm ratio, the drying shrinkage of the concrete mixtures incorporated with 10 and 20% MK were approximately 5 and 15% less than that of the plain concrete, respectively. However, at high w/cm ratio, the effect of MK is more pronounced such that the concretes with 10 and 20% MK had about 13 and 18% lower shrinkage than the plain concrete. Similar observation was found by Brooks and Megat-Johari [6] in that the total shrinkage measured from 24 h was reduced by the use of MK while drying shrinkage was significantly less for the MK concretes than for the control concrete. They reported that the influence of MK was seen to reduce the drying shrinkage of ordinary portland cement concrete by about 50%. Furthermore, the test results presented herein agree with the findings of the study conducted by Al-Khaja [35] and Jainyong and Yan [36] for the effect of the ultrafine mineral admixtures on the shrinkage and creep of concretes. In the study of Al-Khaja [35], it was concluded that the shrinkage and creep of plain concrete were considerably or moderately reduced with the incorporation of silica fume, showing a 1-month reduction in strain of 34.9 and 18.5% for shrinkage and creep, respectively, which led to a reduction in the total deformation of 20.8%. Jainyong and Yan [36] have also showed that ultrafine ground granulated blast-furnace slag and silica fume can substantially promote hydration of cement and increase in the amount of AFt crystal hydrates and C–S–H gel hydrates in cement paste, which offers a hardened concrete with a stronger structure and higher resistance to deformation caused by applied forced. Moreover, these two binders may fill small pores and voids harmful to the structure of concrete. That might be the mechanism of reducing effect of ultrafine mineral admixtures (i.e. GGBS, SF) on creep and drying shrinkage of concrete.

Test results on drying shrinkage in Fig. 5 also indicated that the concretes with low w/cm ratio had a tendency of higher shrinkage than those with high w/cm ratio. At the end of the drying period, indeed, the concrete mixture containing 20% MK had a shrinkage strain of 592 and 448 microstrain at low and high w/cm ratios, respectively. However, the shrinkage data from the earlier investigations indicated that the effect of lower w/cm ratio was to reduce drying shrinkage of concrete as a result of enhancement in strength and refinement in microstructure [37]. One possible explanation of such behavior observed in this study may be that self-desiccation and autogenous shrinkage could have contributed to this higher drying shrinkage of concretes with lower w/cm ratio.

The relationship between the shrinkage after 60 days and the replacement levels of MK can be seen in Fig. 6. It was observed that there was an

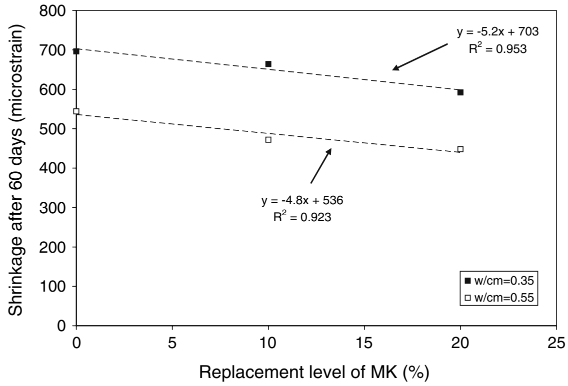

Fig. 6 Relationship between shrinkage after 60 days and replacement level of MK

inverse type of relationship, indicating that the drying shrinkage of the concrete for both w/cm ratios decreased with increasing MK content with fairly good correlation coefficient. It was also noticed that MK had a shrinkage-reducing or compensating properties. It might be used as an additive in concrete application where high shrinkage should be avoided or undesirable.

