16th East Asia-Pacific Conference on Structural Engineering & Construction (EASEC16)
Edited by C.M. Wang, V. Dao and S. Kitipornchai
Brisbane, Australia, December 3-6, 2019

INFLUENCE OF PORE STRUCTURE CHANGED BY CARBONATION USING GGBFS CEMENT ON WATER PERMEABILITY

J. NAKAMURA*, H. MIZUNO and T. IYODA

Graduate School of Engineering and Science, Shibaura Institute of Technology, Tokyo, Japan
Emails: me18091@shibaura-it.ac.jp, me17099@shibaura-it.ac.jp, iyoda@shibaura-it.ac.jp
*Corresponding author

Abstract. *In the cement industry, ground granulated blast furnace slag, which is an admixture, is used as an effort to reduce environmental impact. There are various characteristics of ground granulated blast furnace slag which can be useful as a substitute material for cement. However, carbonation resistance is low, and it can be a problem. In this study, it was investigated the effect of carbonation using ground granulated blast furnace slag on water permeability and it was also measured the porosity by Archimedes method and mercury intrusion porosity method. It was investigated the alteration by measuring the pore structure before and after carbonation of using ground granulated blast furnace slag. As a result, it was found that using blast furnace cement can easily permeate water after carbonation. About the influence of different curing periods, when the curing period was short, it was found that water can easily permeate in the samples. The result measured by Archimedes method showed that the porosity increased when carbonation occurred. As a result of mercury intrusion porosity method, there are many small diameter pores when carbonated, and it has a complicated pore structure. In conclusion, carbonation when using blast-furnace cement is considered to reduce the mass transfer resistance by forming a continuous pore structure.*

Keywords: *Ground granulated blast furnace slag; Carbonation; Water permeability; Mass transfer resistance; Pore structure;*

1. INTRODUCTION

Recently, the construction industry is promoting the use of admixtures from the viewpoint of reducing the environmental impact. There are various kinds of admixtures. Generally, fly ash and ground granulated blast furnace slag fine powder (GGBFS) are used in Japan. By using the admixture as an alternative material for cement, it is possible to reduce the CO_2 emissions significantly. Especially GGBFS can replace the cement in high volume and, as a result of that, it can greatly contribute to reduce environmental impacts. In addition, GGBFS cement characteristics such as increase salt damage resistance, suppression of ASR, enhancement of long-term strength and mass transfer resistance is also improved by curing. However, its resistance to carbonation can decrease.

Carbonation, which is one of the deterioration phenomena of reinforced concrete structures (RC), destroys the passive film of reinforced bar by decreasing the alkalinity in concrete and causes rebar corrosion. In general, carbonation of concrete is represented by equations (1) and (2).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

$$C\text{-}S\text{-}H + CO_2 \rightarrow CaCO_3 + SiO_2 + H_2O \qquad (2)$$

Carbonation of concrete proceeds by reaction of cement hydration products such as calcium hydroxide and C-S-H (Calcium Silicate Hydrate) with carbon dioxide. In addition, it is also reported that calcium carbonate, which are different in crystal morphologies (Calcite and Vaterite), is formed by carbonated hydrates and the Calcium and Silica ratio (Ca/Si) of C-S-H.

According to researches using actual structures in recent years, even if carbonation of concrete has progressed near to the rebar, corrosion cannot be seen or progressed slowly in a dry environment without rain. It has been reported that rebar corrosion progresses more in an environment where drying and moisture occurs repeatedly. In other words, it is thought that water is necessary for the occurrence of corrosion. From this, it is necessary to examine rebar corrosion due to carbonation of the concrete structure from both carbonation and water penetration. Not only the rate of carbonation progress of concrete but also the rate of water penetration has to be considered. The difference between carbonated hydrates and the calcium carbonate formed is also different, it is conceivable that the pore structure in the cement paste also changes. Previous studies have reported that carbonation of calcium hydroxide forms a dense pore structure while carbonation of C-S-H causes the coarse pore structure. In particular, the tendency is remarkable in the carbonation of C-S-H having a low Ca/Si ratio. The Ca/Si ratio can decrease when using admixtures additives such as GGBFS. If the cement paste using GGBFS is carbonated and the pore structure is coarsened, the penetration of water, which causes rebar corrosion, may be simplified. In this study, we made concrete using GGBFS, and examined the influence of the carbonation of the concrete on the water permeability when the carbonated hydrate changes.

