

CARBONATION PROGRESS MECHANISM OF CEMENT CONTAINING DIFFERENT AMOUNTS OF POWDER ADMIXTURES

TAKESHI IYODA*

Department of Civil Engineering, Shibaura Institute of Technology, Tokyo, Japan
Email: iyoda@shibaura-it.ac.jp

Abstract. *The cement industry is also reducing carbon dioxide emissions to prevent the global warming. As one of the methods, the use of many powder admixtures are considered. While the use of admixtures is highly advantageous in various terms of durability, it is known that carbonation resistance is inferior when compared to ordinary Portland cement. In this study, we investigated the progress mechanism of carbonation using cement with high content of powder admixtures. First, we compared the progress of carbonation in the real environment and accelerated environment. As a result, it was confirmed that, although carbonation is delayed in a real environment, the progress of carbonation is quicker than when not using large amount of admixtures. The effect is more remarkable as the curing period decrease, and it is found that it has correlation with the compressive strength. Next, the progress of carbonation was considered to be influenced by the pH and the hydrate products of the sample. The pH and hydrate and carbonate products were evaluated quantitatively at depth positions from the surface before and after carbonation. As a result, it was confirmed that the carbonation depth increased as the pH was lowered by the high content of the admixture, and the calcium hydroxide is converted to calcium carbonate. It was also confirmed that the type of calcium carbonate produced was different. Furthermore, with the change of the pore structure, the tendency of carbonation to accelerate was also recognized. On the other hand, it was also confirmed that the carbonation depth identified by the phenolphthalein solution was different from the actual formation position of calcium carbonate.*

Keywords: *Carbonation; Blast furnace slag; Fly-ash; Calcium hydrate; Calcium carbonate;*

1. INTRODUCTION

According protect for global warming, we are working to reduce carbon dioxide in cement production. Cement has a significant amount of carbon dioxide emissions during clinker production, and reducing clinker production is most effective for carbon dioxide emission limitation. Therefore, active use of admixture materials such as ground granulated blast furnace slag (BFS) and fly ash (FA) is important in the cement industry. Table 1 shows the carbon dioxide emission of each materials for concrete shown in “Guideline for checking the environmental performance of concrete structures” of Japan Society of Civil Engineers. Cement that burns at high temperature during production generates a large amount of carbon dioxide, while replacing industrial by-products such as BFS and FA with a part of the cement can significantly suppress the emission of carbon dioxide. So, it is very effective to use admixtures for concrete in terms of environmental impact reduction. In addition, mixed cement in which cement is replaced with admixture material has advantages such as improvement of salt damage resistance and chemical resistance, and improving of long-term strength. However, on the other hand, resistance to initial strength and carbonation decreases due to the small amount of cement.

In this study, we focused on the carbonation resistance, which is considered to be a drawback of this mixed cement.

Table.1 Carbon dioxide emission on each cementitious materials

Cementitious material	Unit carbon dioxide emission (kg-CO ₂ /t)
Ordinary Portland Cement	757.9
Blast furnace slag cement type B	457.7
Fly-ash cement Type C	622.8
Ground granulated Blast furnace slag	24.1
Fly-ash	17.9

When carbonation progresses in the RC structure, the passive film of the rebar is broken, the rebar corrodes, and the expansion pressure causes the concrete to crack. The JSCE Standard specifications for concrete structures [Design edition] proposes a carbonation progress prediction formula, and for concrete using admixtures, the carbonation rate is evaluated by using a constant determined for each admixture. Concrete using blast furnace slag fine powder is said to have low resistance to carbonation. However, this regression does not take into consideration the effects of curing and environment of concrete. Also, Matsuda et al. reported that the carbonation depth in the actual environment was almost same between normal concrete and concrete using blast furnace slag fine powder. Generally, calcium hydroxide [Ca(OH)₂] or calcium silicate hydrate is achieved by replacing a part of the cement with the admixture as a reason for the decrease in carbonation resistance in the cement in which the admixture is substituted. It is considered as one of the factors that the pH in concrete is reduced by the decrease of cement-derived hydrates such as CSH. In this research, we focused on the cement which highly replaced the admixtures in order to reduce the environmental impacts and examined the following two points. In Series 1, compare the carbonation depth in cement with high admixture replacement in accelerated environment and real environment, and verify the difference in carbonation resistance due to the difference in admixture replacement ratio and carbon dioxide gas concentration. And in Series 2, focusing on the relationship between pH and hydrate in mortar, we analyzed in the depth direction and evaluated pH and hydrate products with the color change area of phenolphthalein solutions in accelerated carbonation condition, and we examined the cause that is progressing of carbonation quickly on mixed cement.

