Elucidation of Calcite Structure of Calcium Carbonate Formation Based on Hydrated Cement Mixed with Graphene Oxide and Reduced Graphene Oxide

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ABSTRACT: In this study, the carbonation of Portland cement by direct chemical interaction with graphene oxide (GO) and reduced graphene oxide (rGO) at 7 and 28 days was examined. During the carbonation reaction, the calcium-bearing phases (calcium hydroxide, calcium silicate hydrate, and ettringite) formed calcium carbonate polymorphs, along with amorphous silica gel, gypsum, and alumina gel. These reaction products were examined using XRD (X-ray diffraction), XPS (energy-dispersive spectrometry), and FTIR (Fourier transform infrared). XRD patterns showed that the intensities of the calcium hydroxide and calcium carbonate peaks in the hydrated cement mixed with GO and/or rGO are higher than the corresponding peaks in the hydrated cement without any additives. The morphology of the reaction products was also characterized by SEM (scanning electron microscopy) measurements, which showed that a needle-like phase of calcium carbonate develops on the hydrated cement. The obtained microstructure parameters enabled the development of a more precise carbonation model.

1. INTRODUCTION

Recently, the increased attention on civil infrastructure enhancement has motivated research on the possible modification of cement-based materials to fulfill the growing requirements for sustainability in the construction field. Modification is performed by some selective additives and adjusting the cement composition. Several attempts have been done to enhance the hardness, durability, and tensile properties of the cement by utilizing different kinds of reinforcing materials, from carbon fibers, steel fibers, and polymer fibers to nanomaterials, such as carbon nanotubes, graphene derivatives, and nanosilica. In addition, multiple studies have been committed to investigate the carbonation effects on the reinforced cement durability and environmental factors such as temperature, relative humidity, and partial pressure of carbon dioxide have been found to have enormous effects on the carbonation of hydrated cement. Indeed, the carbonation of hydrated cement implies an intricate effect on the microstructure; mild CO₂ exposure enhances the compressive strength, while extended exposure might negatively influence the mechanical properties. More importantly, Pavlik demonstrated that the reaction of the hydrated cement with atmospheric CO₂ is generally a slow process and is highly dependent on some environmental factors such as the concentration of atmospheric CO₂, temperature, and permeability of the material. Moreover, a few studies have been conducted on the combination of graphene oxide (GO) with cement-based materials, but they were essentially focused on improving microstructural and mechanical properties, without realizing the possibility of the existence of a direct chemical interaction between GO and hydrated cement. Li et al. showed that the addition of 0.04 wt % GO enhanced the tensile strength by 67% in comparison with the plain cement paste. Lv et al. indicated that the addition of GO at ratios of 0.03, 0.05, and 0.07% increases the compressive strength values of the GO/cement composites from 150 to 177 MPa. With the 0.05% GO ratio, the compressive and flexural strengths were 176.64 and 31.6 MPa, respectively. Lu et al. demonstrated that the addition of 0.05% GO to the cement paste increased the compressive and flexural strengths to 11.1 and 16.2%, respectively. Until now, there have been no reports on the direct interaction mechanism of GO with hydrated cement-based materials, although we previously reported that GO and/or reduced GO (rGO) in their direct chemical interaction with either Ca(OH)₂ or CaO could be used to synthesize pure...
polymorph CaCO₃ crystals with consistent morphology and size. 38,41–46 This is related to the oxygen functional groups that decomposed on the surfaces of GO or rGO in specific alkaline media releasing CO, CO₂, and water. 38,41–46 The objective of the current research was to elucidate the mechanism of the chemical interaction of GO or rGO with hydrated cement-based materials, which is related to the oxygen functional groups that decomposed on the surfaces of GO or rGO in specific alkaline media to react with calcium-bearing phases in cement paste (CP), such as calcium hydroxide (CH), calcium silicate hydrate (C-S-H), and ettringite (AFT), which contributed substantially to CaCO₃ polymorph formation, and showed that the formed CaCO₃ amount far exceeded that which could be obtained from complete CH dissolution. On the other hand, the chemical interaction of the cement paste (CP) with GO or rGO could be utilized to achieve specific economic and environmental benefits. This can be viewed as a promising opportunity to take advantage of this chemical reaction.

