

Study of carbonation mechanism of blast-furnace slag cement with different carbon dioxide concentrations

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ABSTRACT: In general, it is known that the blast-furnace slag cement has more small resistance for carbonation compared with ordinary Portland cement. However, that the wonder is that universal? According to recent research, as a result of investigating the actual structures that it was built using ordinary Portland cement and blast-furnace slag cement, carbonation depth was similar in concrete using each cement. However, the result of accelerated carbonation test using these concrete cores, the carbonation depth of blast-furnace slag cement is increased significantly. This is a great property of blast-furnace slag cement. According to these results, it is affected by moisture into concrete. However, the mechanism of carbonation progress on using different cement types would be not same on different situation such as different concentration of carbon dioxide. Therefore it is considered possible to clear the mechanism is important scientifically.

1 INTRODUCTION

There is carbonation into one of the deterioration of reinforced concrete structures. Carbonation occurs in concrete, the steel in concrete will be corroded for destroying the Oxide layer around steel, therefore carbonation is a factor to deteriorate the structural performance and durability. Usually, in order to determine the resistance of carbonation in a short time, the accelerated test by high concentrations of carbon dioxide that is different from actual concentration is performed. Lots of reports are available on the carbonation resistance of concrete using accelerated testing that is influence of mix proportions, materials and curing conditions. Resistance of carbonation is very low on concrete with blast furnace slag cement comparing with using ordinary Portland cement.

In Japanese standards, the use of the carbonation accelerated test has been found. However, it is possible to determine the carbonation ratio is difficult. The reason is because different materials, mix proportions, initial curing periods and shape of specimens. Therefore it is required of carbonation test with actual environment exposure or real structure by concrete with same mix proportions. Since the research results of concrete with ordinary Portland cement is implemented more generally, it is possible to be converted into the ratio of carbonation coefficient in real environment from obtained that in the case of carbon dioxide concentration different. However in

case of different cement type, it is difficult to be converted for less of the research results.

It is thought that carbonation resistance is low on blast furnace slag cement by comparing the ordinary Portland cement. Because of the amount of calcium hydroxide produced by blast furnace slag cement is less than that by ordinary Portland cement, also pH has been low. However it is not possible to explain the differences in the carbonation progress only to difference in pH. It has been reported that the carbonation progress in real environment is not observed difference in the ordinary Portland cement and blast furnace slag cement. It can be considered such as water supply by surrounding environment has influenced in a real environment. However it is reported that it is large difference on different cement type using concrete cores from same carbonation progress. It was showed that the progress of carbonation increases considerably in concrete using blast furnace slag cement in accelerated test. The carbonation mechanism is different in the case where the carbonation dioxide concentration is different and that the nature and amount of cement hydrate is different by mixing cement and type of ground granulated blast furnace slag is different.

This research aimed at clarifying the carbonation progress on different concentration of carbon dioxide and type of cement. It is investigated carbonation mechanism on different carbon dioxide concentrations using different amount of blast furnace slag cement. It investigated the hydration products and difference of calcium carbonates.

Table-1 Chemical components on using materials

	Density (g/cm ³)	Blaine (cm ² /g)	ig.loss	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
BFS	2.91	4280	0.17	34.05	14.65	ND	43.15	5.94	ND	0.26	0.28	0.57	0.01	0.33	ND
L	3.22	3440	0.64	ND	ND	ND	ND	0.67	2.49	ND	ND	ND	ND	ND	0.004