2. EFFECT OF CARBONATION ON WATER PENETRATION RESISTANCE

2.1. Materials and Mix Proportion

Table 1 shows the details of the materials used in this research. Table 2 shows the mix proportion of concrete. The water binder ratio was set to 60 % in order to accelerate the progress of carbonation. Concrete was prepared by replacing GGBFS with 0 %, 50 %, and 70 % of the cement.

Table 1. Details of materials used

Materials	Symbol	Types and Physical Properties
Water	W	Tap Water
Binder	OPC	Ordinary Portland Cement (Density: 3.16 g/cm^3, Fineness: 3240 cm^2/g)
	GGBFS	Ground Granulated Blast Fine Slag Powder (Density: 2.91 g/cm^3, Fineness: 4290 cm^2/g)
Fine Aggregate	S	Crushed Sand (Density: 2.62 g/cm^3, Absorption: 1.71 %, Fineness modulus: 2.59)
Coarse Aggregate	G	Limestone (Density: 2.70 g/cm^3, Absorption: 0.32 %, Fineness modulus: 6.61)

Table 2. Mix proportion of concrete

Symbol	W/B (%)	Replacement of GGBFS (%)	Air (%)	s/a (%)	Unit Weight (Kg/m^3)				
					W	Binder		S	G
						OPC	GGBFS		
OPC	60	0	4.5	46	165	275	0	847	1025
B50		50				138	138	843	1019
B70		70				83	193	841	1017

2.2. Specimen Specifications

Table 3 shows the curing condition of the specimens. The samples were cylindrical with the size of Φ100×50 mm. The curing condition were non-curing (S1) and sealed curing 7 days (S7). After curing, the specimens were allowed to stand in a constant temperature and humidity chamber (temperature 20±2 °C, relative humidity 60 %) until the age of 28 days. The carbonated specimens were allowed to stand after 28 days in an accelerated environment (inside a chamber with concentration 5 % of CO_2). In order to investigate the effect of carbonation on water permeability, all the tests were conducted at the 20th week of age when the test specimens placed in the accelerated environment were completely carbonated. A prismatic specimen was also prepared, and it was judged that carbonation of the cylindrical specimen was completely finished when the carbonation depth reached 25 mm.

Table 3. Mix proportion of concrete

<table>
<tr><th>Curing</th><th colspan="2">0
Day</th><th></th><th colspan="2">1
Day</th><th></th><th colspan="2">1
week</th><th></th><th colspan="2">4
weeks</th><th></th><th>20
weeks</th></tr>
<tr><td>S1</td><td rowspan="4">Cast</td><td rowspan="4" colspan="2">Form Placement</td><td rowspan="4">Demold</td><td colspan="8">Constant Temperature and Humidity Room (temperature 20±2°C, relative humidity 60%)</td><td rowspan="4">Test</td></tr>
<tr><td>Carbonation S1</td><td colspan="6">Constant Room</td><td colspan="2">Accelerated Carbonation</td></tr>
<tr><td>S7</td><td rowspan="2" colspan="3">Sealing Curing</td><td colspan="5">Constant Room</td></tr>
<tr><td>Carbonation S7</td><td colspan="3">Constant Room</td><td colspan="2">Accelerated Carbonation</td></tr>
</table>

2.3. Water Penetration Test

The water penetration test was conducted with reference to the standard specification for concrete structure [test method and specifications] of Japanese Society of Civil Engineering (JSCE). Figure 1 shows the test method. The side of the specimen was sealed with aluminum tape and the top and bottom were left opened. The water absorption method was immersed to a height of 10 mm from the lower end of the specimen. Tap water was used as a test solution. The specimens were split at 1, 2, 3 hours after immersion and sprayed with an indicator. The water penetration depth was measured at 5 points using an electronic caliper for the colored part by the indicator, and the average value was taken.

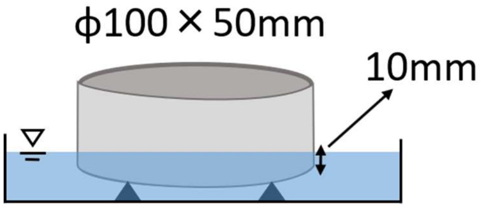

Figure 1. Water penetration test method

3. RESULT OF WATER PENETRATION TEST

Figure 2 shows the fractured surface of the specimen after 3 hours of water absorption. The blue part shows that water has penetrated. Water penetration was found to be smaller in GGBFS than OPC in uncarbonated samples. On the other hand, when carbonation is carried out, the water penetration of GGBFS significantly increased.

