

Effect on mechanism of carbonation in different concentration of carbon dioxide and using ground granulated blast-furnace slag

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ABSTRACT

Carbonation of concrete is one of the phenomena that contribute to the degradation of reinforced concrete structures. This phenomenon is caused by a decrease in the pH due to the chemical reaction of hydration products with atmospheric carbon dioxide. However, the characteristics and amount of hydrates in concrete may change depending on the type of cement, and differing humidity and carbon dioxide concentrations may change the mechanism of carbonation. It has been reported that carbonation depths in existing structures are not significantly different even when using different cement types, but the cement type remarkably affects the results of the accelerated carbonation test. This mechanism is not clear. In this study, the effect of differing carbon dioxide concentrations on the amount of calcium carbonate and calcium hydroxide, as well as the pore structure, of ordinary Portland cement and blast furnace slag cement pastes is investigated using TG-DTA and MIP. In addition, analyses were carried out at various depths in cores taken from existing concrete structures. It was found that the type of calcium carbonate and pore structure was affected by different concentrations of carbon dioxide as well as the use of ground granulated blast furnace slag.

1. INTRODUCTION

In order to determine the resistance to carbonation in a short period of time, the accelerated carbonation test, which uses a high concentration of carbon dioxide, is generally utilized. This concentration, however, is different from the actual concentration under real exposure conditions. It is difficult to evaluate the results of the accelerated test relative to the actual exposure because the acceleration amplification factor depends on materials, mix proportion, poor early curing, and so on. Therefore, the carbonation mechanism for existing concrete structures under natural weathering conditions is not entirely clear. There are many reports that focus on changing test factors, but generally use only ordinary Portland cement (OPC). Consequently, it is possible to convert the carbonation coefficient of the accelerated test to the actual condition for OPC, but it is difficult for other cements due to a lack of data.

It is believed that cement with ground granulated blast furnace slag (BFS) lowers carbonation resistance compared to OPC because more replacing OPC with BFS results in less calcium

hydroxide. The original pH concentration may thus be lower. However, carbonation progress cannot be explained by the pH concentration alone.

Figure 1 shows the progress of carbonation depth in concrete. In the actual environment, there is no observable difference in the carbonation depth when comparing OPC and BFS cement. It has been reported that carbonation depth in existing structures using BFS cement are not significantly different from OPC structures, but large differences occur when conducting the accelerated carbonation test using cores from the same place^{1,2)}. In short, BFS cement suffers from rapid carbonation progress when in an accelerated environment. As a result, in the case of BFS cement, there is the possibility to wrongly interpret the carbonation progress in the actual environment when using data from the accelerated carbonation test.

In this study, the effect of differing carbon dioxide concentrations on the amount of calcium carbonate and calcium hydroxide, as well as the pore structure, of ordinary Portland cement and blast furnace slag cement pastes is investigated using TG-DTA and MIP. In addition, analyses were carried out at various depths in cores taken from existing concrete structures.

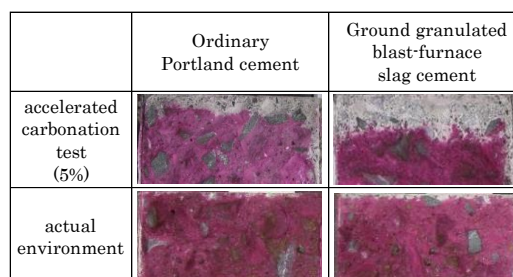


Figure 1. Carbonation depth¹⁾

2. MECHANISM OF CARBONATION IN DIFFERENT ENVIRONMENTS

2.1 Experimental outline

The carbonation mechanism in different environments was examined by measuring the changes caused by carbonation after various time periods. We changed water-cement ratio, concentration of carbon dioxide and cement type such as Ordinary Portland cement and blast-furnace slag cement.

(1) Sample of cement paste

The study Ordinary Portland cement was used for eliminating the influence of mixing extender for preparation of specimens. The types of cement used were OPC (N) and cement with 50% of OPC replaced by BFS (BB). Figure 2 shows the test specimen, which was made using cement paste and had a size of 5×10×100 mm, used for the TG-DTA and mercury intrusion porosimetry (MIP) tests. This size was prepared in consideration of the effect of bleeding. The water-binder ratio was set at 100%.

