EFFECT OF ZEOLITE POWDER ON THE HYDRATION AND MICROSTRUCTURE EVOLUTION OF HARDENED CEMENT PASTE AT LOW WATER-BINDER RATIO

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In order to promote the application of zeolite powder in concrete, the hydration and microstructure evolution of hardened cement paste containing zeolite powder at low water-binder ratio have experimentally been investigated by compressive strengths, non-evaporable water, mercury intrusion porosimetry (MIP), scanning electron microscope (SEM) and nanoindentation. The results indicate that compared with the control cement paste, the addition of zeolite powder reduces compressive strengths of hardened cement paste at early ages, but 10% zeolite powder increases the compressive strength at later ages. The variation of non-evaporable water of hardened cement paste is similar with that of the strength. Zeolite powder degrades the internal structure to increases the porosity of hardened cement paste at 28 days, but the addition of 10% zeolite powder improves the microstructure to reduce the porosity at 60 days. Zeolite powder increases the volume fractions of UHD C-S-H.

Keywords: *zeolite powder, hydration, microstructure, hardened cement paste, low water-binder ratio*

1. Introduction

Supplementary cementitious materials (SCMs) such as fly ash, silica fume, slag and metakaolin are often used to prepare concrete, which not only improves the properties of concrete, but also reduces the cost of concrete production, showing good benefits [1]. Nowadays, SCMs have already become one of essential components for preparing the modern concrete, especially special concrete such as ultra high performance concrete, self compact concrete and so on. With the rapid increase of concrete consumption, the reserve of traditional SCMs can not meet the prepared need of modern concrete. It is urgent to seek and explore relatively new SCMs. Zeolite powder is an especial type of natural pozzolan with a three dimensional frame structure. Najimi et al. [2] reported that zeolite showed more pozzolanic activity than amorphous natural pozzolans, which was also used as one SCM due to its high activity [3].

In general, zeolite powder can obviously improve the properties of concrete such as strengths, durability and shrinkage [4, 5], attracting more and more attention. However, the related mechanism of zeolite powder in concrete needs still further to explore. The hydration and microstructure evolution of cementitious materials is basic work to reveal the mechanism. Uzal and Turanlı [6] reported that the blended cement containing high volume of natural zeolites had no free calcium hydroxide (CH) in hardened paste at the end of 28 days of hydration, and similar compressive strength to the control Portland cement at 28 days. Kocak et al. [7] proved that the addition of zeolite affected the physical and mechanical properties of the blended cement depending on the amount of zeolite. The water demand of cement paste was increased with zeolite powder substitution ratio, and the initial and final setting times of cement paste containing zeolite powder were almost similar to those of control cement paste. Perraki et al. [8] found that the usage of zeolite in cement contributed to the consumption of CH formed during the cement hydration and the formation of cement-like hydrated products. Girskas and Skripkiūnas [9] also obtained the similar results.

Based on the above analysis, it can be seen that the hydration and microstructure of cementitious materials containing zeolite powder focus mainly on the high water-binder ratio, and however, there is no published information at low water-binder ratio which is important to support the application of zeolite powder in concrete at low water-binder ratio. Water-binder ratio has a great effect on the hydration and microstructure evolution of cement, and the microstructure of concrete at low water-binder ratio is completely different from that at high water-binder ratio. Hence, in this study, the effect of zeolite powder contents on the hydration and microstructure evolution of cement paste at low water-binder ratio was investigated by

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Table 1

Chemical compositions of cement and zeolite powder (wt. %)

Type	SO_3	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	LOI
Cement	1.92	20.01	3.29	3.71	63.11	1.48	3.45
Zeolite powder	0.69	64.11	1.25	17.33	3.68	0.63	4.37

Table 2

Mix proportions of cement paste containing zeolite powder (g)

Type	Cement	Zeolite powder	Water	Superplasticizer
C	100	0	20	2
C-10ZP	90	10	20	2
C-20ZP	80	20	20	2

testing compressive strength, non-evaporable water, pore structure, scanning electron microscope (SEM) and nanoindentation. The results will help to understand the mechanism of zeolite powder on the properties of concrete at low water-binder ratio.

