Semi-quantitative Evaluation of Concrete Carbonation by XRD Analysis

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ABSTRACT: Carbonation is a major cause in the degradation of concrete. The resulting reduction of pH around the reinforcement inside concrete creates an environment favoring corrosion. In general, the effect of carbonation is examined by spraying an indicator on the cross section of the concrete core so as to measure the carbonation depth by observing the discoloration. The differential thermal analysis and X-ray spectrometry are also widely applied but the X-ray spectrometry is generally adopted complementarily to examine the variation of the results and conduct comparative analysis of the detected components because of the limited exploitability of the non-quantitative results provided by this method. This study performs carbonation test on specimens fabricated with water-to-binder ratios of 0.40, 0.45 and 0.50. The change in the carbonation depth is measured with respect to the duration of carbonation using a phenolphthalein solution. The contents in calcite and portlandite are analyzed by TG-DTA and XRD. The comparison of the TG-DTA and XRD analysis results reveals the possibility to achieve semi-quantitative evaluation of the carbonation by XRD.

KEYWORDS: Carbonation; Concrete; Paste; XRD; TG-DTA.

I. INTRODUCTION

Fresh concrete paste is highly alkaline (pH = 12–13) due to the presence of large quantities of calcium hydroxide ($Ca(OH)_2$; portlandite) generated during the hydration of concrete caused by the reaction of cement with the minerals contained in water. Even if the calcium hydroxide does not contribute to the development of strength, it plays a crucial role in preventing the corrosion of the reinforcing bars arranged in concrete by creating a passive protective oxide film. During the carbonation process of concrete, the carbon dioxide in the air (about 0.035%) penetrates through the capillary pores from the surface of concrete and enters in contact with the pore solution containing dissolved calcium hydroxide inside concrete. This contact transforms the carbon dioxide into calcium carbonate ($CaCO_3$; calcite) and water. This carbonation process generates the reaction products listed in Table 1. The calcium carbonate precipitates on the pore walls and densifies the structure of concrete whereas water evaporates or continues to be used in the chemical reaction. Especially, efflorescence may also occur when concrete is sufficiently wet by the continuous and gradual precipitation of calcium carbonate or alkaline carbonate that is, sodium chloride ($NaCO_3$) and potassium carbonate (KCO_3), on the concrete surface outflowing from the internal structure of concrete toward the surface together with the water present in the pores of concrete. Since the calcium carbonate precipitated on the pore walls inside concrete is neutral, the pH turns gradually from highly alkaline to neutrality according to the extent of the transformation of calcium hydroxide to calcium carbonate. Carbonation develops progressively from the surface prone to the penetration of carbon dioxide and water. This carbonation process of concrete is accelerated in concrete exhibiting large pores, poor water tightness and high water-to-binder (W/B) ratio in terms of quality, and in environment with high concentration in carbon dioxide and where adequate humidity is preserved (50~75%). A too high humidity prevents the carbon dioxide penetrate in the internal pores of concrete and will obstruct the carbonation. Finally, carbonation progresses rapidly in environment experiencing repeated cycles of drying and moisture.

Table 1 - Concrete carbonation products

Portland cement hydration product	Carbonation product
Calcium hydroxide	Calcium carbonate and water
Calcium silicate hydrate	Calcium carbonate, silica gel, and water
Calcium aluminate hydrate	Calcium carbonate, alumina gel, and water
Hydrated ferrite phases	Calcium carbonate, ferric oxide, alumina gel, and water
Ettringite and calcium monosulfoaluminate	Gypsum, alumina gel, and water

The carbonation of concrete creates an environment favoring the corrosion of the rebar in concrete. Despite of the presence of the passive protective oxide film, this environment induces corrosion by letting the chloride ion penetrate and by lowering the pH of concrete around the rebar as explained above. Pourbaix [1] reported that the corrosion of the reinforcement begins at pH of 10.4 with the failure of the passive protective oxide film covering the surface of the rebar. The fact that the pH of the highly alkaline concrete has dropped below 10.4 indicates that moisture and oxygen have already gained access in the concrete due to carbonation. It is well known that carbonation generates calcium carbonate and water. If carbonation attains the depth of the rebar, it can be expected that the rebar will be exposed to a corrosive environment. Parrott [2] found out that the fastest corrosion by carbonation occurs under relative humidity of 95% to 98% because the supply of moisture and oxygen are primordial in the development of corrosion. This author also stated that corrosion does practically not occur when the relative humidity is lower than 60% even if carbonation has started. The rust of steel expands the original volume by about 2.5 to 7 times causing the deterioration of the durability of the structure like the development of cracks inside concrete, the loss of bond strength of the rebar, the failure of cover concrete, and the cross-sectional reduction of the rebar. In view of these phenomena, carbonation shall be examined in term of the durability.

