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Property improvement of Portland cement by incorporating with metakaolin and slag

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Abstract

The physical and mechanical properties of Portland cement (PC) containing metakaolin (MK) or combination of MK and slag and the compatibility between such materials and superplasticizers were investigated in present study. After MK was incorporated into PC, the compressive strength of the blended cement was enhanced. However, the fluidity of MK blended cement became poorer than that of PC at the same dosage of superplasticizer and the same water/binder ratio. When both MK (10%) and ultra-fine slag (20% or 30%) were incorporated into PC together, not only the compressive strength of the blended cement was increased, but also the fluidity of the blended cement paste was improved comparing to MK blended cement. This indicates that ultra-fine slag can improve the physical and mechanical properties of MK blended cement. The physical and chemical effects of two mineral admixtures were also discussed.

Keywords: Workability; X-ray diffraction; Admixture; Metakaolin; Blended cement

1. Introduction

Metakaolin (MK) is a thermally activated aluminosilicate material with high pozzolanic activity comparable to or exceeded the activity of fume silica (SF) [1]. MK is quite useful in improving concrete quality, such as enhancing strength, shortening setting time [2] (whether this characteristic is advantageous or disadvantageous depends on the application of cements), decreasing autogenous shrinkage [3], controlling alkali aggregate reaction [4], reducing risk of chloride-induced corrosion of embedded steel [5], controlling hydrate transformation of high-alumina cement [6], and improving the durability of concrete [1,7]. Therefore, MK is a promising supplementary material for manufacturing high-performance concrete (HPC).

In order to increase the fluidity of fresh concrete for pumping, increase strength and prolong durability of hardened concrete, a small quantity of superplasticizers are often added into concrete mixture. As it is well known, there is often a compatibility problem between superplasticizers and cements. The compatibility may be characterized by the fluidity of cement paste and its loss with time [8]. Generally, the fluidity of cement paste increases with the increase in the dosage of superplasticizer. When the dosage of superplasticizer reaches a certain amount, the fluidity of the paste does not increase significantly. The threshold dosage of the superplasticizer is called the saturation point [9]. The better the compatibility, the lower the dosage of superplasticizer needed, the higher the fluidity of cement paste, and the lower the loss of fluidity with time. It is therefore desirable to minimize the amount of superplasticizer used while enhancing the fluidity of slurry and strength of hardened concrete.

In the present study, the authors measured the compatibility between cement containing MK and superplasticizers, and used ultra-fine slag to improve it. The results show that ultra-fine slag not only improved the compatibility between superplasticizer and cement, which is incorporated with MK, but also increased the compressive strength (at the same water/binder ratio). Perhaps the method provides a new route for manufacturing HPC in an easy way. The mechanism is mainly the compounding

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Table 1
Chemical analysis of raw materials (%) by weight

Oxides	Portland cement	MK	Ultra-fine slag
SiO_2	20.12	49.55	32.71
Al_2O_3	5.34	40.25	15.75
Fe_2O_3	2.46	2.5	1.38
CaO	60.26	2.71	42.11
MgO	2.08	1.02	6.83
Na_2O	0.45	0.11	0.23
K_2O	0.32	0.24	0.26
TiO_2	0.34	0.75	0.05
SO_3	3.23	0.99	0.28
L.O.I	1.42	2.04	0.32
Free CaO	2.01	–	–
Bogue potential compound			
C_3S	49.36		
C_2S	20.76		
C_3A	9.70		
C_4AF	7.48		

effect of MK and fine slag in chemical and physical aspects.

2. Materials and experiment method

2.1. Materials

The materials used in this study were Portland cement (PC), which was obtained from a vertical kiln cement factory, MK (kaolin material was obtained from a ceramic factory, ground in a Bond test mill and thermally activated at 800 °C in our laboratory), and ultra-fine granulated blast furnace slag (from Jinan Steel). The chemical composition, average particle size (fineness), and binder compositions are given in Tables 1–3, respectively. Two superplasticizers of sulphonated, naphthalene formaldehyde condensate, NF-2 and FDN-A, were utilized in this study. NF-2 was a dark brown solution containing 30% solids, the other superplasticizer, FDN-A, was a bright brown powder.