The reason in the reduction of shrinkage owing to the use of MK is surely the decrease in shrinkage rate. The shrinkage rates in Fig. 5 have been calculated and presented in Fig. 7. The critical comparison of the curves given in Fig. 7 for the plain and MK modified concretes indicated that the average shrinkage rates of MK concretes were lower than the plain concretes during the 60-day drying period, irrespective of replacement level and w/cm ratio. It is evident from the figure that the higher MK content, the

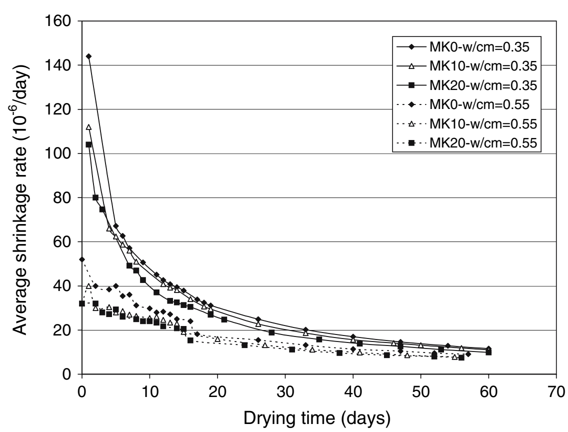

Fig. 7 Average shrinkage rate vs. drying time graphs of plain and MK concretes having w/cm ratios of 0.35 and 0.55

slower the shrinkage rate of concretes, especially for the high w/cm ratio. It was also noted that both the plain and the MK concretes with low w/cm ratio showed a somewhat faster development of shrinkage than those with high w/cm ratio.

The results of weight loss due to drying for different concrete mixtures are also shown in Fig. 8. It was clear from the figure that the concrete mixes with higher unit water contents showed higher weight loss. Similar to the drying shrinkage test results, inclusion of MK to the concrete mixes decreased considerably the weight loss for both w/cm ratios. During 60 day drying period, the difference of weight loss between plain and MK blended cement concretes were more distinguishable. This is true for all drying time and the difference increases with increasing the drying time. It was observed after 60 day drying that the MK concretes exhibited a weight loss up to 48% less compared to plain concretes, depending mainly on replacement level of MK and w/cm ratio. It seems that the rate of weight loss for MK concretes slows down earlier than that of the plain concrete. This may be because there is less evaporable water available in the mixes as hydration and pozzolanic reactions used up significant amount of free water. Overall, the foregoing trends lead to confirm that the MK concretes have a lower porosity and finer pore structure which encourages loss of water by self-desiccation rather than by diffusion to the outside environment [6, 34].

In Fig. 9, the drying shrinkage is plotted against the corresponding weight loss for all mixtures investigated in order to obtain the relationship between them. For all mixtures, the shrinkage was approximately proportional to the loss of water. However, in the case of the mixtures with a w/cm ratio of 0.55, it was observed that the water loss during 60 day drying stage was somewhat high. Therefore, the slope of the curves for the high w/cm mixtures deviated considerably as compared to those for the low w/cm mixtures. This may be explained that the water coming from the large capillary pores within the high w/cm mixtures results in greater weight loss [29]. Bissonnette et al. [38] also studied the relationship between the shrinkage and weight loss for the paste, mortar, and concrete mixtures. They observed that irrespective of the mixture type, the shrinkage is almost proportional to the loss of water. Moreover, it was found that the water–cement ratio was very effective on this correlation.

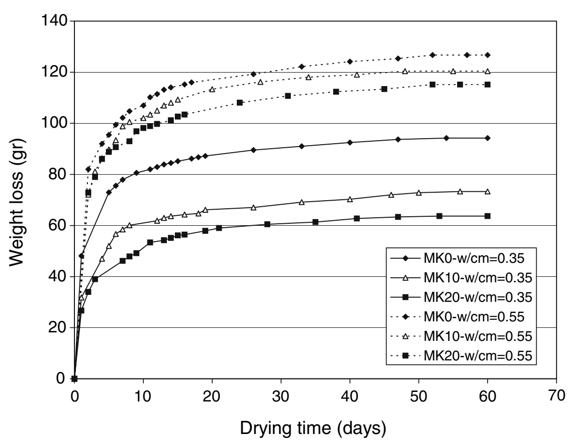

Fig. 8 Weight loss vs. drying time graphs of plain and MK concretes having w/cm ratios of 0.35 and 0.55

