



STUDY ON CARBONATION MECHANISM IN DIFFERENT CONCENTRATION OF CARBON DIOXIDE

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Abstract

The carbonation is a degradation factor of reinforced concrete. Currently, it was operated by accelerating carbonation test on selecting cement type. However, the accelerated carbonation test is performed in the 100 times concentration compared with natural environment. It was considered that the mechanisms are different on the different cement type and the different concentration of carbon dioxide. In this research, it was cleared that the mechanism of carbonation on different concentration of carbon dioxide. We had measured the changing pore structures and the amount of producing calcium carbonate and consuming calcium hydroxide. As a result, it is different mechanism for carbonation on ordinary Portland cement and slag cement, and also different concentration of carbon dioxide.

Keywords: Carbonation mechanism, porosity, XRD, calcite, vaterite

1. INTRODUCTION

There is carbonation into one of the deterioration of reinforced concrete structures. Carbonation was 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 actually concentration is performed. Lots of reports is 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

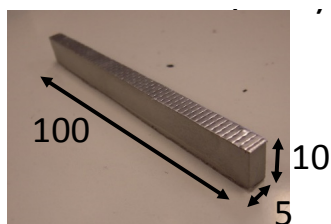


Photo-1 Cubic specimen for porosity and TG

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 ordinary Portland cement and blast furnace slag cement. It was investigated the changing pore structure on carbonation, the hydration products and difference of calcium carbonates on before and after carbonation.

2. OUTLINE OF EXPERIMENT

2.1 Samples

It was used for this research, 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), and Blast Furnace slag cement Type B (BB). BB is a replacement ratio 50% of ground granulated blast furnace slag on ordinary Portland cement. Therefore, the water binder ratio is constant as 100% for accelerating the carbonation. It use the chemical admixture on high quality of viscosity for preventing the separation of cement pastes. The test specimen for measurement of porosity was a cement paste of the size of 100*5*10mm in order to consider the bleeding and accelerating carbonation as shown photo-1. After mixing, the top of specimen was rapped with glass plate for 1 day. After remolding at 1 day, it was sealed curing at

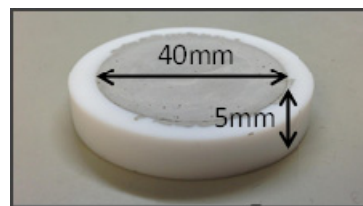


Photo -2 Disk specimen for XRD measurement

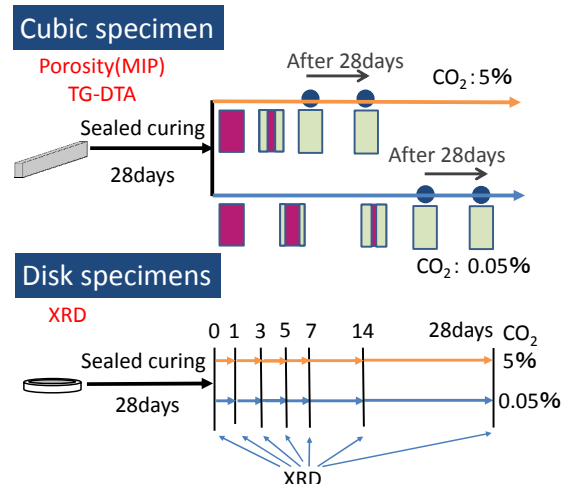


Fig.1 Test schedule on curing and measurement

28 days for progress of hydration. After these curing, only 2 areas opened on 10*100mm, the other area will be sealed using aluminium tapes. After few days on carbonation environment, test specimens were cutting repeat as shown Fig-1, it sprayed phenolphthalein solutions on the cutting area, and it kept the carbonation until no colour completely on the cutting area. On the other hand, it use a cement paste of the size of D40*5mm for using X-ray Diffraction test as shown photo-2. XRD measured continuously.

