Quantitative Depth Analysis of Carbonated Concrete

*In-Seok Yoon[1], Hyung-Gyu Choi[2], Young-Min Kim[3], Gyu-Yeol Jeong[4] and Gyung-Il Son[5]

[1] Department of Construction Info. Engineering, Induk University, Seoul 01878, Korea
[2], [3], [4], [5] Department of Construction Info. Engineering, Induk University, Seoul 01878, Korea
[1] isyoon@induk.ac.kr*

ABSTRACT

Carbonation is the result of the dissolution of CO_2 in the concrete pore fluid and this reacts with calcium from calcium hydroxide and calcium silicate hydrate to form calcite ($CaCO_3$). Normal concrete pore solution is saturated with calcium hydroxide and also contains sodium and potassium hydroxide; the pH is typically 13.0 to 13.5. Concrete with a pore solution of pH 10 ~ 12 is less alkaline than sound concrete but would still produce a strong color change with phenolphthalein indicator. It therefore follows that the indicator test is likely to underestimate the depth to which carbonation has occurred.

According to the previous research of author, the indicator has not changed color near the top and bottom surfaces, suggesting that these near-surface regions are carbonated to a depth of at least 3 mm from the top surface and 5 mm from the lower surface. Where the indicator has turned purple - the center of the slab - the pH of the concrete pore fluid remains high (above 8.6, probably nearer 10). Although the strong purple indicator color is clear, a more complete assessment would require chemical investigation. Indicator is not applied to the concrete at the right of this image and so the concrete retains its original color.

Based on the above technical background, this study was devoted to examine the depth analysis of carbonated concrete quantitatively. By means of micro-profiler, concrete powder was obtained with 1 mm depth. The powder sample was examined thermo-chemically by means of TGA. CH and Calcite profiles were described and the work was compared with the carbonation depth obtained by phenolphthalein indicator.

1. INTRODUCTION

Carbonation is the result of the interaction of carbon dioxide gas in the atmosphere with alkaline hydroxides in the concrete
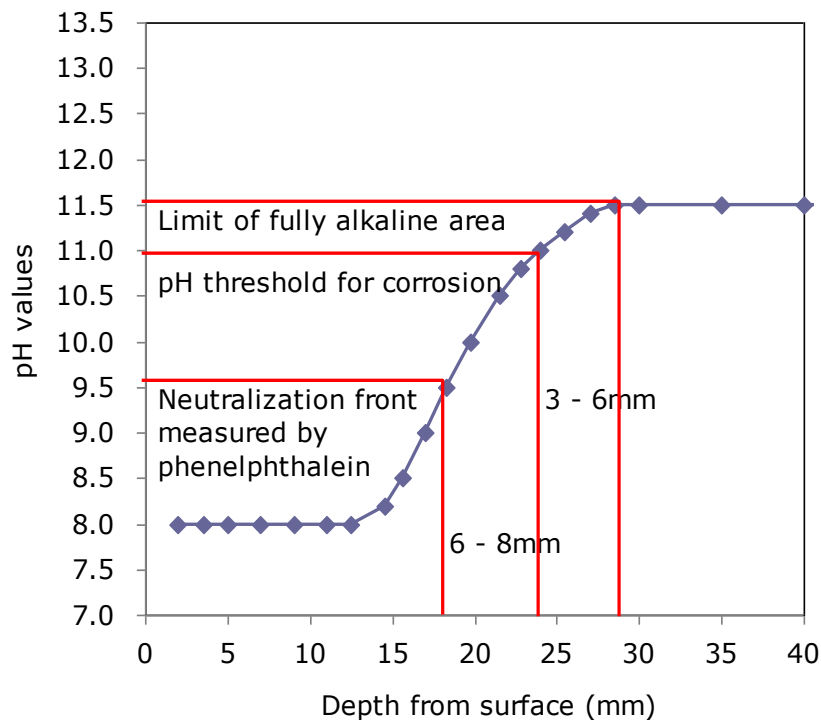
Fig. 1 Schematic of the carbonation from and its relationship to the corrosion behaviour and the color change for phenolphthalein indicator (Broomfield, 1997)

Table 1 Effect of carbonation on concrete durability (updated from Yoon et al, 2015)