2. COMPARISON OF CARBONATION PROGRESS IN REAL ENVIRONMENT AND ACCELERATED ENVIRONMENT (SERIES 1)

It is pointed out that the use of a large amount of various admixtures for reducing the content of OPC and reduces the resistance to carbonation. Here, the purpose is to experimentally clarify whether there is a difference in the progress by comparing the accelerated and the real environment.

2.1. Outline of experiment

2.1.1 Binder ratio examined

Table 2 shows a list of cements used in the tests conducted to understand the difference between the progress of carbonation in the real environment and the accelerated environment. Ten types of cement were prepared by changing the combination using ground granulated blast furnace slag having hydraulic properties and fly ash having pozzolan material based on ordinary Portland cement. A mortar was produced using these binders. The water-binder ratio was 0.5, and the sand-cement ratio was 3. The mortar was set to 40*40*160 mm, and was deformed 24

hours. It was carried out during 7 days and 28 days of sealed curing. The change in curing expressed the difference in initial strength.

Table.2 Mix proportions on Series 1

Series.1 Cement type	W/B (%)	S/C (%)	Binder ratio(%)		
			OPC	GGBFS	FA
<i>N100</i>	0.5	3	100	-	-
<i>B60</i>			40	60	-
<i>B50F15</i>			35	50	15
<i>B70</i>			30	70	-
<i>B50F25</i>			25	50	25
<i>B60F15</i>			25	60	15
<i>B70F15</i>			15	70	15
<i>B85F5</i>			10	85	5
<i>B85F10</i>			5	85	10
<i>B70F25</i>			5	70	25

2.1.2 Measurements

A mortar strength test based on JIS R 5201 was performed after curing. The specimen which sealed by the aluminum tape was prepared except one side surface for carbonation test. The samples were allowed to stand in an accelerated carbonation test (20 degrees Celsius, RH 60%, concentration of carbon dioxide is 5%) and in real condition test as constant temperature and humidity chamber (20 degrees Celsius, RH 60%, concentration of carbon dioxide is about 0.05%). The specimen was cut at setting age, and the carbonation depth was measured in accordance with JIS. A phenolphthalein solution was sprayed, and 6 points of a portion colored in red purple from the surface were measured, and the average value was taken as the carbonization depth.

2.2. Results of carbonation

2.2.1 Compressive strength

Figure 1 shows the relationship between the contents of OPC in the binder and the compressive strength. It can be seen that the compressive strength decreases with the decrease in the contents of OPC in the binder. In addition, it was confirmed that the strength was progressed in any of kind of binders by increasing the curing periods.