(2) Measurement conditions

The chemical analysis was carried out as illustrated in Figure 3. After curing for 28 days, test pieces were separated into two environmental chambers. One was a controlled room with 0.05% carbon dioxide concentration, to simulate the actual concentration, and the other was carbonation chamber at 5% concentration, following the accelerated environment. The humidity was set at 60% RH and the temperature was 20 degree Celsius for all tests. Test pieces were then continuously cut at 5 mm thickness after set periods and sprayed with a 1% solution of phenolphthalein to check the progress of carbonation; that is, observation of coloration change to purplish-red. Carbonation was regarded as finished when none of the surface was purplish-red.

MIP and TG were measured after the initial 28 days of sealed curing and after the conclusion of carbonation. In addition, tests were also carried out 28 days after carbonation finished (hereafter referred to as 28 days after carbonation) because the pH value at carbonation area

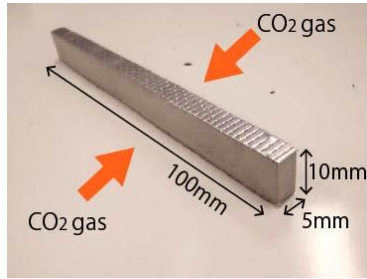


Figure 2. Size of test specimen

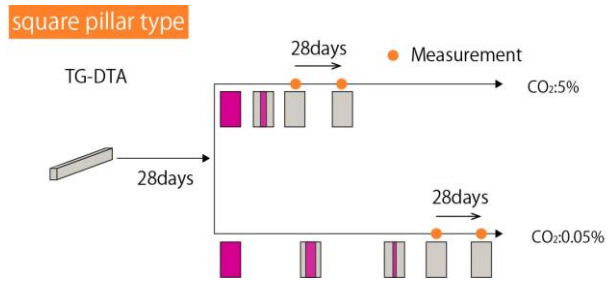


Figure 3. Measuring date of each test

which is judged by phenolphthalein is about 8.2-10.0 pH, so there is some possibility of reducing the alkaline pH after no coloration.

(3) Microstructure and chemical analyses

The pore structure was examined using MIP and the generated amounts of calcium carbonate and calcium hydroxide were measured using TG-DTA. In the MIP test, pore size distribution and cumulative pore volume were measured. In the TG-DTA test, the production of calcium carbonate (CaCO_3) and calcium hydroxide (Ca(OH)_2) was calculated using the weight change in the TG curve from the inflection point of the DTA curve.

