

Study of carbonation mechanism and post-carbonation permeability in a cement with high content of blast furnace slag

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ABSTRACT

Considering the reduction of the environmental impacts, the use of mixed cement is becoming important. Cement using highly replace ground granulated blast furnace slag fine powder has various characteristics, such as resistance for penetration of chloride ion, ASR e.t.c. On the other hand, resistance to carbonation is known to decrease than ordinary Portland cement. In this study, the carbonation behavior and its mechanism using highly replacement of blast furnace slag cement was discussed. In addition, the characteristics of penetration for water and gas after carbonation were investigated. As a result, it was found that carbonation of C-S-H excels predominantly in highly replacement of blast furnace cement and many vaterite is produced than calcite. Furthermore, it was revealed that after the carbonation with the collapse of C-S-H, the pore structure became coarse and the penetration resistance remarkably decreased. In particular, it was confirmed that the permeability of gas and moisture remarkably increased. Meanwhile, chloride ion permeation can be suppressed by taking advantage of the characteristics of the blast furnace slag fine powder. It is probably due to the influence of electrical adsorption performance.

1. INTRODUCTION

In order to suppress global warming phenomena, it is necessary for industry to take an action against carbon dioxide emission. Particularly in the construction industry, carbon dioxide emissions, especially during cement production, are considerably high. There are many methods to reduce carbon dioxide emissions. Among them, the use of admixture as a substitute for cement is currently carried out actively because of its effectiveness. Recent years, Japan has been actively making developments of cements which raised the replacement rate of ground granulated blast furnace slag and fly ash. This study target on the characteristics of cement with large replacement of ground granulated blast furnace slag.

Because there are many steel mills in Japan, a large amount of blast furnace slag is available. Therefore, it is possible to manufacture cement which can reduce the environmental impacts by replacing in it large quantities of blast furnace slag. In addition, improvements are known as effects of using blast furnace slag in concrete, such as suppression of hydration heat generation and durability. On the other hand, there are problems that are likely to occur by using this type cement, such as delay in initial strength development, increase in carbonation rate and cracking due to drying shrinkage.

In this study, attention was focused on the progress of carbonation and the penetration characteristics after carbonation using cement with high replacement of blast furnace slag. Cement with high content of blast furnace slag was setting and the carbonation was promoted by various environments. The hydrated products were compared before and after carbonation by XRD. Subsequently, the pore structures before and after carbonation were compared. Furthermore, mortar was evaluated for water permeability before and after carbonation.

2. COMPARISON OF HYDRATES BEFORE AND AFTER CARBONATION

Hydration products of cement are carbonated by carbonation, such as calcium carbonate from calcium hydroxide. However, the calcium carbonate has some different crystal structures such as calcite, vaterite and aragonite. Carbonation of ettringite, monosulfate and calcium silicate hydrate is conceivable as vaterite or aragonite was produced after carbonation. Here, it was decided to compare differences in hydration product before and after carbonation using cement with high volume of blast furnace slag.

2.1 Outline of experiments

2.1.1 Specimen overview

In order to exclude the influence of a small amount of mixed components in preparing the test specimen, the ordinary Portland cement was used for this research. The chemical compositions of materials are shown in Table 1. As cement types, ordinary Portland cement (N), B20 (BFS 20% replacement), B50 (BFS 50% replacement), and B90 (BFS 90% replacement) were used. The specimen did not receive the influence of bleeding as much as possible and, in order to be able to measure X-ray diffraction with a small amount, a disk type of $\phi 40 \times 5$ mm was used as shown in Figure 1. The water to binder ratio was set constant for cement paste as 50%. After manual mix, it was casted and sealed with a glass plate. On the next day, it was demolded and sealed cured until 28 days for hydration promoting.