2. Experimental

2.1 Materials

Cement used in this study was Portland cement which had the strength grade of P·O52.5, which accorded with Chinese standard GB 175-2007. Zeolite powder was from the grinding of natural zeolite, whose fineness was planned and adjusted according to the requirements. Chemical compositions of cement and zeolite powder are shown in Table 1. SiO_2 content of zeolite powder is highest, Al_2O_3 content secondly, which are greater than those of cement. The results of fineness of cement and zeolite powder are presented in Fig. 1. As regards the mean sizes, zeolite powder particles have smaller sizes than cement particles, showing the micro filler effect. In addition, one polycarboxylic superplasticizer admixture with a specific gravity of 1200 kg/m^3 was also used with the water-reducing rate of 30% and solid content of 32%.

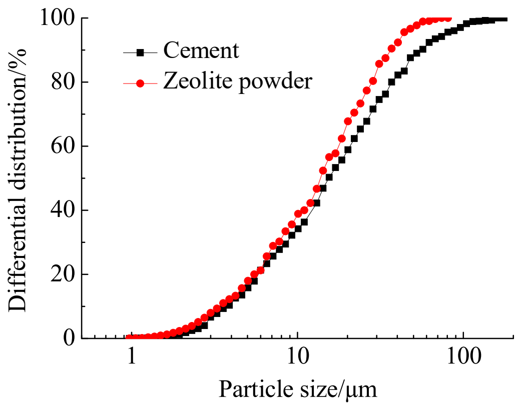


Fig. 1 - Grading curves of cement and zeolite powder.

2.2 Mix proportions

Zeolite powder was used to replace cement, and three types of cement paste were prepared according to zeolite powder contents. The water-binder ratio was constant, only 0.2, and zeolite powder contents were 10% and 20%, respectively. The constant superplasticizers were used to ensure the workability of cement paste. In addition, the control cement paste without zeolite powder was also prepared. Mix proportions of cement paste containing zeolite powder are shown in Table 2.

2.3 Test methods

Firstly, cement and zeolite powder were mixed evenly according to the proportions, and then water and superplasticizer were also stirred together in the cement paste mixer to form the cement paste with the size of 40mm × 40mm × 40mm. The cement paste with mould was cured for one day at normal temperature, and then demoulded and put into the standard room for curing to the specified ages. The compressive strengths of cement paste at 3, 28 and 60 days were tested. After that, the broken fragments of cement paste were soaked in alcohol for testing SEM, pore structure and non-evaporable water. The pore structure was determined by mercury intrusion porosimetry (MIP). Based on the reference [10], the process of SEM and MIP were obtained. The test procedure and calculation method of non-evaporable water were found in the reference [11]. The detailed process of nanoindentation technique of cement paste was gained in the reference [12].

3. Results and discussions

3.1 Compressive strength

Fig.2 presents the compressive strength variations of hardened cement paste containing zeolite powder at different ages. It can be seen from Fig.2 that the addition of zeolite powder reduces compressive strengths of hardened cement paste at 3 and 28 days, and with the increase of zeolite powder contents, the reduction is more obvious. However, the compressive strength of hardened cement paste containing 10% zeolite powder is more than that of the control cement paste at 60 days, and that of hardened cement paste containing 20% zeolite powder is always lowest, indicating the optimum content of zeolite powder should be 10%.

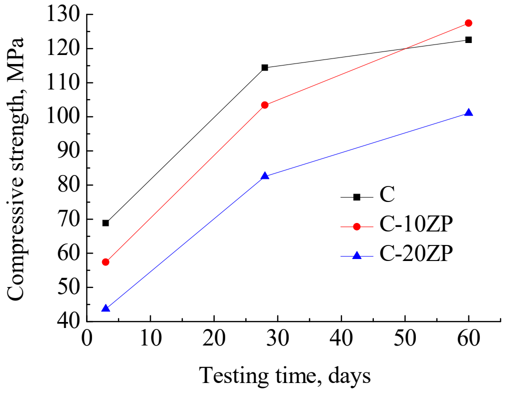


Fig.2 - Effect of zeolite powder on compressive strengths of hardened cement paste.