Effect	Consequences for durability of structures	Consequences for durability testing
Reduction of alkalinity	causes reinforcement corrosion	detected with phenolphthalein solution
Decrease in transport coefficients	causes carbonation rate to decrease. Reduction of chloride and sulphate transport is significant	Surface durability tests such as Initial Surface Absorption will give misleading indication of improved durability
Decrease in chloride adsorption	causes chloride adsorption to decrease. Risk of reinforcement corrosion is very severe.	Determined from ratio of total chloride content to free chloride content.
Decrease in electrical resistivity	questions	Measurements of resistivity and rest potential give misleading results. Reliability of electrical chloride migration tests could be affected
Shrinkage	can cause cracking	threaten durability, in particular, penetration of harmful substances through micro-cracks

. Carbon dioxide dissolved in water to form calcite. It is known that CH more easily carbonated than C-S-H. The effect of carbonation on physical properties of concrete was summarized in Table 1. There is a lot more calcium hydroxide in the concrete pores than can be dissolved in the pore water. This helps maintain the pH at its usual level of around 12 or 13 as the carbonation reaction occurs. However, all the locally available calcium hydroxide reacts, precipitating the calcite and allowing the pH to fall to a level where steel will corrode. The passive layer on the reinforcement surface becomes unstable. As a result of carbonation, the pH of the pore solution drops down to 9.0. The passive layer of reinforcement is destroyed due to the reduction of pH. Finally the corrosion reduces the serviceability and safety performance of reinforced concrete. Thus, it is very important for concrete engineer to understand the effect of carbonation on deterioration of concrete structures. This is illustrated in Fig. 1.

Therefore, it is very important that carbonation can lead to reinforcement corrosion in concrete. The simple method to evaluate the carbonation of concrete is to measure carbonation depth by using 1% Phenolphthalein indicator. However, this method cannot provide a reasonable carbonation depth so that critical threshold depth to start reinforcement corrosion can be misunderstood. For this reason, many researches reported that reinforcement corrosion can start before carbonation depth reaches to the level of reinforcement.

The purpose of this study is to provide further evidence and improved understanding of the effects of carbonation on the change of hydration products. This study is devoted to obtain the carbonation profiles (contents of CH and calcite) and to conduct quantitative depth analysis around the borderline of carbonation depth. The work can be expected as a framework to estimate the durability condition of carbonated concrete structure reasonably.

2. EXPERIMENT DESIGN

2.1 Preparation of the specimen

A commercial cement, Type I KS L 5201 Ordinary Portland Cement (OPC), was used with a water-cement ratio (w/c) of 0.45, 0.50, and 0.55, as shown in Table 2. Cylindered specimens were fabricated for each w/c ratio and then cured before concrete accelerating testing. The size of each specimen was determined to be 100 mm (D) and 200 mm (H). The curing temperature was 20 °C in water.

Table 2 Mixing proportion of concrete

Air (%)	Slump (cm)	W/C	Unit weight (kg/ m^3)			
			Water	Cement	Sand	Gravel
4.5±1.5	15±1	0.45	185	411	706	1001
4.5±1.5	15±1	0.50	185	370	720	1021
4.5±1.5	15±1	0.55	185	336	732	1038

2.2 Test Methods

(1) Carbonation of concrete

After water curing were completed, specimens were exposed in an accelerating carbonation chamber at a temperature of 20 °C, relative humidity of 65%, and 5 % CO_2 in order to make carbonated concrete. Duration of carbonation was a month. A 1% on the fracture of the specimens, and a Venire caliper was employed to measure the depth of carbonation of each specimen. After carbonation, two methods were used to estimate carbonation depth. Firstly, phenolphthalein-alcohol solution was sprayed. The carbonation depth was measured at 3 or 4 parts and the average value was obtained. Secondly, for improving data accuracy, micro-profiler grinding kit was used to take concrete powder at suitable increments. The specimen was drilled along the vertical direction from the surface(see Fig. 2). Two samples were taken from each mixture.
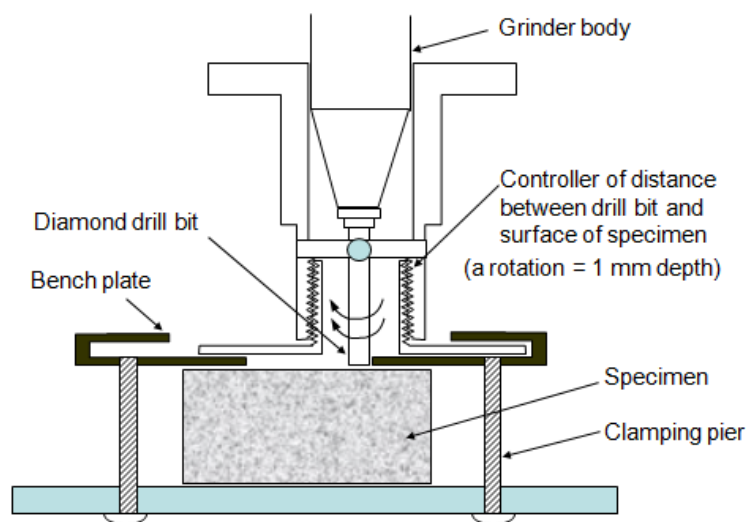

