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CHLORIDE PENETRATION AND MICROSTRUCTURE DEVELOPMENT OF FLY ASH CONCRETE

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Abstract

In the past decades, supplementary materials have been widely used in cement production. Fly ash (FA) with cheaper in price and with latent hydraulic properties, is one of the widely used supplementary materials. However, the addition of supplementary materials could influence the concrete properties. In general, the durability of concrete is associated with its transport properties. The transport properties, such as permeability, diffusivity and sorptivity are mainly resulted from the development of microstructure.

In this study, the chloride migration coefficient measurement of FA concrete and the microstructural observation of cement paste blended with FA were carried out on the samples curing up to one year. Rapid Chloride Migration (RCM) test was used to determine the chloride migration coefficient of concrete. Meanwhile, Mercury Intrusion Porosimetry (MIP) method was conducted to obtain total porosity and pore size distribution of blended cement paste. Test results show that FA concrete has good resistance to chloride ion after the curing age of 28 days compared to ordinary Portland cement concrete. Although cement paste blended with FA has a higher total porosity, less capillary pore exist if compared to cement paste. Except the chloride binding capacity of FA hydrates, the difference in microstructure is probably one of the main reasons why FA concrete has a lower chloride migration coefficient.

1. INTRODUCTION

Chloride-induced corrosion of reinforcements has a significant influence on the durability of reinforced concrete structures. Chloride migration coefficient, D_{RCM}, is a measure of the resistance of concrete to chloride diffusion. Meanwhile, the chloride penetration in concrete is controlled by the microstructure development of cement paste. In the past decades, supplementary materials have been widely used with cement to enhance the performance of concrete. In other words, the addition of supplementary materials could influence the concrete properties. Many researchers [1 - 4] reported that the high-volume of FA blended into cement has very low chloride penetration. Cox and Zhang [5, 6] indicated that with a high volume of FA, concrete has a much higher chloride migration coefficient at 28 days. Meanwhile, Cox [5] also proposed that FA concrete shows a good chloride migration resistance after 3 months. A number of researches on chloride penetration in FA concrete have been done, but the research of the relation between chloride penetration and microstructure is hardly found. But Cox [5] discussed the permeable porosity of FA concrete and capillary transport, which is probably the most dominant invasion mechanisms for chlorides. The microstructure development of blended cement paste is also could be linked to the durability properties of concrete. Moreover, the relationships between chloride penetration and microstructure development for FA concrete or paste at long-term curing age is still unclear. More researches about chloride penetration test were limited to short-term curing age (3 months).

The objective of this paper was to investigate the influence of microstructure development of cement paste blended with FA on chloride penetration in FA concrete at long-term curing ages up to 1 year. In this study, Rapid Chloride Migration (RCM) test is carried out to determine the chloride migration coefficient of FA concrete. MIP test is used to measure the porosity and pore size distribution of cement paste blended with FA. The blended cement paste was made with a water to binder (w/b) ratio of 0.4, the curing age up to 1 year. The FA content is 30% by weight as the replacement of cement in the blended cement paste. Meanwhile, the reference and FA concrete were casted for RCM test with the same condition except the addition of aggregate. In the end, the relationships between chloride penetration and microstructure are discussed.

2. MATERIALS AND METHODS

2.1 Materials

Table 1 shows the chemical compositions of ordinary Portland cement and FA. The crystalline phase of FA was about 41.29% determined by XRD method. The portion of mullite and quartz was 13.26% and 25.14%, respectively. Figure 1 shows the BSE image of FA particles. It is clear that almost all particles are spherical except some hollow particles.