In order to further explain the results, the growth rate variations of strength of hardened cement paste containing zeolite powder are calculated, shown in Fig.3. According to Fig.3, with the increase of curing ages, the growth rates of strength of hardened cement paste containing zeolite powder are greater and greater. Compared with the control cement paste, the hardened cement paste containing zeolite powder has greater growth rates of strength, and with the increase of zeolite powder contents, the growth rate of strength is greater and greater, which indicates that zeolite powder can effectively increase the growth rates of strength of hardened cement paste.

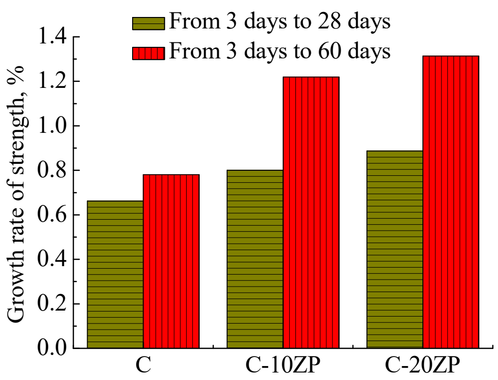


Fig.3 - Effect of zeolite powder on growth rates of strength of hardened cement paste

3.2 Non-evaporable water

Non-evaporable water variations of hardened cement paste containing zeolite powder are shown in Fig.4. According to Fig.4, zeolite powder reduces non-evaporable water of hardened cement paste at 3 and 28 days, and however, the non-evaporable water of hardened cement paste containing 10% zeolite powder is greater than that of the control cement paste at 60 days. The hardened cement paste containing 20% zeolite powder always presents the lowest non-evaporable water. Combining Fig.2 with Fig.4, compressive strengths and non-evaporable water of hardened cement paste containing zeolite powder show the similar variation tendency.

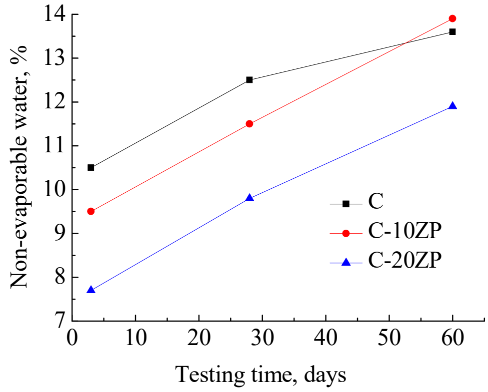


Fig.4 - Effect of zeolite powder on non-evaporable water of hardened cement paste.

The growth rate variations of non-evaporable water of hardened cement paste containing zeolite powder are also obtained, shown in Fig.5. It can also be found from Fig.5, zeolite powder increases the growth rates of non-evaporable water of hardened cement paste. Combining Fig.3 with Fig.5, the growth rates of strength of hardened cement paste containing zeolite powder show the similar tendency with the growth rates of non-evaporable water, indicating that the variation of compressive strengths corresponds with that of non-evaporable water.

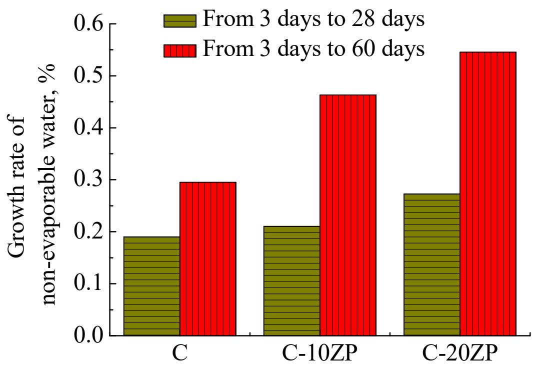
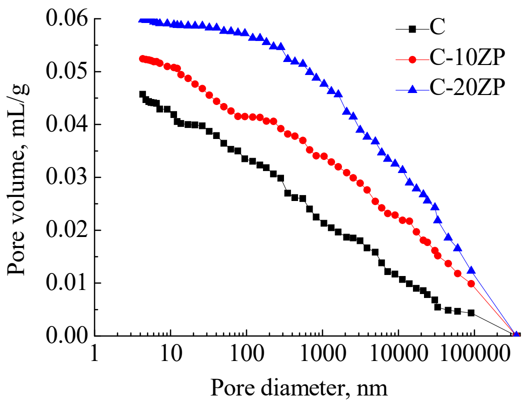