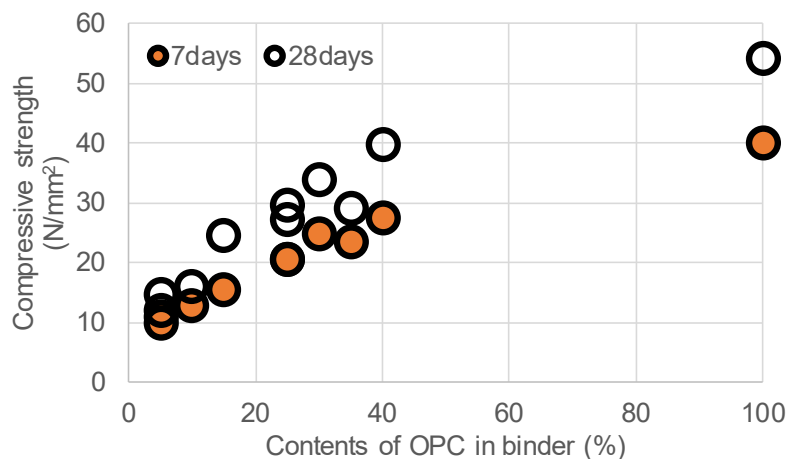


Figure 1. Compressive strength on different binders

2.2.2 Comparison of carbonation depth of accelerated and real environment

Figure 2 shows the relationship between the OPC ratio in the binder and the carbonation depth on accelerated and real environment. It can be seen that the accelerated carbonation depth and the real environment carbonation depth increase with a decrease in the contents of OPC in the binder. However, it can be seen that the difference between the accelerated carbonation depth and the real environment carbonation depth is large when the contents of OPC in the binder decreased. In addition, even if the curing days were set long from 7 to 28 days, the accelerated carbonation depth was significantly large when the contents of OPC in the binder decreased. From these results, it can be said that the difference between the carbonation depth in the accelerated environment and in the real environment is large in which the contents of OPC in the binder decreased.

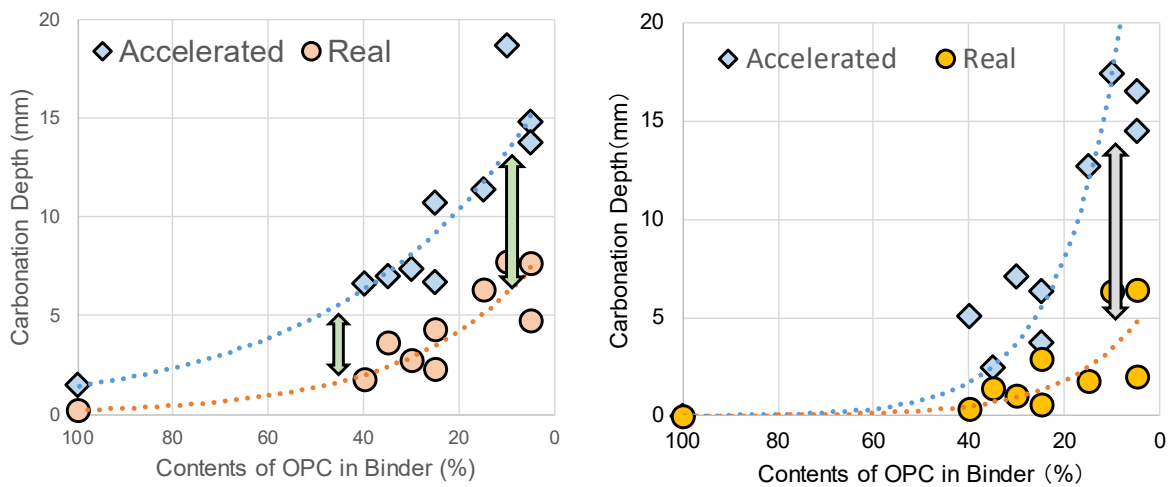


Figure 2. Relationship between contents of OPC in binder and Carbonation depth on accelerated and real carbonation environments (Left: 7-day curing, Right 28-day curing)

2.2.3 Comparison of compressive strength and carbonation depth

Figure 3 left shows the relationship between compressive strength and the real environment carbonation depth. It can be seen that the carbonation depth decreases as the compressive strength increases, regardless of the curing periods and the contents of OPC in binder. Next, Figure 3 right shows the relationship between compressive strength and the accelerated carbonation depth. Also the carbonation depth generally decreases as the compressive strength increases regardless of the contents of OPC in binder. However, the result of on 28 days curing period was different from the result of the real environment, that cement with a small amount of OPC in binder did not decrease the carbonation depth while the compressive strength increased. That is, although the strength is progressed by the extension of curing, it can be said that the carbonation resistance is not increased by the accelerated test.

From these results, it is necessary to consider curing period when examining compressive strength and carbonation resistance in accelerated tests on highly replacement for admixtures (especially when the contents of OPC in binder is less than 15%) is necessary. However, if the contents of OPC in binder is less than 15%, the compressive strength at 28 days is considered to be insufficient in strength expression, so it is necessary to further study on long term curing periods in the future.