Table 1: Chemical compositions of FA and cement

Chemical compositions (% by mass)	SiO_2	Al_2O_3	CaO	free-CaO	Fe_2O_3	P_2O_5	K_2O	MgO	SO_3	Na_2O
CEMI42.5N	20.36	4.96	64.4	0.6	3.17	0.18	0.64	2.09	2.57	0.14
FA	48.36	31.36	7.14	-	4.44	1.90	1.64	1.35	1.18	0.718

The FA concrete mixtures were casted using 70% of Portland cement CEM I 42.5 N, 30% of FA (Low calcium), aggregate (the maximum size of 16 mm), and tap water. The w/b ratio was 0.4. Meanwhile, the reference concrete mixtures without FA was casted with the same w/b ratio and curing condition.

All mixtures were cast in a standard cylindrical mould with the dimension of $\Phi 100\times300$ mm. After 1 day, the specimens were demoulded and cured in a saturated limewater bath until preconditioning for testing in 28 days, 91 days, 180 days, and 365 days. Blended cement paste with 30% of FA was also casted in order to research the development of microstructure.

For MIP tests, the blended cement pastes were sealed and cured in a plastic bottle for 1, 3, 7, 14, 28, 91, 180, and 365 days at room temperature. The reference sample was cement paste with a w/b ratio of 0.4.

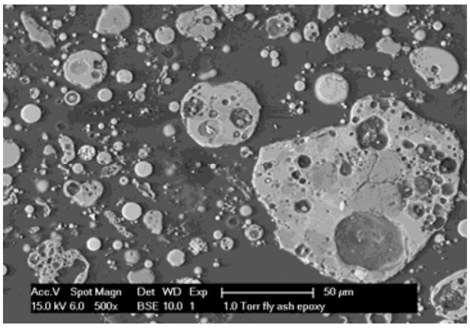


Figure 1: BSE image of FA particles

2.2 Methods

The chloride migration coefficient in concrete was determined according to NT Build 492 method, i.e., rapid chloride migration test at non-steady-state [7].

The preconditioning includes four steps, 1) cutting a 50 ± 2 mm thick slice from the central portion of the cylinder, three specimens could be obtained from one concrete cylinder, with enough space (50 mm) left at the sides to avoid any side effect; 2) placing specimen in the vacuum machine for three hours; 3) immersing saturated $Ca(OH)_2$ solution for one hour; 4) keeping the specimens in the solution for 18 ± 2 hours. After preconditioning, the test specimens were put in a rubber sleeve and fastened with two stainless steel clamps. The RCM set-up was shown in figure 2. The substrate surface was immersed in the anolyte solution of 0.3 M NaOH and the bottom surface was immersed in the catholyte solution of 10% NaCl. Turn on the power, with the voltage preset at 30 V, and record the initial current through each specimen [7].

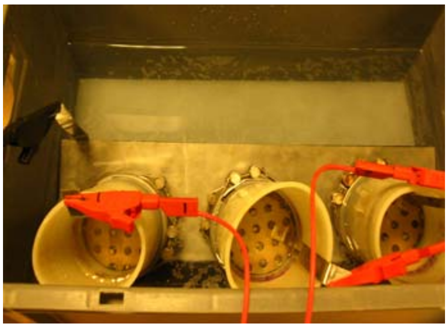


Figure 2: The migration set-up in laboratory

Based on the initial current, a corrected voltage and appropriate test duration were chosen. After testing, each specimen were split into two pieces and 0.1M silver nitrate solution was sprayed over the freshly split section. After 15 minutes, the migration depth of chloride ion and the thickness of each specimen were recorded. The non-steady-state migration coefficient was calculated using equation (1). The room temperature during the test was 20 ± 1°C.

$$D_{RCM} = \frac{0.0239\cdot(273)+T)\cdot L}{(U-2)\cdot t}\cdot\left(x_d - 0.0238\sqrt{\frac{(273+T)\cdot L\cdot x_d}{U-2}}\right) \quad (1)$$

D_{RCM}: Non-steady-state migration coefficient, $\times10^{-12}$ m^2/s;
U: Absolute value of the applied voltage, V;
T: Average value of the initial and final temperatures in the anolyte solution, °C;
L: Thickness of the specimen, mm;
X_d: Average value of the penetration depths, mm;
t: Test duration, hour.