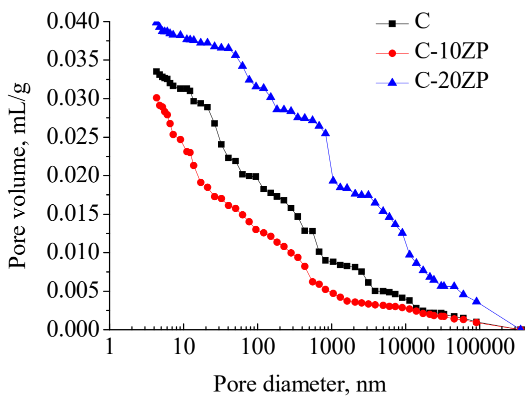
Fig.5 - Effect of zeolite powder on growth rates of non-evaporable water of hardened cement paste

3.3 Pore structure

Pore structure has an important effect on the properties of hardened cement paste, and the results of pore structure obtained by MIP at different ages are presented in Fig.6.



(a) At 28 days



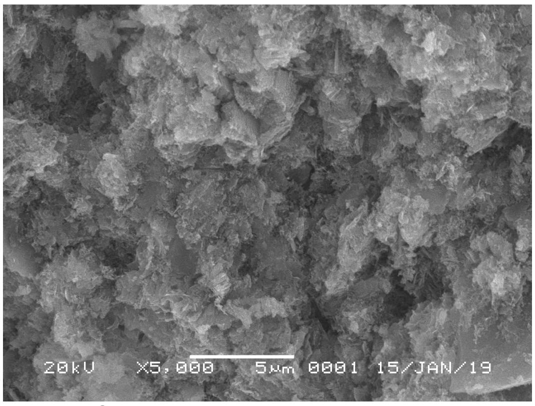
(b) At 60 days

Fig.6 - Effect of zeolite powder on cumulative porosity of hardened cement paste.

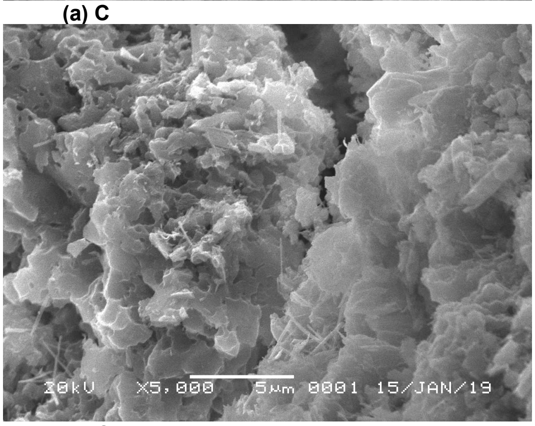
It is observed that the usage of zeolite powder increases the porosity of hardened cement paste at 28 days, and the hardened cement paste containing 20% zeolite powder shows the greatest porosity, indicating the lowest strength presented in Fig.2. This should be attributed to the fact that zeolite powder mainly shows the micro filler effect due to the low activity at 28 days. With the increase of ages, compared with the control cement paste, the usage of 10% zeolite powder reduces the porosity, but 20% zeolite powder still increases the porosity of hardened cement paste at 60 days. The pozzolanic reaction of 10% zeolite powder produces more hydration products, combining with its micro filler effect, to reduce the porosity. However, the usage of excessive zeolite powder (20%) leads to the reduced cement content, which causes the less CH, and hence, the pozzolanic reaction of zeolite powder is not sufficient, which results in the increased porosity of hardened cement paste.