2. RESULTS AND DISCUSSION

2.1. Mechanism of GO and rGO Reaction with Hydrated Cement. Portland cement is a mixture of heterogeneous compounds in an anhydrous state. This mixture originally consists of alite (C₃S, Ca₃SiO₅), belite (C₂S, Ca₂SiO₅), tricalcium aluminate (C₃A, Ca₃Al₂O₆), and tetracalcium aluminoferrite (C₄AF, Ca₄(Al,Fe)₂O₁₀) as well as limited quantities of other impurities, such as magnesium sulfate (MgSO₄), sodium sulfate (Na₂SO₄), potassium sulfate (K₂SO₄), and gypsum (CaSO₄·2H₂O). 1,2,47–49 During normal hydration, Portland cement will undergo a complex hydration (MgSO₄), sodium sulfate (Na₂SO₄), potassium sulfate (K₂SO₄), and gypsum (CaSO₄·2H₂O), and ettringite (AFT), which contributed substantially to CaCO₃ polymorph formation, and showed that the formed CaCO₃ amount far exceeded that which could be obtained from complete CH dissolution. On the other hand, the chemical interaction of the cement paste (CP) with GO or rGO could be utilized to achieve specific economic and environmental benefits. This can be viewed as a promising opportunity to take advantage of this chemical reaction.

2.1.1. CH-Phase Carbonation. In a lower alkaline environment, CH (portlandite, Ca(OH)₂) is the first component to start dissolution. 24–26,28–30,47–49,51–53,55,56,61–63 Inducing the process of the oxygen functional group decomposition at the surfaces of GO or rGO to release CO₂, CO, and H₂O, which appears to be responsible for calcium carbonate (CaCO₃) polymorph formation 18,21–23,38–46 according to eq 1:

\[
\text{nCaOH}_2 + \text{nGO} + \text{nH}_2\text{O} \\
\rightarrow \text{nCaCO}_3(\text{s}) + (\text{n} + 1)\text{H}_2\text{O}
\]  

We believe that the reaction of GO or rGO with hydrated cement is governed by the total amount of the oxygen functional groups located on the surfaces of GO and/or rGO. The determination of oxygen groups on the surfaces of various carbon materials was analyzed by both the Boehm titration and the thermal-programmed desorption (TPD) methods. 41–43,65,66 TPD gives quantitative information about the total number of surface oxygen groups, which break down at various temperatures to release CO, CO₂, and H₂O, even though the Boehm titration method provides both qualitative and quantitative information solely regarding acidic and basic groups (which include phenols, lactone groups, and carboxylic acids). The acidic nature of the oxygen functional groups could be equalized by bases of various strengths such as NaHCO₃, Na₂CO₃, and NaOH.

2.1.2. C-S-H-Phase Carbonation. The results strongly indicate that the direct reaction of C-S-H with GO or rGO results in the formation of amorphous silica gel and various CaCO₃ polymorphs according to eq 2:

\[
\text{nCaO-SiO}_2\cdot\text{mH}_2\text{O} + \text{nGO} + \text{nH}_2\text{O} \\
\rightarrow \text{nCaCO}_3(\text{s}) + \text{nSiO}_2(\text{H}_2\text{O})_\text{m} + (\text{n} - \text{m})\text{H}_2\text{O}
\]  