2.2 Concentration of carbon dioxide

After curing, it was carbonated for different concentration of carbon dioxide. Concentration of carbon dioxide are 0%, 0.05% and 5%. It was set up 5%, for based on the carbonation test on JIS A 1153. The concentration of 0.05% was assumed to be comparable to the real environment, it was at the laboratory room. Furthermore, 0% was kept in sealed state even after completion of curing. It was kept on the 20 degree Celsius and relative humidity 60%.

2.3 Experimental test

(1) Measurement of Porosity

Measurement of porosity were two methods. One is the Mercury Intrusion porosimeter (MIP) for measurement of pore size distribution. The

other is Archimedes' method for measurement of total porosity. It was prepared by cutting to 5mm cube for samples. It was used the test specimen as no coloured by phenolphthalein solution on whole area by carbonation. Porosity was measured at before starting carbonation test, the time at the moment on no colour specimen on carbonation and moreover after 28 days continuously carbonation.

(2) TG-DTA for amount of carbonated products

It was measured the production of calcium carbonate (CaCO_3) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) 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, the end time of carbonation at whole area and after 28days from that. The sample made from specimen as shown photo-1. After carbonation, it was grinding samples and measured TG-DTA test.

(3) X-ray Diffraction

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 of specimen. 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. It was analysed 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 intensity. After allowing carbonated samples in