Table 1. Mineral composition of materials

kind of binder	Density (g/cm ³)	Blaine (cm ² /g)	LOI(%)	Chemical components (%)											
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cl
N	3.16	3480	0.62	21.36	2.28	2.66	65.02	1.46	2.08	0.29	0.48	0.27	0.24	0.09	0.013
GGBFS	2.91	4280	0.17	34.05	14.65	ND	46.15	5.94	ND	0.26	0.28	0.57	0.01	0.33	ND

2.1.2 Setting carbon dioxide concentration

After curing, carbonation environments were set with different concentration of carbon dioxide. The concentrations of carbon dioxide were 0%, 0.05%, 0.5%, 5%. The carbon dioxide concentration of 5% was based on the accelerated carbonation test method for concrete (JIS A 1153). The value of 0.5%

promoted low concentration environment, 1/10 of 5%. In addition, the concentration of 0.05% was set in the laboratory because it reflects the actual environment. The 0% carbon dioxide environment remained in the sealed state even after curing. For all environments, constant temperature of 20 degrees Celsius and the humidity of 60% RH were maintained.

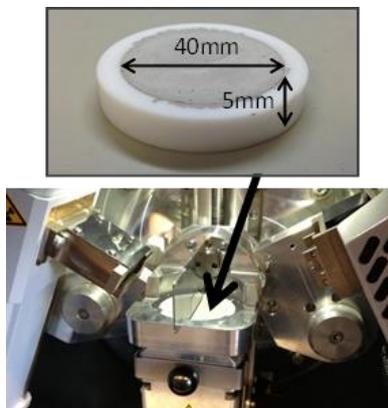


Figure 2. Specimens size and XRD setting images

2.1.3 Surface X-ray Diffraction Test Using the Same Specimen

In the powder X-ray diffraction test, it is difficult to distinguish between the carbonated part and the non-carbonated part. In addition, troubles are involved in the process up to the measurement such as crushing, errors are generated because the specimens are different each time, and so on. Therefore, in this research, as shown in Figure. 1, the surface layer of the non-grinded samples was used for the X-ray diffraction test. Since it was considered that carbonation progresses from the surface of the specimen, this study considered that progress of carbonation can be clarified by surface using X-ray analysis. In addition, since the specimens are not grinded, it is possible to use the same specimen, reducing errors due to the specimen.

X-ray measurement conditions were tube voltage 40 kV, tube current 250 mA, scan speed 0.25 deg/min, sampling interval 0.025 deg. In this study, focusing on the formation of calcium carbonate by carbonation, the integrated intensity was calculated from the diffraction peak (calcite: 29.4 °, vaterite: 27.03 °), and it was taken as the production amount. After the specimen was carbonated under each carbon dioxide concentration environment, Surface X-ray diffraction test was carried out on the same specimen was used at the age of 0.2, 0.4, 1, 2, 4, 7, 10, 14, 21, 28 days from the start of carbonation.

2.1.4 Differential thermogravimetric analysis (TG-DTA)

The amount of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and calcium carbonate (CaCO_3) produced was measured by differential thermogravimetric analysis. The amount of production was calculated from the inflection point of the DTA curve using the weight change of the TG curve. The measurements were made after the curing and after the start of carbonation over time.

2.2 Results of Hydration products – Relationship between cement type and carbonation

Figure 2 shows the changes in the amount of calcium carbonate produced with the progress of the carbonation over time for N and B50. N and B50 confirm that both calcite and vaterite calcium carbonate increase as the age progresses. At any concentration of N, much calcite was produced compared to vaterite. B50 was different from N, the amount of vaterite produced tended to be larger at any carbon dioxide concentration compared to calcite. The calcite and vaterite have different crystal structures and densities, and the stability of vaterite is lower than that of calcite. Compared with calcite, vaterite is reported to be formed from calcium silicate hydrate (CSH) having a low C/S ratio and monosulfate. For B50 mixed with blast furnace slag fine powder, it is considered that a lot of vaterite was generated due to the low C/S ratio on CSH.

