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Quantitative evaluation of cement paste carbonation using Raman spectroscopy

Tangwei Mi¹, Yongqiang Li¹, Wei Liu¹, Weiwen Li¹, Wujian Long¹, Zhijun Dong², Qianyi Gong², Feng Xing¹ and Yaocheng Wang¹✉

Carbonation induced corrosion is one of the major durability issues for reinforced concrete structures. To address this issue, it is essential to understand the underlying mechanism of carbonation by detecting the ingress of the CO₂ and carbonation depth quantitatively. This paper demonstrates the potential of Raman spectroscopy, as a powerful technique, to implement quantification analysis of cement paste carbonation. In present work, the correlation between the content of the CO₃²⁻ and the Raman peak intensity was initially established by using several standard specimens premixed with certain amount of CO₃²⁻. The established correlation was then used to investigate the carbonation of the cement paste in a CO₂ diffusion scenario, and the results show a good agreement with that obtained by thermogravimetry measurements. Therefore, the feasibility of the Raman spectroscopy to quantify the carbonation degree of the cement paste can be demonstrated.

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INTRODUCTION

As one of the major degradation types, carbonation of cement paste has attracted extensive attentions with attempts to understand the underlying mechanism. Portland cement is one of the most common construction materials around the world, benefiting from its excellent mechanical property and relatively well durability. Hydration of the Portland cement mainly produces portlandite (Ca(OH)₂) and other calcium-bearing phases like C–S–H¹, which contributes to the development of the mechanical properties and alkalinity of the material. These properties would, however, be affected by the carbonation, which is one of the major degradation issues for cementitious material². Essentially, the carbonation begins with the ingress of the CO₂ into the pore solution to form carbonic acid which mainly reacts with Ca(OH)₂ (Reaction 1) and calcium-bearing phases (such as C–S–H (Reaction 2)) to form CaCO₃, resulting in the neutralization of the alkaline environment³. The consumption of the hydroxides would certainly reduce the pH and potentially initiate corrosion of the steel reinforcement^{4,5}. On the other hand, the precipitation of CaCO₃ may form a denser structure than uncarbonated cement⁶. To assess the above effects, it is of great significance to precisely follow the carbonation evolution so that the carbonation induced corrosion and alteration of the mechanical property could be followed precisely. Thereby, development of a quantitative analysis technique is attracting increasing attentions.

To explore the carbonation evolution, several techniques have been well documented by former researchers, such as phenolphthalein indicator^{7,8}, X-ray diffraction (XRD)⁹, thermogravimetric (TG) analysis^{10,11}, and Infrared spectroscopy (IR spectroscopy)^{8,12}. Spraying the phenolphthalein indicator on the carbonated cement is one conventional method to assess the carbonation depth⁸ and it is recognized as the most convenient method to capture the color

change boundary between the carbonated and uncarbonated concrete where the pH is around 9¹³. Though phenolphthalein indicator is capable to give a continuous picture of the carbonated and uncarbonated zone, it can only identify the degree of carbonation above/below 50% (i.e., the pH is higher/lower than 9)⁷ and the less carbonated location is impossible to be identified. In addition, XRD and TG are also widely employed to investigate the carbonation depth by characterizing the hydrated and carbonated products⁹. In principle, XRD is capable to investigate the crystal structure of carbonated products and thus determine the carbonation degree and carbonation front, and TG is dependent on the different decomposition temperature of Ca(OH)₂ (420–600 °C)¹⁴ and CaCO₃ (440–800 °C)¹⁵. Both XRD and TG could achieve quantitatively analysis and have provided valuable information to assess the carbonation of the concrete^{10,16}. However, both XRD and TG are traditional bulk analysis techniques¹⁷, and powder sample should be prepared prior to each test. As it is almost impractical to obtain powder at different depth at a microscale, high resolution spatial analysis on the carbonation depth is thereby rarely achieved, which is sometimes of significant importance. Apart from the above techniques, infrared (IR) spectroscopy⁸ and Raman spectroscopy have also been used to investigate the carbonation of cement paste, benefiting from their capability to follow identify the carbonated products in accordance with the characteristic peak of the C–O stretching bond. These two techniques are discussed below.