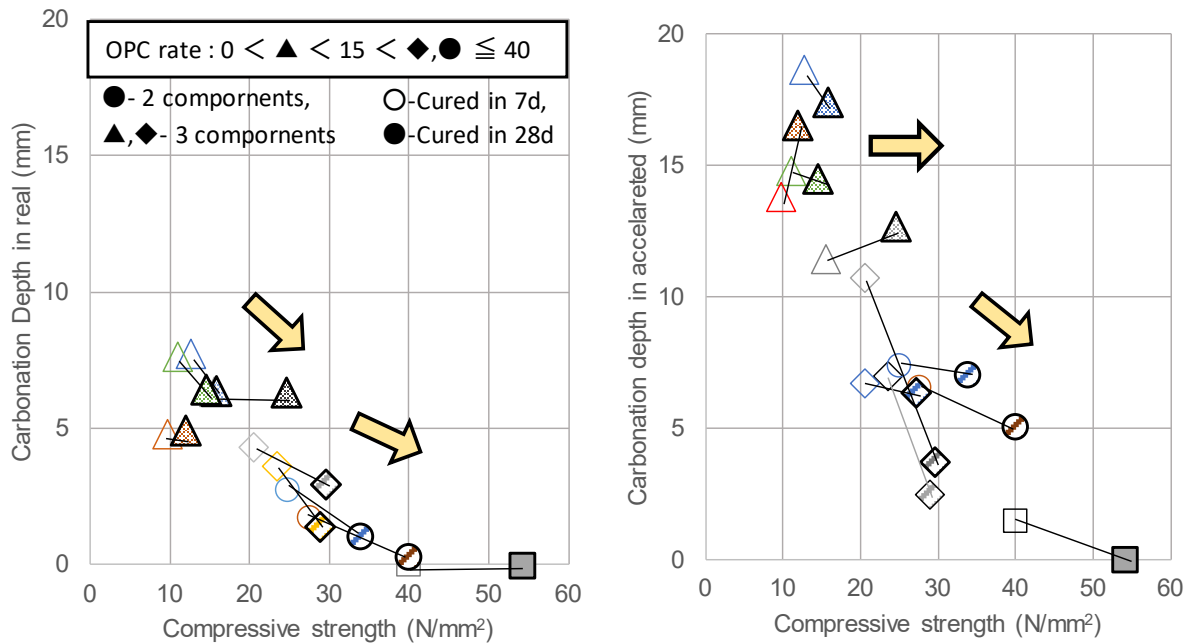


Figure 3. Relationship between the compressive strength and carbonation depth on different environments (Left: in real, Right: in accelerated)

3. EXAMINATION OF CHANGE OF PH AND HYDRATE BEFORE AND AFTER CARBONATION (SERIES 2)

With regard to the progress of carbonation under the accelerated environment obtained by the above study, it was decided to compare the decrease in pH with the amount of hydration product. Investigate the relationship between the decrease in pH and the amount of carbonation products in the mixed cement, which is inherently low in pH, and consider why carbonation is fast.

3.1. Outline of experiment

3.1.1 Binder ratio examined

Table 3 shows the composition of the mortar which examined pH and a hydration product in a depth position. In Series 2, three blast furnace cements were used. Such as B50 equivalent to blast furnace cement type B, B65 equivalent to blast furnace cement type C, and B85, which have a higher BFS replacement ratio. In addition, in each of B50, B65 and B85, a study was made on a ternary cement in which 15% of BFS was replaced with FA.

Table3. Mix proportions on Series 2

Series.2 Cement type	W/B (%)	S/C (%)	Binder ratio (%)		
			OPC	BFS	FA
<i>N100</i>	0.5	3	100	-	-
<i>B50</i>			50	50	-
<i>B35F15</i>			50	35	15
<i>B65</i>			35	65	-
<i>B50F15</i>			35	50	15
<i>B85</i>			15	85	-
<i>B70F15</i>			15	70	15

3.1.2 Measurements

After curing, the specimen was split before accelerated carbonation, and samples were taken to determine the pH before carbonation and the amount of hydration products. After that, the specimen sealed with aluminum tape except for one side was left in the accelerated carbonation test. After measuring the carbonation depth in the same method as in Series 1, cutting was performed each 6 mm in the depth direction, and samples for measuring the pH of each layer and the amount of hydration products were analyzed.