Fig. 2 Micro-profiler to extract powder with depth

(2) TGA experiment

Thermogravimetric analysis (TGA) is the method to provide quantitative information about the decomposition or dehydration of minerals as a function of temperature. The mass of powder samples was 30 ~ 40 mg. The contents of main hydration product (CH) and calcite (Ct) were calculated from the weight loss of samples from TGA curves. The typical TGA results for concrete are shown in Fig. 3. The well-dried powder sample was heated at the rate of 1℃ / sec. In the TGA curves of noncarbonated samples, the weight loss in the range of 40 ~ 400℃ is normally related to the dehydration of C-S-H phase. The mass loss related to CH dehydroxylation usually occurs in the range of 450 ~ 550℃. The technique makes a correction for the concurrent dehydration of other compounds. The decomposition of calcite mainly happens in the range of more than 600 ℃.
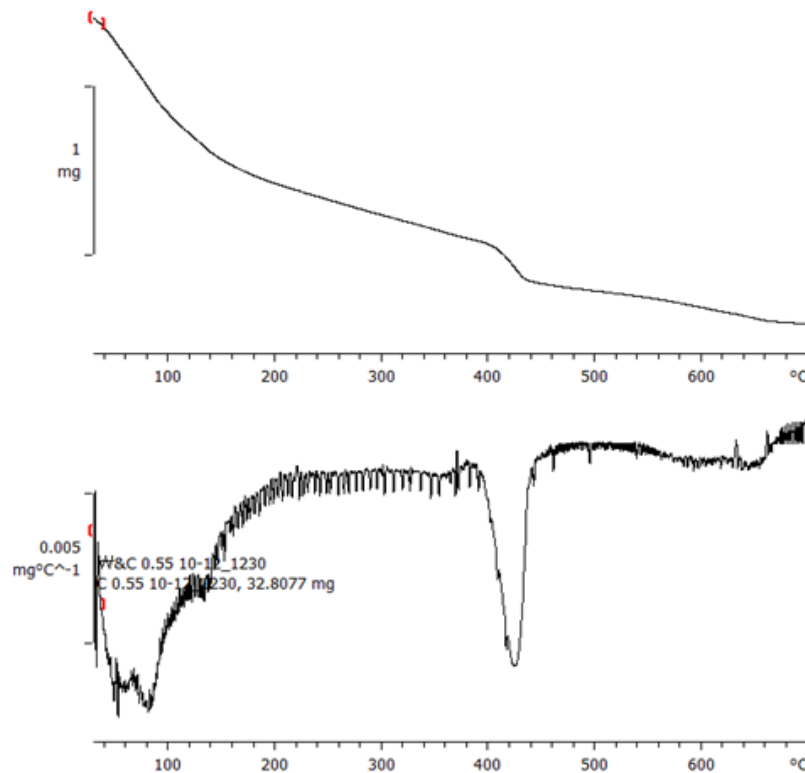
Fig. 3 Thermal behavior curve and 1st derivative curve by means of TGA