Raman spectroscopy, a scattering based technology with high chemical fingerprint sensitivity, is a complementary technique to IR spectroscopy¹⁸. Raman spectroscopy has attracted increasing attention since it was first employed to characterize the cement-based materials in 1976¹⁹, which was followed by several systematical work on the spectrum of the main compounds of the cement^{20,21}. In addition, Raman spectroscopy was also extensively applied to characterize of the deterioration products of cement-based materials under carbonation, sulfate, and alkali–silicate reactions attacks²². Overall, Raman spectroscopy has demonstrated its potential to study both hydration and

¹Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen Durability Centre for Civil Engineering, College of Civil and Transportation Engineering, Shenzhen University, Shenzhen, Guangdong, China. ²Institute of Technology for Marine Civil Engineering, Shenzhen Institute of Information Technology, Shenzhen, Guangdong, China. ✉email: wangyc_szu@126.com

deterioration of cement-based materials in the literature. In comparison with IR spectroscopy, almost no preparation is required, and thus the negative effects induced by sample preparation could be minimized²³. Furthermore, the spectra of the CaCO_3 , as the main carbonation products, obtained by Raman spectroscopy exhibits a much sharper peak corresponding to the C–O vibration modes in CO_3^{2-} group than that obtained by IR spectroscopy²⁴. The Raman spectroscopy is thus more sensitive than IR spectroscopy to determine the carbonation evolution. Therefore, there is a few attempts to use Raman spectroscopy to evaluate the carbonation evolution and the obtained carbonation

maps showed relative high resolution^{25–27}. For instance, Torres-Carrasco et al.²⁷ investigated the weathering effect on the deterioration of the anhydrous cement by using Raman spectroscopy, which main focused on the carbonation effect. In addition, Raman spectroscopy has followed the carbonation depth of carbonation reaction of lime paste successfully²⁶. The ability of Raman spectroscopy to evaluate the spatial distribution of the carbonation products of Portland cement was further confirmed by Corvisier et al.²⁵. It can be seen that using Raman spectroscopy to investigate the distribution of carbonation products in cement has shown great potential^{25,26}, the quantitative analysis is still absent due to the lack of the correlation between the Raman intensity and content of the carbonation products.

Aim of the current work is thus to achieve the quantitative analysis of the carbonation products in hydrated cement paste by using Raman spectroscopy. To achieve this aim, standard reference specimens premixed with different dosages of CO_3^{2-} were prepared and tested with Raman spectroscopy. Thereby, correlation between content of CO_3^{2-} and intensity of the Raman characterization peak was established. To verify the accuracy of the established correlation as well as the feasibility of the quantitative analysis of the carbonation evolution, an investigation into the carbonation of the Portland cement was also completed. The obtained correlation was then used to characterize progress of carbonation in hardened cement paste exposed to an accelerated carbonation scenario, so as to explore in-depth mechanism of carbonation. Meanwhile, the most commonly used techniques, i.e., XRD and TG, were used to determine distribution of CaCO_3 in the tested samples to further verify accuracy and suitability of the Raman mapping technique in studying progress of carbonation.

Fig. 1 Raman spectrum obtained from analytical grade CaCO_3 powders. Raman spectrum showing typical characteristic peaks and associated vibrational modes.

Fig. 2 Experimental results of the Raman spectroscopy measurements on the surface of the type (1) samples. **a** Appearance of test areas under optical microscope. **b** Mapping results of intensity of the 1084 cm⁻¹ Raman peak. **c** Box chart of Raman peak intensities against content of CO_3^{2-} and the fitting result.