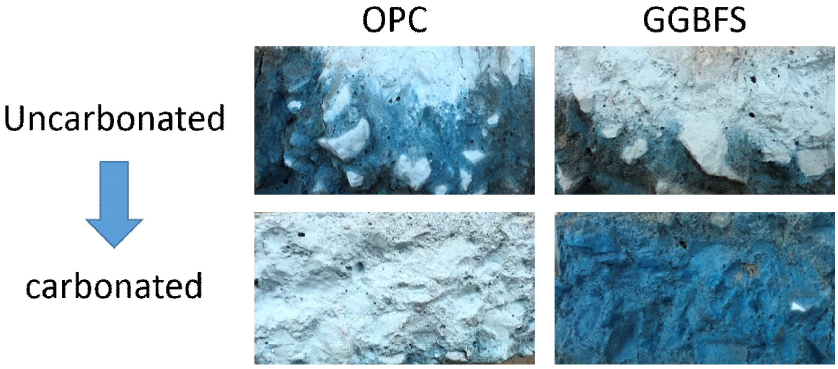

Figure 2. Surface view of split after water penetration test

Figures 3 and 4 show the results of measuring the water penetration depth of S1 and S7. In S1, the water penetration depth is smaller as GGBFS is replaced, and it can be seen that water penetration is suppressed by GGBFS replacement. The water penetration depth for S7 had around the same value at any replacement rate.

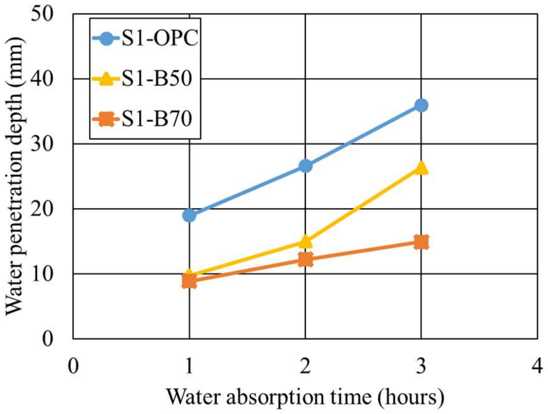

Figure 3. Water penetration depth (S1)

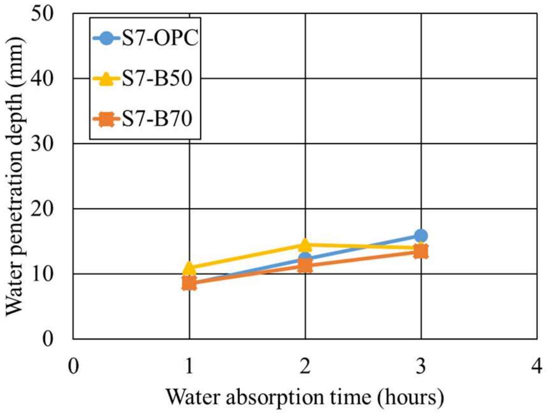

Figure 4. Water penetration depth (S7)

Figures 5 and 6 show the measurement results after carbonation of S1 and S7. The water penetration depth in OPC was significantly reduced by carbonation. On the other hand, the water penetration of B50 and B70 were increased by carbonation. Particularly in S1, the penetration depth of water reached 50 mm in 2 hours of water absorption. From the above, it was shown that the resistance to water penetration is lowered when blast furnace cement samples were carbonated.

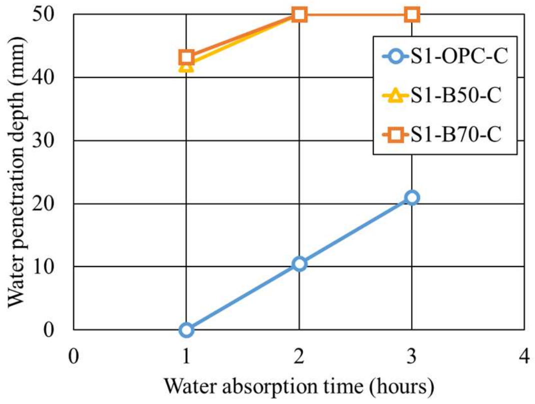

Figure 5. Water penetration depth after carbonation (S1)