2.2. The compatibility test method

According to Kantro [9], the compatibility of cement–superplasticizer can be measured by the fluidity (degree of spread) of cement paste and the loss of fluidity with time. The fluidity test results of cement paste (fluidity at saturation point dosage of superplasticizer, fluidity, and its loss with time) were related to the slump loss of concrete. The fluidity of cement paste was measured using mini-slurry cone test [9,10]. In this study, the mini-slurry cone has an upper inner diameter of 36 mm, a bottom inner diameter of 64 mm, and a height of 60 mm.

Table 2
Fineness of raw materials

Fineness	PC	MK	Ultra-fine slag
Passing, 80 μm (%)	94.5	96.8	99.7
Specific surface, Blanine (m^2/kg)	320	310	630
Median grain size (μm)	19.63	20.96	5.70

Table 3
Mixture proportions

Mixture no.	PC content (%)	MK content (%)	Slag content (%)
PO	100	0	0
M1	90	10	0
S2	70	10	20
S3	60	10	30

The cement paste was mixed in a paste mixer (the mixer was in accordance with the Chinese Standard GB1346 for the setting time test of cement paste) and the water-to-binder ratio was held constant at 0.28. The mini-slump cone was placed on a glass plate, and was filled with cement paste. The upper surface of the paste was finished with a trowel and the cone was lifted vertically. The cement paste slumped on the glass plate, and the average spread diameter of cement pastes—fluidity (F) was measured with a ruler. The fluidity (spread degree) of cement paste was measured immediately after completing the mixing approximately 5 min after adding water (F5), after 30 min rest (F30), and after 60 min (F60).

2.3. Test method of physical and mechanical properties of cements

The physical and chemical properties of the cements were determined in accordance with Chinese Standard GB1346 and GB177, respectively. The water-to-binder ratio was 0.44, and the compressive strength of cement mortar was determined at 3, 7, and 28 days. The cement-to-sand ratio was 1:2.5. The mortar specimens were formed in $40 \times 40 \times 160$ mm prism triple-gang molds. The cement paste samples for X-ray diffraction (XRD) analysis were prepared by a water/binder of 0.28.

3. Results and discussion

3.1. Fluidity results

The fluidity test results for cements and the superplasticizer NF-2 are given in Fig. 1, and the fluidity test results for cements and the superplsticizer FDN-A are given in Fig. 2.

Fig. 1 shows that the fluidity of cement paste increases with the increase in the dosage of NF-2 superplasticizer. The saturation point of NF-2 for the 5-min fluidity (F5) of cement PO, M1, S2, and S3 are about 1.2%, 1.6%, 1.4%, and 1.4%, respectively, At these points, S3 and S2 had the highest fluidity (the fluidity of cement S2 and S3 was similar), and M1 had the lowest fluidity. With the progress of hydration of cement, the fluidity of cement paste will lose some after it was mixed for a while. In the present test, the fluidity after 30 and 60 min (F30 and F60) was determined.