3.4 SEM analysis

In order to investigate the effect of zeolite powder on the morphology and microstructure of hardened cement paste, the SEM images of hardened cement paste are gained at different ages, shown in Fig.7 and Fig.8.

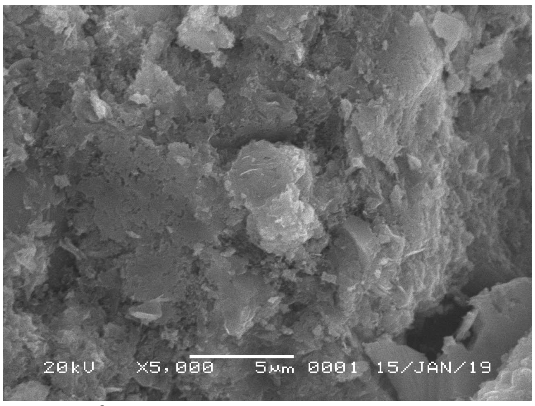


(a) C

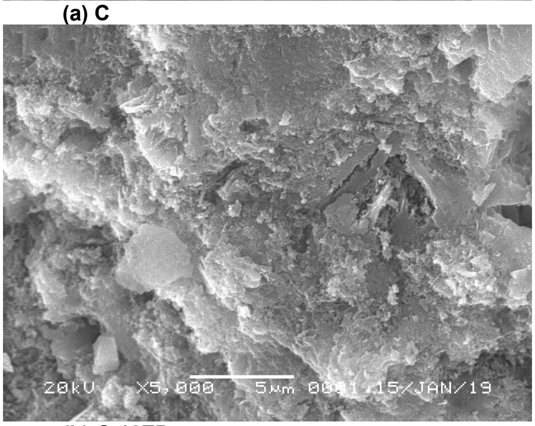


(b) C-10ZP

Fig.7 - SEM images of hardened cement paste containing zeolite powder at 28 days.



(a) C



(b) C-10ZP

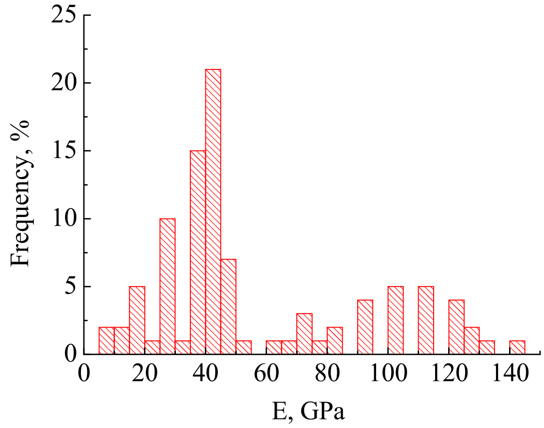
Fig.8 - SEM images of hardened cement paste containing zeolite powder at 60 days.

Observing the images at 28 days shown in Fig.7, the control cement paste has abundant hydration products which overlap each other to form a relatively compact structure, and has no obvious micro cracks. In addition, some pores with the small sizes intersperse. Compared with the control cement paste, the hardened cement paste containing 10% zeolite powder has less hydration products, and the obvious micro cracks and large size pores interconnects to form a channel which results in the divided internal structure. The results are agreement with the porosity shown in Fig.6. With the increase of curing ages, the internal structure of hardened cement paste at 60 days becomes more and more compact, presented in Fig.8. The amount and size of pores are smaller and smaller in the control cement paste, and the hardened cement paste has a similar compact structure with the control cement paste due to the overlapped and more and more hydration products. The results of SEM images also correspond well with compressive strengths of hardened cement paste shown in Fig.2.

