Life-Cycle of Structures and Infrastructure Systems – Biondini & Frangopol (Eds)

Influence of various admixture materials on pore structure and mass transfer characteristics

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ABSTRACT: Durability is important for the life cycle of reinforced concrete structures. Pore structure and mass transfer characteristics are related. Understanding the pore structure is necessary but difficult. It has been shown that gas and liquid have different mass transfer characteristics, and we thought that this difference could be express the pore structure. In this study, air permeability tests, Water penetration rate coefficient test, and porosity measurements were conducted. Various admixtures were used because the porosity is different depending on the admixture. As a result, it's clear that the mass transfer characteristics are different depending on the admixtures and amount of its content. Silica fume and blast furnace slag fine powder in high proportion showed high mass transfer resistance, and the water penetration rate coefficient was about 1/2 that of N. The difference between the air permeability and water penetration rate coefficients indicates the possibility of expressing the complexity of pores.

1 INTRODUCTION

Durability is important for the life cycle of reinforced concrete structures. Carbonation and salt damage, which are representative of the deterioration of reinforced concrete structures, cause steel corrosion and cracks in concrete. Since steel corrosion is progressed by the supply of water and oxygen, it is very important to understand the mass transfer characteristics in concrete. In Japan, steel corrosion by water penetration was added to the durability verification in the revision of the Standard Specification for Concrete Design, and a Water penetration rate coefficient test was devised in 2017. deterioration factors such as carbon dioxide, chloride ions, water, and oxygen penetrate the concrete using the pores as movement pathways. Therefore, it is often considered that pore structure and mass transfer properties are very closely related and are often discussed together with durability. Therefore, it is necessary to understand the pore structure of hardened cement in order to understand the mass transfer characteristics. In recent years, the use of various admixtures and chemical admixtures has been focusing in order to improve durability and reduce the effects on the environmental. It is known that the use of admixture materials changes the pore structure. However, it is difficult to accurately determine the pores in concrete because there are pores of different sizes and different shapes, each of which is complexly connected to the others. Thus, we considered inferring the pore structure of hardened cement when various admixtures are used, by using mass transfer characteristics and porosity. In this study, we tested hardened cement used the admixtures such as ground granulated blast-furnace slag, fly ash, silica fume, and C-S-H hardening accelerator agent. Air permeability tests, moisture penetration tests, and porosity measurements were conducted to sort out the pore structure and mass transfer characteristics formed using admixture materials. The combination of these tests was also investigated to understand the pore composition.

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2 OUTLINE OF EXPERIMENT

2.1 *Materials and mass ratio of cement and admixtures of mortar*

In this study, mortar specimens were used to eliminate the influence of coarse aggregate. Also various admixtures were used and specimens were tested with different curing times in order to vary the diameter and distribution of pores. Ordinary Portland cement (OPC, Density 3.16 g/cm^3, Blaine 3080 cm^2/g) was used as cement, and blast furnace slag fine powder (BFS, Density 2.91 g/cm^3, Blaine 4190 cm^2/g), fly ash type II (FA, Density 2.33 g/cm^3, Blaine 4460 cm^2/g), and silica fume (SF, Density 0.27 g/cm^3, Blaine 18.5 m^2/g) were used as admixtures for the mortar. In case of using BFS, anhydrous gypsum was added to the BFS in an amount equivalent to 2% SO_3. Admixtures was replaced by mass ratio to cement. A C-S-H hardening accelerator (ACX) was used as a chemical admixture, which is thought to contribute to pore densification. Table-1 shows the mass ratio of cement and admixtures of mortar. The water-binder ratio was 50% and the binder: fine aggregate mass ratio was kept constant at 1:3.

Table 1. Mass ratio of cement and admixtures of mortar.

	Admixtures	W/B (%)	Mass ratio (%) OPC	Mass ratio (%) Admixtures	ACX (W×%)
N	-	50	100	0	-
B20	BFS		80	20	
B50			50	50	
B85			15	85	
FA30	FA		70	30	
SF30	SF		70	30	
ACX	ACX		100	0	10

2.2 *Porosity test*

The specimen used in the water penetration test was crushed and a 25 mm square specimen was taken out. The samples were saturated with water by a vacuum desiccator. After measuring the saturated weight and the weight in water, the samples were left to dry at 40°C, RH 30% until their weights became constant, and the weight in a dry state was then measured. Porosity was calculated by Archimedes method.