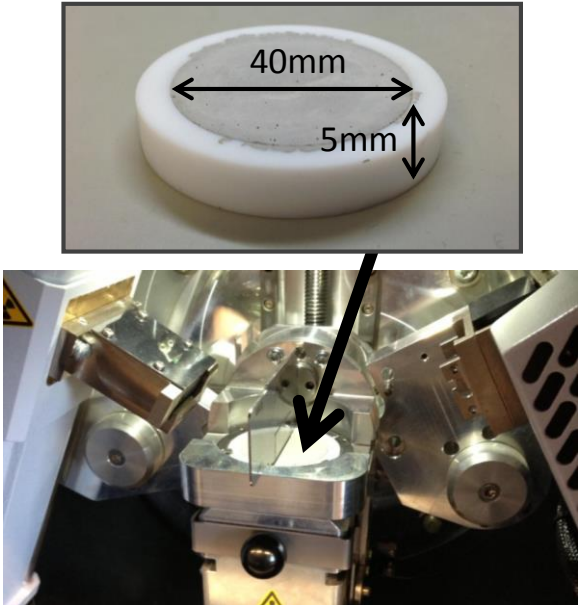


Figure-1 Outline of X-ray Diffraction test

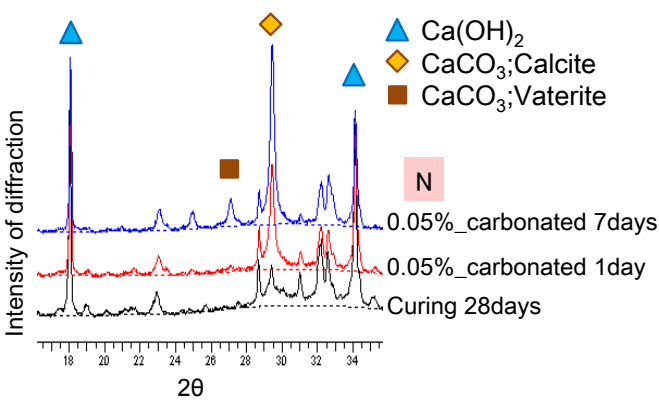


Figure-2 Results of XRD test (one case)

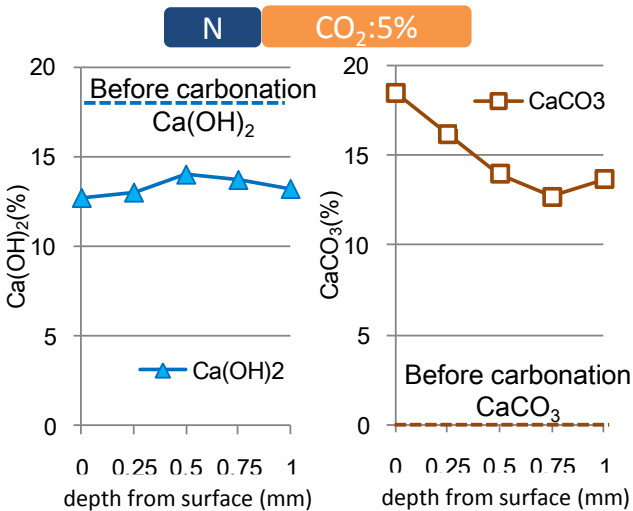


Figure-3 Results of TG-DTA test on each depth from surface layer

2 OUTLINE OF EXPERIMENT

2.1 Samples

It was used for the study ordinary Portland cement in order to eliminate the influence of mixing a minor component for preparation of specimens. Type of cement are used ordinary Portland cement (N), replacement ratio 20%, 50% and 90% of ground granulated blast furnace slag, and Low heat Portland cement (L). Table 1 shows chemical components on these materials. The test specimen was a cement paste of the size of D40*5mm for using X-ray Diffraction test in order to consider the bleeding. Water binder ratio is constant as 50%. After mixing, the top of specimen was rapped with glass plate for 1 day. After remolding, it was sealed curing at 28 days for progress of hydration.

2.2 Concentration of carbon dioxide

After curing, it was carbonated for different concentration of carbon dioxide. Concentration of carbon after completion of curing. It was kept on the 20 degree Celsius and relative humidity 60%.

2.3 X-ray Diffraction test

The original X-ray Diffraction test had been measured as a powder by grinding the samples. Therefore, it is difficult to distinguish the non-carbonation

area and carbonation area. The value of some products obtained by averaging the all area by grinding the samples. It has a problem of the error on the analysis that it can take a long time to process the measurement such as grinding and it is not same samples as pasting age to measure. In this research, it was used for XRD test on the very surface layer without the specimen, as shown in Figure 1. It was considered that it was able to understand the progress of carbonation using the surface XRD analysis with pasting age, because of being gone to carbonation from only surface of samples. It was also thought that it continues to measure the same sample in order to without grinding and be able to eliminated sample between errors. The results show an example in Figure 2 that the XRD test of the same sample was carbonated with concentration of 0.05% carbon dioxide. From this results, it can confirm that the calcium hydroxide (Ca(OH)₂) was decreased, the