Research dedicated to the analysis of carbonation of concrete commenced very early. A representative method to evaluate the carbonation is the use of indicator. The seventies witnessed the start of studies using differential thermal analysis (DTA) for the analysis of the thermal characteristics and hydration of cement. Later, studies used also other methods like the thermo-gravimetry (TG), the derivative thermo-gravimetry (DTG) and the differential scanning calorimetry (DSC) [3-6]. The X-ray diffraction (XRD) method extensively utilized together with TG-DTA as a method analyzing the crystalline structure inside a substance intends to identify qualitatively the amount of portlandite and calcite in concrete. However, XRD is generally used to assess qualitatively the relative amount of a component to another and cannot be employed itself to achieve quantitative evaluation of the component.

This study performs carbonation test on specimens fabricated with various W/B ratios. The carbonation depth per duration of exposure to carbonation and the modification of the chemical composition due to carbonation with respect to the change of W/B are analyzed quantitatively using TG-DTA and qualitatively using XRD. Investigation is conducted by focusing on the semi-quantitative assessment provided by XRD through the comparison of the TG-DTA and XRD results and to prepare criteria enabling to assess carbonation by XRD only.

II. TEST

A. Fabrication of specimens

Table 2 arranges the analysis results of the composition of the binder adopted in this study. The components of the binder are seen to present practically no difference to those of type-1 Portland cement as well as to the results of Bogue's equation. The paste and mortar specimens for the carbonation test are cubes with dimensions of $50 \times 50 \times 50$mm fabricated in compliance with ASTM C 109. The concrete specimens are $\phi 100 \times 200$mm cylinders. All the specimens considered in this study are fabricated with a mass replacement rate of 20% of ordinary Portland cement (OPC) by fly ash (FA). Prior to exposure to CO2 for examining the effect of carbonation, all the specimens were subject to standard

water-curing at temperature of 20±2.5°C during 28 days. A total of 45 specimens were fabricated for evaluating the change in the carbonation depth according to the W/B ratio by adopting 3 specimens for each of the considered W/B ratios of 0.40 (Mix 1), 0.45(Mix 2), and 0.50(Mix 3) and, each considered carbonation acceleration durations of 28, 56, 91, 180, and 365 days of the paste, mortar and concrete specimens. The depth of discoloration due to carbonation was measured at each of the considered duration. TG-DTA and XRD were performed at depth of 10 mm from the surface in each specimen.

Table 2 –Analyzed components of adopted binders

Components	OPC	FA
SiO_2	20.10	54.70
Al_2O_3	5.22	24.80
Fe_2O_3	2.76	8.76
CaO	55.90	2.99
MgO	2.97	1.15
SO_3	1.87	0.32
LOI	1.56	3.56

B. Accelerated carbonation test

A carbonation test chamber set to temperature of 20°C, humidity of 60% and CO_2 concentration was used to accelerate the carbonation of each specimen, and the carbonation depth was measured at durations of 28, 56, 91, 180, and 365 days. The carbonation depth is measured using paste specimens to minimize the effect of the aggregates during the analysis. In order to ease the carbonation of all the specimens during the test, the specimens were disposed at sufficient distance to each other so as to provide harmonious contact with the gas.

C. Carbonation depth measurement by phenolphthalein indicator

A traditional method for measuring the carbonation depth of concrete is the use of phenolphthalein indicator. This method is based upon the pH-dependent discoloration of an originally colorless indicator sprayed on the surface of concrete. However, since this method relies on the pH change, it presents limitations in verifying the extent of carbonation when partial carbonation occurs or when the pH exceeds the discoloration range of the indicator. Especially, the method using phenolphthalein indicator becomes obsolete in case of the recent non-cementitious material where the material itself presents pH lower than 9. Nevertheless, since this method remains the easiest and most preferred one enabling to assess eventual carbonation visually on site, one cannot restrict its application. Accordingly, the method using an indicator to measure the carbonation depth is carried out to secure data to be used for comparative analysis with other methods measuring the carbonation depth by means of the microstructure of fabricated concrete specimens.

The carbonation depth measurement by indicator proceeds first by splitting specimens using a universal testing machine after having been drawn out from the carbonation chamber at each considered duration time. Then, a phenolphthalein solution made by dissolving 1% of phenolphthalein and 99% of ethanol in distilled water is sprayed on the split fragments. The pH indicated by phenolphthalein ranges between 8.3 and 9.5 and this pH range differs according to the adopted indicator as presented in Table 3.

Table 3 - pH ranges of typical pH indicators

Indicator	pH range
Tropaeolin O	pH 11.1 - 12.7
Alizarin yellow R	pH 10.2 - 12.2
Thymolphthalein	pH 9.3 - 10.5
Phenolphthalein	pH 8.3 - 9.5

The identification of the carbonation depth from the cut surface of the concrete core becomes more difficult as much as the structure from which the concrete core is sampled has been in service and the quality of concrete is poor, and as much as time has elapsed from the sampling of the core. This difficulty in identifying the discoloration is caused by the presence of remaining powders generated during the extraction on the surface of the core or in its pores. Following, it is recommended to spray the phenolphthalein solution on the cut surface on site immediately after exposure of the core to air. When measurement cannot be performed on site, the carbonation depth must be measured by spraying the phenolphthalein solution on the concrete interface obtained by cutting the central part of the specimen.