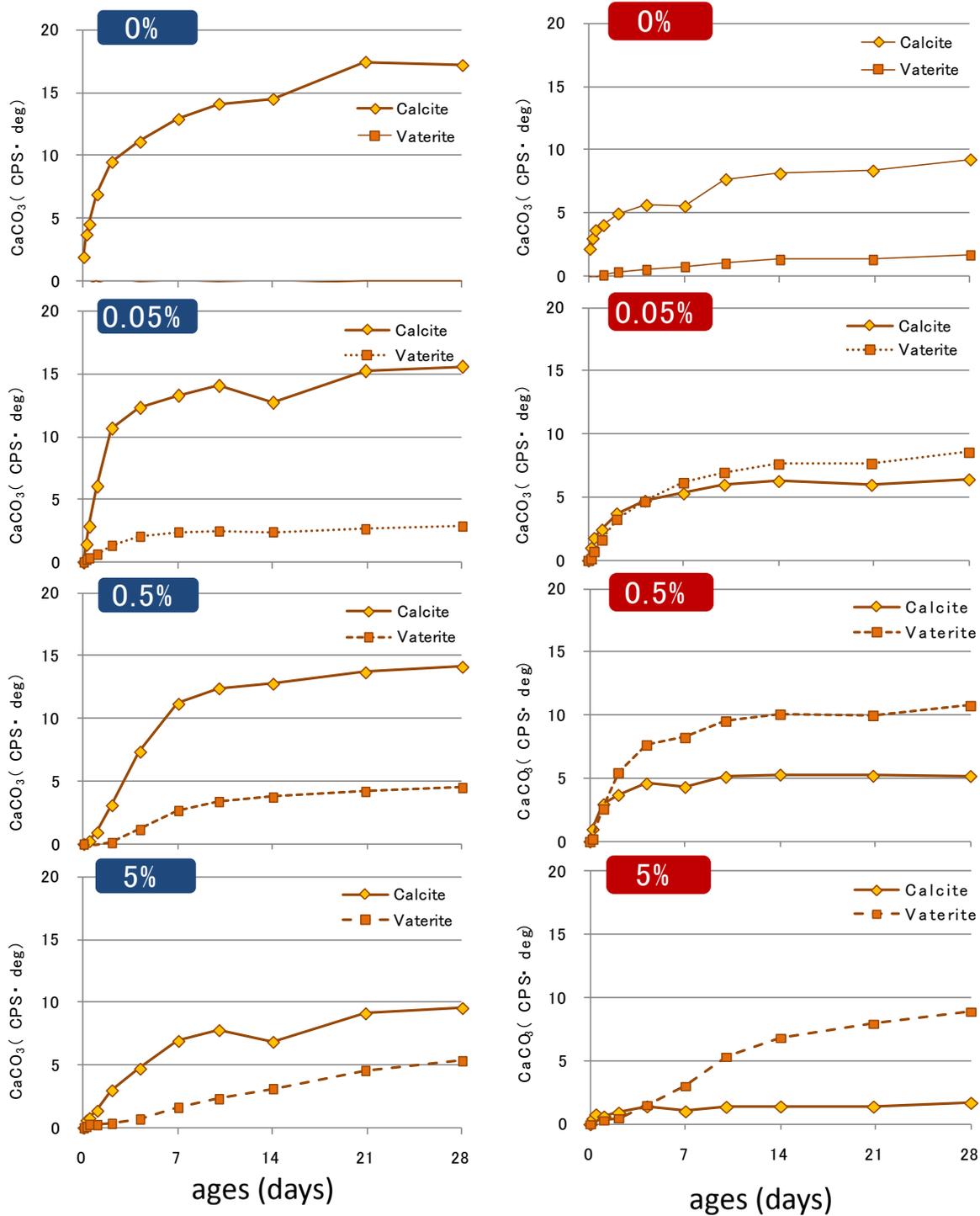


Figure 2. Results of CaCO_3 products on different concentration of carbon dioxide (left: N cement, right: B50 cement)