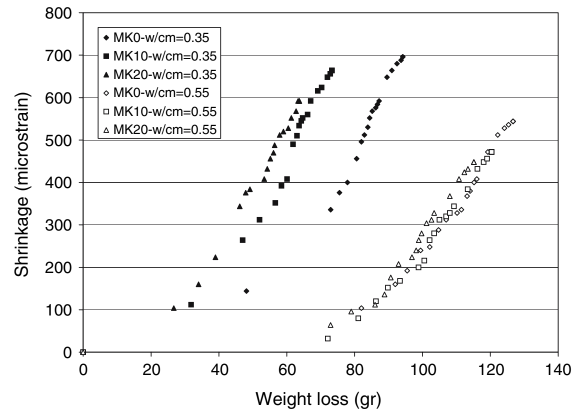

Fig. 9 Relationship between shrinkage and weight loss

3.4 Effect of MK on the pore structure of the concrete

The results of MIP are given in Table 5 and Fig. 10. It can be seen from Fig. 10 that, for similar pore sizes, the pore volume of the samples without MK is higher than those with MK for both w/cm ratios. The pore size distribution curves indicated the marked influence that MK additions had in skewing pore size distribution to the finer sizes compared with the samples without MK. It was also observed from Table 5 that the total porosity decreased substantially with increasing replacement level of MK. The magnitude of this reduction varies between 22

Table 5 Results of mercury intrusion porosimetry test for the low and high w/cm ratio samples tested at 120 days

w/cm ratio	MK (%)	Porosity (%)	Mean pore diameter (μm)	Median pore diameter (μm)
0.35	0	10.7	0.286	0.098
0.35	10	7.3	0.139	0.058
0.35	20	5.5	0.088	0.037
0.55	0	14.6	0.614	0.202
0.55	10	11.4	0.320	0.129
0.55	20	10.2	0.283	0.093

and 49%, depending mainly on w/cm ratio and replacement level of MK. It was also noted that there was a considerable reduction in the mean (or median) pore diameter of the samples due to the inclusion of MK. The effect was particularly beneficial at 20% MK content, where the lowest porosity and pore diameter were achieved.

It is essential to note that MK is a relatively new mineral admixture used in the cement concrete products. MK is highly reactive pozzolana and its reaction mechanism can be divided into physical and chemical aspects. The physical effect is that the ultra-fine particles fill the voids in cement, which makes the microstructure of matrix denser. The chemical effect is the reaction of MK with the cement hydrates. The reaction of MK with cement hydrates is faster since MK has a loose micro-structure after heat activated at a temperature of 800 °C (the chemically bonded water in kaolin is driven out at a higher temperature, and water