In this study, carbonation was measured by cutting the central part of the specimen. Discoloration did not occur in the carbonated parts and the solution turned red in the portions remaining highly alkaline. The carbonation depth was measured by means of the maximum, minimum and average depths on the carbonated parts using Vernier calipers. The carbonation depth is expressed in term of the average depth obtained from measurements on 3 specimens per carbonation exposure duration.

III.   ANALYSIS

A. Preparation of samples for analysis

Series of three specimens were additionally fabricated for each mix composition in order to analyze the chemical change of the paste specimen due to carbonation. The carbonation depth was measured first using phenolphthalein indicator before any change in the microstructure caused by carbonation, then, the paste specimen was cut down to a depth of 10 mm from the surface and pulverized from which powders passing the sieve No. 50 were used for the analysis. Pulverization was performed along the cut surface using fret saw paste and stainless medicine pestle to minimize the additional carbonation effect on the paste specimen due to the frictional heat that can be generated between the specimens during cutting.

B. TG-DTA

Thermo-gravimetric differential thermal analysis (TG-DTA) is a method using loss on ignition, which was developed based on the observation that a substance experiences moisture evaporation, oxidation, and recrystallization according to the elevation of temperature. Since the change in the state of a substance resulting from the gradual elevation of temperature differs according to the characteristics of the substance at hand, the analysis of the state change throughout this process makes it possible to know the extent of the substances contained in the sample. Especially, this method is valuable when assessing quantitatively the degree of carbonation by quantifying the dosage of calcium carbonate and calcium hydroxide. In general, calcite as a representative substance in carbonated concrete decomposes in temperature range of 600°C to 900°C, and portlandite as a major component of concrete decomposes in temperature range of 400°C to 500°C.

The analysis was conducted using model TG/DTA 7300 of Seico Inst by setting the temperature range from ambient temperature to 1200°C, the heating rate to 10°C/min, using carbon dioxide free nitrogen, and the flowing to 10ml/min.

The analysis results are verified by checking the values related to the change of each substance in specific temperature ranges. The transformation temperature change per component of concrete are determined with reference to the temperature ranges listed in Table 4.

Table 4 - Temperature ranges of compounds

Compounds	Temperature Ranges
Gypsum	180°C
Ettringite	250-290°C
Calcium hydroxide	400-450°C
Calcium carbonate	600-900°C

C. XRD

Analysis was performed using the model D8 Focus of Bruker AXS. The adopted analysis conditions were scan range 2θ of $5°$ to $60°$, step size of $0.02°$, scan speed of 0.3s/step, voltage of 40kV, and current of 40mA. The analysis results were verified by exploiting the peak values according to the crystal with reference to JCPDS card. Table 5 lists the corresponding JCPDS numbers.

Table 5 - Compounds and JCPDS No. for XRD method

Compounds	Chemical Formula	JCPDS Card No.
Calcium Carbonate Vaterite, syn	$\mu\text{-}CaCO_3$	025-0127
Calcium Carbnoate Calcium carbonate, syn	$CaCO_3$	005-0586
Calcium Hydroxide Portalndite, syn	$Ca(OH)_2$	004-0733
Calcium Silicate Hydrate	$Ca_{1.5}SiO_{3.5} \cdot xH_2O$ /$1.5CaO \cdot SiO_2 \cdot xH_2O$	033-0306
Calcium Silicate Hydrate	$CaO \cdot SiO_2 \cdot H_2O$	009-0210

### IV.   RESULTS

A. Measured carbonation depths

The carbonation depth is measured at each considered duration time according to the exposure to carbonation by measuring the depth from the surface using the discoloration criteria of the phenolphthalein indicator sprayed on the specimen. The results correspond to the averages measured at each duration time on 3 specimens per mix composition. It can be verified that the results lie within ±10% of the averages.

Fig. 1 compares the results categorized by mix composition with identical type of paste, mortar and concrete according to W/B. The logarithmic regression shows that highly reliable results are obtained for all the mixes with a coefficient of determination (R2) running from minimum 0.929 to maximum 0.994. The carbonation rate is seen to increase in each mix composition according to the increase of W/B. This observation is in agreement with a previous study [7] which reported that the carbonation rate slows down with higher design strength.
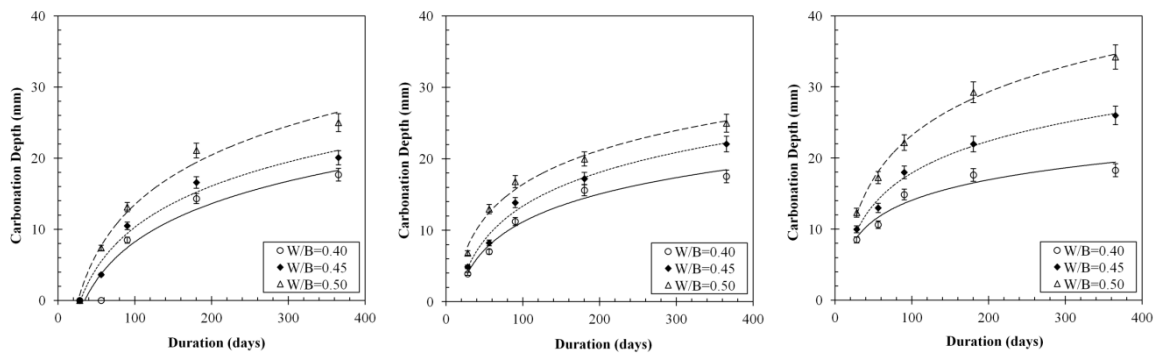
Figure 1. Carbonation depth measured by phenolphthalein indicator per considered mix (a)paste, (b)mortar, (c)concrete