2.1.2.1. C-S-H Gel. As stated in our previous work, 38 the direct reaction of GO or rGO with Ca(OH)₂ or CaO results in CaCO₃ formation. Thus, the rate and degree of the carbonation of the C-S-H gel depend greatly on the amounts of CO₂ and CO released during decomposition, which are associated to the total amount of the oxygen functional groups located on the surfaces of GO or rGO. 38–46 It is well established that carboxyl and lactone groups are responsible for CO₂ production, while aldehyde, carbonyl, and phenols are responsible for the production of CO. 30–45 Taking into account weathering carbonation upon extended exposure to atmospheric CO₂ in the process, C-S-H is believed to be more decalcified and to lose its binding ability accordingly. 24–26,53,54 Carbonation of the C-S-H gel generally results in calcite, aragonite, and vaterite formation. 26 Aragonite and vaterite formation are apparently related to the existence of highly decalcified C-S-H and consequently to high CO₂ (GO or rGO decomposition product) concentrations. 24–26,38–46,52–54 Moreover, we expect that the direct chemical interactions of GO or rGO with hydrated cement-based materials do not necessarily result in full carbonation on the surface of the cement paste but rather that a completely carbonated zone can exist in the core of the paste.

2.1.3. Ettringite-Phase Carbonation. Our results also emphasize the effective chemical interactions of GO or rGO with other calcium-bearing phases. Apart from the CH and C-S-H phases, ettringite and aluminas are other cement phases that decompose upon reaction with GO or rGO, resulting in gypsum (CaSO₄·2H₂O) and alumina gel (Al₂O₃·mH₂O) formation according to eq 3:

\[
\text{nCaO-AL}_2\text{O}_3\cdot\text{nCaSO}_4\cdot\text{mH}_2\text{O} + \text{nGO} + \text{nH}_2\text{O} \\
\rightarrow \text{nCaCO}_3(\text{s}) + (\text{nCaSO}_4\cdot\text{2H}_2\text{O}) + \text{Al}_2\text{O}_3\cdot\text{mH}_2\text{O} \\
+ (\text{n} - \text{m})\text{H}_2\text{O}
\]  

The carbonation of ettringite may lead to vaterite crystal formation. 55–57 Carbonation of all calcium-bearing phases, such as CH, C-S-H, and ettringite, contributes substantially to CaCO₃ polymorph formation, and it is frequently mentioned that the formed CaCO₃ amount far exceeded that which could be obtained from the entire CH dissolution. 24,52–58 Moreover, during carbonation, both GO and rGO eventually decompose to form CO₂, CO, and H₂O, which completely react with hydrated cement (calcium-bearing phases, CH, C-S-H, and ettringite) to form CaCO₃. The Boehm titration method reported that the acidity of the oxygen functional groups on the carbon materials can be equalized by bases of various strengths. The oxygen functional groups decompose at various temperatures to release CO, CO₂, and water. During decomposition, the released CO and CO₂ associated to the total amount of the oxygen functional groups located on the
It is well established that carboxyl and lactone groups are responsible for CO$_2$ production, while aldehyde, carbonyl, and phenols are responsible for the production of CO. Calcium carbonate (CaCO$_3$) formation was detected using Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD) patterns, etc., as will be discussed later. Therefore, this mechanism emphasizes the chemical interaction between hydrated cement and GO or rGO, resulting in the formation of CaCO$_3$ (calcite polymorph), regardless of the variation between GO and rGO, specifically in terms of their physical properties, and the surface morphologies of GO and rGO.

Overall, the carbonation of hydrated cement (formation of CaCO$_3$ with silica gel) can be useful for cement-based materials, as it has previously been reported to enhance the compressive and flexural strengths of cement and reduce the atmospheric carbonation of hydrated cementitious matrices. Conversely, the prolonged carbonation of hydrated cement, such as CH and the C-S-H phase, may lead to corrosion of reinforcing steel bars due to a pH decrease to a certain level (less than 9.7), which may cause serious structural damage.

2.2. XRD Characterization. XRD characterization was implemented to identify the crystalline phases of the solid products. A representative set of diffraction data for the four hydrated cements is shown in Figure 1.

A comparison of the peak intensities between hydrated cement and GO and/or rGO provides some insight into their relative compositions. Evidently, the acidic nature of the oxygen functional groups on the surfaces of GO or rGO (with pH 3.01) has a neutralizing effect on the highly alkaline medium of the hydrated cement with a pH greater than 12.5 in the pore solution. Therefore, the intensities of the CH and CaCO$_3$ peaks in hydrated cement mixed with GO and/or rGO are higher than the corresponding peaks in the hydrated cement without any additives.