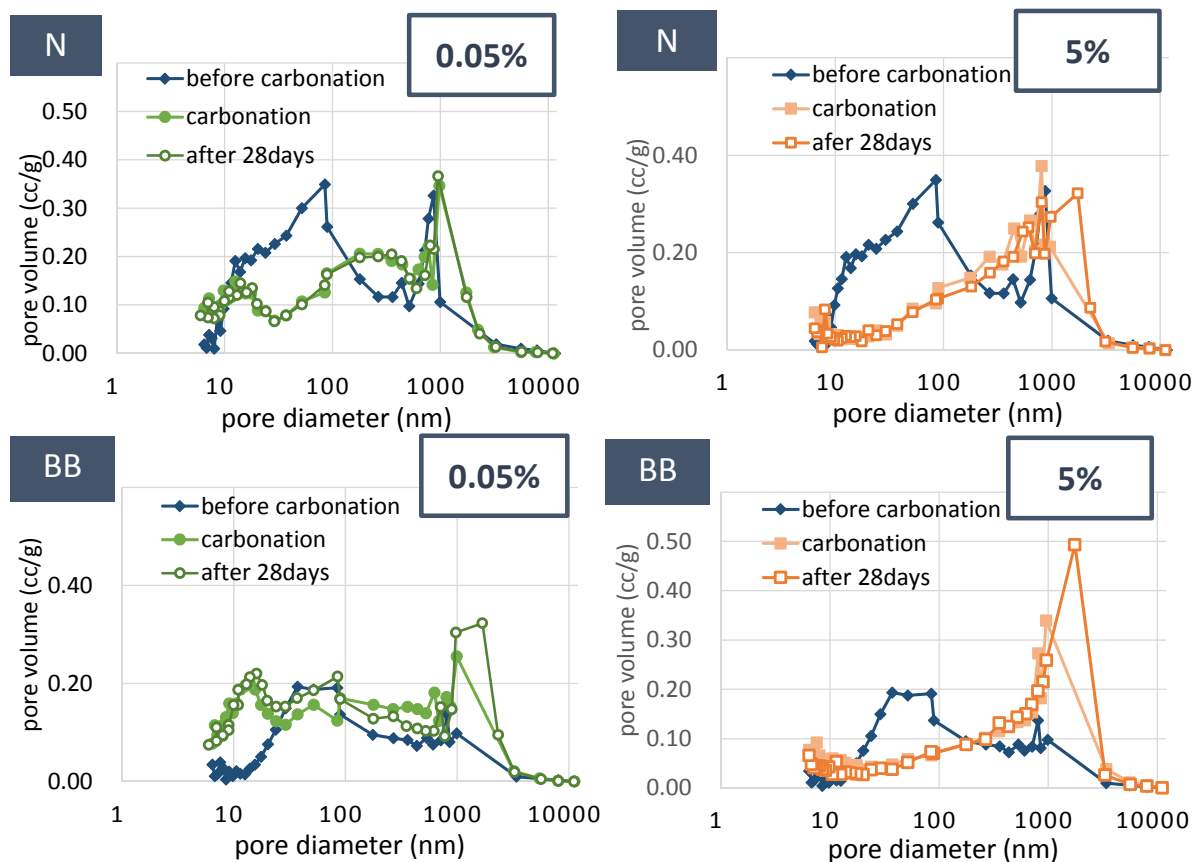


Fig2 Result for pore distribution by MIP

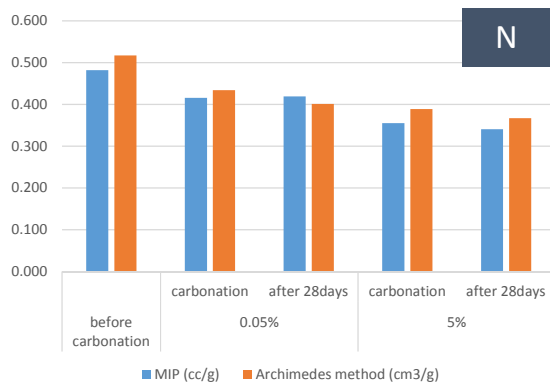


Fig-3 Compare total pore volume on N

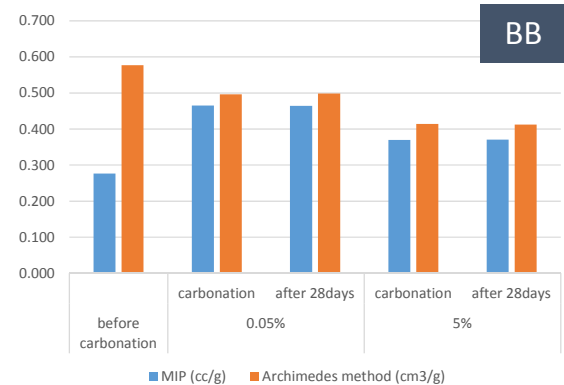


Fig-4 Compare total pore volume on BB

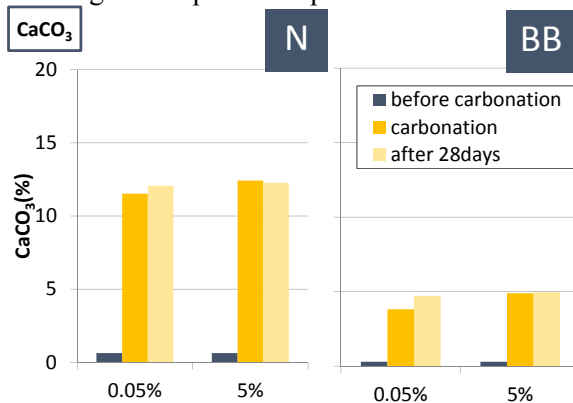


Fig-5 Result of amount of CaCO₃ by TG

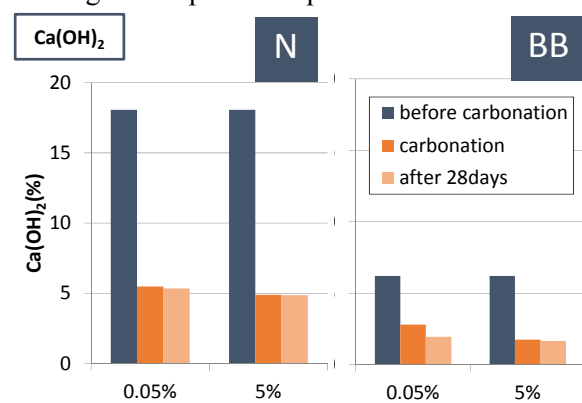


Fig-6 Result of amount of Ca(OH)₂ by TG

concentration of carbon dioxide, it was measured the XRD test using the same sample in the measurement age such as 0,1,3,5,7,14,28 days from the start of carbonation.