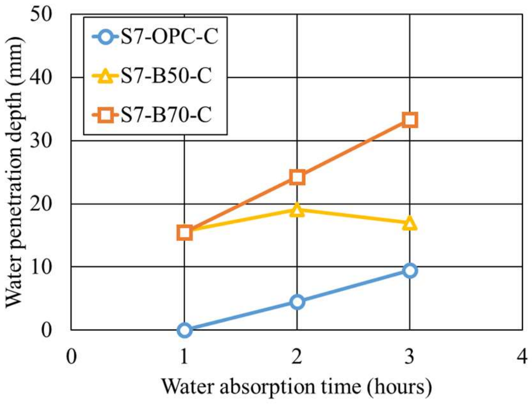

Figure 6. Water penetration depth after carbonation (S7)

4. EXAMINATION OF PORE STRUCTURE CHANGES BY CARBONATION

From the results of the water penetration test, it is considered that the changes in water penetration resistance due to carbonation were because of the modifications in the pore structures. Therefore, the amount of pore and its structure were measured by the Archimedes method and the mercury intrusion method using the specimens subjected to the water penetration test.

4.1. Archimedes Method

The sample was crushed and used with a size of about 5 mm square, so the porosity was calculated by equation (3). The sample was immersed in acetone for 24 hours and vacuum degassed to obtain a dry mass W1. After that, the sample was put in water and depressurized to fill with water inside the air gaps and calculate the water saturated mass W2. The mass in water W3 was calculated using the sample mass when immersed in water.

$$Porosity(\%) = \frac{(W2-W1)}{(W2-W3)} \times 100 \tag{3}$$

Figure 7 shows the results of porosity for uncarbonated and after carbonation of S1. The porosity of the OPC was reduced by carbonation. However, the porosity in GGBFS was increased by carbonation. Figure 8 shows the result of S7. As a result, it was found that the porosity of GGBFS increases after carbonation in S7 as well as in S1. From this fact, carbonation when using blast-furnace cement may increase the pore volume.

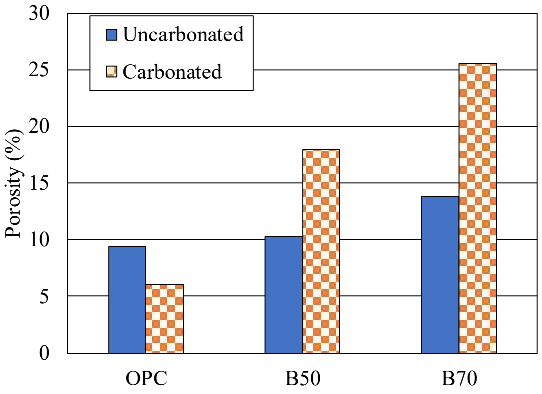

Figure 7. Result of porosity (S1)

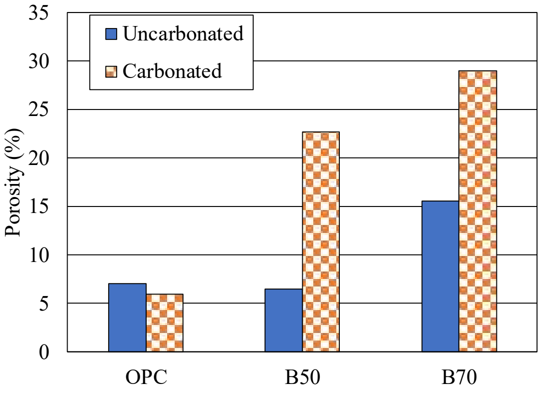

Figure 8. Result of porosity (S7)

4.2. Mercury Intrusion Method

The specimen used were the same as the Archimedes method. In this study, we focused on the continuity of the porosity, which greatly affects the water permeability. The pore in the cement-hardened structures are connected to each other in large and small pores to form a complex pore structure. In the mercury intrusion method, the pore size is calculated on the assumption that mercury continuously penetrates from the large pore size to the small pore size. However, when a large pore such as an ink bottle pore exists, the large diameter pore is evaluated as a small diameter pore. Therefore, assuming the difference as the ink bottle pore effect from the relation of hysteresis generated in the process of pressurization and depressurization of mercury, it was evaluated the continuity of the pores.

Figure 9 shows the result of cumulative pore size of S1. The total pore volume of OPC was the smallest. On the other hand, the total pore volume of B50 and B70 are larger than OPC, resulting in a large pore volume of small diameter pores. That is, when blast furnace slag fine powder is replaced, it is conceivable that many small diameter pores exist and that it has a complicated pore structure.