2.2 RESULT AND DISCUSSIONS

(1) Change of pore size distribution by carbonation

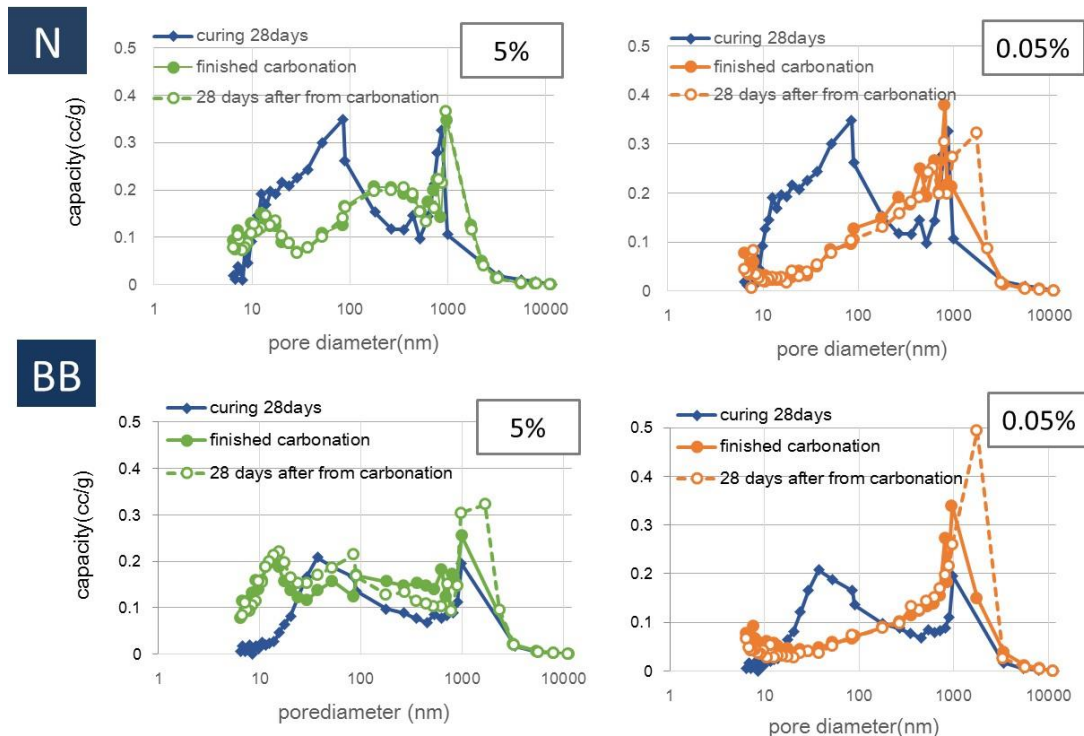


Figure 4. Change of pore size distribution by carbonation

Figure 4 shows the change in pore size distribution due to carbonation using MIP. The pore size distribution shifts in the direction of larger pore sizes for both N and BB. At the actual concentration, pores near 10 nm in size remained in the case of N, however it was produced in BB. It seems that pores of the size under 6 nm, which cannot be measured by MIP, were shifted to the 10 nm size when using BFS. However, for the accelerated test, the small pore size near 10 nm did not remain, and large pore sizes near 100 nm increased. This suggests that, at higher concentrations of carbon dioxide, more small pores shift to a large size than what occurs under the actual exposure conditions.

(2) Change of cumulative pore volume by carbonation

Figure 5 shows the change in cumulative pore volume due to carbonation. The cumulative pore volume decreased in the case of N, however it increased in the case of BB. This suggests that the produced amount of CaCO_3 decreased when using BFS, and the pore size under 6 nm shifted to a larger size. There were no changes observed in the cumulative pore volume between immediately after completion of carbonation and after 28 days. This result suggests