Figure 3 shows the amounts of calcium carbonate of N and B50 obtained by differential thermogravimetric analysis. As a result, the production rate varies depending on the difference in carbon dioxide concentration and, the higher of the concentration, the slower the production rate was obtained. However, after 14 days of carbonation age, regardless of the carbon dioxide concentration, the amount of calcium carbonate produced was about 20% for N and about 15% for B50. Here, when compared with the results of the X-ray diffraction tests at Figure 2, it was found that the production rates of calcium

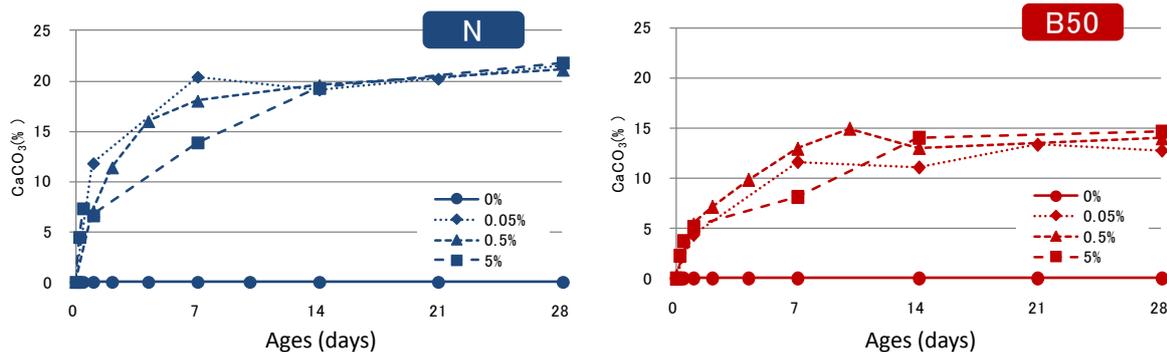


Figure 3. Results of amount of CaCO₃ products on different concentration of carbon dioxide