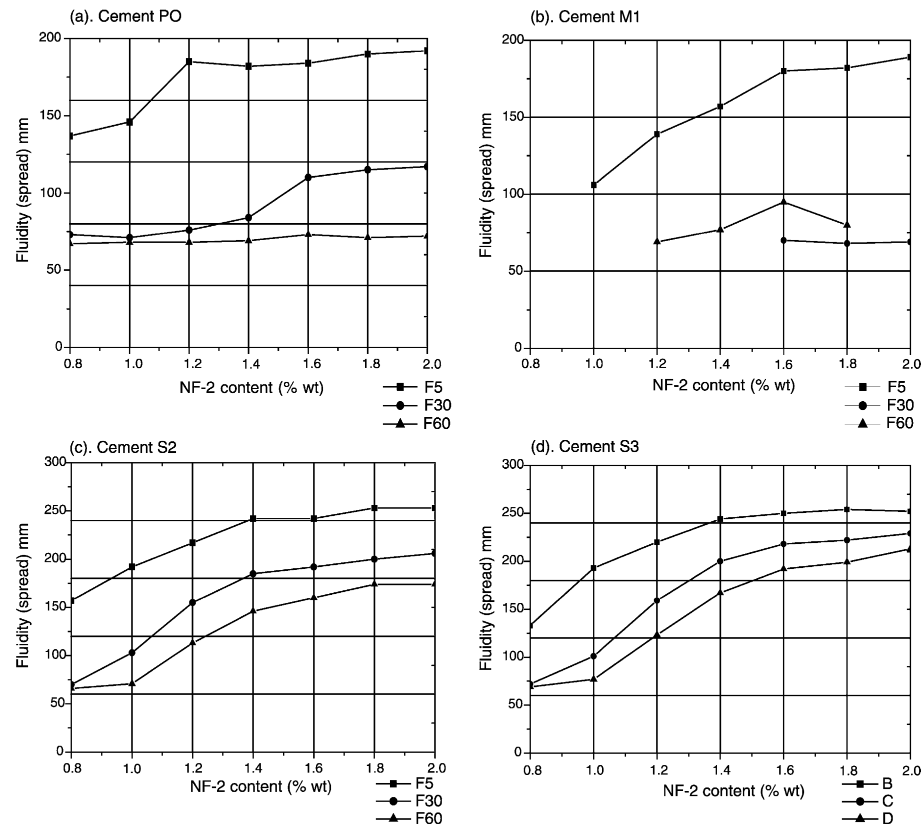

Fig. 1. Fluidity of cement paste mixed with superplasticizer NF-2.

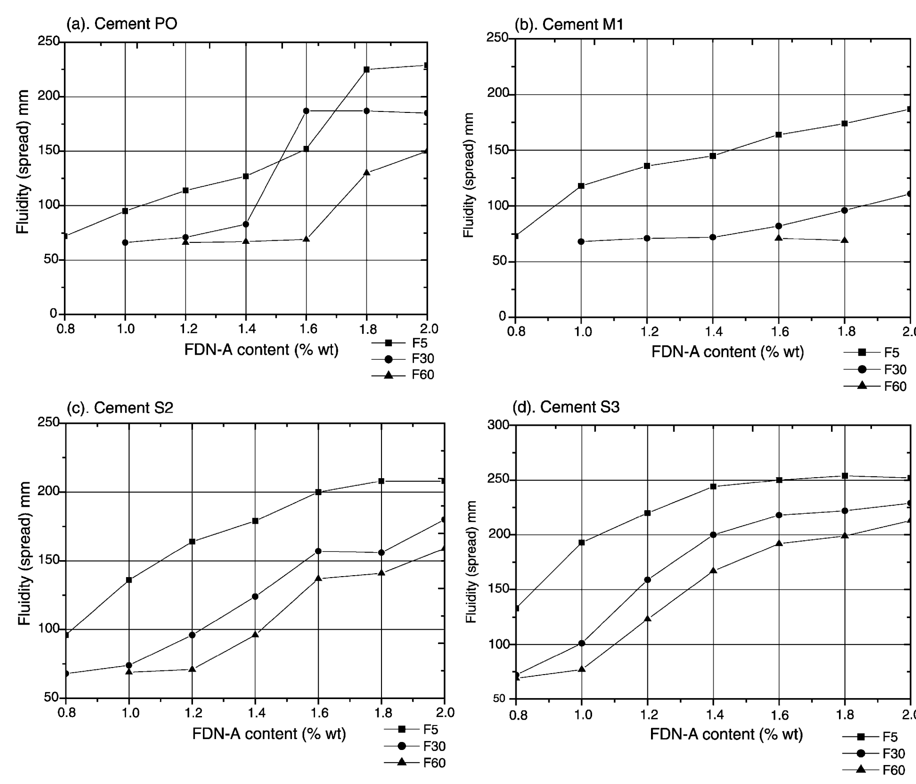

Fig. 2. Fluidity of cement paste mixed with superplasticizer FDN-A.

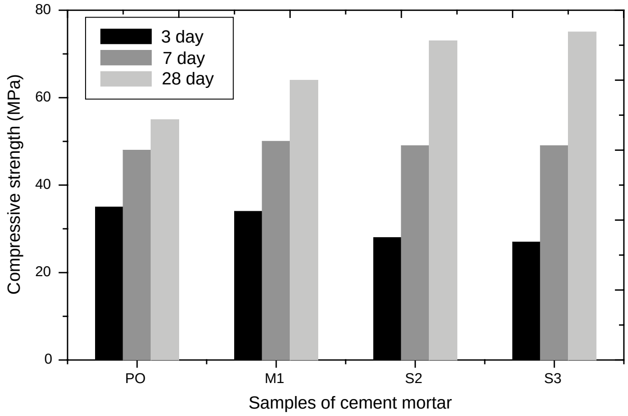

Fig. 3. The compressive strength of cement mortars.