Figure 10 shows the result of cumulative pore size of S7. The total pore volume of OPC was the smallest, and B50 and B70 resulted in a large pore volume of small diameter pores. It follows the same tendency as S1.

Figure 11 shows the results after carbonation of S1. The difference in total pore volume due to the presence or absence of carbonation in OPC is small. On the other hand, B50 and B70 had an increased in the amount of the large diameter pores by carbonation.

Figure 12 shows the results after carbonation of S7. There was no significant change in OPC compared to the results of carbonation of S1. On the other hand, B50 shows that the total pore volume is reduced by carbonation. In addition, the total pore volume of B70 became the largest.

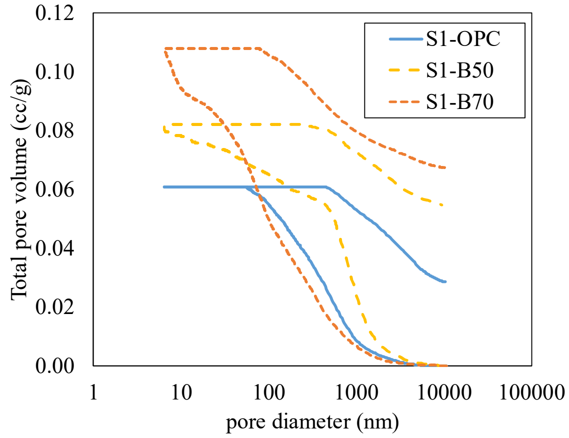

Figure 9. Cumulative pore size (S1)

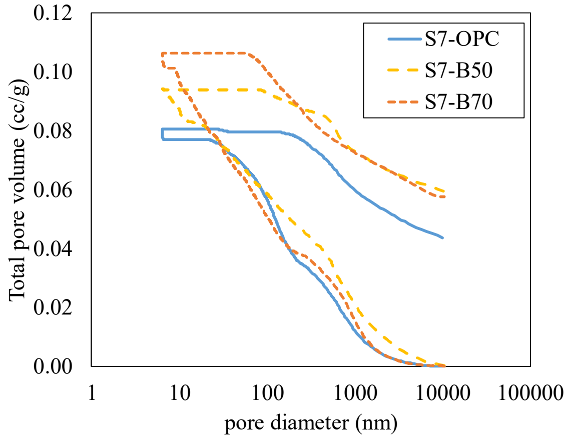

Figure 10. Cumulative pore size (S7)

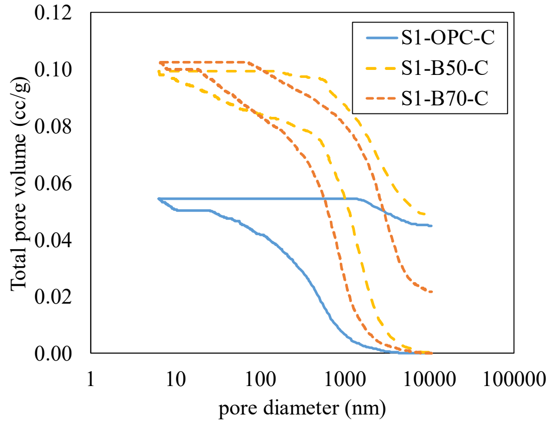

Figure 11. Cumulative pore size after carbonation (S1)

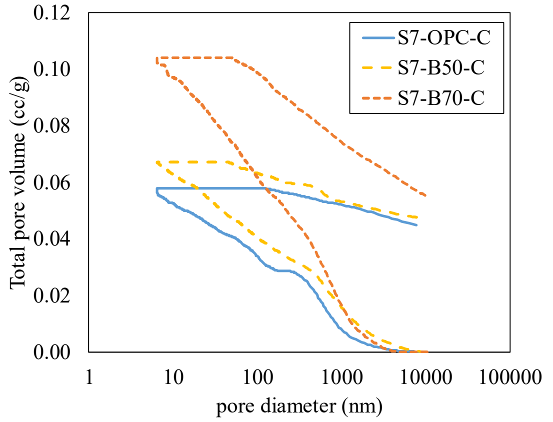

Figure 12 Cumulative pore size after carbonation (S7)