The XRD patterns also show the CaCO$_3$ peak intensity, which increases with GO and/or rGO addition due to the increase in CH, which is available for carbonation as a result of the presence of the oxygen functional groups that decompose on the surfaces of GO or rGO. This process releases CO$_2$, CO, and H$_2$O, which can be precipitated in one or a mix of various polymorphs of CaCO$_3$ (calcite, aragonite, and vaterite). Calcite appears to be the primary crystalline CaCO$_3$ polymorph, with diffraction peaks at 2$\theta$ = 23.5°, 29.3°, 36°, 43°, 48.4°, and 64.3°, which are attributed to calcite. Characteristic peaks of vaterite and aragonite at 2$\theta$ = 25° and 45°, respectively, are evident, but they are relatively low compared with that of calcite. However, the XRD patterns show sharp calcite reflections, confirming the effective formation of calcite. Further, a comparison of the XRD patterns for the CaCO$_3$ particles acquired using GO and/or rGO reveals that the XRD peaks for the hydrated cement mixed with GO and/or rGO are sharper than those of the hydrated cement without any additives.

Typical energy-dispersive spectrometry (XPS) spectra of the chemical interaction of GO or rGO with hydrated cement at 7 and 28 days are shown in Figure 2. The original and fitting curves of the Ca(OH)$_2$ and CaCO$_3$ phases match remarkably well.

Indeed, a GO or rGO reaction with calcium-bearing phases (CH and C-S-H) in hydrated cement can cause chemical–mechanical changes in the microstructure. Due to the acidic nature of the oxygen functional groups on the surfaces of GO or rGO, they will decompose in the highly alkaline medium releasing CO, CO$_2$, and H$_2$O, leading to faster carbonation,
more Ca(OH)2 consumption, and consequently more CaCO3 generation.25,29,38,60

2.3. FTIR Spectrum Analysis. The FTIR spectra of hydrated cement and hydrated cement mixed with GO and/or rGO at 7 and 28 days are shown in Figures 3 and 4. The positions of all of the infrared active modes of calcite found in hydrated cement mixed with GO and/or rGO precisely match those of the calcite reference bands.38,50,64 It can be seen from the infrared spectra (Figures 3 and 4) of hydrated cement mixed with GO and/or rGO that asymmetric stretching (v3) gives rise to a very sharp and broad infrared absorption at 1425 cm\(^{-1}\). Out-of-plane and in-plane bending (v2 and v4) correspond to the fundamental bands of calcite at 872 and 713 cm\(^{-1}\), respectively.19,38 The clear presence of these absorption bands confirms the formation of the calcite phase of CaCO3 particles when either GO or rGO is mixed with hydrated cement.38 It should be noted that no residual peaks of GO or rGO are observable, confirming our predictions about the eventual decomposition to form CO2, CO, and H2O.38−46 In addition, it has been reported that thermal-programmed desorption (TPD) was used to characterize the oxygenated functional groups on the surfaces of the carbon materials,
which break down at various temperatures releasing CO, CO₂, and H₂O. This analysis also confirms the XRD and XPS analysis results presented in Figure 1. In addition, it is crucial to note that more intense/sharper characteristic peaks are observable in the FTIR spectra for the calcite particles acquired using either GO or rGO with hydrated cement than in the spectra for the hydrated cement without any additives. The peaks at 450 cm⁻¹ falls in the range of 400–500 cm⁻¹, which corresponds to the Si–O bending vibration (v2) in SiO₄²⁻, according to refs 19 and 50. Furthermore, both spectra show peaks at 950 cm⁻¹, corresponding to asymmetric Si–O stretching vibrations, which indicates limited polymerization in C-S-H.19,50,61

Moreover, the four spectra show weak bands at 1108 cm⁻¹, falling in the range of 1100–1165 cm⁻¹, which corresponds to SO₄²⁻ vibration (v3) in sulfates.50,62,63 This region has a range of peaks that may overlap due to the polymerization of SiO₄²⁻ and the corresponding vibration (v3).46,50 The water band peaks of the four spectra, which are located at 1642 cm⁻¹, indicate the H–O–H bending vibration (v2) of the adsorbed water molecule.19,50