2.3 *Water penetration rate coefficient test*

This test was conducted in accordance with JSCE-G 582-2018. Figure 1 shows an illustration of the test. Cylindrical specimens of φ50 × 100 mm were made, and after curing, they were placed in the chamber at 40°C and RH30% until their mass became constant. After the specimens were removed from the chamber and the temperature was lowered to room temperature. The sides were sealed with aluminum tape and two sides were open. The mass of the specimen was measured, and 10mm from the bottom of the specimen was immersed in water and removed after 5, 24, and 48 hours. After the mass was measured again, the specimen was split

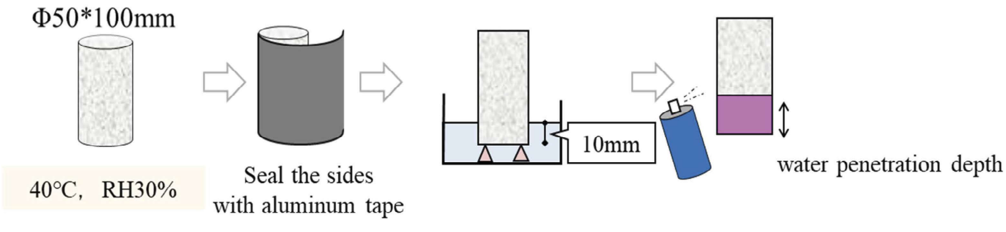

Figure 1. Outline of *water penetration rate coefficient test.*

open and sprayed with a moisture sensing agent. The range of coloration was defined as the water penetration depth, and the slope of the water penetration depth relative to the square root of the soaking time was calculated as the water penetration rate coefficient.

2.4 *Air permeability test*

The test was carried out using the output method with a disk-shaped specimen of φ100 × 20 mm. In the pre-treatment, the specimens that finished the curing period were dried. The specimens were placed in an environment of 40°C, 30% RH and dried until the weight became constant. Air was injected at 0.1 MPa, and after confirming that the air flow had become constant, the permeability was measured using a graduated cylinder by water displacement method (Figure 2). The air permeability coefficient was calculated using the Darcy rule using the following equation (1).

$$K = \frac{2LP_2}{(P_1^2 - P_2^2)} \cdot \frac{Q}{A} \quad (1)$$

where K: Air permeability coefficient ($cm^4/N \cdot s$), L: Specimen thickness (cm), P_1: Loading pressure (N/mm^2), P_2: Outflow side pressure (N/cm^2), Q: Amount of air permeability (cm^3/s), A: permeable area (cm^2)

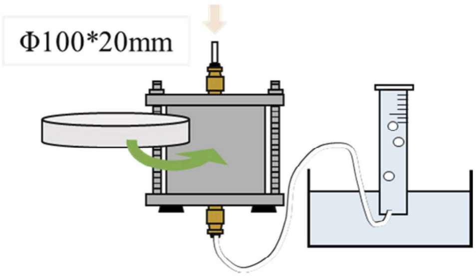

Figure 2. Outline of air permeability test.

3 RESULTS OF TESTS

3.1 *Porosity*

Figure 3 shows the results of porosity calculated by Archimedes' method for each mix proportion. The porosity showed a decreasing trend as the curing period was extended. This may be because of the hydration reaction of the cement, or the reaction caused by the admixture material. It was also clarified that even with the same number of curing days, the porosity was different depending on the type of admixture and the replacement ratio. The porosity is largest in B85, suggesting that the hydration reaction may not be sufficiently complete.

