Compressive strength and pore structure of cement paste with metakaolin

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Abstract: Compressive strength, Ca(OH)₂ content and pore structure of cement paste with metakaolin (MK) were investigated by compressive strength test, diffraction of x-rays, nitrogen adsorption test and mercury intrusion porosimetry. The results show that the addition of MK can improve the compressive strength of cement paste, reduce the content of Ca(OH)₂ of cement paste, and reduce porosity of cement paste.

1. Introduction
At present, cement-based materials are the most widely used building materials. Cement production will consume a lot of energy, emit a large amount of carbon dioxide, nitrogen oxide and sulfur oxide into the atmosphere. It will cause global temperature rise and acid rain formation. The application of supplementary cementitious materials provide a beneficial approach to solve the problems. Metakaolin is a supplementary cementitious material with high pozzolanic activity. Its main components are amorphous silica and amorphous alumina. Metakaolin can react with Ca(OH)₂ to form calcium aluminate hydrate and calcium silicate aluminate hydrate. The results show that MK can improve chloride penetration resistance and the sulfate resistance of cement-based materials, restrain alkaline aggregate reaction[2]-[4].

In this paper, the influence of MK on compressive strength, pore structure and hydration products of cement paste is studied.

2. Materials and method

2.1. Raw materials
Cement is P.I 42.5 standard cement without mineral admixture, which produced in Qufu, Shandong Province, China. MK is produced in Hohhot, Inner Mongolia Province, China. The chemical composition of cement is shown in table1. The chemical composition of Metakaolin is shown in table 2. The morphology and XRD pattern of MK are shown in figure 1. Particle size distributions of MK and cement are shown in figure 2.

Table 1 Chemical composition of cement (mass fraction/wt%)

|  | Si₂O₅ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂Oeq | f-CaO | Cl | Ignition loss |
|---|-------|-------|-------|-----|-----|-----|--------|------|---|--------------|
|   | 21.88 | 4.31  | 3.47  | 62.39 | 1.72 | 2.56 | 0.23  | 1.52  | 0.016 | 1.42          |

Note: Na₂Oeq is content of volatile alkaline, f-CaO is free calcium oxide[5]
Table 2 Chemical composition of MK (mass fraction/wt%)

|         | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | K₂O | N₂O | Ignition loss |
|---------|------|-------|-------|-----|-----|-----|-----|-----|--------------|
|          | 49.40| 43.88 | 0.51  | 0.27| 2.66| 0.14| 0.23| 1.52| 0.59         |

Figure 1 XRD spectrum of MK  
Figure 2 Particle size distribution of MK and cement

2.2. Specimens preparation

In this experiment, the equivalent substitution method is adopted, and three MK contents are used: 5%, 10%, 15% (mass ratio). Corresponding test piece numbers are MK5, MK10 and MK15, and MK0 is ordinary cement. The water cement ratio of cement mortar is 0.4. To ensure that MK is uniformly dispersed in the cement paste, MK is added into mixing water to form a suspension, and then add cement into the suspension to obtain the cement paste. Four groups of specimens (six in each group) were prepared with each MK content of cement paste for compressive strength test. The cement paste inside the compressive strength sample was placed in anhydrous ethanol to stop hydration for 24 hours and drying for 24 hours, which was used for mercury injection and nitrogen adsorption test. The cement paste inside the compressive strength sample is immersed in ethanol to stop hydration for 24 hours and then dried for 24 hours for mercury intrusion porosimetry and adsorption isothermal test.

3. Results and discussion

3.1. Effect of MK on compressive strength of cement paste

Compressive strength of MK cement paste at 7d, 14d, 21d and 28d are shown in figure 3. For the cement paste with the same MK content, the compressive strength of the cement paste increases with the age. Taking M5 as an example, the compressive strength of MK5 at 28d increased by 21.7%, 25.9% and 29.6% compared with 7d, 14d and 21d respectively. For cement paste of the same curing age, the compressive strength of cement paste increases with the increase of MK content. Taking 28d as an example, compared with MK0, the compressive strength of MK5, MK10 and MK15 increased by 6.7%, 21.5% and 35.4% respectively. Previous studies have shown that MK possess high pozzolanic activity, can react with Ca(OH)₂ to form hydrated calcium aluminate and hydrated calcium aluminosilicate[6]. In addition, the MK has a smaller particle size (as shown in figure 2), the effect of dilution and nucleation also promotes the hydration of cement. Under the combined influence of the above two mechanisms, the pore structure of MK cement paste is refined and the degree of density is increased, which results in the phenomenon that the compressive strength of MK cement paste increases with the content of MK.
3.2. Effect of MK on pore structure of cement paste