3. RESULTS AND DISCUSSION

Fig. 4 shows the profiles of CH and calcite at carbonated concrete cured for 90 days. The CH at carbonated concrete is clearly lowed compared with uncarbonated concrete. It should be noticed that CH was not completely dissipated even at carbonated concrete. On the contrary, the production of CH was clearly appeared at noncarbonated concrete. The amount of calcite decreased remarkably with depth from surface of concrete and the trend is very similar to Fickian behavior.
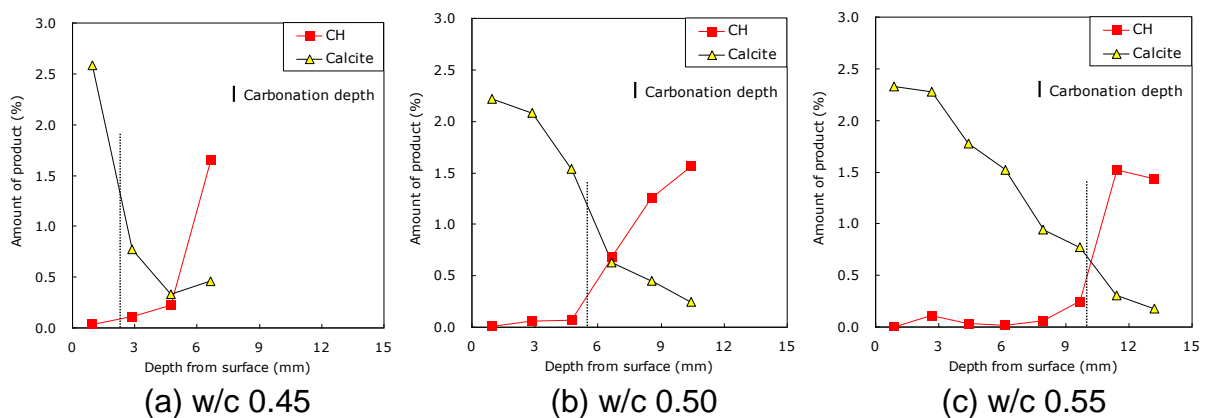

(a) w/c 0.45   (b) w/c 0.50   (c) w/c 0.55

Fig. 4 Amount of CH and calcite in concrete with 90 days

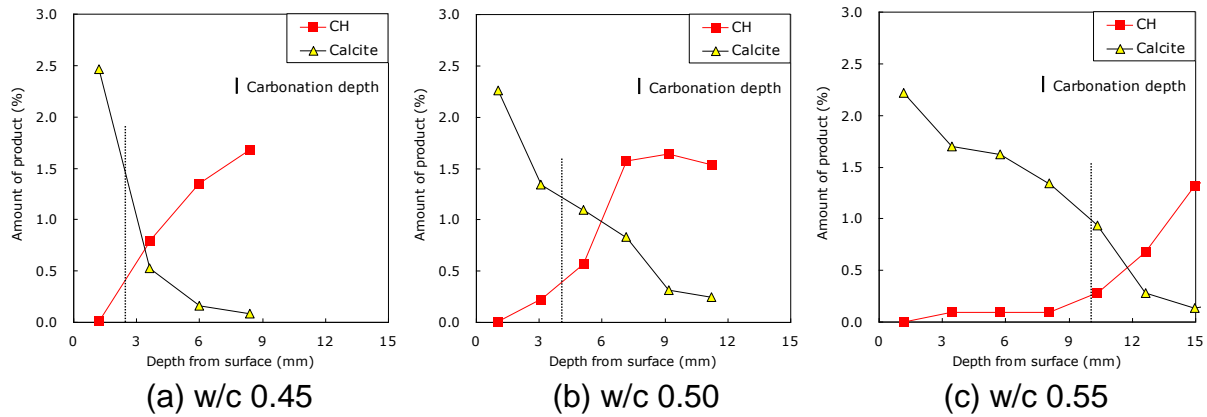(a) w/c 0.45 (b) w/c 0.50 (c) w/c 0.55

Fig. 5 Amount of CH and calcite in concrete with 240 days

Fig. 5 shows the amount of remained CH and calcite at carbonated concrete cured for 240 days. CH was not completely dissipated at the carbonated concrete and that is similar to Fig. 4. The remaining amount of CH was high at the uncarbonated concrete. The amount of CH of concrete with low w/c ratio at the uncarbonated concrete was high because the high volume of cement produced the high amount of hydration products for concrete with low w/c ratio. The amount of calcite at the surface of concrete was remarkably high because of skin effect. That is, surface concrete has not contained coarse aggregate and this leads high volume of hydration product which can be converted into calcite if concrete is carbonated.