MIP measurements were performed by using Micrometrics PoroSizer® 9320 machine. The PoroSizer® 9320 is a 207 MPa mercury intrusion porosimetry, which determines pore size in the range from 7 nm to 500 µm. The relation between the pressure p (MPa) and the pore diameter d (µm) is described by the Washburn equation (2), which is based on a model of cylindrical pores:

$$p = -\frac{4\gamma\times\cos\theta}{d} \quad (2)$$

Where γ is the surface tension of the mercury (mN/m) and θ is the contact angle between the mercury and the pore wall surface of the material. In this study, the contact angle and surface tension of mercury were 139° and 480 mN/m, respectively [8]. Sample preparation for MIP test was referred to [10].

3. RESULTS AND DISCUSSION

3.1 Chloride penetration of FA cement concrete

Figure 3 presents chloride diffusion coefficient (D_{RCM}) of reference concrete and the concrete blended with 30% of FA (FA concrete) with the same w/b ratio of 0.4 at different curing ages up to 1 year.

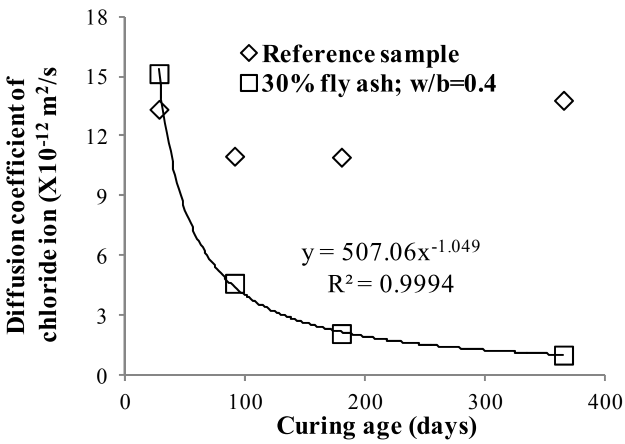


Figure 3: Diffusion coefficient (D_{RCM}) of reference concrete and FA concrete

At 28 days, the reference concrete has a lower D_{RCM} value than FA concrete. That could be caused by the reason that the Pozzolanic reaction of FA is slow in short-term curing age, even at 28 days. FA remains as filler material in concrete, which results in decreasing the amount of hydration products and thus higher porosity.

However, after curing age of 28 days, the D_{RCM} value of FA concrete decreases dramatically. FA concrete shows good resistance to chloride penetration. The curve of reference concrete also shows a similar tendency. But the reduction is much smaller than FA concrete. The D_{RCM} value of FA concrete is much smaller than reference concrete after 91 days, which is in consistence with findings in the literature [1-6].

3.2 Pore size distribution of blended cement pastes

Figure 4 presents cumulative pore size of reference sample and the sample blended with 30% of FA with a w/b ratio of 0.4 at different curing ages up to 365 days.