RESULTS

Building up the database for quantitative analysis

Prior to the quantification analysis, a criterion to evaluate quantify the carbonation of cement paste is essential to be established. As the main carbonation product in cement paste is CaCO_3 , the carbonation can thus be linked to the content of the CO_3^{2-} directly³. A typical Raman spectrum was obtained from analytical grade CaCO_3 powders, as shown in Fig. 1. It can be seen that the spectrum present a strongest peak at 1084 cm^{-1} , which should be assigned to the symmetric stretching of the CO_3 group (ν_1) in CaCO_3 as depicted in the spectrum²⁸. Meanwhile, three minor peaks can also be identified at 281, 711, and 1435 cm^{-1} , which are associated with Ca–O lattice vibration mode, double degenerate in-plane bending mode and asymmetric stretching mode, respectively^{28–30}. However, only this strongest peak can be observed when there is a small amount of CO_3^{2-} . Consequently, using the intensities of the peaks at 281, 711, and 1435 cm^{-1} as for quantification analysis might be not sensitive enough to identify the paste with low CO_3^{2-} content. To improve the sensitivity to quantify CO_3^{2-} with a minor content, the most intense peak at 1084 cm^{-1} was used as indicator to prove the existence of carbonated minerals and evaluate the carbonation degree in all the analyses²⁶.

Figure 2 shows the experimental results of the Raman spectroscopy measurements on the surface of the type (1) samples which were premixed with different dosages of CaCO_3 . As explained above, three random regions were selected in each sample and the images of these regions under optical microscope are displayed in Fig. 2a. It can be seen from the optical microscope images, mixes with a higher CO_3^{2-} content presented a brighter and homogeneous color appearance, which is consistent with the color of CaCO_3 powder³¹. Figure 2b presents color mapping results revealing intensity of the 1084 cm^{-1} Raman peak ($\nu_1\text{ CO}_3$) in the areas listed in Fig. 2a. Based on the differences of the mapping results, it can be easily derived that the intensity of the 1084 cm^{-1} Raman peak is associated with amount of the CO_3^{2-} compounds.

Figure 2c presents a box chart revealing the correlation between the Raman peak intensity and the CO_3^{2-} content of the test samples. Based on these data points, a linear relationship between CO_3^{2-} content and intensity of the 1084 cm^{-1} peak is clearly illustrated as red dash line, which is similar to correlation between intensity of Raman peak and content of other compounds, e.g., salicylic acid and pharmaceutical compound, as reported elsewhere^{32,33}. Therefore, the obtained fitting line, i.e.,

$$y = 49500x \quad (1)$$

(where x is the CO_3^{2-} content and y is the intensity of the Raman peak at 1084 cm^{-1}) with an R^2 of 0.96, can be used to convert Raman spectra signal to CO_3^{2-} content in hardened cement paste samples. In such manner, potential of using the 1084 cm^{-1} Raman peak for quantification of CO_3^{2-} content in hydrated cement paste is thus proved.

Verification on feasibility of the established correlation to evaluate progress of carbonation

To validate the accuracy and feasibility of the above established correlation for the carbonation process in a CO_2 diffusion scenario, an attempt was made to use Raman spectroscopy to quantify the carbonation evolution of the cement paste under accelerated carbonation. TG measurements was also carried out to validate the quantification results obtained by Raman spectroscopy.

As stated, the Raman mapping measurements was applied on slice samples sliced from type (2) samples after 0d, 1d, 3d, 7d, 14d, 28d, and 56d of accelerated carbonation. At the depth ranging from 0 to 10 mm, Raman mapping analyses were conducted, and results were collected. By using the correlation obtained from Fig. 2c, statistic results from the 1084 cm^{-1} Raman peak can be

Fig. 3 Raman mapping showing the carbonation degree of the specimen after different ages of accelerated carbonation. Different colors representing the CO_3^{2-} converting from the intensity of Raman peak at 1084 cm^{-1} by using the correlation obtained from Fig. 2c.

Fig. 4 The concentration of CO_3^{2-} at different depth. An area graph illustrating the increase of the CO_3^{2-} content with the time under accelerated carbonation against the distance to the exposure surface (the CO_3^{2-} content at each depth is the averaged results of 8 points and the line was smoothed by Origin™).

converted to the distribution of CO_3^{2-} content, as presented in Fig. 3. From the CO_3^{2-} content mapping results, evolution of the carbonation process and the development of carbonation at certain location can be clearly observed.

As can be seen in Fig. 3, no CO_3^{2-} was detected at 0 day, which confirms that good preparation and condition procedures were carried out prior to the accelerated carbonation. It can also be found that carbonation has started from the exposure surface, and the

Table 1. Results obtained from Fig. 4, including depth of the carbonation front (X_c), depth of the fully carbonated zone (X_f), and the total CO_3^{2-} content.