With regard to the effect of the aggregate, the measurements of the carbonation depth reveal that concrete experiences larger development of carbonation than the paste or mortar whereas the carbonation rate is the fastest for the paste as much as the exposure duration is longer as shown in the plots of the carbonation depth of the mixes per W/B in Fig. 2.
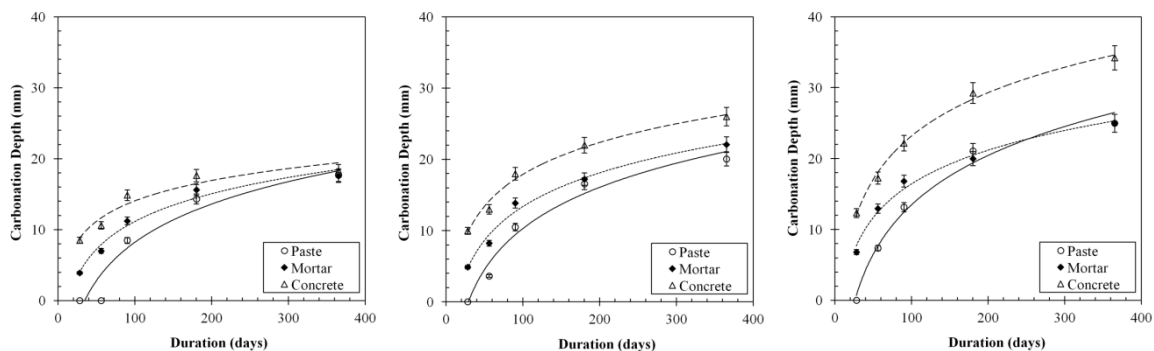
Figure 2. Carbonation depth measured by phenolphthalein indicator per considered W/B, (a)W/B=0.40, (b)W/B=0.45, (c)W/B=0.50

The analysis of the logarithmic scaling of each mix shows that the carbonation depth with respect to W/B ranges between 7.78 and 10.05 for paste, and 4.15 and 8.83 for concrete, which can be expected to be paste > mortar > concrete by descending order if carbonation is assumed to continue its progress after 365 days. This result can be explained by the fact that early carbonation initiates faster because of the easier penetration of the carbonate ion through the capillary pores generated by the effect of the bleeding and inter-transition between the cement paste and aggregate at the surface of concrete. However, the carbonation rate of concrete slows gradually down with longer exposure duration to carbonation due to the presence of the aggregate obstructing the penetration of the carbonate ion migrating in the cement paste matrix [8].

B. TG-DTA

Numerous studies on the carbonation of concrete analyzed quantitatively the degree of carbonation by TG-DTA as an indispensable method. Numerous studies were also conducted on the temperature range at which each of the crystals dissociates for the analysis using TG-DTA. Hacelbach arranged Table 6 which lists the TG-DTA methods conducted to date. In view of Table 6, it appears that the dehydration and decomposition of the major components of concrete, portlandite and calcite, occur mainly at temperature ranges of 300 to 360°C and 500 to 950°C, respectively, and that

these ranges can be set as the largest temperature ranges [9]. The analysis of the weight loss by means of the dehydration and decomposition in these temperature ranges is widely adopted as a quantitative method enabling to compute the molarity of the crystal and the results are also used to validate other analysis results. Equation 1 expresses the decomposition of portlandite during the analysis process using TG-DTA and Equation 2 formulates the decomposition process of calcite to carbon dioxide.

$$Ca(OH)_{2(S)} \rightarrow CaO_{(S)} + H_2O_{(g)} \tag{1}$$

$$CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)} \tag{2}$$

Table 6 - Decomposition temperature ranges in previous research [9]

Author	$Ca(OH)_2$ TGA decomposition	$CaCO_3$ TGA Decomposition
Chang and Chen (2006) [10]	425-550	550-950
Papadakis et al. (1992) [11]	460	
Papadakis et al. (1991) [12]	400-500	600-800
Huntzinger (2006) [13]	300-500	500-800
Huijgen et al. (2005) – slag [14]		>500
Taylor et al. (1985a,b) [15,16]	450-650	
Ramachandran et al. (1964) [17]	464(DTA)	850-950 Calcium carbonate
Cole and Kroone (1960) [18]		600-750 poorly crystallized 820 well crystallized
Stern (2001) [19]		827-927 Calcium carbonate