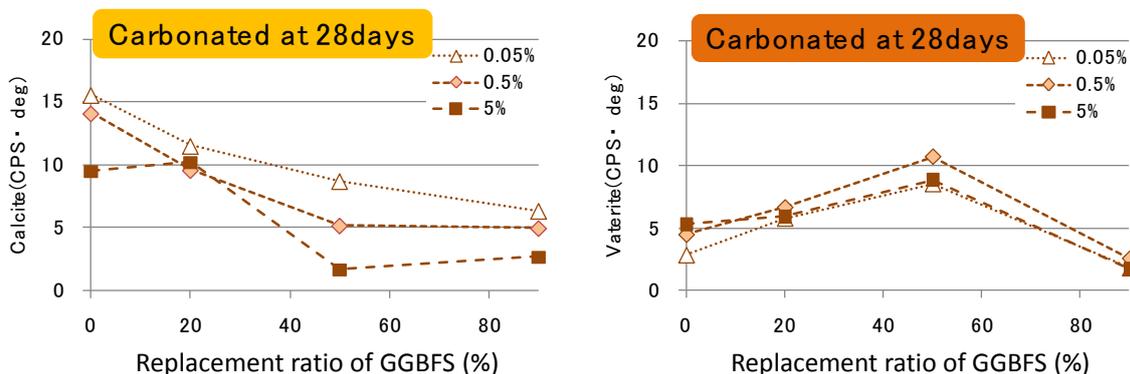


Figure 4. Relationship between replacement ratio if GGBFS and calcite, vaterite

carbonate in N and B50 are different from each other, and the higher the concentration, the slower the formation rate. As mentioned above, many vaterite was produced compared to calcite due to contamination of blast furnace slag fine powder. Therefore, Figure. 4 shows the relationship between blast-furnace slag fine powder replacement rate and production amount of calcite and vaterite. Calcite decreased as the replacement rate of blast furnace slag fine powder was higher. This showed the same tendency as slag replacement rate and calcium hydroxide production amount. That is, the more calcium hydroxide before carbonation, the more calcite is produced. Vaterite showed a tendency to increase with increasing slag replacement rate, reaching the maximum value at 50%, and then decreasing as the substitution rate increased. It is thought that carbonation progresses due to the formation of calcium carbonate, the decrease of calcite, and the increase of vaterite, up to the slag substitution rate of 50%. The relationship between the amount of calcium hydroxide produced on the 28 days and the amount of calcite produced at 28 days of carbonated age is shown in Figure 5. The more calcium hydroxide produced, the more calcite was produced, and the same tendency was observed even when the carbon dioxide concentration changed. However, the lower concentration showed a tendency to increase the amount of calcite formation. This suggests that the amount of calcite produced from the amount of calcium hydroxide produced before carbonation may be largely determined for each concentration in this study.

3. COMPARISON OF PORE STRUCTURE BEFORE AND AFTER CARBONATION

3.1 Outline of experiments

3.1.1 Specimen overview

The materials used were the same as in section 2.1, the specimen to analyse the progress of carbonation with cement paste was as shown in Figure 6. After achieve carbonation, a sample of

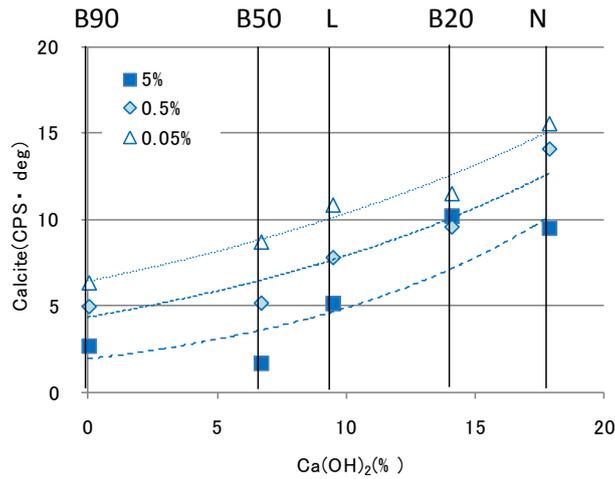


Figure 5. Relationship between Ca(OH)_2 and calcite products

5×10×100 mm square prismatic type were submitted to mercury intrusion porosimetry method. In order to carbonate the entire specimen in a short period of time, the water binder ratio was set to be constant at 100%. In order to prevent material segregation, a high-performance special additive was used as an admixture. The addition rate was 1.0% over the unit water amount.

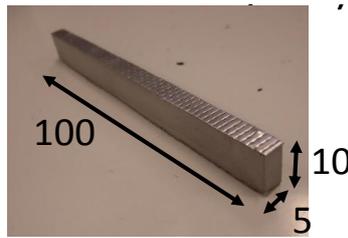


Figure 6. Specimens size for measurement of porosity

3.1.2 Test environment

With reference to the test conditions in section 2.1, the carbon dioxide concentration was set to be two kinds: 0.05% in the laboratory under the actual environment and 5% as the accelerated test environment based on JIS with humidity of 60% RH. The specimen was covered with aluminium tape except for both side faces of 10×100 mm so that carbon dioxide could penetrate from two directions. After leaving the specimen under each environment, in order to ascertain the degree of progress of carbonation, it was occasionally split and sprayed with phenolphthalein to observe the change in coloration. The time when the entire surface no longer change color was taken as completion of carbonation. The timing of the conclusion of carbonation varies depending on the concentration of carbon dioxide, and it was about 28 days for 0.05% and 7 days for 5% after carbonation started for both N and B50.

3.1.3 Pore structure (mercury intrusion porosimeter)

Pore size distribution and cumulative pore volume in the specimen were measured by a mercury intrusion porosimeter. For the sample, a specimen was cut into 5 mm squares and used. As a pre-treatment, it was dipped in acetone and degassed under vacuum.