	Duration						
	0d	1d	3d	7d	14d	28d	56d
X_c (mm)	0	1.875	3.125	6.750	9.125	N/A	N/A
X_f (mm)	N/A	N/A	0.125	0.75	1	1.25	1.5
Total CO_3^{2-} content (%)	0.00	1.57	4.00	7.23	8.94	11.92	19.98

Fig. 5 Quantification of the CO_3^{2-} content. TG and DTG results for the cement paste specimens.

carbonation front gradually increases with the time of accelerated carbonation. Although the distribution of the CO_3^{2-} can be evaluated in Fig. 3, the exact quantities of the CO_3^{2-} at all depths can be hardly compared so that the depth of the carbonation front and fully carbonated zone could be determined. Therefore, an area graph is depicted in Fig. 4 to present the contents of the CO_3^{2-} at all depth for the specimens. The carbonation front could be easily found by looking at point where the CO_3^{2-} content reaches 0. The depth of the carbonation front has been labeled in Fig. 4 and recorded in Table 1. Based on the carbonation front, the diffusion coefficient could be calculated according to Eq. (2) (Where X_c is the depth of carbonation front, k is diffusion coefficient and t is time). As the values of X_c and t are both available in Table 1, the diffusion coefficient can be calculated as 2.37. For the fully carbonated zone, the threshold of CO_3^{2-} content should be established. In the literature, the content of the CO_2 in the fully carbonated cement paste has been reported to range from 22% to 26%^{9,10}. To convert CO_2 content to CO_3^{2-} content, Eq. (3) was employed (Where $C_{\text{CO}_3^{2-}}$ is the content of CO_3^{2-} ; C_{CO_2} is the content of CO_2 ; $M_{\text{CO}_3^{2-}}$ is molecular mass of CO_3^{2-} and M_{CO_2} is molecular mass of CO_2). Based on calculation, the CO_3^{2-} content should be between 30 and 36% for fully carbonated cement paste. The depth of the fully carbonated zone is thus defined as the point where CO_3^{2-} content exceeds 30%, which has been labeled in Fig. 4 and listed in Table 1. Furthermore, the overall carbonation degree could be evaluated by

Fig. 6 Comparison between the results obtained by TG and Raman measurements. Plot of the content of CO_3^{2-} obtained by Raman and TG measurements.

the total CO_3^{2-} content within the specimen, which can be calculated by ratio of the area for each specimen to the whole area ($100\% \times 10 \text{ mm}$) as depicted in Fig. 4. The results have been listed in Table 1.

$$X_c = k\sqrt{t} \quad (2)$$

$$C_{\text{CO}_3^{2-}} = C_{\text{CO}_2} \times \frac{M_{\text{CO}_3^{2-}}}{M_{\text{CO}_2}} \quad (3)$$

The Raman spectroscopy has demonstrated its capacity to detect the distribution of the CO_3^{2-} content over the sample surface, and this information can be used to evaluate the carbonation evaluation. To verify the above results, either comparing the similar results in the literature or carrying out complementary experiment is needed. However, it is almost impossible to compare the results with that reported in the literature because of the variation in experimental condition, such as the pretreatment, water/binder ratio and material, which has been proved to affect the carbonation depth significantly³⁴. Complementary experiment, thermogravimetry analysis (TGA) was thus performed.

The TG measurements, as a conventional technique to quantify the content of CO_3^{2-} , have been performed to verify the Raman results. Figure 5 depicts the TG/DTG plots of cement paste specimens after 0, 1, 3, 7, 14, 28, and 56 days of accelerated carbonation. As explained earlier, DTG plots are employed to determine the decomposition intervals by inspecting the beginning and end of the peaks³⁵. It can be seen that there are three peaks in Fig. 5, which are around 100, 410, and 700 °C. According to the temperature required for the decomposition of possible compounds in the carbonated cement paste specimens, these three peaks should be attributed to the evaporation of free water (100 °C), dehydration of $\text{Ca}(\text{OH})_2$ (410 °C)^{14,36} and decomposition of CaCO_3 (700 °C)^{10,37}. As the purpose of TG measurements is to verify the quantification results, the peak for the decomposition of CaCO_3 is analyzed only.