In this study, the degree of carbonation is analyzed by extracting samples of 10 mm at the surface according to the duration of exposure to carbonation. Fig. 3 plots the DTG and DTA results measured at carbonation exposure durations of 28 and 91 days. Referring to the temperature ranges of previous studies listed in Table 6, the largest changes indicated in the graph are set between 400°C and 500°C for portlandite and between 600°C and 900°C for calcite. It can be verified that the value of 150 µg/min measured at 28 days in the DTG results of portlandite reduces by more than a half at 91 days to become approximately 60 µg/min. On the contrary, the DTG value of calcite is more than doubled from about 70 µg/min at 28 days to 140 µg/min at 91 days. Changes can also be verified for the DTA values in the portlandite and calcite ranges where large change is observed at 28 days in the portlandite range whereas small change occurs in the calcite range.
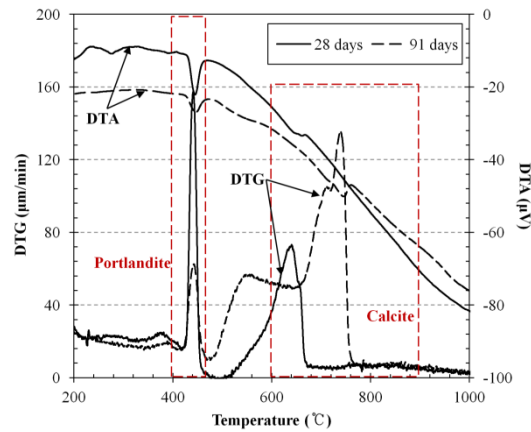
Figure 3.DTA and DTG changes of paste at 28 and 91 days of carbonation test

Based upon the temperature ranges of 400 to 450°C for portlandite and 600 to 900°C for calcite, the TG results are analyzed to measure the molarity of the components decomposed in each temperature range. Here, the total weight of the sample is converted to 100 and the corresponding weight ratios are plotted in Fig. 4. The formulae for the calculation of the molarity of portlandite and calcite are expressed as follows.
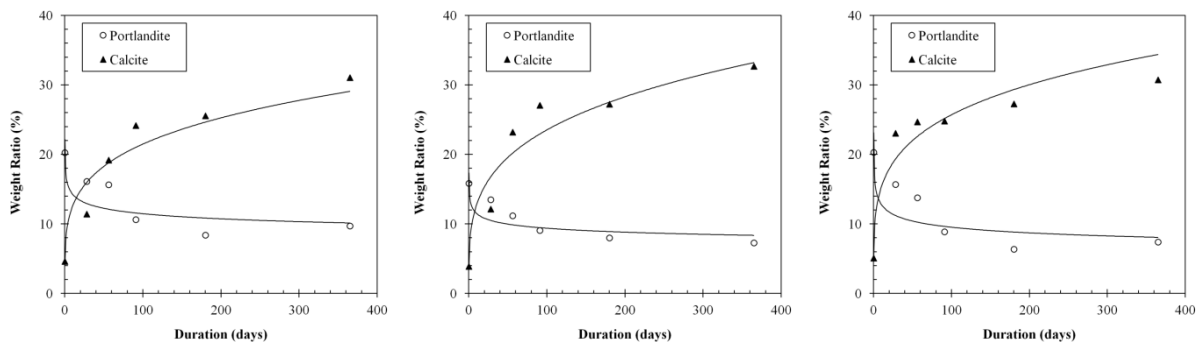
Figure 4. Changes of portlandite and calcite by TG per W/B according to carbonation exposure duration
(a)W/B=0.40, (b)W/B=0.45, (c)W/B=0.50

In the graphs, the result at 0 day is used as indicator for identifying the degradation of the component with respect to the non-degraded state immediately after 28 days of curing. The computation provided contents of 3.9 to 5.1%/wt. for portlandite and 15.8 to 20.3%/wt. for calcite. The computed content in portlandite is in good agreement with the work of Dweck et al. who performed TG-DTA and found out that the content in portlandite of the cement paste after 28 days of water curing ranged around 20% [20].

C. XRD

XRD, which was employed to analyze the crystals inside cement paste, presents the disadvantage of being unable to compute quantitatively the amount of crystal but remains widely utilized owing to the accessibility and convenience provided by the latest equipment. In this study, XRD is also applied simultaneously to DT-TGA to allow qualitative comparison with the results with respect to the carbonation exposure duration. The results are presented graphically in Fig. 5 by plotting the changes from 28 days to 365 days, where P and C stand for portlandite and calcite, respectively.