When MK was substituted for part of the cement, the fluidity of MK blended cement (M1) paste was smaller than that of PC paste at the same dosage of NF-2. We can say that the fluidity of MK blended cement paste at the same superplasticizer dosage becomes poorer. After the MK blended cement was modified by adding the ultra-fine slag, the fluidity of MK-slag blended cement paste increased. Among the four cements, S2 and S3 had the best fluidity, and M1 cement had the poorest fluidity.

Fig. 3 indicates that the fluidity of cements paste also increases with the increase of the dosage of FDN-A. The saturation point of superplasticizer for the 5-min fluidity (F5) of cement PO, S2, and S3 are about 1.8%, 1.6%, and 1.4%, respectively. To the cement M1, it appears that there is no saturation point in the test range. The fluidity of cement M1 increases with the addition of FDN-A. The saturation point of cement M1 will be identified by more tests in the future. For the F30 and F60, the fluidity of cement paste decreasing trend was similar to that of F5. From Figs. 1 and 2, we can observe that the changing trend of fluidity of four cements with FDN-A was similar to that of cements with NF-2.

According to previous research [11], many factors influence the compatibility of cement and superplasticizers, such as the content of C_3A and C_4AF phase in PC clinker, total alkali amount, cement fineness, the type and the amount of calcium sulphate. When PC was given, however, the type and mixing amount of mineral admixtures will play an important role on the compatibility.

MK is a soft material produced by decomposition of kaolin at a temperature of 650–900 °C, it tends to absorb water to form kaolin [4]. MK mainly contains amorphous silicon dioxide and aluminum oxide. After it was added in PC, it prompts the hydration of cement and shortens the setting time. However, the MK blended cement needs more water to achieve the same workability. Therefore, MK degraded the fluidity under the condition of adding the same dosage of superplasticizer.

Granulated blast furnace slag is a latent hydraulic material. When it was incorporated with PC, the reaction of slag must be initiated by calcium hydroxide released from PC hydration. Therefore, it defers the hydration of the blended cement, and prolongs the setting time of cement. Also, the ultra-fine slag particles fill the space among cement particles and make the particle size distribution better than before. The fluidity of cement paste can be improved by adding sufficient slag due to these two aspects.

3.2. Physical and mechanical properties of cements

3.2.1. Physical properties

The water requirement and setting times of cements investigated are summarized in Table 4. For all cements, the water required to achieve the standard consistency of cement paste was in the range of 26.3–29.1%. PC (PO) has the lowest water requirement, but MK blended cement M1 has the highest water requirement. After the slag was mixed with MK blended cement, the water requirement of cement S2 and S3 was reduced, but it was still higher than that of PC.

The initial and final setting times of the cement incorporating 10% MK were shorter than those of PC, while the initial and final times of S2 and S3 cements were longer than those of PC. MK contains actively amorphous silicon dioxide and aluminum oxide, they can react with hydrates of cement to form C-S-H gel and calcium sulphoaluminate (ettriginte, AFt), then form the framework of cement paste in the early hydration period. Hence, this process shortened the setting time and increased the water requirement of cement. However, slag reacted very little in the early period of cement hydration because its hydration depends on the hydration of PC clinker. Thus, it can retard the formation of paste framework by slow hydration.

3.2.2. Mechanical properties

The compressive strength of cement mortar is presented in Fig. 3. It shows that MK has a function in enhancing the strength, and the 28-day compressive strength of cement mortar M1 is about 8 MPa higher than that of PC mortar. According to other investigations, concrete has the best compressive strength when PC was replaced by 10 wt.% MK [1,2,7]. When PC was mixed with MK and ultra-fine slag at the same time, the 3-day compressive strength of S2 and S3 cement mortars is lower than that of PC and cement M1. However, after 7 days, the strengths of S2 and S3 were higher than that of the M1 and PC mortars. After 28 days,

Table 4
Physical properties of cement paste

Mixture no.	Water required for standard consistency (%)	Setting time (H/M)	
		Initial	Final
PO	26.3	1:36	3:27
M1	29.1	1:11	2:12
S2	28.4	1:55	4:34
S3	28.0	2:19	6:15