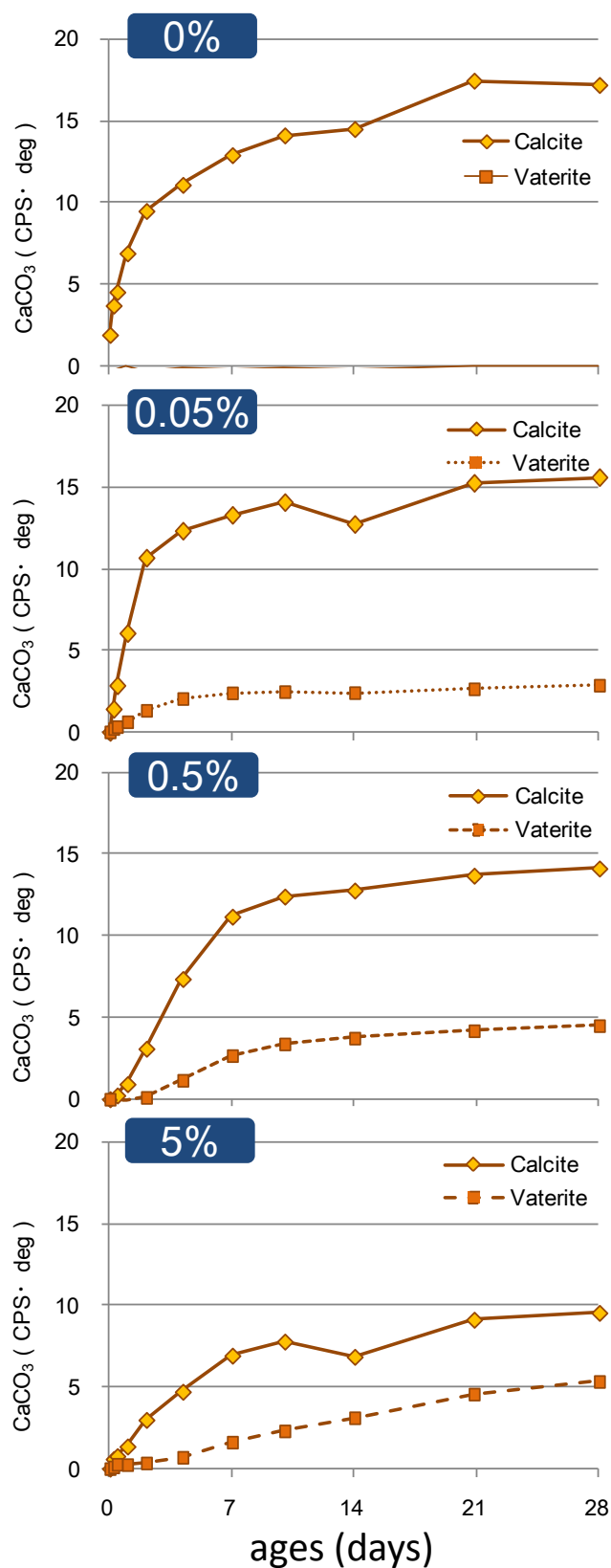


Figure-4 Results of CaCO_3 products on different concentration of Carbon dioxide (N cement)

generation of calcium carbonate with pasting age. Moreover it can confirm that the diffraction intensity of calcite was increased and the amount of vaterite after 7 days past. It was thought that XRD test using same sample was effective as a means for confirming the change of the product by carbonation.