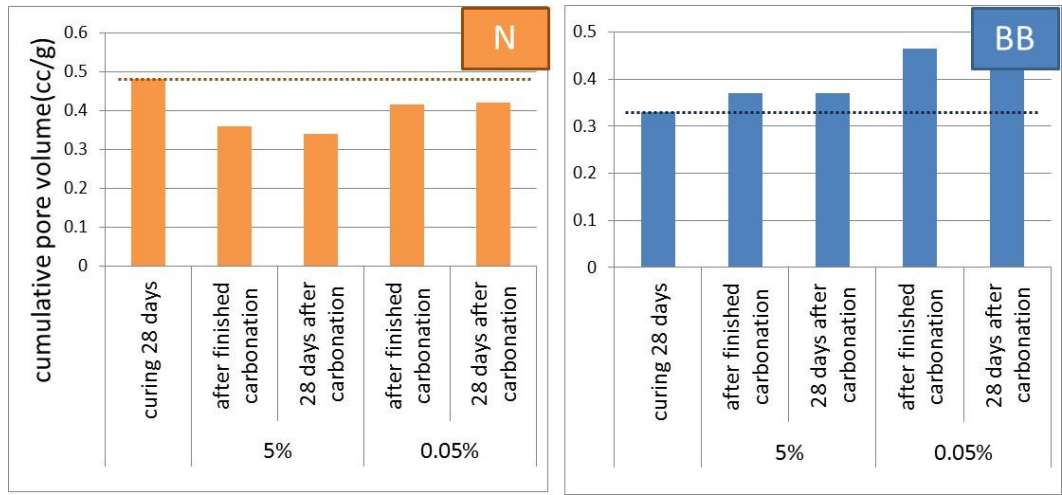


Figure 5. Change of cumulative pore volume by carbonation

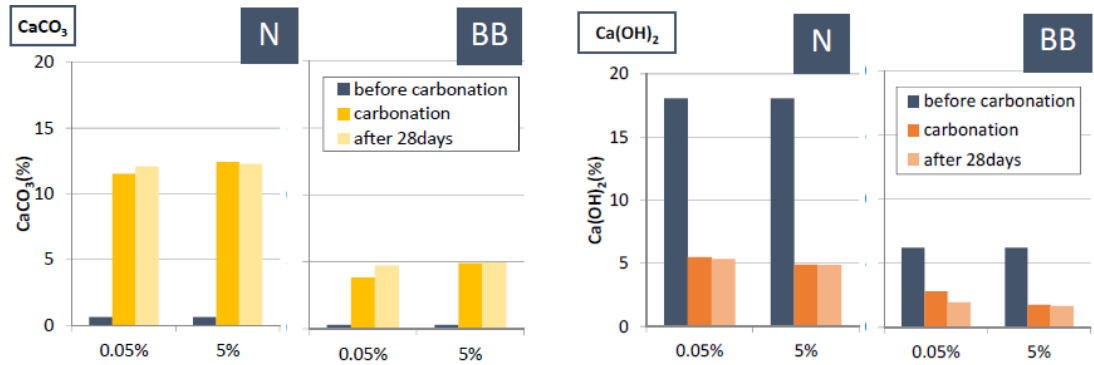


Figure 6. Change of production amount by carbonation

that either no further change in the voids of the cement paste will occur after carbonation, or that any changes to the void space take longer than one month to occur.

(3) Change of production amount by carbonation

Figure 6 shows the changes in the produced amounts of Ca(OH)_2 and CaCO_3 using TG-DTA. Overall, the produced amount of Ca(OH)_2 was less for BB than N, but carbonation caused a decrease in the amount of Ca(OH)_2 for both of N and BB. Additionally, the speed of carbonation was different depending on the carbonation ratio; however, regardless of the carbonation ratio, the final produced amounts of Ca(OH)_2 and CaCO_3 were almost the same for both cement types. There was no significant change between immediately after completion of carbonation and after 28 days, similar to the results in section 3.2 It is suggested that the produced amount of Ca(OH)_2 and CaCO_3 became either fixed or decreased after reaching a constant value. Finally, for different concentrations of carbon dioxide, there was no large effect on the produced amount of CaCO_3 .

(4) Examine of Carbonation mechanism.

Figure 7 shows the material balance of CaCO_3 derived from the amount of Ca(OH)_2 . The calculated amount of CaCO_3 is the amount produced only by carbonation from Ca(OH)_2 as measured by TG-DTA. For N, the amount of CaCO_3 measured by TG-DTA was 1.1-1.3 times the amount calculated of CaCO_3 , and for BB it was 1.7-2.0 times. This means that CaCO_3 is produced not only by Ca(OH)_2 but also other hydrates. In addition, when using BFS, the measured CaCO_3 was higher than the calculated amount of CaCO_3 , and the original produced amount of Ca(OH)_2 was lower than for OPC.

It is reported that is CaCO_3 produced not only by Ca(OH)_2 but only C-S-H which has a low ratio of C/S and monosulphat³⁾. For BFS, it is suggested that a lot of CaCO_3 is produced by hydrates such as C-S-H. Also, in the case of low concentration of carbon dioxide, the pore structure was filled by the produced CaCO_3 . However in the case of high concentration of carbon dioxide, carbonation from C-S-H happened as well, also producing CaCO_3 .

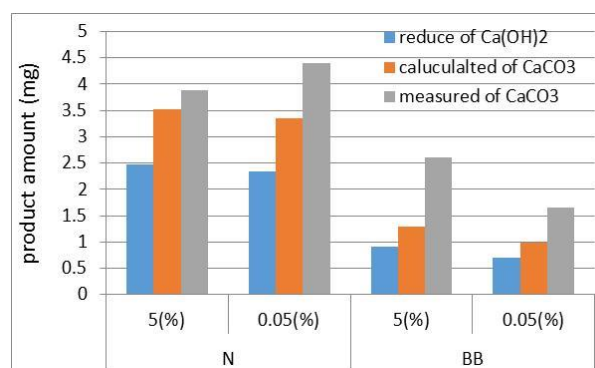


Figure 7. Material balance of CaCO_3 derived by amount of Ca(OH)_2

3. CARBONATION PROGRESS IN DEPTH USING CONCRETE CORE

3.1 Experimental outline

The change in carbonation at various depths was measured to examine the carbonation progress over a long period. A concrete core from an existing structure that was made from blast furnace cement was used.