3.2 *Water penetration characteristics*

Figure 4 shows a specimen that had been cured for 28 days and was sprayed with a water sensing agent on the split surface of the specimen after 48 hours of immersion. It was confirmed that the use of admixture materials suppressed water penetration. B50 and SF30 showed smaller depths of water penetration than N, and SF30 showed higher resistance to water penetration, less than 1/2 that of N. On the other hand, the water penetration characteristics were different depending on the admixture and its amount of content. Especially, it was observed that the higher the BFS replacement ratio, such as B85, the more water was penetration at the sides of the cylindrical specimen and the greater the water penetration depth compared to the

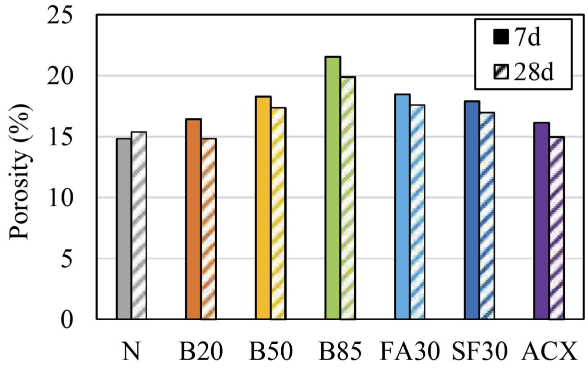

Figure 3. Results of porosity test.

center of the specimen. This was reported in previous studies to be caused by changes in the pore composition affected by drying in the case of high BFS replacement. This result may have been obtained in B85 because drying was performed as a pretreatment. While the effect of drying was small for N, however, B85 was greatly affected by drying before the test was conducted, and the water penetration behavior was different between the center and the sides of the specimen. Therefore, it is clear that the water penetration behavior is different depending on the mixed material and its content.

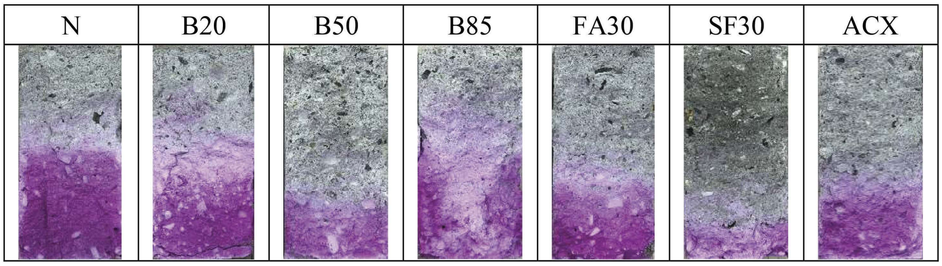

Figure 4. Results of water penetration characteristics.

3.3 *Air permeability coefficient*

Figure 5 shows the air permeability of each mix proportions calculated from the results of the pressure air permeability test. As a general trend, the permeability decreased as the number of curing days increased. FA30 shows a significant decrease at 28 days of curing compared to 7 days of curing. It is considered that this is because of the densification of the pores due to the long-term occurrence of the pozzolanic reaction of FA in addition to the hydration reaction of cement. In addition, regardless of the number of curing days, B85 and FA30 showed significantly higher values of permeability than the other mix proportions. On the other hand, B20, B50, SF30, and ACX showed similar or slightly smaller values than N. Thus, it can be seen that the use of admixtures improves the mass transfer resistance.

4 DISCUSSION AS EXPRESSION OF PORE COMPOSITION BY MASS TRANSFER TEST

4.1 *Relationship between water penetration rate coefficient and air permeability coefficient*

Figure 6 shows the relationship between the water penetration rate coefficient and the air permeability. No correlation was observed between them. This may be because the water penetration rate coefficient test and the air permeability test are affected by different factors. Group

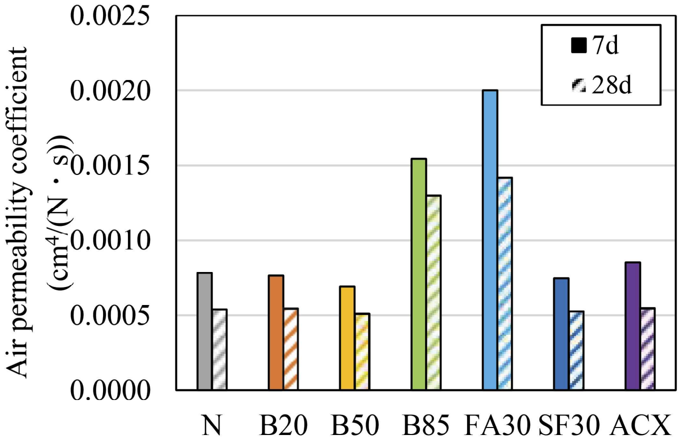

Figure 5. Results of air permeability coefficient.