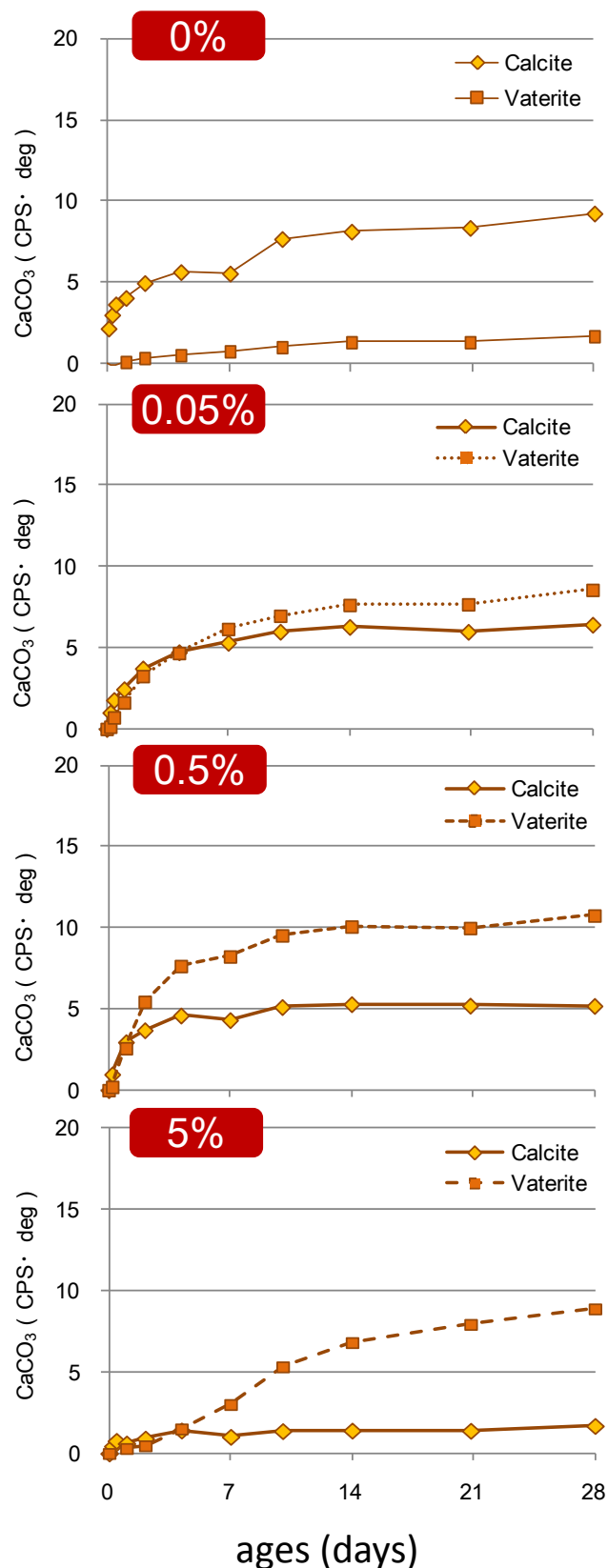


Figure-5 Results of CaCO_3 products on different concentration of carbon dioxide (B50 cement)

It was analyzed qualitatively using D2 PHASER by Bruker AXS. Measurement conditions of XRD, voltage was 30kV, current 10mA, scan speed 0.25deg/min, sampling interval 0.025deg. In this research, we focused on the generation of calcium carbonate as diffraction peak (calcite: 29.4° , vaterite: 27.03°) was calculated from the integrated intensi-

ty. After allowing carbonated samples in carbon dioxide concentration of each environment, it was measured the XRD test using the same sample in the measurement age such as 0.2,0.4,1,2,4,7,10,14,21,28 days from the start of carbonation.

2.4 TG-DTA test

It was measured the production of calcium carbonate (CaCO_3) and calcium hydroxide (Ca(OH)_2) by TG-DTA. It was calculated using the change in weight in TG curve from the inflection point of the DTA curve at after curing time and during the carbonation time. Here, Figure 3 shows the result obtained by the TG-DTA analysis measured by sample carved to a depth 1mm by 0.25mm intervals. It is the result of the one week accelerated carbonation with 5% carbon dioxide concentration atmosphere on cement paste with ordinary Portland cement. It can be confirmed that Tend to calcium hydroxide is reduced compared to before carbonation, the calcium carbonate is increased. Calcium hydroxide is reduced over all layer, however calcium carbonate has decreased in the depth from surface, the most surface layer is produced most extremely. It is thought that it is able to capture the progress of carbonation by measuring most surface layer of sample. Therefore the measurement by X-ray diffraction test was similarly used samples were powdered only carbonation of the surface.

3 RESULTS AND DISSCUTIONS

3.1 Relationship between cement type and carbonation

It shows the change in calcium carbonate production amount due to the carbonation with past age on N and B50 in Figure-4 and 5. It can confirm that both of calcium carbonate calcite and vaterite is increasing with passage on both of N and B50. Calcite has been generated compared with vaterite on N cement at any concentration. On the other hand, on B50 cement is different from N cement. There was a ten dency production of vaterite is large compared to the local site at any carbon dioxide concentration. The density and crystalline structure is different from vaterite and calcite, stability of vaterite is lower than calcite. It has been reported to be generated from the monosulfate and C-S-H on low C/S ratio is vaterite. It is considered that C/S ratio on C-S-H decrease using cement containing ground granulated blast Furnace slag, and vaterite has generated much more than N.

Figure-6,7 show the amount of calcium carbonate on N and B50 obtained by TG-DTA. The results of production rate depends on the difference on carbon dioxide concentration, the generation speed decreases as the high concentration is obtained. However

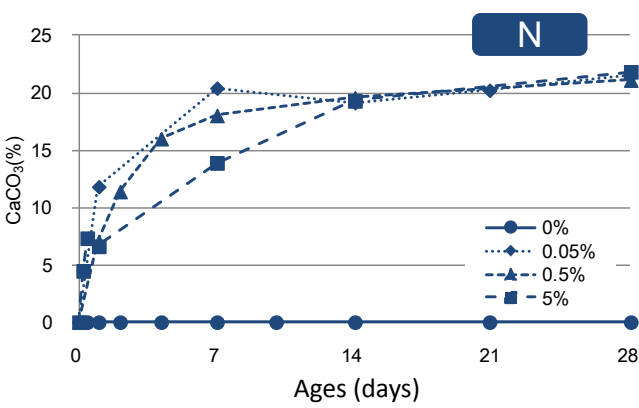


Figure-6 Results of the amount of CaCO_3 by TG-DTA (N cement)