3.2.1. Nitrogen adsorption test

The nitrogen adsorption curves of MK cement pastes for curing 28d are shown in figure4. It can be seen from the trend of nitrogen adsorption curves that the isotherm adsorption curve of MK cement paste belongs to II class nitrogen adsorption curves. When the relative pressure ($P_0 / P$) is low, the nitrogen adsorption curves rise steadily. This stage is the adsorption process of nitrogen molecular layer on the pore surface of cement paste. When the relative pressure ($P_0/P$) is high, adsorption volume of nitrogen increase rapidly. In this stage, nitrogen molecules are adsorbed on the surface of pores in multiple layers, and capillary condensation occurs. With the increase of MK content, the adsorption isothermal curve of cement paste moves to the negative longitudinal axis, adsorption volume reduced significantly. It show that the higher MK content is, the smaller adsorption volume of nitrogen is. The above phenomena preliminarily show that MK refines the pore structure of cement paste and increases the density of cement paste.

3.2.2. Mercury intrusion porosimetry

To obtain the pore structure characteristics of MK cement paste, mercury intrusion porosimetry test was carried out on the cement paste with MK for curing 28 d (the results are shown in figure 5). As shown in figure 8, with the increase of MK content, the pore diameter of MK cement paste decrease. Compared with MK0, the average aperture of MK5, MK10 and MK15 decreased by 35.1%, 37.1% and 44.3%; the median particle size decrease by 50.8%, 57.6% and 59.8%, the porosity decrease by 5.7%, 5.8% and 20.5%; the specific surface area increase by 39.2%, 47.4% and 48.8%.
3.3. Effect of MK on hydration products of cement paste

3.3.1. Effect of MK on hydration products

Figure 6 shows the XRD pattern of cement paste with MK for curing 28 d. As shown in figure 6, for curing 28 d, with the increase of MK content, the diffraction peak intensity decreases. The reasons for the above phenomena are: (1) the pozzolanic effect of MK consumes Ca(OH)$_2$; (2) MK replaces part of cement and reduces Ca (OH)$_2$.

To accurately measure the information of Ca (OH)$_2$ and other hydration products. Figure 7 shows the TG / DTG curves of cement pastes with MK for curing 28 d. It can be seen from Figure 7 that the DTG curves of different samples are similar. There are three major weightlessness peaks: (1) 30-
300°C is weightlessness stage of C-S-H and C_2ASH_8; (2) 370-450°C is weightlessness stage of Ca(OH)_2; (3) 530-660 °C is weightlessness stage of CaCO_3[7]. It is shown figure 7 that the content of C-S-H and C_2ASH_8 in cement paste increases with the raise of MK content. However, the content of the content of Ca(OH)_2 decrease. This shows that MK consumes Ca(OH)_2 of in cement paste and generates more hydration products (such as C-S-H and C_2ASH_8). MK improves the density, reduces the porosity and raise the compressive strength of cement paste.

![Therogravimetric curves of MK cement pastes at 28d](image)

**4. Conclusion**

By means of compressive strength test, XRD test, mercury intrusion porosimetry and nitrogen adsorption test, the compressive strength and pore structure characteristics of cement paste with MK are studied. The main conclusions are as follows:

(1) MK improves the compressive strength of cement paste. For curing 28d, compared with MK0, the compressive strength of MK5, MK10 and MK15 increased by 6.7%, 21.5% and 35.4% respectively.

(2) MK refines the pore structure and increases the density of cement paste. For curing 28d, compared with MK0, the average aperture of MK5, MK10 and MK15 decreased by 35.1%, 37.1% and 44.3%; the median particle size decrease by 50.8%, 57.6% and 59.8%, the porosity decrease by 5.7%, 5.8% and 20.5%; the specific surface area increase by 39.2%, 47.4% and 48.8%.

(3) MK consumes Ca(OH)_2 and increases the content of C-S-H and C_2ASH_8 of cement paste.

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