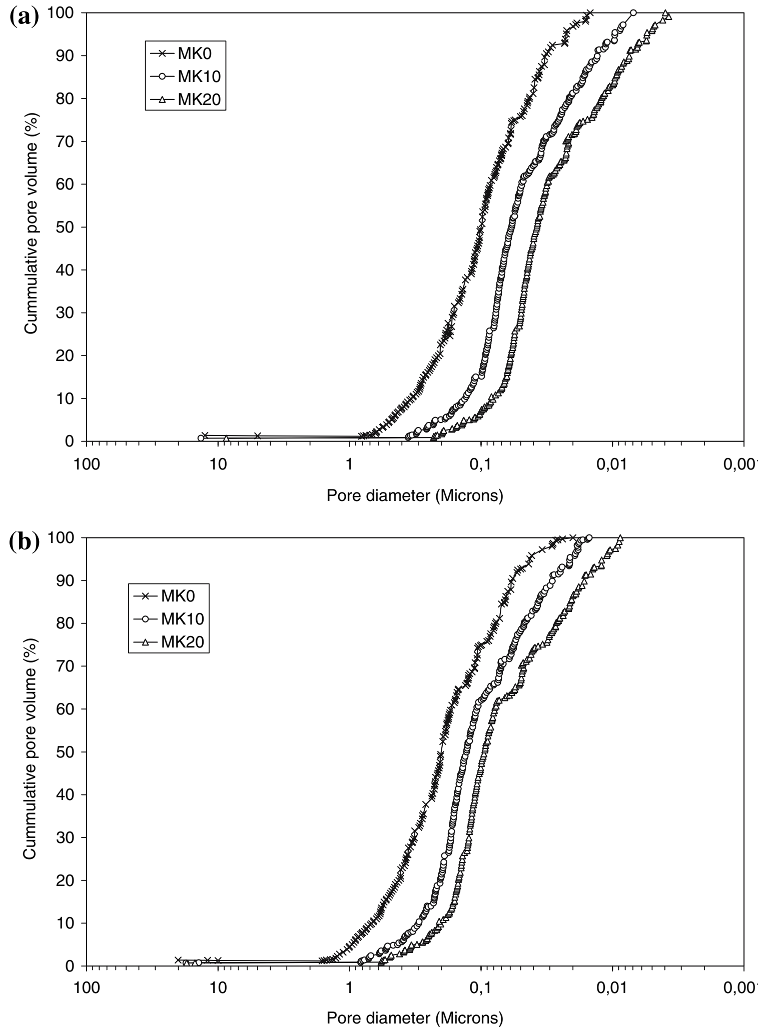

Fig. 10 Effect of MK addition on the pore-size distribution of the samples tested at the age of 120 days (**a**) w/cm ratio: 0.35; and (**b**) w/cm ratio: 0.55

molecules enter MK more easily when met with water again). During the chemical reaction, the precipitated calcium hydroxide ($Ca(OH)_2$) is transformed into secondary C–S–H (C = CaO; S = SiO_2; and H = H_2O) gel, resulting in refinement of the pore structure (transformation of coarser pores into finer pores). Owing to the net reduction in $Ca(OH)_2$ content in the hydrated matrix due to pozzolanic reaction, the volume of continuous capillary pores is proportionally decreased; the higher the $Ca(OH)_2$ content in the hydrated matrix, the higher the volume of continuous pores [11, 39].

Based on the experimental results, the relationship between the porosity measured at 120 days and the corresponding 120 day compressive strength of the concrete is also examined. In the literatures, it has been shown that the porosity is not only the parameter influencing the strength of concrete, but many other factors such as pore size distribution, microcracks, interface, and so on are also important factors that determine mechanical properties of cementitious materials [25, 40, 41]. However, porosity, which can be semiemprically and concisely used to describe the relationship between strength and microstructure of porous materials, is still being studied [42–45]. To observe the relationship between the porosity and compressive strength of the sample containing MK, the plot of the porosity versus the corresponding compressive strength, as shown in Fig. 11, is used. Additionally, the variation in the strength with the porosity from this experimental study and several other relations for predicting the compressive strength from the porosity forwarded by the other researchers is also given in Fig. 11 for the comparison purposes. It was evident from the figure that the model proposed by Poon et al. [42] remarkably overpredicted the compressive strength of the mortar containing MK while the Balshin model proposed by Bouguerra et al. [44] greatly underestimated the compressive strength. However, the Ryshkewitch model [44] and the model proposed by Chan et al. [45] provided relatively more reasonable prediction of the experimental data.

In order to analyze the interdependence between the porosity and water absorption measured in the present investigation, the correlation between the porosity and the corresponding 120 day water absorption of the concrete specimens with and without MK was also studied. The plot is illustrated in Fig. 12. It was observed that the relationship between the two variables was almost exponential with a relatively high correlation coefficient (R^2) of 0.76. As clearly seen from the figure, the water absorption increased exponentially with increasing porosity. On the other hand, the higher porosity mixtures absorbed significantly greater amount of water. From these results, it could be concluded that the mixtures with higher absorption are potentially less durable than those with lower absorption owing to their greater porosity.