Several additional weak bands between 3000 and 2000 cm⁻¹ are overtone modes. Meanwhile, the peaks at 3390 cm⁻¹, which fall in the range of 3100–3400 cm⁻¹, correspond to the O–H stretching vibrations (v1 and v3) in the water molecules.19,48 The peaks at 3640 cm⁻¹ (Figures 3 and 4) correspond to CH, which is formed as silicate phases in the hydrated cement. It is clear that the intensities of the characteristic peaks of CH decrease markedly when either GO and/or rGO is mixed with hydrated cement, compared to their intensities in the spectra of the hydrated cement without any additives. This difference is mainly due to the reaction of CH with liberated CO₂ from the decomposition of the oxygen functional groups of GO or rGO.19,38,46,48,50,62,63,65 These findings also confirm the XRD and XPS analysis results discussed previously and prove that GO and/or rGO have high reactivity with hydrated cement, leading to nano-calcium carbonate generation.50 Nano-calcium carbonate can block the
pores in the hardened cement, which may or may not improve the mechanical properties.

2.4. SEM. The microstructures of hydrated cement mixed with 0.07% of GO and/or rGO were examined using scanning electron microscopy (SEM). The SEM results presented in Figures 5 and 6 depict the microstructures of the hydrated cement mixed with GO and/or rGO at 7 and 28 days. Figure 5A,B shows the microstructure of the hydrated cement without GO and/or rGO, 5C,D with 0.07% of GO, and 5E,F with 0.07% of rGO at 7 and 28 days.
any additives, proving that the microstructure is an amorphous solid with a large amount of microcracks, porosity, and pore size distribution. When compared with Figure 5C−F, the results prove that the hydrated cement composites mixed with a 0.07% dosage of GO and/or rGO have a certain amount of needle-like crystal products and form compacted microstructures, which strongly prove that, due to the acidic nature of the oxygen functional groups located on the surfaces of GO or rGO, they will decompose in a highly alkaline medium releasing CO, CO$_2$, and H$_2$O$^{38,41-45}$ which accelerate the dissolution rate and the hydration of cement at the first few minutes of the starting reaction. The acceleration phase of CaCO$_3$ formation starts due to the direct carbonation reaction of cement hydrates with GO and/or rGO at different times (Figure 5C−F). Moreover, the results indicate that the direct reaction of GO and/or rGO with hydrated cement produces a certain amount of CaCO$_3$ crystals that participate in forming the cross-linking and interweaving microstructure, which leads to enhancing the mechanical behavior of the hydrated cement paste. Figure 6A−D shows different portions and magnifications of a relatively higher growth of the calcite phase of CaCO$_3$ in the hydrated cement mixed with GO and/or rGO at 7 and 28 days. Simultaneously, a needle-like phase develops on the cement particles. This needle-like phase has been linked to the calcite structure in earlier studies.$^{38,48,50}$ The distribution of CaCO$_3$ crystals in hydrated cement composites could be identified by inspecting the CaCO$_3$ crystals in a whole SEM image using energy-dispersive X-ray spectroscopy (EDX). The EDX-inspected areas are marked as white boxes in Figure 6A−D. The EDX test results indicate that the needle-like crystals of CaCO$_3$ is uniformly distributed within the whole inspected area (Figure 7). These results also suggest that the needle-like phase formed continuously during hydration and grew even more after 28 days of hydration. As a matter of fact, the various morphologies of CaCO$_3$ particles resulted from the variations in the concentration and type of the oxygen functional groups on the surfaces of GO and rGO, which serve as active sites and play an essential role in such reactions.$^{38-45}$ However, both GO and rGO eventually decompose to form CO$_2$, CO, and H$_2$O in a highly alkaline medium, which completely react with hydrated cement (calcium-bearing phases, CH, C-S-H, and ettringite) to form needle-like crystals of CaCO$_3$. These findings also confirm the XRD, XPS, and FTIR analysis results and prove that GO and/or rGO have high reactivity with hydrated cement.
3. CONCLUSIONS