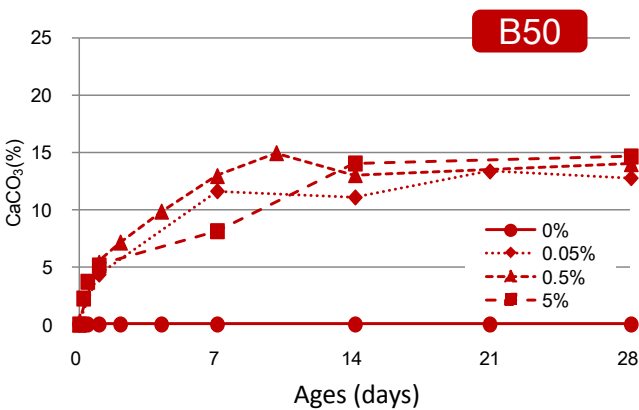


Figure-7 Results of the amount of CaCO_3 by TG-DTA (B50 cement)

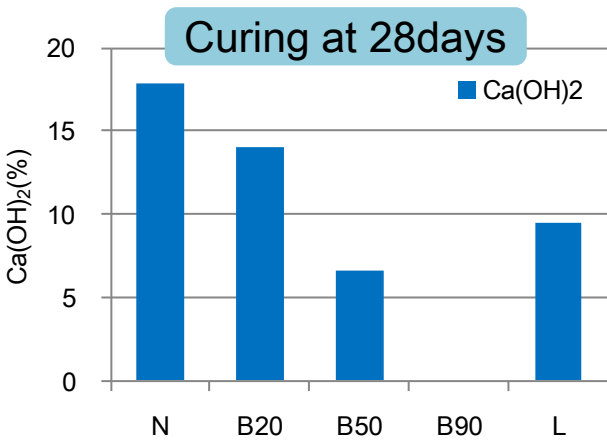


Figure-8 Compare with amount of Ca(OH)_2 on different cement type

the amount of calcium carbonate was about 20 % on N and 15% on B50 at 14 days after carbonation age. It doesn't depend on the concentration of carbon dioxide. Here when compared with the results of X-ray Diffraction analysis of Fig-6,7 production rate of calcium carbonate each in N and B50 also different, it was found that the generation speed decreases as the concentration increases.

It is shown in Figure-8 the calcium hydroxide production on different replacement ratio of blast furnace slag at the end of curing. Amount of calcium hydroxide decreased with increase in the replace

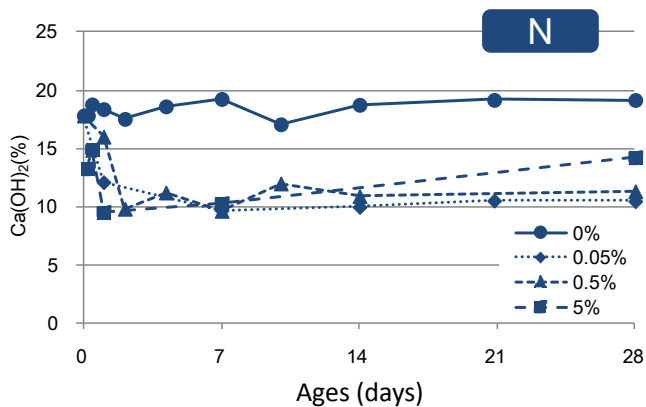


Figure-9 Amount of Ca(OH)_2 on different concentration of carbon dioxide (N cement)

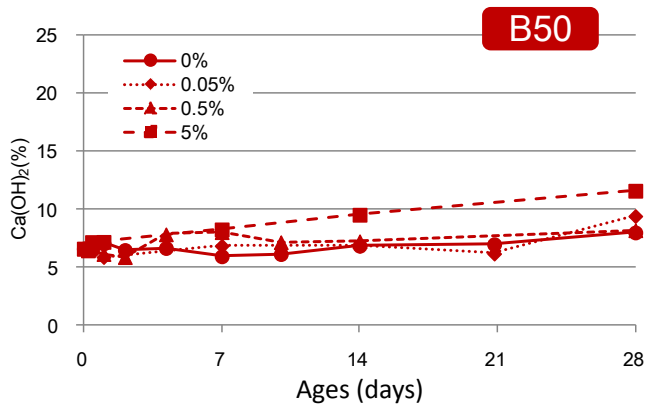


Figure-10 Amount of Ca(OH)_2 on different concentration of carbon dioxide (B50 cement)

ment rate, amount of that was 0 in B90 such as 90% replacement. Furthermore, generation of calcium hydroxide amount becomes less L because of less C_3S compared to N. then it changes over time due to carbonation of calcium hydroxide amount due to TG-DTA in Figure-9 and 10. At any concentration environment, the amount of calcium hydroxide is reduced at an early stage from stating carbonation, however after that, it is not have trend the downward of calcium hydroxide. It is believed that the amount of calcium carbonate was not change on surface layer even though calcium hydroxide is remained in Figure-11 Relationship between replacement ratio if GGBFS and Calcite harden paste. This can indicate that all of the calcium hydroxide produced in not made by the calcium carbonate.