The three peaks indicated for each component in Fig. 5 are the peaks with the largest changes according to the exposure duration sorted out from the peaks listed in JCPDS. For example in Fig. 5(b), the intensity change at 34.089° corresponding to 2θ of portlandite can be seen to experience clear reduction from 28 days to 365 days. The positions of such peaks showing clear increase or decrease trend are indicated in Fig. 5(a). Consequently, the reduction of portlandite and the augmentation of calcite can thus be clearly identified. The qualitative expression of such qualitative changes is represented in Fig. 6 showing the changing trend by summing up the intensities at the three selected peaks that is at 28.662°, 34.089°, 47.124° for portlandite, and at 26.998°, 29.406°, 32.778° for calcite. This approach enables to verify graphically the reduction of portlandite and the augmentation of calcite with relative accuracy in comparison to the TG-DTA results expressed in Fig. 4.
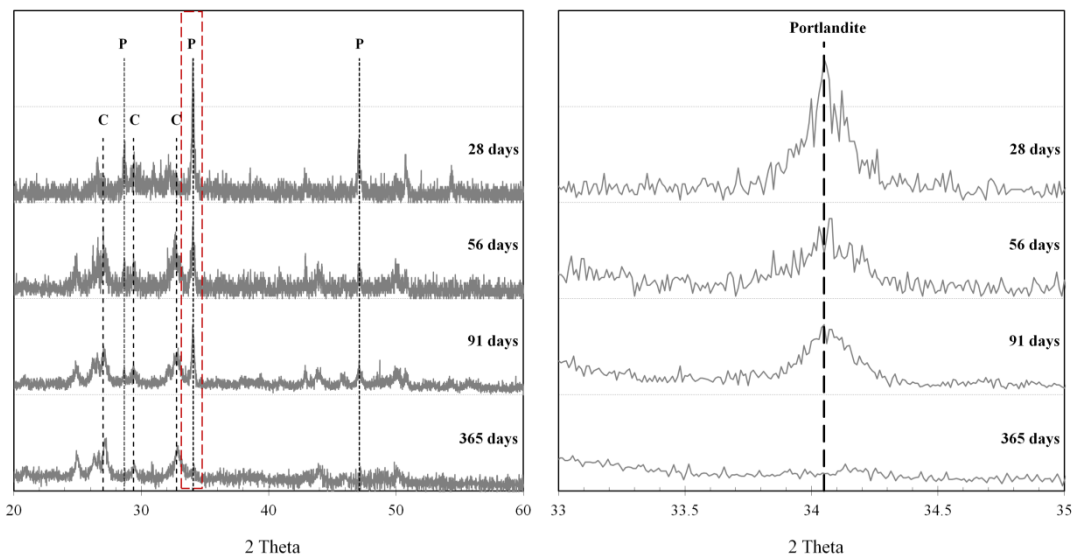
Figure 5. Variation pattern of XRD results according to carbonation exposure duration**(**a) Variation of XRD of paste according to carbonation exposure duration(b) Variation of XRD intensity in portlandite range
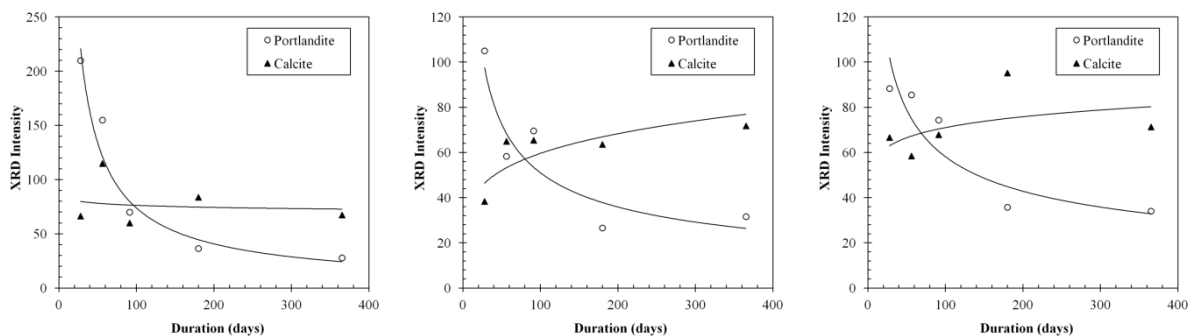
Figure 6. Qualitative evaluation of change in portlandite and calcite quantities using XRD intensity (a)W/B=0.40, (b)W/B=0.45, (c)W/B=0.50

V.   DISCUSSION

Despite of numerous other degradation conditions, this study assumed only the degradation of the paste caused by carbonation. Even if the environmental condition of the fabricated paste specimens created in the accelerated carbonation test is harsher than the actual condition, the test assumed that the observed tendency is similar to that encountered in reality.

The dehydration and decomposition of C-S-H gel during the carbonation process is known to occur over a wide temperature range extending from 110°C to 1000°C, and the decomposition of portlandite from ambient temperature to 110°C [21]. Due to the excessively wide decomposition temperature range of C-S-H gel, the effect of the carbonation of C-S-H gel is not considered in this study. In addition, portlandite at low temperature range is also discarded considering that various crystals form when water dehydrates around 100°C. The analysis of the change in the composition of portlandite and calcite in the temperature ranges mentioned above is the most accurate method representing the effect of carbonation as shown through the evaluation of carbonation in the previous figures. Following, this study applies only the changes in these two components as being the most commonly used method in TG-DTA and XRD analyses.

The DTA and XRD graphs of Fig.4 representing the composition change per W/B according to the duration of exposure to carbonation indicate only the tendency with respect to the exposure duration to carbonation. Therefore, the results are expressed in term of the calcite/portlandite weight ratio for further relative comparison.