The development of GO and rGO cementation actions is a significant area of interest in the construction field. The impressive ability of GO to release CO$_2$, CO, and H$_2$O through the decomposition of the oxygen functional groups in certain alkaline media, which appears to be behind the carbonation of Portland cement, is a phenomenon that could be employed to elucidate the mechanism of this chemical interaction. Toward this end, this study was focused on investigating the critical reaction mechanism using GO, rGO, and Portland cement and on how these materials may influence CH, C-S-H, and ettringite carbonation. The rate and degree of CH and C-S-H gel carbonation depend fully on the quantities of CO$_2$ and CO released during decomposition, which are associated to the total amount of the oxygen functional groups located on the surfaces of GO or rGO. These processes result in an obvious pH reduction to a certain level (less than 9.7). The ettringite and aluminate phases decompose upon reaction with GO or rGO, resulting in gypsum and alumina gel formation. XRD, XPS, and FTIR were used to confirm the CaCO$_3$ polymorph formation. The SEM

Figure 7. EDX analysis of CaCO$_3$ particles obtained: (A) hydrated cement, (B, C) hydrated cement mixed with 0.07% of GO at 7 and 28 days, and (D, E) hydrated cement mixed with 0.07% of rGO at 7 and 28 days.
images also corroborated the needle-like phase attributed to the calcite polymorph. Principally, the current study has evidently established the usefulness of GO and/or rGO with hydrated cement for obtaining CaCO₃, which could be beneficial for the cement industry, as it has previously been reported to increase the compressive and flexural strengths of CP and reduce the atmospheric carbonation of hydrated cementitious matrices.

4. EXPERIMENTAL SECTION

4.1. Preparation of Cement–GO. GO was synthesized from graphite powder (200 mesh, Alfa-Aesar) utilizing the Hummers’ method. Ordinary Portland cement (type 52.5, Green Island, Hong Kong) was utilized in this work, and the chemical composition collected by X-ray fluorescence is listed in Table 1. Table 2 details the mixture ratios of the GO and/or GO–rGO with hydrated cement. The produced samples were cured in ambient conditions for 24 h, demolded, and placed into a curing room (25 °C for 1 h). They were then kept in an air-tight container to prevent any air exposure until testing.

4.2. Preparation of Cement–rGO. rGO was prepared following the same method that was reported previously. Table 2 details the mixture ratios of the GO and/or rGO with modified cement paste. The mixture was prepared first by ultrasonication of the aqueous solution of rGO for 15 min, which was then slowly mixed with cement (at a ratio of 0.4 water to cement by weight) at the speed of a high rate for 8 min before casting into molds and covering with plastic sheets. The samples were cured in ambient conditions for 24 h, demolded, and placed into a curing room (25 °C/RH 95%) until testing.

4.3. Material Characterization. The produced samples were characterized by XRD patterns, which were collected by a PW1830 (Philips) system at 2 kW, using a Cu anode and a graphite monochromatic system. XPS measurements were performed by a Kratos Axis Ultra DLD Multitechnique using a graphite monochromatic system.

Table 1. Chemical Composition of Cement

| component | CaO   | SiO₂  | SO₄  | Al₂O₃ | Fe₂O₃ | MgO | K₂O | TiO₂ |
|-----------|-------|-------|------|-------|-------|-----|-----|------|
| content (%) | 65.40 | 19.47 | 5.71 | 3.86  | 3.00  | 1.58 | 0.49 | 0.26 |

Table 2. Mixed Proportions of GO- and rGO-Modified Cement Paste

| sample          | cement (g) | H₂O (g) | GO (mL) | rGO (g) | dosage (wt %) |
|-----------------|------------|---------|---------|---------|---------------|
| hydrated cement | 400        | 140.0   |         |         | 0.00          |
| cement–GO       | 400        | 70.0    | 70.0    |         | 0.07          |
| cement–rGO      | 400        | 70.0    |         | 70.0    | 0.07          |

6700F scanning electron microscope equipped with an energy-dispersive X-ray analyzer.

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