Therefore, uncarbonation depth is very important because carbonation depth is not sufficient to estimate integrity of concrete durability rationally. It was reported that reinforcement corrosion begins when so-called "the uncarbonation depth" (see Fig. 6) of the concrete equals about 8mm without presence of chloride ions. The uncarbonation depth denotes the distance between the carbonation depth and the surface of reinforcement bar. This value becomes 20 mm for the concrete structures containing chloride ions(JSCE, 1999). These findings often result into ambiguity of interpretation. One of the explanations for this phenomenon could be the fact that carbonation depth measured by the phenolphthalein indicator could usually be highlighted in the range of pH 8.3 ~ 9.5, while reinforcement corrosion is triggered within the range of pH 11.0 ~ 11.5. Yoon (2012) suggested that when uncarbonation depth is 3~5 mm, the reinforcing bar corrodes at concrete without chloride ions. Based on the technical report above, one of the best ways to estimate of carbonation of concrete should be expressed as "degree of carbonation." In this study, the remaining degree of CH and the production of calcite in the carbonated depth were suggested as following;

$$R_{CH} = \frac{W_{CH}^c}{W_{CH}^{nc}} \qquad (1)$$

$$R_{Ct} = \frac{W_{Ct}^c}{W_{Ct}^s} \qquad (2)$$

where, W_{CH}^{nc} : amount of CH at uncarbonated concrete, W_{CH}^{c} : remaining amount of CH at carbonation depth, W_{Ct}^{c} : amount of calcite at carbonation depth, W_{Ct}^{s} : amount of calcite at carbonated surface concrete.
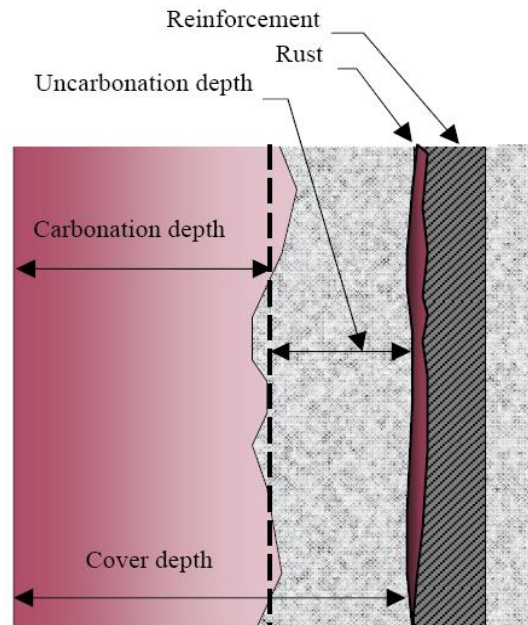

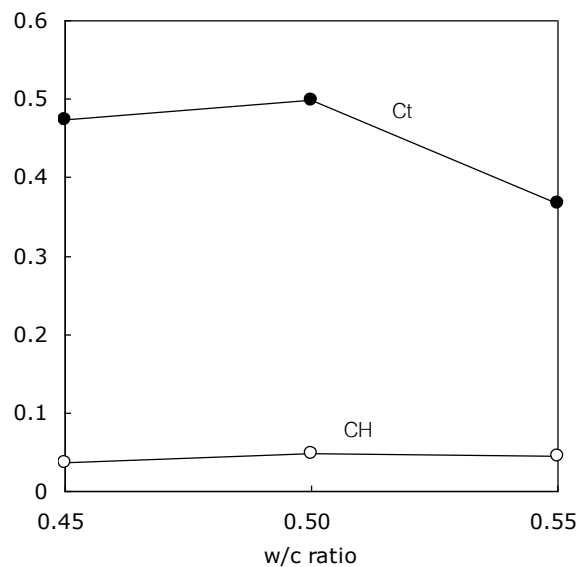Fig. 6 Definition of uncarbonation depth (Yoon, 2012)

Fig. 7 Degree of carbonation of concrete with w/c ratio

Fig. 7 represents the degree of carbonation of concrete with various w/c ratios, based on the profile of CH and calcite. The degree of production of calcite around carbonation depth was 0.37 to 0.50, however, the degree of production of CH was 0.037 to 0.048, which was equivalent to around 1/10, compared with the degree of production of calcite. CH is more sensitive than calcite at carbonation depth. This is

because of a rapid rate of reaction of carbonation. That is, concrete is rapidly carbonated by acceleration experiment and this indicates that CH is not immediately converted into the calcite even if concrete is carbonated.

4. CONCLUSIONS

(1) CH was not completely dissipated at the carbonated concrete and remaining amount of CH was high at the uncarbonated concrete. The amount of calcite at the surface of concrete was remarkably high because of skin effect. The amount of calcite decreased remarkably with depth from surface of concrete and the trend is very similar to Fickian behavior.

(2) The degree of production of calcite around carbonation depth was 0.37 to 0.50 and the degree of production of CH was 0.037 to 0.048. Thus, CH is more sensitive than calcite at carbonation depth. This is because of a rapid rate of reaction of carbonation.

ACKNOWLEGMENTS

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