The reason for representing the results by the calcite/portlandite ratio in Fig. 7 relies on the fact that this ratio is the best one expressing the tendency in the reduction of portlandite and increase of calcite considering the carbonation process in which portlandite combines with CO_2. In Fig. 7, the coefficient of determination (R2) reaches 0.90 to 0.97 for TG-DTA, which indicates indirectly the high reliability of the tendency. Moreover, in Fig. 7(d) plotting the 3 graphs together for relative comparison, it can be seen that the increasing rate of the calcite/portlandite ratio becomes larger with higher W/B and that this tendency remains constant according to the age despite of some difference with respect to the W/B. This tendency is similar to that observed through the graphs plotting the change in the carbonation depth according to the carbonation exposure duration. Accordingly, this opens room for predicting the carbonation rate at identical depths with respect to the acceleration duration.
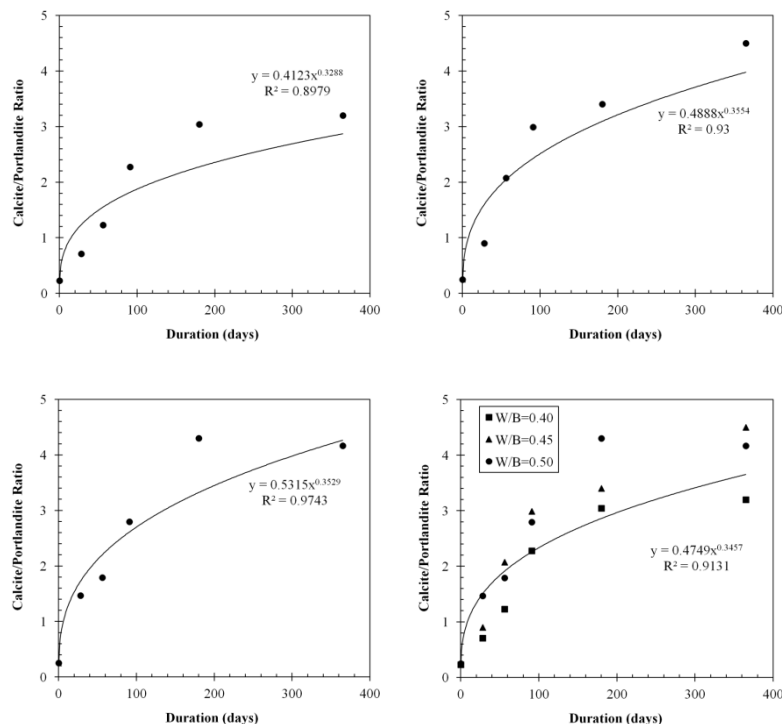

Figure 7. Change of calcite/portlandite ratio according to exposure duration using TG-DTA (a)W/B=0.40, (b)W/B=0.45, (c)W/B=0.50, (d)Total

In addition, the calcite/portlandite ratio using the XRD results shows increasing tendency similarly to the TG-DTA results. In Fig. 8, despite of a relative loss of accuracy compared to the TG-DTA results, the calcite/portlandite ratio provides relatively high determination coefficient (R^2) ranging between 0.74 and 0.93. However, it is still difficult to identify the relationship with carbonation according to W/B because of the small change and nearly similar graphs obtained with respect to W/B.
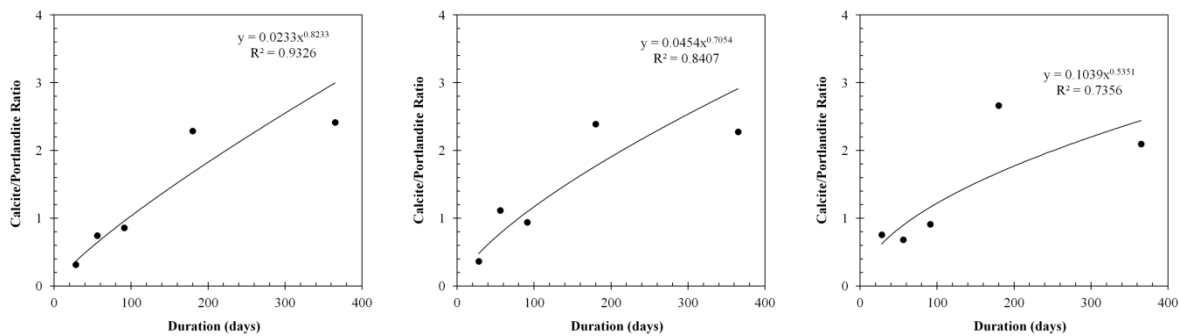
Figure 8. Change of calcite/portlandite ratio according to exposure duration using XRD (a)W/B=0.40, (b)W/B=0.45, (c)W/B=0.50