3.2 Results of Pore structures - Change by carbonation

Figure 7 shows the pore size distribution of N and B50 before and after carbonation and 28 days after carbonation. Regardless of the concentration of carbon dioxide in both pore diameters of N and B50, the pore diameter showed a peak by carbonation shifted to the larger pore size. In N and B50, the peak and cumulative pore volume did not differ greatly even if the carbonation period was long. In addition, when the carbon dioxide concentration was different, the carbon dioxide concentration was 0.05%

regardless of the cement type and, the peak of the pore diameter was observed not only in the larger ones but also in the smaller ones. There was no change in the cumulative pore volume of N and B50 even at the carbonating age, but as the carbon dioxide concentration became higher, the pores of 100 nm or more increased. In B50, pores of 1000 nm or more increased with the progress of the carbonation age, and especially at the carbon dioxide concentration of 5%, it occupied about 40% in the cumulative pore volume. Since this study was conducted with a water binder ratio of 100%, it is considered that the pore structure was influenced. Saeki et al. reported that the pore size distribution and the pore volume change when the water cement ratio increases in mortar. Although the presence of water is necessary for the carbonation, the moisture inside the concrete evaporates simultaneously with carbonation. Evaporation is faster as the diameter of the larger pores increase, whereas no change occurs in the amount of pores, since carbonation does not occur where the water does not exist due to evaporation. Therefore, when the water binder ratio is low, the pore size shifts to a smaller diameter due to the formation of calcium carbonate, but when the water binder ratio is high, the pore having a large diameter increases. In addition, Asaga measured the characteristics of the hardened cement paste with a ratio of 1 using powder, the pore diameter shifted to the larger side by carbonation. The position of the peak was near 700 nm for the OPC sample and as slag was added for the samples, it shows results of 1000 nm. As shown in Figure 7, in this study, the reason why the gap of 1000 nm or more increased was that it was affected by evaporation of water because it was carried out with high water binder ratio to promote carbonation.