Amount of vaterite was generated more compared with calcite by contamination of ground granulated blast furnace slag. Figure 11 and 12 show the relationship between the amount of calcite, vaterite and replacement ratio of ground granulated blast furnace slag. Amount of calcite was reduced as the high replacement ratio of ground granulated blast furnace slag. It showed a trend similar to between amount of calcium hydroxide and slag replacement ratio. So that the calcium hydroxide exist so much before carbonation, calcite is generated more. It had a trend of increasing vaterite as increased the slag replacement ratio. The amount of vaterite was reached a maxi

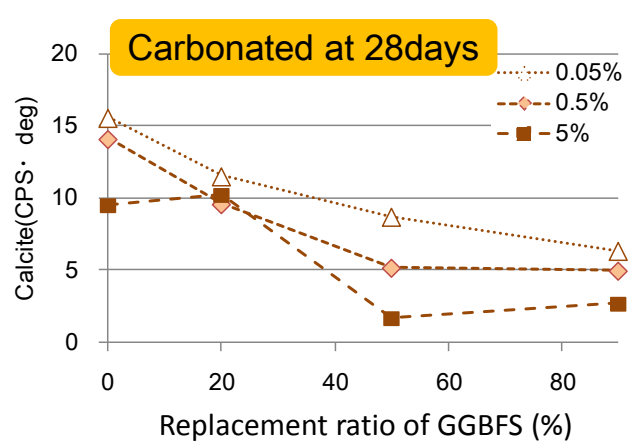


Figure-11 Relationship between replacement ratio if GGBFS and Calcite

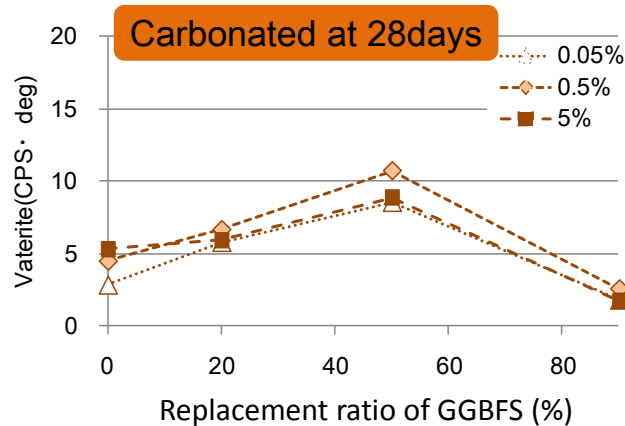


Figure-12 Relationship between replacement ratio if GGBFS and Vaterite

mum value at 50 % replacement slag, and after that vaterite decreased as slag replacement ratio was increased. It is believed that between 0% and 50% of slag replacement ratio, there is a phenomenon of a decrease in calcite and increase in vaterite in all calcium carbonate production. Both calcium carbonate of vaterite and calcite are product, not observed calcium hydroxide in B90. It is believed that all calcium carbonate generated from C-S-H and mono-sulfate. It is believed that the vaterite is to decrease the high replacement of slag, and because hydrate reacts with carbon dioxide in the cement hydrate to produce calcium carbonate is significantly less. It is considered the relationship between production of calcite and calcium hydroxide before carbonation. On the other hand, production of vaterite is unknown from calcium hydroxide or property of C-S-H or effect of other hydration products. It is necessary to further work.

The calcite and the vaterite generation rate which were generated as of age 28 days of each cement are shown in Figure-13. The value in a graph is a rate when the sum of the calcite and vaterite is set to 1, obtained by X-ray diffraction. If carbon dioxide concentration is different in every cement, it can check that the generation rates of both calcium car-

bonate is different. For this reason, it is thought that carbonation mechanisms is different under the environment where concentration of carbon dioxide is different. If it compares for every kind of cement, a difference will be found by the generation rate of both calcium carbonate into the cement in which N and containing ground granulated blast furnace slag. About B90, the rate of both the generated calcium carbonate showed similar to N. the hydrate which generated vaterite originates in few on B90. Therefore, it is thought that the rate of vaterite decreased as a whole. L has few rates of calcite compared with N. It is thought that carbonation mechanisms is different because different of the quantity and the character of hydration product on different kinds of cement.

3.2 Relationship between hydroxide and carbonation

When the result had many amounts of calcium hydroxide generation on curing age at 28 days, it was checked that the amount of calcite generation increases. Then, the relationship between the amount of calcium hydroxide generation on curing age at 28 days and the amount of calcite generation on carbonation age at 28 days in a different kind of cement as shown in Figure-14. Many calcite was generated, there was much generated calcium hydroxide. And the tendency was the same even if carbon dioxide concentration was changed. However the amount of generation of calcite had much one where carbon dioxide concentration is lower. It was suggested the possibility that the amount of calcite generated would be determined in general by the amount of calcium hydroxide generation and concentration of carbon dioxide before carbonation. On the other hand, it is thought that the amount of generation of vaterite depends on the amount of calcium hydroxide generation or on Ca/Si ratio of C-S-H in few things.