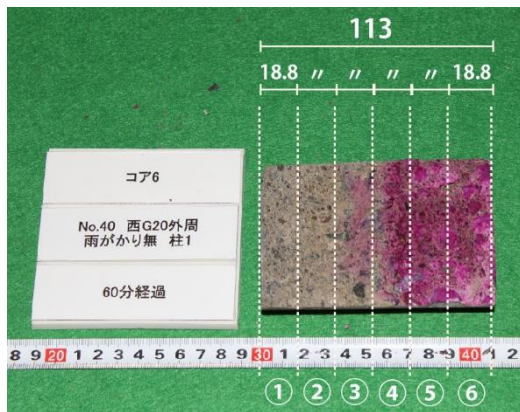


Figure 8. Sample taken from core

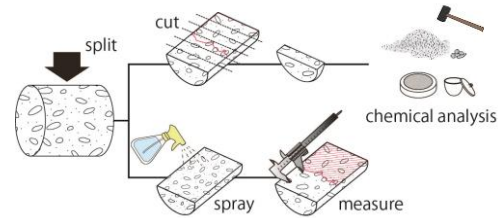


Figure 9. Test flow

(1) Core sample of existing structure

The target structure was 60 years old and made with blast furnace cement concrete. A sample is shown in Figure 8, and Figure 9 shows the test flow. Concrete core samples 75 mm in diameter were collected using a wet core drill. After the splitting test, one half was sprayed with a 1% solution of phenolphthalein at the broken cross-section, and the other half was used for chemical analysis. To stop hydration, samples were granulated by hammer and preserved in acetone after drying in a vacuum (D-dry).

(2) Produced amount of $\text{Ca}(\text{OH})_2$ and CaCO_3 in sample with aggregates

The production of CaCO_3 and $\text{Ca}(\text{OH})_2$ were measured using the weight change of the sample temperature at 200, 500 and 800 degrees Celsius. The weight loss from 200 degrees Celsius to 500 degrees Celsius was regarded as the emission amount of H_2O from $\text{Ca}(\text{OH})_2$, and the weight loss from 500 degrees Celsius to 800 degrees Celsius was regarded as the emission amount of CO_2 from CaCO_3 . The produced amounts was then calculated from those emission amounts. In the normal situation cases, these are measured by TG-DTA. However, as it is a microanalysis, the result can vary a great deal depending on the amount of aggregates. If the aggregates are removed, then $\text{Ca}(\text{OH})_2$ around the aggregates is also removed. Therefore, the afore-mentioned method was used in place of TG-DTA. Each test was conducted with a roughly 1.5 g sample. After acetone treatment, the fine powder on the sample was adjusted using a mill. Heating times were 30 minutes at each temperature. After cooling in a desiccator for 30 minutes, weight was measured.

(3) Produced amount of $\text{Ca}(\text{OH})_2$ and CaCO_3 in sample without aggregates

As described in chapter 2.4, the produced amount of CaCO_3 and $\text{Ca}(\text{OH})_2$ was measured by using TG-DTA. Aggregates were removed from samples and the powder prepared by the same method.

(4) pH value

The change in pH at various depths was measured using a pH meter. Samples were percolated by water at 50 degree Celsius for 30 minutes, and then filtered. Test solutions were produced one at a time with 20 g sample and 200 ml of water.