3. RESULT AND DISSUSIONS

3.1 Porosity

Fig-2 show the result of changing the pore size distribution measuring by MIP on progressing of carbonation. In each of N and BB cement, porosity is formed on dense pore in sealed curing finished (such as before stating carbonation). Comparing the carbonation at concentration of carbon dioxide at 0.05% (low) and 5.0% (high), a different was observed in a small pores of about 20 nm. In 5.0% concentration of faster carbonation progress condition, the pore of about 20nm is not much observed. However, at 0.05% concentration of slower carbonation progress condition, the pore of about 20nm is many observed. Therefore, the differences were observed in pore formed due to the difference on carbonation environments as concentration of carbon dioxide. Then, in Fig-3and Fig-4, it was compared by the total pore volume measured by MIP and Archimedes'

method on the difference carbonation concentration. Regardless of the difference in concentration of carbon dioxide, the total pore volume is reduced after carbonation in N. On the other hand, the total pore volume has increased at any concentration of carbon dioxide in BB.

3.2 Carbonation products by TG

Fig-5 and -6 show the results of the amount of calcium carbonate and calcium hydroxide measuring by TG-DTA. On each cement as N and BB, calcium carbonate was increased and calcium hydroxide was decrease due to carbonation. The amount of changing each products in N were larger than that in BB. After 28days past from the end time of carbonation, such as no colour in cutting area by phenolphthalein solution, it was not change the amount of calcium carbonate and calcium hydroxide on long periods for carbonation. The amount of calcium carbonate was same as different concentration of carbon dioxide. However, if it was focus on the calcium hydroxide, that of N for 5% of concentration of carbon dioxide was mostly decreased. On BB was also decreased, but not so much as N.