4 EXAMINATION OF VARBONATION MECHANISM

From these results, it was checked that a carbonation mechanism changes with concentration of carbon dioxide and kinds of cement. Then, it is examined how it changes with concentration of carbon dioxide and kinds of cement into concrete with actual environment. It is shown that the result of having investigated the carbonation depth on different kinds of cement and concentration of carbon dioxide by concrete in Figure-15. Kinds of cement are N and B50, it was made to carbonation age to 110 days under 0.05%, 0.5% and 5% on concentration of carbon dioxide after curing age at 28 days. Temperature is constant as 20 degree Celsius and Relative humidity

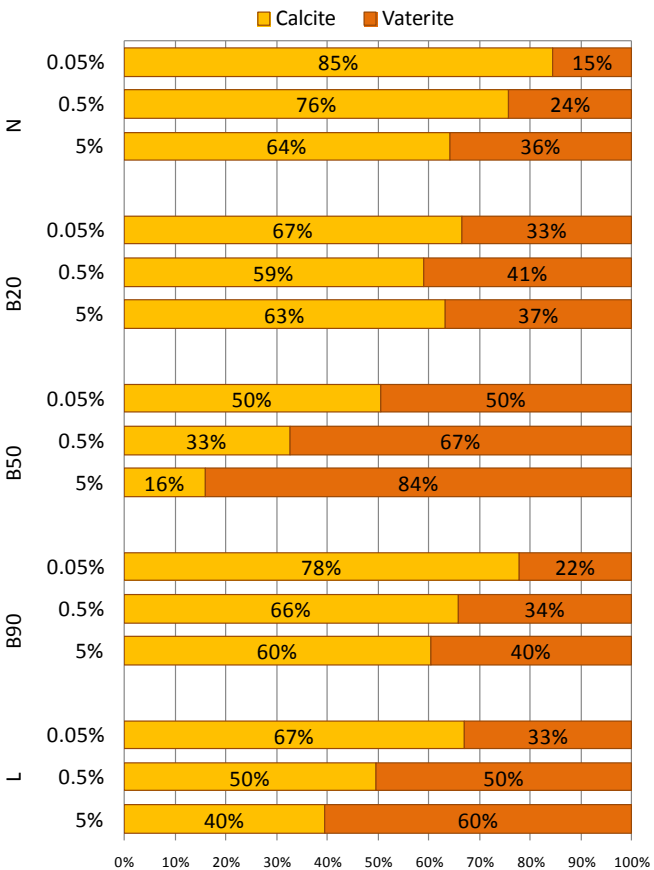


Figure-13 Compared with ratio of calcite and vaterite on different cement type and concentration of carbon dioxide

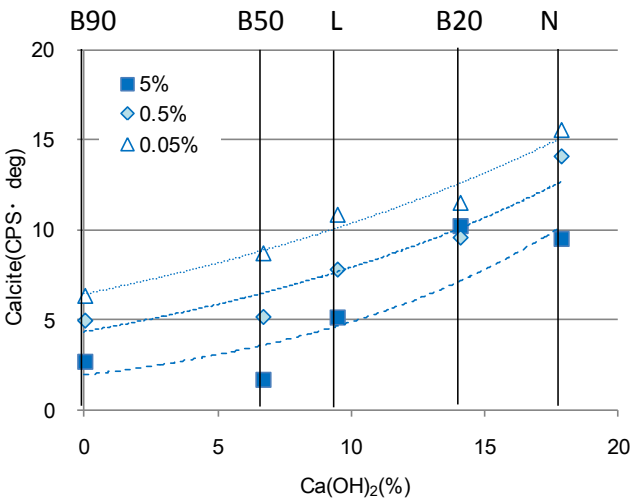


Figure-14 Relationship between Ca(OH)₂ and calcite products

is also constant as 60% in each environment. B50 compared with N, the carbonation depth became large in every concentrations. It does not have the difference of carbonation depth on ordinary Portland cement and blast furnace slag cement in actual carbonation environment. However, it has a small difference as the kind of cement on carbonation depth in testing condition, such as controlled temperature and relative humidity. As this cause, it has influence of circumstance environment as moisture in actual

environment, it is thought that most of the difference is not admitted.