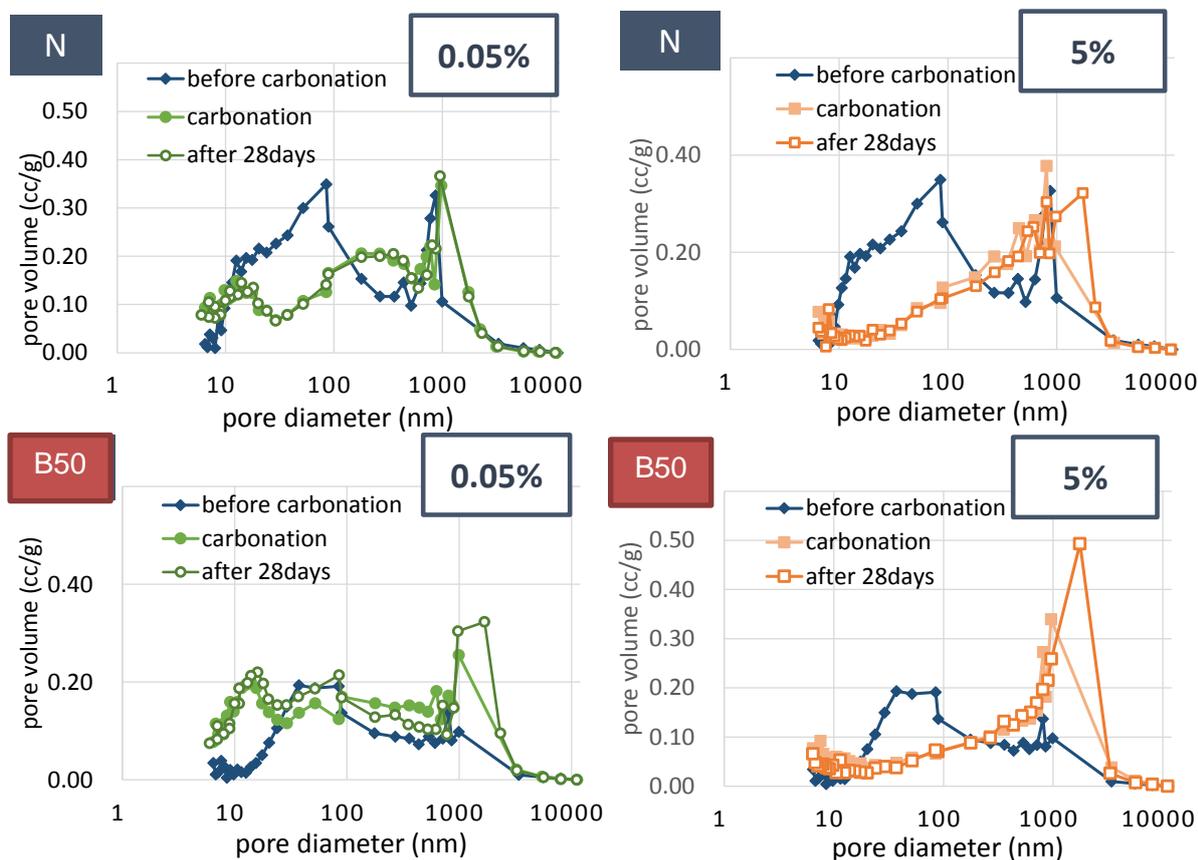


Figure 7. Pore distribution on pre and post carbonation by different cement

From the above, it is considered that in N, calcium hydroxide produced calcium carbonate by the carbonation and fills the pores, but in B50 the amount of calcium hydroxide produced was small, so the pores were not sufficiently densified. In addition, as B50 produces low CSH of Ca/Si ratio and changes in the structure of CSH due to carbonation. It is considered that CSH decomposes by carbonation, which causes increasing of the pore structure rather than densification by calcium hydroxide carbonation.

4. EVALUATION OF WATER PENETRATION CHARACTERISTICS BEFORE AND AFTER CARBONATION

4.1 Outline of experiments

In this section it was examined how the change in the pore structure after carbonation observed in section 3, affects water penetration resistance. The sample was a standard mortar made according to JIS with water binder ratio of 50% and sand cement ratio of 3. The cements were used N and B50 and B70 with replacement ratio of 50% and 70% of blast furnace slag respectively. Mortar was made with dimensions of 40×40×160 mm and curing periods were 1, 3, 7 days. After the curing was finished, it was left standing for 28 days in a dry atmosphere free of carbon dioxide not be affected by carbonation. After 28 days drying, it was cut using the mortar cutter to a thickness of 10 mm to prepare a sample of 40×40×10 mm. This is because carbonation occurs in all areas. Thereafter, the system was allowed to stand until all the areas were carbonated in an accelerated carbonation environment on temperature of 20 degrees Celsius, Relative humidity of 60% and a concentration of Carbon dioxide as 5%. After confirming that all area was carbonated, the measuring of the weight change for the sample by applying water and moisture absorption rate was calculated as shown in Figure. 8.