In the DTG curve, the peak at around 700 °C starts from the temperature 440 °C and continues till 800 °C, which is owing to the different polymorphs of CaCO_3 ^{9,38,39}. The weight loss corresponding to the decomposition of CaCO_3 is thus evaluated between 440 and 800 °C, and the exact ranges are determined according to the actual starting and ending points of the peak at each curve. As the weight loss results represent the weight of CO_2 , which are then converted to the CO_3^{2-} by Eq. (3). To compare the total CO_3^{2-} content obtained by TG and Raman measurements, they are

plotted in Fig. 6. As can be seen that the content of CO_3^{2-} obtained by TG and Raman measurements are almost the same. Therefore, the quantification results obtained by Raman measurements could be verified.

DISCUSSION

It might be worth noting that Raman results report a slightly less quantity of the CO_3^{2-} content, especially for the specimen after 56 days of accelerated carbonation, which might be caused by the different polymorphs of the CaCO_3 as explained above. It has been well-established that there are three polymorphs of CaCO_3 , i.e.,

calcite, aragonite and vaterite, and calcite is known to be the main carbonation products⁴⁰. Both calcite and aragonite pronounce a strongest peak at around 1084 cm^{-1} . As explained in previously, quantitative analysis in present work is based on the intensity of the peak at 1084 cm^{-1} , the existence of aragonite might not affect the quantification results. However, for vaterite, the main peak splits into a doublet at 1074 and 1090 cm^{-1} ^{130,41}. The presence of vaterite would thus potentially induce slight underestimation of carbonation degree. To verify the existence of vaterite, XRD measurements was performed for verification.

The XRD patterns of the cement paste specimens after 0, 1, 3, 7, 14, 28, and 56 days of accelerated carbonation have been depicted in Fig. 7. The assignments of the peaks have been well documented and labeled above the patterns. Among all the composition detected in the carbonated cement paste specimens, two polymorphs of the CaCO_3 were found, i.e., calcite and vaterite. The presence of calcite could be confirmed by a strongest peak at 29.4° 2θ , along with many weak peaks as marked in Fig. 7^{42,43}. Vaterite has its strongest peak at 27.0° 2θ as well as other 4 peaks at 24.9° , 32.8° , 43.9° , and 50.0° 2θ ^{9,37}. Therefore, the presence of the vaterite could be confirm. Based on the peak intensities, the quantity of the vaterite is neglectable before 3 days, which gradually increases after 7 days. In the meantime, the amount of calcite, as the main carbonation products, rises much more dramatically as shown in the XRD pattern (Fig. 7). Therefore, the CO_3^{2-} content results obtained by Raman spectroscopy is representative to assess the carbonation degree, although the existence of vaterite may induce the minor underestimation.

Overall, in present work, the correlation between the Raman peak intensity and the content of CO_3^{2-} were established initially by a linear equation: $y = 49500x$. The established correlation was employed to study the accelerated carbonation of the cement paste in a CO_2 diffusion scenario. The results clearly show the distribution and quantity of the carbonation products. In addition, the accuracy of the obtained quantification results by Raman spectroscopy were confirmed by TG results. Overall, the feasibility of employing the Raman spectroscopy for quantitative analysis of the cement paste carbonation has been fully demonstrated.

METHOD

Material and sample preparation

In this study, two types of samples were manufactured in lab, viz. (1) cylindrical hardened cement paste, with a dimension of $\phi 20\text{ mm} \times 10\text{ mm}$, as depicted in Fig. 8a, and (2) a $\phi 28\text{ mm} \times 150\text{ mm}$ cement sample as depicted in Fig. 8b. The previous group of samples involving eight groups of hardened cement paste samples containing 0%, 5%, 10%, 20%, 30%, 40%, 50% and 60% of CO_3^{2-} , respectively, which was achieved by adding analytical grade calcium carbonate during mix. Two groups of type (1) specimens were prepared to improve the reproducibility of the experimental results, namely group A and group B. To facilitate a reasonable hydration of cement and a meaningful carbonation speed, a water/binder (w/b) ratio of 0.45 was designated for all the eight mixes. For the latter type of sample, the cement

Fig. 7 Characterization of the chemical composition of carbonation products. XRD pattern of cement paste specimens after 0d, 1d, 3d, 14d, 28d, and 56d of accelerated carbonation.