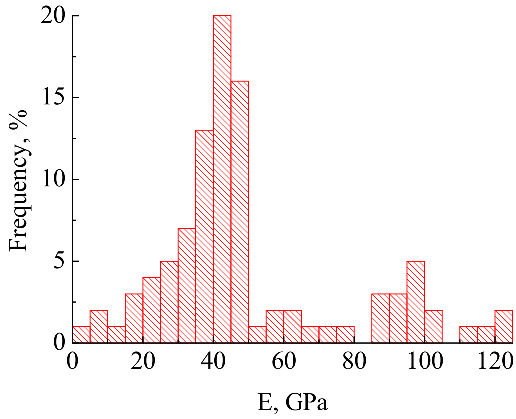
3.5 Nanoindentation investigation

In general, hardened cement paste mainly consists of pores, CH, calcium silicate hydrate (C-S-H), other hydration products with small amounts and unhydrated particles. C-S-H can be classified into three types: low density C-S-H (LD C-S-H), high density C-S-H (HD C-S-H) and ultra-high density C-S-H (UHD C-S-H) according to the different mechanical properties. The different phases of hardened cement paste have a relatively constant range of elastic modulus and hardness, and it is generally acknowledged that the ranges of elastic modulus of porosity, LD C-S-H, HD C-S-H, CH and unhydrated particle agree with less than 14GPa, 14-24GPa, 24-35GPa, 35-50GPa and greater than 50GPa, respectively [13]. UHD C-S-H has similar ranges of elastic modulus with CH, and however, the amount of CH is very small which can be ignored at low water-binder ratio especially at later ages [14].

During this nanoindentation test, the 10×10 grid containing 100 points with the distance between two adjacent points of 10μm was conducted. According to the curve of indentation depth and load, the elastic modulus of each phase was obtained to calculate the frequency histograms of elastic modulus of the control cement paste and hardened cement paste containing 10% zeolite powder at 60 days, shown in Fig.9.



(a) C



(b) C-10ZP

Fig.9 - Effect of zeolite powder on frequency histogram of elastic modulus of hardened cement paste at 60 days.

Based on the results in Fig.9, the proportions of different phases at 60 days can also be gained, presented in Table 3.

It can be observed from Fig.9 and Table 3 that the volume fraction of CH or UHD C-S-H is maximum, followed by the volume fraction of unhydrated particle. In view of CH with the small amount at low water-binder ratio which can be ignored, the maximum hydration product should be UHD C-S-H, and a number of unhydrated particles are remained in hardened cement paste. Zeolite powder increases the volume fractions of hydration products especially UHD C-S-H, which indicates that C-S-H produced by the pozzolanic reaction of zeolite powder is mainly UHD C-S-H. In addition, zeolite powder reduces the volume fraction of porosity and unhydrated particles. This is largely

Table 3

Volume fractions of constituent phases in hardened cement paste (%)

Sample	Porosity	LD C-S-H	HD C-S-H	CH or UHD C-S-H	Unhydrated particle
C	4.21	6.32	11.58	45.26	32.63
C-10ZP	4.12	7.22	12.37	50.52	25.77

attributed to the fact that the pozzolanic reaction of zeolite powder results in the reduction of unhydrated particles to produce more hydration products to fill micro cracks and refine the pore structure. The results conform to the above-mentioned compressive strengths in Fig.2 and other microstructure results.

4. Conclusions

This paper presents the effect of zeolite powder on the compressive strengths, non-evaporable water and microstructure of hardened cement paste at low water-binder ratio. The following conclusions can be gained:

(1) The addition of zeolite powder reduces compressive strengths of hardened cement paste at 3 and 28 days. However, zeolite powder increases the growth rate of strength, and compressive strength of hardened cement paste containing 10% zeolite powder is more than that of the control cement paste at 60 days.

(2) Non-evaporable water of hardened cement paste containing zeolite powder has a similar variation tendency with the strength.

(3) Zeolite powder increases the porosity of hardened cement paste at 28 days due to its low pozzolanic reaction, and however, the addition of 10% zeolite powder reduces the porosity at 60 days because of its high pozzolanic reaction and micro filler effect.

(4) Zeolite powder increases the volume fractions of hydration products especially UHD C-S-H, and reduces the volume fractions of porosity and unhydrated particles of hardened cement paste at 60 days.

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