The measurement of pH was performed according to "the method of measuring pH (JIS Z 8802)" using a digital pH meter of the glass electrode method. The calibration reagent was a two-point calibration using 0.01 mol/L aqueous sodium borate solution and 0.05 mol/L aqueous potassium hydrogen phthalate solution. The pH measuring device used had a measuring range of 0.00 to 14.00 and a measuring resolution of 1/100 pH specification. The measurement method was based on the previous research, and the measurement sample was mixed with distilled water so that the powder concentration in the solution was 1%, and the pH was measured after stirring for 5 minutes.

In addition, the content of calcium hydroxide $[\text{Ca}(\text{OH})_2]$ and calcium carbonate $[\text{CaCO}_3]$ as hydrates were measured using differential thermogravimetric analysis (TG-DTA).

3.2. Results of carbonation

3.2.1 pH and hydration products before carbonation

Figure 4 shows the pH before carbonation. The pH slightly decreases with the decrease of the OPC ratio in the binder. However, except for B85 and B70F15, the proportion of OPC in the binder was 15%, the pH values were almost the same. Focusing on admixtures, it can be seen that the ternary cement has a slightly higher pH than the binary cement. The reason for this is considered to be that the pH is raised by replacing part of BFS with FA, which is a low alkali. Next, Figure 5 shows the contents of $\text{Ca}(\text{OH})_2$ and CaCO_3 before carbonation. It is confirmed that the amount of CaCO_3 shown the small amount of mixed component contained in OPC. That is, the amount of CaCO_3 decreases at a rate corresponding to the decrease in the rate of OPC in the binder. On the other hand, it can be seen that the hydrate $\text{Ca}(\text{OH})_2$ decreases as the mixing and mixing interest of the admixture increases due to the effect of hydration.

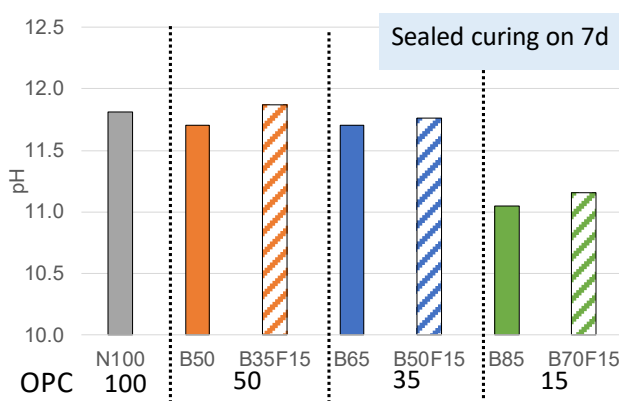


Figure 4. pH value before carbonated

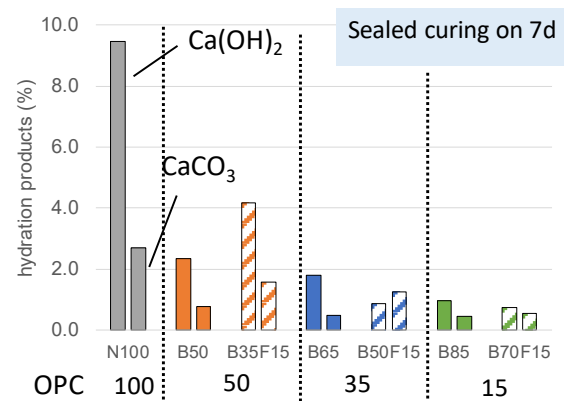


Figure 5. Components before carbonations

3.2.2 pH and $\text{Ca}(\text{OH})_2$ and CaCO_3 content at depth position after carbonation

Figures 6 to 8 show the pH and the contents of the amount of $\text{Ca}(\text{OH})_2$ and CaCO_3 on each depth. Here, the results of B65, B85 and B70F15 are shown. First, focusing on the pH, the pH decreases in carbonation zone with phenolphthalein. It can be confirmed that this is related to