Figure 13 and 14 show the volume ratio of the ink bottle pore contained in the total pores. The result is the value obtained by dividing the difference between the pressurization process and the decompression process by the total pore volume. This value is defined in this research as the ink bottle pore existing in the cement hardened structure. The larger this value is, the smaller the difference between the pressurizing process and the depressurizing process, which means that the structure has a complicated pore structure. In the case of uncarbonated S1, the value becomes larger when GGBFS is replaced when compared with OPC, and it is considered that a complex pore structure is obtained by replacing GGBFS. However, in the results after carbonation, the value of OPC increases, but the value GGBFS replacement results in a smaller value. From this result, it is considered that the carbonation of OPC densifies the pore structure to form complicated pores with ink bottle pores. On the other hand, it is considered that when the GGBFS is replaced, carbonation changes the pore structure from densified to continuous. Also, in the result of S7, the value for OPC increased due to carbonation. On the other hand, in the case of GGBFS replacement, the difference due to the presence or absence of carbonation was small.

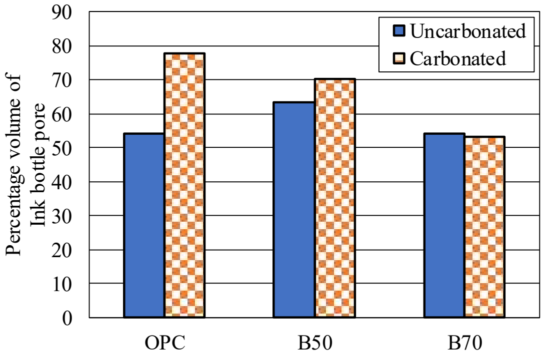

Figure 13. Volume of ink bottles (S1)

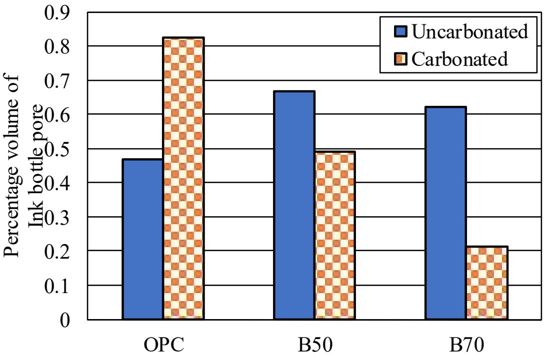

Figure 14. Volume of ink bottles (S7)

From the above, it was considered that the hardened cement structures for blast furnace cement had a complex pore structure but became a continuous pore due to carbonation. And the tendency was remarkable as the number of days for curing decreased. Previous studies have shown that the carbonate which hydrates when GGBFS is substituted is superior to calcium hydroxide in carbonation of C-S-H. From previous studies (5), it has been reported that C-S-H is superior to calcium hydroxide in carbonation when GGBFS is replaced. From this, it is shown that carbonation of C-S-H forms a continuous pore structure and reduces the mass transfer resistance such as water permeability.

5 CONCLUSIONS

In this study, we investigated the effect of carbonation on the water permeability in hardened cement structures using blast furnace cement, focusing on the changes in pore structure. The results obtained are described below.

(1) When the concrete using blast furnace cement is carbonated, the resistance to water penetration decreases, and the tendency becomes remarkable for the early days of curing.
(2) As a result of measuring the porosity by the Archimedes method, when the cemented material of the blast furnace cement is carbonated, the porosity increased when compared with the uncarbonated one.
(3) From the results of mercury intrusion method, the hardened cement structures for blast furnace cement had many small diameter pores and had a complicated pore structure.
(4) carbonation of C-S-H forms a continuous pore structure and reduces the mass transfer resistance such as water permeability.

REFERENCES

Suzuki, K., Nishikawa, N. & Hayashi, T., (1989), Carbonation of the C-S-H with various Ca/Si ratios, Cement science and concrete technology, No. 43, 18-23

Maehara, S. & Iyoda, T., (2018), Study on the effect of rain exposure on carbonation-induced spalling / falling of the cover concrete, Journal of japan society of civil engineers, Vol. 74 (No. 2), 80-87

Harasawa, Y., Honda, K. & Iyoda, T., (2014), Effects of different carbonation environments on pore characteristics and carbonation progress, Proceedings of the japan concrete institute, Vol. 36 (No. 2), 808-813

Japan social of civil engineers, (2018), Test method for water penetration rate coefficient of concrete subjected to water in short term, The standard specification for concrete structure [test method and specifications] of JSCE, 448-452

Ito, T., Iyoda, T., (2017), Investigation of carbonation progress mechanism in cement with high replacement of admixtures, Proceedings of the japan concrete institute, Vol. 39 (No. 1), 637-642