A and Group B in Table 2 show some mix proportions with similar porosity. The relationship between the water penetration rate coefficient and the air permeability coefficient in these mix proportions shows that some hardened materials with the same porosity show similar values in group A but group B shows different values. In other words, even hardened materials that have the same porosity, but they are expected to show different trends depending on the pore composition, the material used in the mass transfer test, and the driving force of the test.

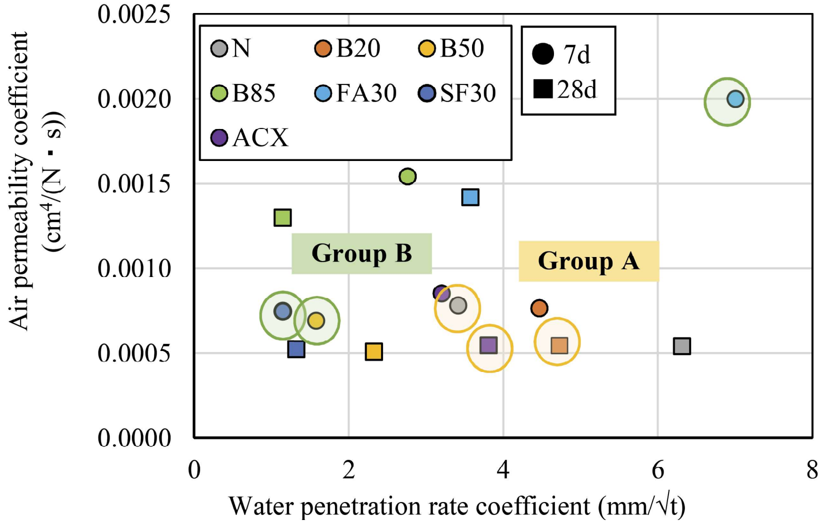

Figure 6. Relationship between water penetration rate coefficient and air permeability coefficient.

4.2 *Relationship between porosity and mass transfer tests*

Figure 7 shows the relationship between porosity and air permeability coefficient, and Figure 8 shows the relationship between porosity and water penetration rate coefficient. Figure 7 shows a positive correlation between porosity and permeability coefficient, with a decrease in permeability coefficient with decreasing porosity. On the other hand, Figure 8 shows a slightly negative correlation between porosity and water penetration rate coefficient. This relationship was different from that of the water penetration rate coefficient.

This result suggests that both of the water penetration rate coefficient test and the air permeability test evaluated the mass transfer in the hardened cement in the same way, but the results were affected by different factors, which may have caused the differences in the air

Table 2. The mix proportions with similar porosity.

Group	Mix proportion	Curing days	Porosity(%)	Marks
A	N	7	14.81	●
	B20	28	14.84	■
	ACX	28	15.00	■
B	SF30	7	17.89	●
	B50	7	18.26	●
	FA30	7	18.43	●

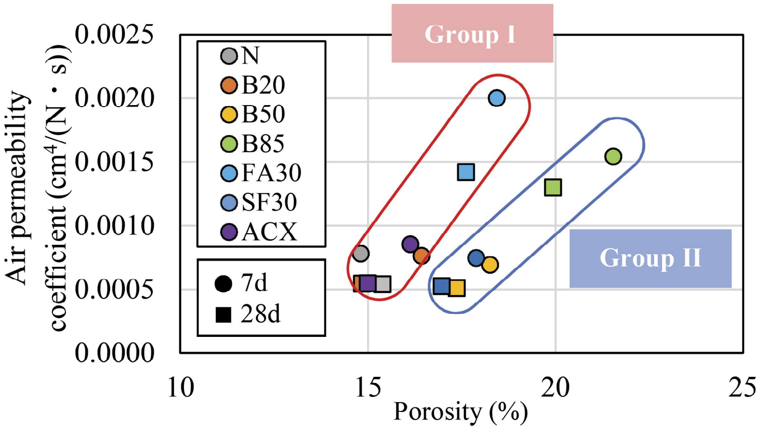

Figure 7. Relationship between porosity and air permeability coefficient.