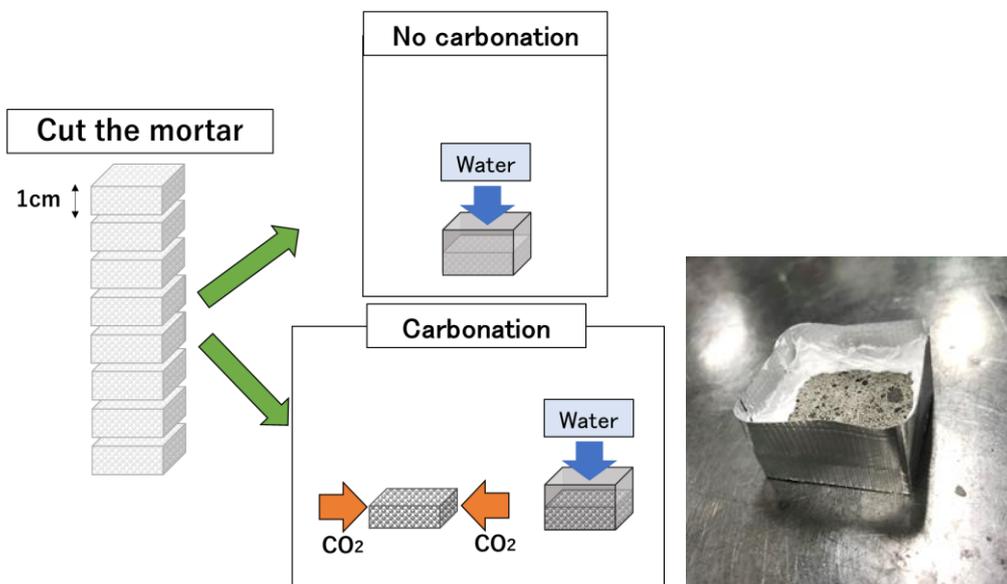


Figure 8. Outline of experiment and specimens size

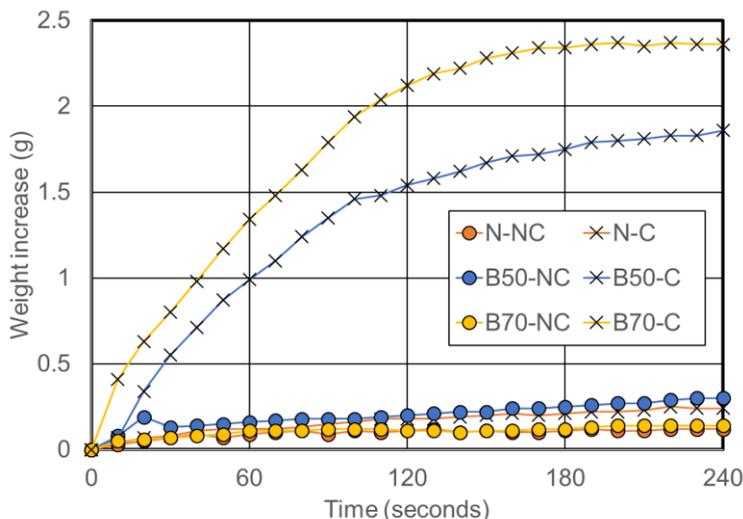


Figure 9. Results of water permeability test

4.2 Experiment results

Figure 9 shows the state of moisture penetration for all cases. Comparing the sample in which carbonation did not take place, it is found that the moisture permeation rate is slower in B 70, which has higher substitution rate, than in N. This is thought to be due to the improved water penetration resistance because blast furnace cement forms a dense pore structure as clarified by previous studies. On the other hand, when carbonated samples are compared, there are almost no difference from the un-carbonated sample in N, however in B50 and B70 it is significantly faster than before carbonation.

5. CONCLUSIONS

In this study, it was regarded to the carbonation of cement in which blast furnace slag fine powder mixed, the effects of the difference in the carbonation environment and the difference in the mixing amount of blast furnace slag fine powder are examined. As a result, it was found that calcite is superior in formation of vaterite in carbonation of ordinary Portland cement, on the other hand, vaterite is superior in formation of calcite in blast furnace slag cement. In addition, as a change in pore structure due to carbonation, densification due to carbonation was confirmed in ordinary Portland cement, however large pore was confirmed in blast furnace slag cement. As a result, it can be confirmed that the permeation of water into the hardened after carbonation becomes extremely large, and it is necessary to consider the influence on the rebar corrosion. In particular, it is assumed that degradation of CSH occurs, which suggests that the pore structure becomes large and the water penetration resistance decreases intensely.

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