Fig. 8 Schematic diagram for the sample preparation. **a** Standard cement specimens. **b** Cement paste specimens. **c** Slices of the cement paste specimen.

Fig. 9 Diagrams showing the test points for data collection. **a** Test points for type 1 specimens. **b** Test points for type 2 specimens.

paste cover was a hydrated Portland cement with a w/b of 0.45. The procedure for mixing pastes followed ASTM C305⁴⁴. The porosity of all samples should be consistent with that reported in the literature.

After cast, all the samples were cured in a vacuum dryer for 24 h to avoid carbonation. After curing, type (1) samples were ready for the Raman spectroscopy measurements; while type (2) samples were placed in a carbonation chamber with a condition at ~74% RH, 20% CO₂, 20 °C. Prior to carbonation of the type (2) samples, two ends of the specimen were sealed to make sure that only the side of the cylinder was exposed to CO₂. At the age of 0, 1, 3, 7, 14, 28, and 56 days of the accelerated carbonation, as depicted in Fig. 8c, a 20 mm long cylinder sample was cut off to test the development of carbonation with Raman spectroscopy, TG and XRD. It is worth pointing out that the slice obtained at 0 day was used to verify that no carbonation happened during the sample preparation.

Raman spectroscopy

Raman spectra were acquired by using a Reinshaw inVia Raman spectroscopy, which is equipped with a 532 nm laser and a charged coupled device detector. Laser was focused via a Lecia $\times 50$ (N.A. = 0.55) into a spot size of 1.40 μm in diameter on test samples. To avoid possible decomposition of carbonation products under applied energy, power of the tests was limited within 0.82 mW. All the spectra were recorded with an exposure time of 10 s and two accumulations to improve the signal-to-noise ratio.

For the type (1) sample, three regions with an area of $150 \times 60 \mu\text{m}$ were selected randomly from group A and group B, named A0–A2 and B0–B2. In each region, 35 spectra forming a matrix of 7×5 were collected, as depicted in Fig. 9a. For the sliced disc specimens, the Raman spectroscopy was collected from a threadlike testing area ranging from surface to a depth of 10 mm and covered a width of 70 μm . In each of this area, 640 spectra forming a matrix of 8×80 were collected and the intervals of the analyses for the parallel and vertical directions were 10 and 125 μm , respectively, as shown in Fig. 9b.

The Raman spectra obtained from cement are always accompanied with unwanted sloping background, which may be caused by the intrinsic fluorescence as well as the incorporation of optics^{45,46}. The background is thus subtracted by using WIRE 5.1 via an “intelligent fitting” process with a polynomial value of 11.

X-ray diffraction (XRD) and thermogravimetry (TG) analyses

After the Raman measurements, the disc specimens were crushed into powder with particle size of lower than 70 μm . Subsequently, the powder was immediately analyzed with TG and XRD for their CaCO₃ contents and composition of the carbonation products, so as to verify the quantification results obtained by Raman spectroscopy.

The TG measurements were carried out by using a TA SQT-Q600, and the temperature range was from 30 °C to 1000 °C with a heating rate of 10 °C/

min. The XRD measurements were carried out using a Bruker D8 Advance diffractometer. A scanning range between 5 and 70° with a scanning rate of 0.02°/step was selected.

DATA AVAILABILITY

All the data associated with this study are available from the corresponding author upon request.

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AUTHOR CONTRIBUTIONS

T.M. conceived the idea and wrote the draft of paper. T.M. and Y.L. conducted the experiments and paper revision. Weil. and WeiwenL. contribute to the data analysis of the TG measurements and overall formatting of the paper. W.L. and F.X. contributed to establishing the experimental approaches and figure plotting. Z.D. and Q.G. contributed to data analysis for the Raman measurements. Y.W. supervised the whole project and revised the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Correspondence and requests for materials should be addressed to Y.W.

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