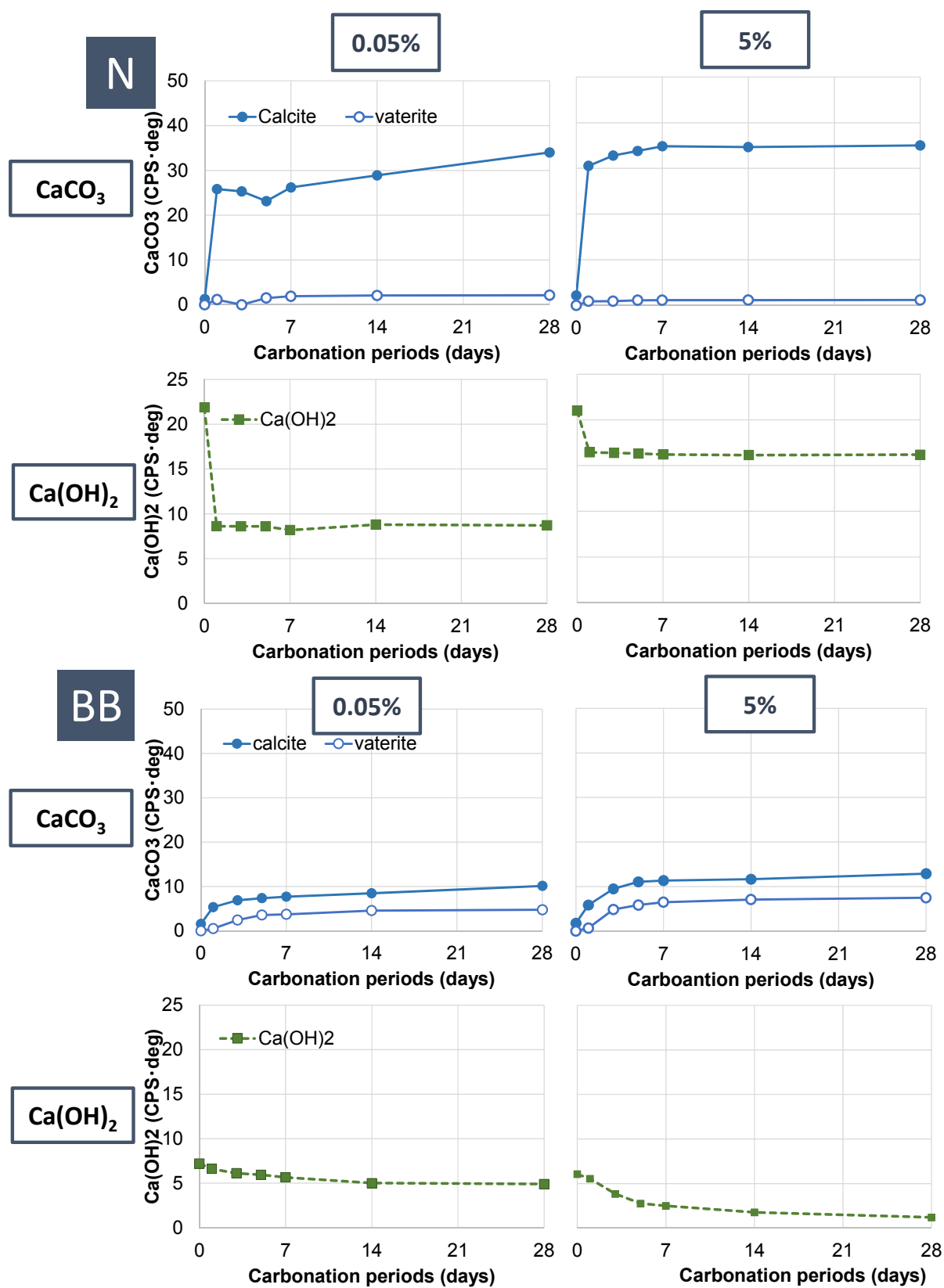


Fig-7 Results of amount of CaCO₃ including calcite and vaterite, and Ca(OH)₂ by XRD

3.3 Carbonation products by XRD

Fig-7 shows the result of quantities on calcium carbonate and calcium hydrate products on each carbonation periods. Each cement of N and BB, it was observed the calcite on early carbonation periods. The production of calcite increased rapidly in the early carbonation period in N. however the amount of calcite in BB was a tendency to increase gradually. Therefore, BB took time to production of calcite is constant, compared to N. Also, stating carbonation on BB, the production amount of vaterite increased. This tendency can be seen that when more carbonation concentration of 5% stronger than the 0.05%. Then, it was compared for the production of calcium hydroxide. In N, after stating carbonation, the amount of calcium hydroxide decreased immediately. After that, it became a constant regardless of the carbonation concentration. On the other hand, regardless of the carbon dioxide concentration, the amount of calcium hydroxide in BB decreases gently compared with N.

In N and BB, due to the difference in carbonation concentration, the difference was observed the porosity, the formation of calcium carbonate and the consumption of calcium hydroxide.

4. CONCLUSION

This research examined in order to clear the carbonation mechanism under different concentration of carbon dioxide environment at different cement. The knowledge is shown as following.

- 1) After carbonation, the radial peak of pre diameter was moved to large diameter. On the total pore volume, N became dense, but BB is increased pore.
- 2) The amount of production of calcite is often in N, however the amount of vaterite is often in BB.
- 3) Regardless of the carbon dioxide concentration, the amount of calcium hydroxide was reduced immediately after the stating carbonation in N. On the other hand, it has gradually decreased in BB.

However I think that there is a need to consider any practical W/B in the future work. The reason for the result in order to accelerating carbonation, were tested in high W/B (such as 100%) in this research.

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