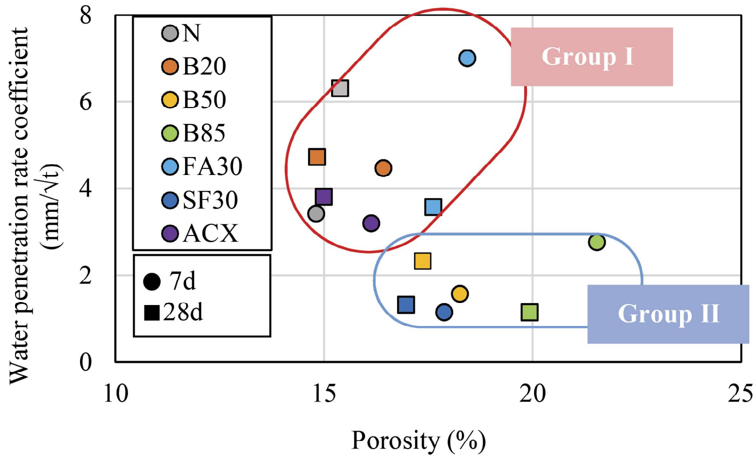

Figure 8. Relationship between porosity and water penetration rate coefficient.

permeability test, a correlation was observed between them, suggesting that the pore volume in the hardened cement affects the air permeability. However, a different trend was observed in the water penetration rate coefficient test, which suggests that other factors besides pore volume, such as the complexity of the pore composition, may have an effect on water penetration. In Figure 7 and Figure 8, the two groups shown in Table3 are N, ACX, FA30, and B20 (Group I) and B50, B85, and SF30 (Group II).

In Group I, it can be seen that both the water penetration rate coefficient and air permeability coefficient decrease with decreasing porosity. On the other hand, in Group II, the air permeability

Table 3. Groupings in Figures 7 and 8.

group	Mix proportion	Color of the mark
I	N	● ■
	ACX	● ■
	FA30	● ■
	B20	● ■
II	B50	● ■
	B85	● ■
	SF30	● ■

coefficient decreases with decreasing porosity as in Group I. However, the water permeability rate coefficient does not change so much with decreasing porosity. From these results, it was considered that B50, B85, and SF30, which were classified as Group II, had complex porosity. The complexity of the porosity composition may have affected the water permeability rate coefficient, resulting in a smaller water penetration rate coefficient, even with a large porosity. In addition, even if the porosity is the same, the air permeability coefficient of Group II shows a slightly smaller value than that of Group I. The relationship between porosity and air permeability coefficient also suggests that Group II has a complex pore composition. Therefore, it is suggested that the complexity of the pore composition can be expressed by combining the results of the water penetration rate coefficient test with the porosity and air permeability coefficient.

5 CONCLUSION

(1) The mass transfer characteristics and porosity showed different trends depending on the admixture material and its content. In particular, the mix proportion with a high replacement of blast furnace slag fine powder showed large water penetration at the side of specimen and that is significantly different from that of other mix proportion.
(2) It was found that even hardened cements having similar porosity showed different tendency in several mass tests depending on the test method transfer such as air and water.
(3) The water penetration rate coefficient may be affected by the complexity of the pore composition, suggesting that the complexity of the pore composition may be expressed by evaluating the combination of the air permeability coefficient and porosity.
(4) Since the size and diameter of each pore in this study were not measured, in the future a mercury intrusion porosimeter will be used to measure the porosity in detail.
(5) Only gas pressure injection and water permeation have been conducted, so we hope to understand the pore structure more clearly by conducting mass transfer tests using different materials and driving power.

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