From these results, we are considered the carbonation mechanism of compared with ordinary Portland cement and blast furnace slag cement under different concentration of carbon dioxide in Figure-16. When concentration of carbon dioxide is high, there are many invading amounts of carbon dioxide, and then only the surface area of hydration product is carbonated. After that, it reacts to the hydrate of the following layer immediately. Advance of carbonation from this becomes quickly. On the other hand, since there is also little invading carbon dioxide when concentration is low, it reacts to a hydrate gradually. After the reaction is completed, the reaction advances in the following layer. Thus, it is not based on kinds of cement, carbonation mechanism is determined by the difference in concentration of carbon dioxide. On the other hand, when ground granulated blast furnace slag is contained, it can consider the following reason that resistance of carbonation becomes very small in an accelerated testing conditions. One is a little calcium hydroxide generated and the other is the Ca/Si ratio of C-S-H being low that it is the cause of the calcium carbonate generated serving as vaterite easily. A part of frame on C-S-H collapses by carbonation, and it is thought that the part will be porous. Therefore, when concentration of carbon dioxide is high, carbon dioxide invades easily to a deep position.

5 SUMMARY

This research examined in order to clear the carbonation mechanism under different concentration of carbon dioxide environment at the tie changing mixing and kinds of cement using ground granulated blast furnace slag. The knowledge is shown as following.

- 1) It is based on neither kinds of cement nor concentration of carbon dioxide, calcite and vaterite are generated by carbonation as calcium carbonate.
- 2) In the result measured by surface X-ray diffraction test, many calcite was generated, so that concentration of carbon dioxide is low. On the other hand, the amount of vaterite generation was not dependent on concentration of carbon dioxide.
- 3) It is found the difference by generation rate of calcium carbonate because concentration of carbon dioxide is different. Moreover, a generation rate changes also kinds of cement. It can be said that carbonation mechanism is different from this.

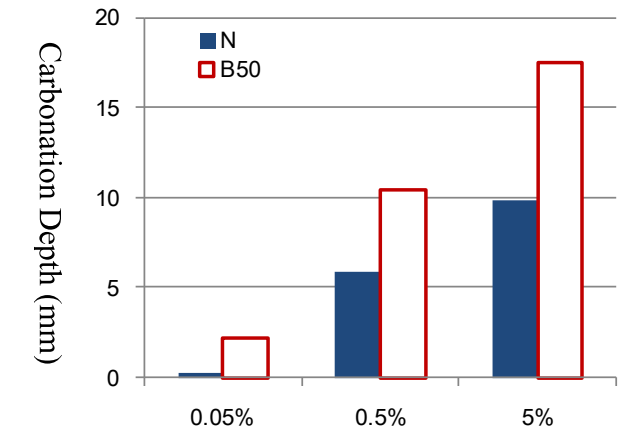


Figure-15 Compared with carbonation depth on different concentration of carbon dioxide using concrete

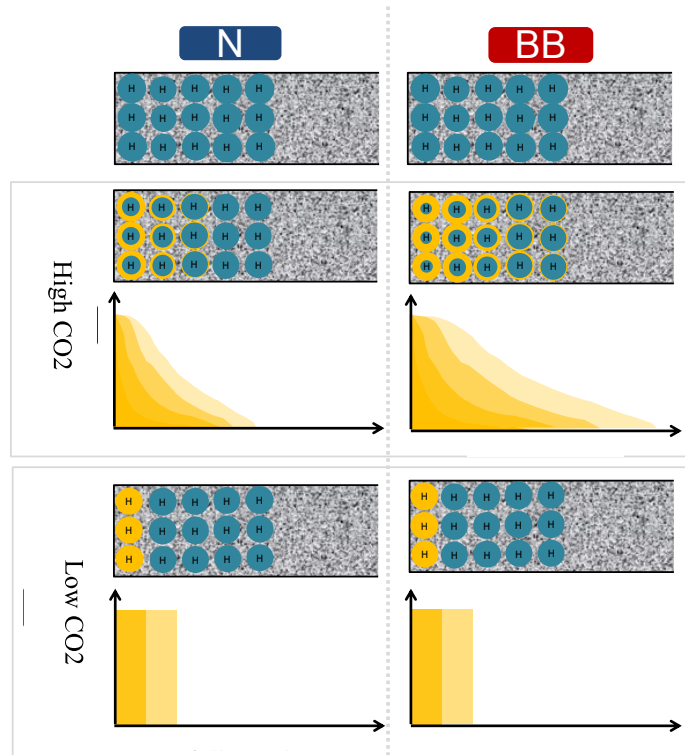


Figure-16 Image of the carbonation mechanism on this research

- 4) When there was much generated calcium hydroxide, it was seen the tendency which calcite generates mostly. On the other hand, the amount of vaterite generation was unknown in this research.
- 5) In the examination by concrete, the carbonation depth was not based on concentration of carbon dioxide on blast furnace slag cement compared with ordinary Portland cement. In the case of actual environment, it is considered to be based on the influence of circumstance as moisture, it is not difference on kinds of cement.

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