10.2 to 10.3 of the color boundary of phenolphthalein. With the progress of the carbonation, the pH at the measurement position decreases and we can be clearly confirmed the progress of the carbonation from pH value. In B65, focusing on the change in pH in the first layer, pH value significantly decreases from pre-carbonation to the second week of accelerated carbonation. If the rebar corrosion because of carbonation is due to the decrease of pH, the decrease rate of pH and the value of pH after judging as the carbonation zone with phenolphthalein are very important. Next, we focused on the mineral content. In the case of highly substituted admixtures with cement as in this study, the amount of Ca(OH)_2 formed is very small. Although the difference is not clear in all figures, it can be said that Ca(OH)_2 disappears as much as the progress of carbonation. On the other hand, focusing on the amount of CaCO_3 produced by carbonation, it can be seen that although a large amount of CaCO_3 is produced in the carbonation zone, there is no significant difference in the amount for each composition.

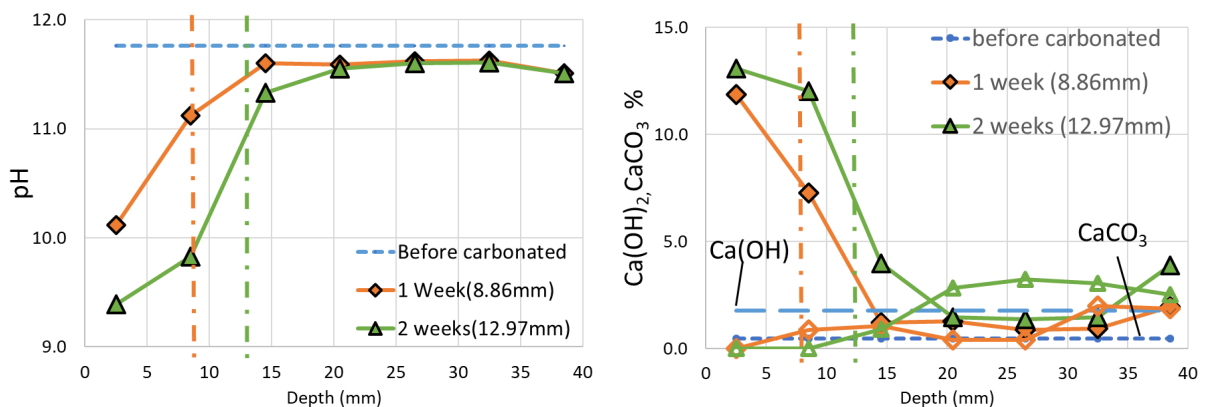


Figure 6. Result of pH and contents of amount of Ca(OH)_2 and CaCO_3 on each depth [B65]

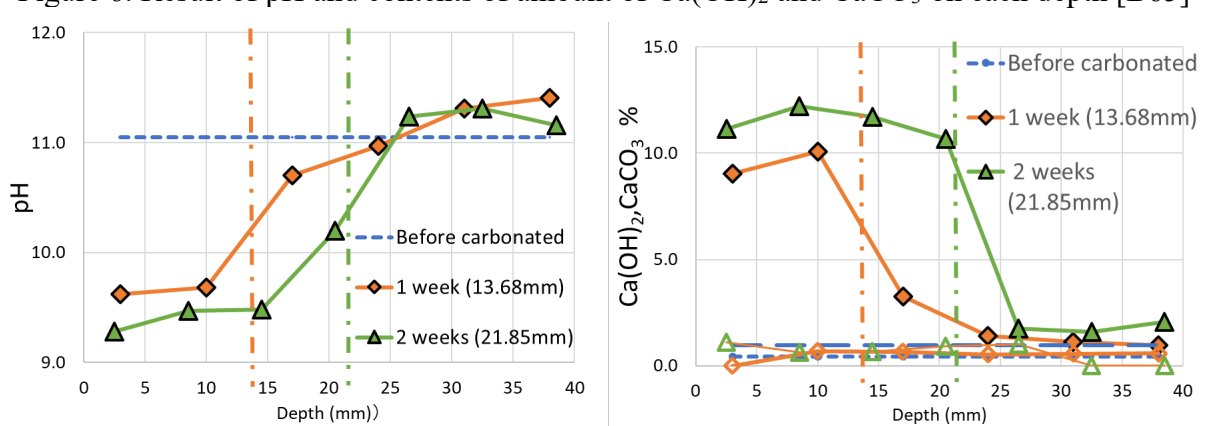


Figure 7. Result of pH and contents of amount of Ca(OH)_2 and CaCO_3 on each depth [B85]