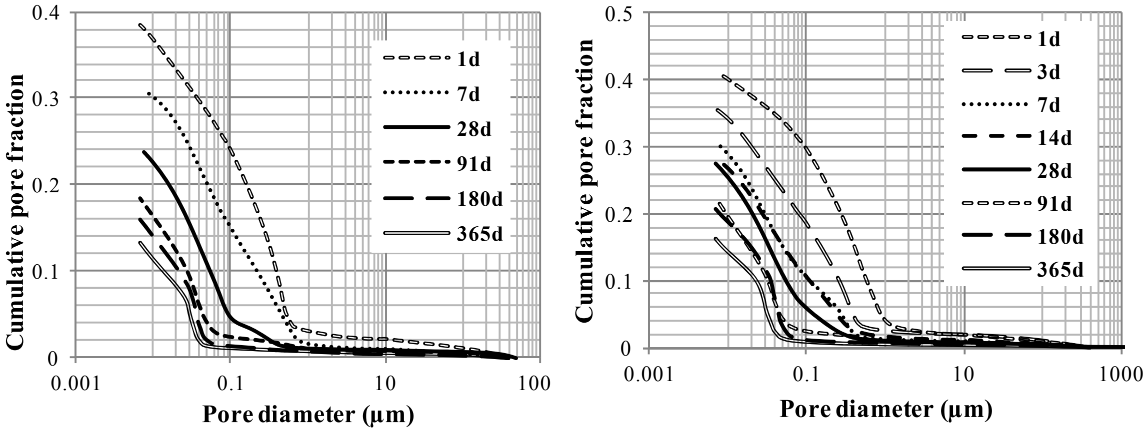


Figure 4: Cumulative pore size of reference sample (left) and the sample blended with 30% FA (right) with a w/b ratio of 0.4 at different curing ages

Total porosity is the fractional volume of pores with respect to bulk volume of the material, which is expressed as the higher value in figure 4. Figure 5 presents the porosity of reference sample and the sample blended with 30% FA at different curing ages.

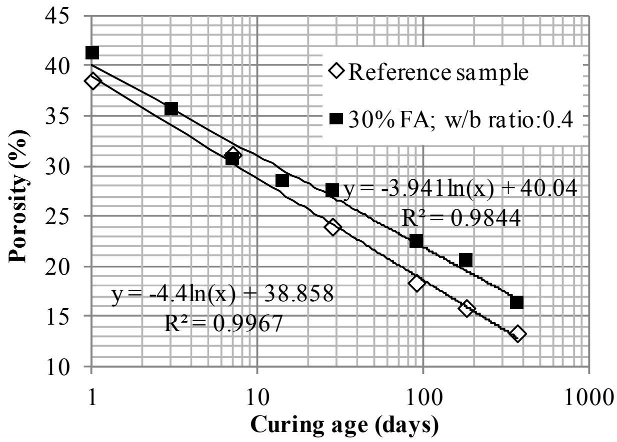
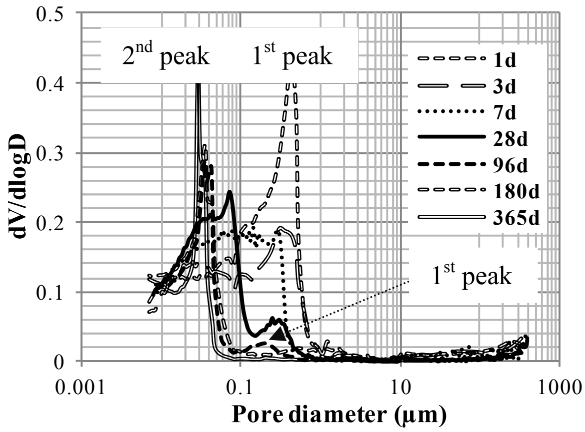


Figure 5: Porosity of reference sample and the sample blended with 30% FA at different curing ages

Obviously, as shown in figure 4 and 5, the sample blended with FA has a higher total porosity than reference sample, especially in long curing stage. FA shows a negative influence on the development of total porosity in binary system. The total porosity decreases with curing age regardless of the type of sample. For reference sample, total porosity decreases sharply with the increase of curing age from 1 to 91 days. The total porosity is 18.39% at 91 days, which is a half of 38.55% at 1 day. After 91 days, total porosity decreases slowly resulting from more and more denser structure in cement paste. For the sample blended with FA, the change in total porosity is smaller than reference sample, which can be detected from figure 5. A similar trend appears between 96 and 180 days. This is probably because FA takes place slows pozzolanic reaction. It is notable that in semi-log scale, the porosity has a linear relationships with curing ages. In later study, the porosity for two kinds of samples under 2 and 3 years will be determined, which can be used to validate the linear relationships .

By differentiating the cumulative distribution curve, the differential distribution curve is plotted in Figure 6.