Fig. 9 plots the XRD intensity with respect to the TG-DTA weight ratio (%) per corresponding sample in order to examine the correlation between the TG-DTA and XRD results. However, the corresponding results show random pattern and disregard the changing tendency according to W/B and exposure duration. There is also no particular pattern enabling to distinguish clearly portlandite and calcite. This absence of clear pattern can be attributed to the fact that the tendency exhibited by the XRD results differs with respect to the measurement day even if analysis is done with the same equipment and same conditions.
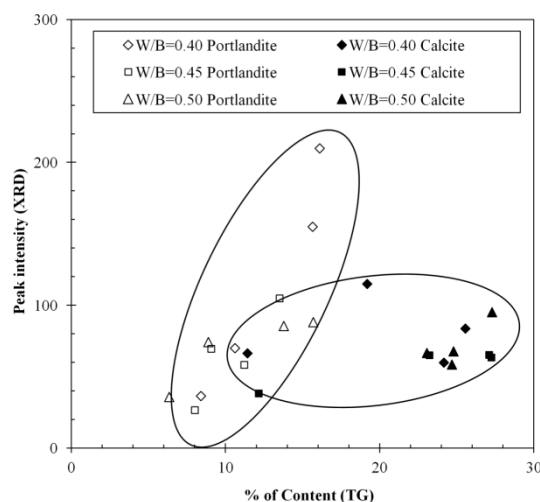

Figure 9. Comparison of XRD intensity and TGA contents per component

In view of the lack of reliability of these results, the XRD results are used only for qualitative and relative comparison and the dosage should be computed by measuring concurrently the reference substances and sample to achieve

quantitative analysis. Moreover, for the latter, substances present in small quantities are not appropriate for the quantification since the XRD of powder requires dosage of ±5~10%.

Fig. 10 describes the correlation between the TG-DTA and XRD results by converting the results in calcite/portlandite ratio in a will to evaluate the amount of each substance. Unlike Fig. 9 which simply compared the TG-DTA and XRD results without finding clear pattern, it can be verified that the results expressed in term of calcite/portlandite ratio show a definite orientation with respect to the exposure duration and W/B. Moreover, the coefficient of determination (R^2) is found to be 0.76 that is close to 0.8, which can be seen as being relatively high.
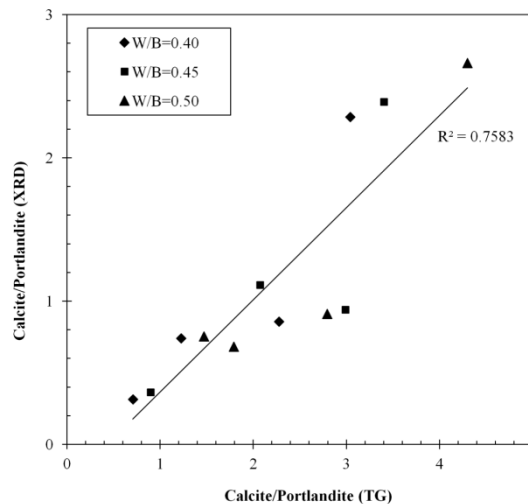
Figure 10. Comparison of XRD and TG-DTA results converted into calcite/portlandite ratio

Accordingly, an empirical formula can be derived to predict the TG-DTA results by converting the XRD results. This predictive formula expressed in Equation 3 converts the accelerated carbonation test results analyzed by XRD into TG-DTA values. In addition, Equation 4 computes the duration of the accelerated carbonation test using the TG-DTA values calculated by Equation 3.

$$B = 1.1784A + 0.8704 \tag{3}$$
$$C = 8.62B^{2.89} \tag{4}$$

where A =calcite/portlandite (XRD); B =calcite/portlandite (TG-DTA); and, C =duration (days).

These equations can be used to compute the duration of accelerated carbonation (Equation 4) and the change in the TG-DTA results by means of the XRD results during the accelerated carbonation test (Equation 3).

VI.   CONCLUSION

The following conclusions can be drawn from the present study.

The traditional method measuring the carbonation depth using an indicator showed that the initial carbonation is faster for concrete as much as the duration of carbonation is longer and as much as W/B is higher but, in a long term, it was seen that the carbonation rate slowed down gradually in the sequential order paste > mortar > concrete. This could be explained by the fact that early carbonation initiates faster because of the easier penetration of the carbonate ion through the capillary pores generated by the bleeding at the surface of concrete. However, the carbonation rate of concrete slows gradually down with longer exposure duration to carbonation due to the presence of the aggregate obstructing the penetration of the carbonate ion migrating in the cement paste matrix.

1. From TG-DTA, the dehydration and decomposition of portlandite and calcite appeared to occur at temperature ranges of 400 to 450°C and 600 to 900°C, respectively. The tendency of portlandite to increase

and calcite to decrease could be identified visually in these temperature ranges and computation provided contents of 3.9 to 5.1%/wt. for portlandite and 15.8 to 20.3%/wt. for calcite.

2. The change in the intensity was analyzed by XRD from 28 days to 365 days at the diffraction angles corresponding to portlandite and calcite. The reduction in the intensity of portlandite and the increase in the intensity of calcite could be identified clearly and the sum of the intensities corresponding to the selected peaks at which these tendencies could be distinguished clearly was expressed graphically. The resulting graphs verified the reduction of portlandite and the augmentation of calcite.

3. Finally, the XRD and DT-TGA results were compared after converting them in term of the calcite/portlandite ratio. This conversion enabled to verify similar orientation and consistent tendency of the XRD and DT-TGA results, which revealed the possibility to achieve semi-quantitative evaluation of the carbonation by XRD only. Additional study will be conducted to derive prediction formulae using XRD analysis.

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