3.2 Result and discussions

(1) Produced amount of $\text{Ca}(\text{OH})_2$ and CaCO_3

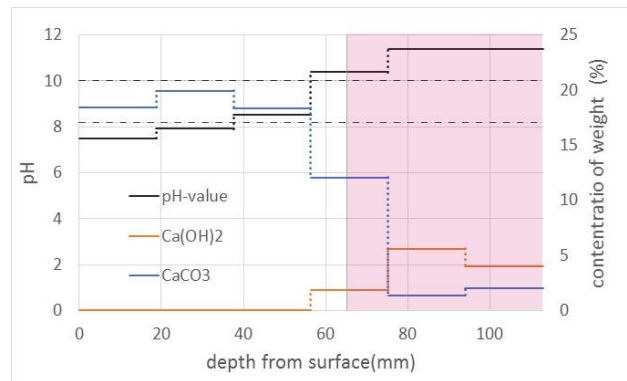


Figure 11. pH and production amount change at each depth

Figure 10 shows the changes in calcium carbonation and calcium hydroxide at various depths. Both samples with aggregates and without aggregates exhibited change in sections 3 to 5. Ca(OH)_2 increased and CaCO_3 decreased from the carbon depth front (62.53 mm). However, the amount of Ca(OH)_2 in samples with aggregates showed higher value than those without aggregates. Also, it was slightly higher than the standard amount in concrete. In the case of samples without aggregates, the amount was slightly lower. It was suggested that Ca(OH)_2 around the aggregates had an effect and the lower limit temperature was not appropriate. In general, H_2O in Ca(OH)_2 evaporates between 450 and 500 degrees Celsius, so the results for Ca(OH)_2 may actually include another material as well. It is necessary for increasing the heat in lower limit temperature on electric furnace test or using samples that include aggregates in the TG-DTA test.

(2) Production amount of Ca(OH)_2 and CaCO_3 , and pH value of concrete core

Figure 11 shows the change in pH value and produced amount of Ca(OH)_2 and CaCO_3 at various depths. There was a large change near the progress front of carbonation depth (65.23 mm). Calcium hydroxide changed to calcium carbonate due to carbonation in the area 56-75 mm from the surface, which was not carbonated according to the phenolphthalein test. The pH value is 10.39 in this area. Therefore, the carbonation depth as indicated by the pH and phenolphthalein test was different than that indicated by the changing of Ca(OH)_2 into CaCO_3 .

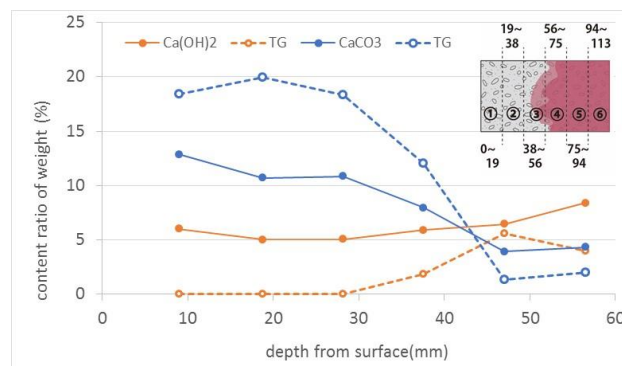


Figure 10. Change in produced amount

4. CONCLUSION

- 1) Regardless of the carbon dioxide concentration, the pore size distribution shifted toward larger size pores due to carbonation. It also shifted when using BFS.
- 2) At low concentrations of carbon dioxide, pores around 10 nm in size remained after carbonation when using OPC, but they were produced in the case of BFS. At high concentrations of carbon dioxide, the number of pores around 10 nm in size decreased and shifted to larger pores.
- 3) After carbonation, the cumulative pore volume decreased when using OPC, but increased when using BFS.
- 4) There was difference in speed of carbonation depending on the concentration of carbon dioxide. However no difference was observed in the produced amount of Ca(OH)_2 and CaCO_3 when comparing the cement types.
- 5) CaCO_3 is produced not only by Ca(OH)_2 but also other hydrates, such as C-S-H.
- 6) In the case of BFS, the produced amount of Ca(OH)_2 was less than OPC.
- 7) The produced amount of Ca(OH)_2 was less in specimens without aggregates because removal of the aggregates also removed Ca(OH)_2 around the aggregates.
- 8) CaCO_3 was observed in areas that were indicated as non-carbonated when sprayed with phenolphthalein.

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