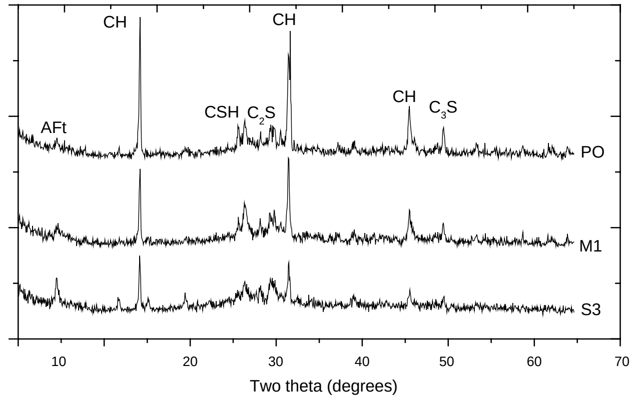

Fig. 4. XRD for cement paste hydrated 28 days.

the strength of S2 and S3 had greatly surpassed that of the two former cement mortars.

Both MK and slag belong to active mineral admixtures, they can improve the microstructure and mechanical properties of blended cement [1,2,11,12]. When both of them were utilized in cement at the same time, the 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 cement paste denser. The chemical effect is the reaction of MK and slag with the cement hydrates. The reaction of MK with cement hydrates is faster than that of the slag, because MK has a loose microstructure after heat activated at a temperature of 800 °C (the chemically bonded water in kaolin was driven out at a higher temperature, and water molecules enter MK more easily when met with water again). However, slag has a very dense structure hydration. When mixed with PC, slag is activated by the CH and alkali which the latter produces. The slag reacts considerably more slowly than the alite, and strength development is therefore slower to an extent that increases with the proportion of slag. Generally, the strengthening effect of slag to the compressive strength of PC concrete will be seen after the concrete was cast for a long time, for example, after 91 days [13]. If the slag was ground into ultra-fine, it can improve the strength of blended cement in 28 days age [12]. Our results indicate that the reaction among MK, slag, and cement improves the strength of cement mortars to a large extent in the first 28 days. This phenomenon is a synergistic effect of mineral admixtures, also called compounding effect [11]. We can analyse this phenomenon by combining with XRD patterns of cement paste.

Fig. 4 shows the XRD patterns of the cement PO, M1, and S3 hydrated after 28 days. The main $Ca(OH)_2$ (CH) peaks in cement PO is the highest among the three cement paste, cement S3 has the lowest peaks of CH, and the CH peaks in M1 is medium. This was caused by the reaction of CH with MK and ultra-fine slag. CH cannot directly produce strength to the cement paste, only after it was translated to C-S-H gel by pozzolanic reaction with active minerals. Both MK and slag can absorb CH to form C-S-H, making the microstructure denser. CH often occurs in the form of crystal and produce interfaces (weak combination) inside the cement matrix. However, C-S-H has a tremendous specific surface, which produces a greater combination force inside the paste, and it is a continuum structure (there is no interface). The more of CH was consumed, the more C-S-H was formed, and the higher the strength of cement. On the other hand, the size of the XRD peak attributed to AFt also indicated that more AFt was formed in cements M1 and S3. This is very helpful to the early strength development of cement mortar.

4. Conclusion

MK is a new active mineral admixture used in cement concrete products. It has a good effect on the mechanical properties of cement. However, MK blended cement has a poorer fluidity compared to PC under the condition which used the same amount of superplasticizer. However, this can be improved by adding ultra-fine slag. By incorporating 10% MK and 20% or 30% ultra-fine slag jointly into PC, not only the fluidity of blended cements was improved, but also the 28-day compressive strength of the cements was enhanced. MK is a high active pozzolanic mineral admixture and slag is a latent hydraulic mineral. The former can prompt the hydration of PC, shorten the setting time of cement, increase the water requirement, and increase the fluidity losing of the fresh paste. However, slag can defer the reaction of cement hydration and prolong the setting time of cement paste. Both MK and slag can react with CH released by cement clinker hydration to produce secondary C-S-H gel inside the cement paste. The secondary formed C-S-H gel improves the microstructure of cement paste matrix, therefore, the macroscopic property of cement was also improved. XRD analysis indicates that more $Ca(OH)_2$ was consumed after adding both mineral admixtures.

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