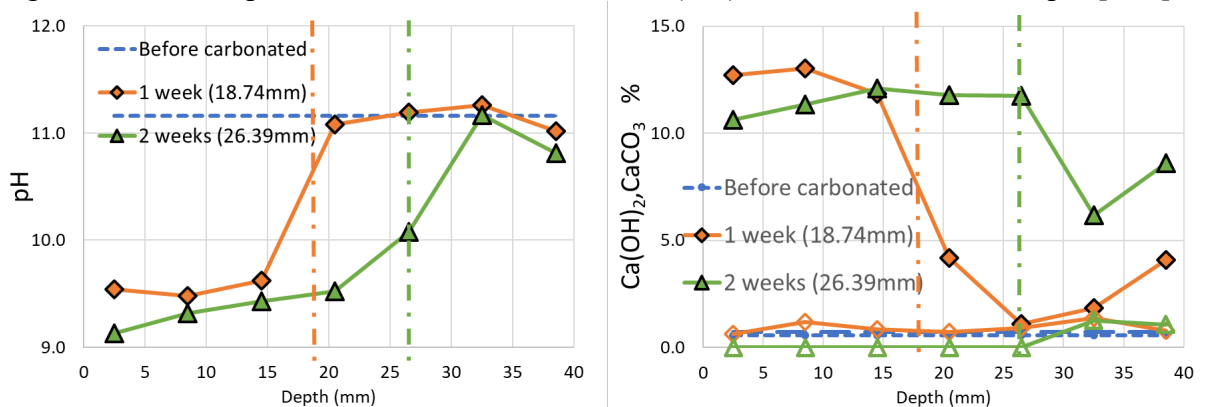


Figure 8. Result of pH and contents of amount of Ca(OH)_2 and CaCO_3 on each depth [B70F15]

Moreover, in B70F15, the amount of CaCO_3 increases greatly over the innermost layer. This is considered to be due to insufficient sealing when sealing the specimen with aluminum tape. There was no difference between the two-component cement (B85) and the three-component cement (B70F15) in which the proportion of OPC in the binder was the same.

From these results, when the different mix proportions were compared, it was found that, in the region judged to be a carbonation zone with phenolphthalein, the change of pH and the lower limit pH value were different, however the amount of CaCO_3 was almost the same. This indicates that care should be taken for carbonation of C-S-H in cements with low $\text{Ca}(\text{OH})_2$ such as cements with highly substituted admixtures. There are two types of CaCO_3 present in concrete, Calcite and Vaterite. Toyomura et al. reported that the CaCO_3 produced changes with the change of the replacement rate of ground granulated blast furnace slag. Also, Harasawa et al. reported changes in pore size distribution before and after carbonation for each cement type, and that the cumulative pore volume after carbonation increased with the combination of 50% blast furnace slag. From these reports, it is assumed that substituted with admixture materials such as ground granulated blast furnace slag in cement, CaCO_3 is generated by carbonation, and the pores are coarsened along with by progressing carbonation. In the future, it will be necessary to distinguish between the types of CaCO_3 generated during carbonation in the ternary cements, Calcite and Vaterite. Then, it is necessary to examine the pore size distribution of each area judged to be the carbonated area and the un-carbonated area with phenolphthalein, and to investigate the change of the pore before and after the carbonation.

4 CONCLUSIONS

- (1) In highly admixture material replacement cements, the tendency differs between the carbonation by the accelerated environment and by the real environment. Especially in the accelerated environment, the carbonation depth did not show \sqrt{t} law.
- (2) The relationship between pH and the amount of hydration products was investigated before and after carbonation. The pH value of the portion judged to be a carbonation area with phenolphthalein showed a different value for each composition. On the other hand, the amount of CaCO_3 was almost the same.

ACKNOWLEDGEMENTS

This research is in master work of Mr. Takafumi Ito who is graduated student from Shibaura Institute of Technology.

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