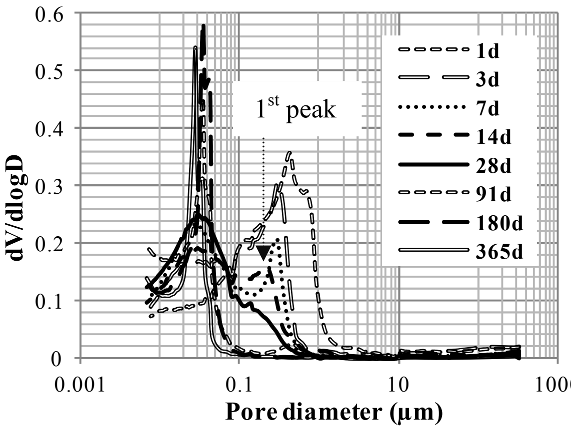


Figure 6: Differential pore size distribution of reference sample (left) and the sample blended with 30% FA (right) with a w/b ratio of 0.4 at different curing ages

Two main peaks are described in figure 6. The 1st peak is referred to capillary pore and the 2nd peak is referred to gel pores or medium capillary pores [10]. The 1st peak plays a dominant role in transport property of cement paste. It is obvious that the 1st peak becomes smaller and the 2nd peak appears and grows dramatically with the increase of curing age.

For reference sample, at 96 days, the 1st peak almost disappears. In contrast, the 2nd peak is more pronounce at 28 days and becomes sharper with the increase of curing age. For the sample blended with FA, the 1st peak almost disappears at 28 days, and the 2nd peak appears at 14 days.

3.3 Discussions

During the research of chloride penetration in FA concrete, many reasons could lead to lower chloride migration coefficient of FA concrete under long-term curing age, such as more C-S-H gel produced by the Pozzolanic reaction of FA, more Ca^{2+}, Al^{3+}, $AlOH^{2+}$, and Si^{4+} ions in FA concrete [9]. In other words, more C-S-H gel could absorb more chloride ions and these ions have lower diffusing ability .

In the other hand, the durability of concrete is also related to microstructure development of blended cement paste. And the capillary pores play an important role in transport property of concrete. As mentioned above, it can be concluded that the reference sample has lower total porosity, but capillary pores (1st peak) still exist until the curing age of 96 days. On the contrary, even though the sample blended with FA has a higher total porosity, the capillary pores disappear at the curing age of 28 days. This probably could be the main reason why the FA concrete has a lower diffusion coefficient (D_{RCM}) because capillary pores dominate the transport property of concrete.

4. CONCLUSION

This study discussed the chloride penetration of FA concrete and microstructure development of cement paste blended with FA under long-term curing age up to 1 year. Then the relationships between microstructure development and chloride penetration in FA concrete were explored. The following conclusions can be given based on the results obtained in this research.

1. At the curing age of 28 days, FA concrete has a higher chloride migration coefficient than reference concrete. But after 28 days, FA concrete shows good resistance to chloride ion, which is in consistence with findings in the literature. But in most literatures [1-6], the FA concrete has lower chloride penetration resulting from more than 50% of FA was mixed in concrete as replacement of cement by weight. In this study, the dosage of FA as replacement of cement is 30% in FA concrete, which also show lower chloride migration coefficient.
2. Reference sample always shows lower total porosity than cement paste blended with FA under different curing ages up to 1 year. Moreover, in semi-log scale, there are a linear relationships between the total porosity and curing age regardless of the type of cement paste.
3. Although cumulative pore size curve can identify the total porosity of blended cement paste, differential pore size curve shows more the development of pore size and pore type in binary system mixing with FA under different curing age. Two peaks are found in differential pore size curve. The 1st peak in cement paste blended with FA disappeared at 28 days, which is earlier than that in reference sample at 91 days.
4. Although reference sample has lower total porosity, more capillary pores exist compared with the sample blended with FA. It could be explained that FA concrete have lower diffusion coefficient (D_{RCM}).

5. ACKNOWLEDGEMENT

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