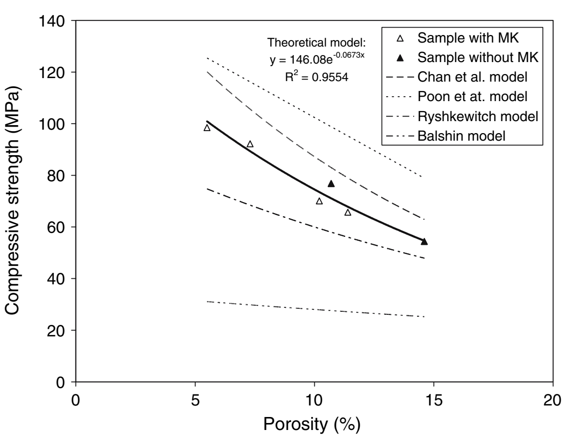

Fig. 11 Relationship between porosity and compressive strength

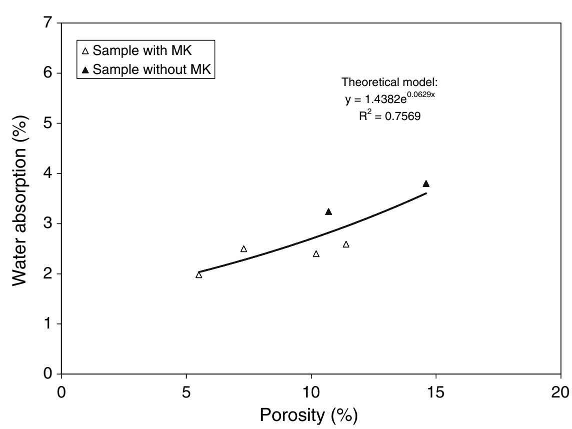

Fig. 12 Relationship between porosity and water absorption

4 Conclusions

The effectiveness of using MK on the performance properties of concretes were investigated in this study. From the above experimental results, the following conclusions are drawn:

- Concretes with high strength and low shrinkage can be made by using Portland cement blended with ultrafine MK.
- The study showed that the MK provided a significant increase in both the compressive and splitting tensile strengths when used as a modifier in concrete with varying amounts. When MK replaces cement, its positive effect on the concrete strength generally starts at early ages and also noticeable increase in the strength was observed at later ages. It was observed that the strength of concretes incorporated with MK was up to 30% greater than that of the plain concretes, depending mainly on replacement level of MK, w/cm ratio, and testing age.
- For all replacement levels, the MK modified concretes exhibited remarkably lower shrinkage in comparison to the plain concretes, irrespective of w/cm ratio. It is known that the drying shrinkage is influenced by many factors. The results demonstrated that the w/cm ratio was the dominating factor because both the plain and especially the MK modified concretes with high w/cm exhibited relatively low drying shrinkage.
- With regard to the rate of drying shrinkage, it is evident that both plain and MK concretes with low w/cm ratio showed a somewhat faster development of shrinkage than those with high w/cm ratio. However, the drying shrinkage rates of the concretes had a decreasing tendency with increased drying time, particularly for the MK concretes.
- The inclusion of MK as a partial cement-replacement material provided an excellent improvement in the pore structure of concrete. Irrespective of w/cm ratio, the pore size distribution was shifted to the smaller pore size range due to the incorporation of MK. The total porosity decreased substantially with increasing replacement level of MK. The magnitude of this reduction ranged from 22 to 49%, depending mainly on w/cm ratio and replacement level of MK. Moreover, there was a considerable reduction in the mean (or median) pore diameter of the samples due to the inclusion of MK. The effect was particularly beneficial at 20% MK content, where the lowest porosity and the pore diameter were achieved.

Acknowledgments The authors would like to thank to Mr. Vakıf Kiriş for his invaluable assistance during the laboratory phase of the study.

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