
Abstract: In the present study, the efficiency of five different carbonation and/or water curing conditions on the properties of belite-rich cement mortar and ordinary Portland cement mortar was investigated. The hybrid curing of samples was carried out by submerging samples at different levels in water or in a lime-saturated solution kept under carbonation curing conditions. The compressive strength was measured to compare the physical properties of the cement mortars, and X-ray diffraction and thermogravimetric analysis results were analyzed to compare the physicochemical properties. The results revealed that the supply of additional moisture during carbonation curing tends to decrease carbonation curing efficiency and that the hydration products of cement paste are predominantly affected by the depth at which the specimen was immersed in the liquid rather than the type of liquid used.

Keywords: carbonation; curing; cement; lime-saturated water; compressive strength

1. Introduction

The growth in industrial activities has led to the high consumption of energy, which in turn has led to significant amounts of carbon dioxide being emitted into the atmosphere [1]. Carbon dioxide emissions have resulted in global warming and other harmful climate-change-related phenomena, causing irreparable damage to the earth’s ecosystem [2]. The mitigation of calamities caused by the rise in temperature has emerged as a global agenda [3]. However, the emission of carbon dioxide into the earth’s atmosphere reached an all-time high in 2019 [4].

According to the IEA (International Energy Agency)’s Global Status Report for Buildings and Construction 2019, the building and construction sector produced nearly 40% of all carbon dioxide emissions in 2018, out of which 11% was generated during the manufacturing processes of building materials and products such as cement [5]. Cement is one of the most widely used human-made materials in the world, and it has been reported that cement production worldwide will reach 3.7 billion to 4.4 billion tons by 2050 due to rapid infrastructure development [3,6,7]. Concrete, being an important material for infrastructural needs, requires efforts in a sustainable direction that reduce both its overall use and the emissions of related pollutants, specifically carbon dioxide [8]. As a way to improve the sustainability of concrete, carbon capture, utilization and sequestration in concrete have recently attracted attention [9].

In particular, various studies are being conducted to strengthen the physical properties of concrete by combining carbon dioxide with concrete [10,11]. Hardened concrete when exposed to atmospheric carbon dioxide results in the decomposition of C-S-H (calcium silicate hydrate) gel into silica gel, leading to a loss of the binding capacity and compromising the durability of this material. This phenomenon can be referred to as natural carbonation,
weathering carbonation, or neutralization [12,13]. On the other hand, carbonation curing, a mineral carbonation process, is a method of curing by exposing fresh concrete to a carbon dioxide-rich environment during its curing period under low pressure [12]. During this curing process, carbon dioxide as an agent reacts with anhydrous cement minerals directly, resulting in the formation of carbonate minerals in the binding matrix [12,13]. Equations (1)–(3) show the chemical reactions governing the carbonation curing process of portlandite (normal hydration products, Ca(OH)$_2$), alite (C$_3$S), and belite (C$_2$S), respectively [14,15]. Equation (4) also shows the process by which C-S-H gel is eventually converted to SiO$_2$ and CaCO$_3$ through carbonation [13,16].

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (1)$$
$$\text{C}_3\text{S} + (3-x)\text{CO}_2 + y\text{H}_2\text{O} \rightarrow \text{C}_x\text{SH}_y + (3-x)\text{CaCO}_3 \quad (2)$$
$$\text{C}_2\text{S} + (2-x)\text{CO}_2 + y\text{H}_2\text{O} \rightarrow \text{C}_x\text{SH}_y + (2-x)\text{CaCO}_3 \quad (3)$$
$$\text{C-S-H} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 + \text{H}_2\text{O} \quad (4)$$

The carbonation of calcium silicates to produce C-S-H gel can occur rapidly and can also explain how strength develops [17]. Previous studies of the mineral carbonation of cement clinkers reported that if early-age carbonation curing is applied to concrete, it not only improves the mechanical properties of concrete, such as the compressive strength, the drying shrinkage, and the densification of the pore structure, but also accelerates the strength development rate [1,18]. Several studies have sought to determine the effects of carbonation curing on various types of cement-based materials, as well as ordinary Portland cement, which is commonly used [19–21]. Jeon et al. reported that carbonation curing could have a positive effect on the hydration and microstructure of concrete [19], and Qin et al. reported that the application of carbonation curing to concrete manufactured by replacing parts of the cement with limestone powder, fly ash, or blast furnace slag could improve the compressive strength of concrete [20]. Meanwhile, Jang and Lee reported that the effect of carbonation curing on belite-rich cement concrete is more noticeable [21]. In their study, Jang and Lee revealed with higher belite contents in cement, more carbonation is promoted, resulting in a dense microstructure of the concrete matrix [21].

Several factors affect the carbonation curing efficiency of concrete, including the concentration of carbon dioxide, the temperature, and the humidity [22]. In general, it is known that the highest carbonation rate of concrete can be achieved in an environment of 50–70% R.H. and that higher humidity levels decrease the carbonation rate [23]. The presence of internal moisture also has a profound effect on the carbonation efficiency of concrete [24], because when curing concrete under the carbonation conditions, CO$_2$ gas from the surface moves along the internal pores of the concrete. Concrete, which contains a considerable amount of moisture in its internal pores, has a much lower carbonation rate because the water-filled pores inhibit the penetration of CO$_2$ into the concrete matrix [16,25]. If the pores of the concrete are completely saturated with water, the diffusion of carbon dioxide into the concrete matrix is restricted [16].

On the other hand, studies have also been conducted to increase the physical strength of concrete by utilizing lime powder or lime water in the carbonation curing process [26,27]. Tu et al. studied the effect of lime powder mixed as an admixture material on carbonation curing, and the results of the study revealed that the pressure condition during carbonation curing determines the ratio of poorly crystallized calcium carbonate to highly crystallized calcium carbonate [26]. Gao et al. argued that the synergism between carbonation curing and Ca(OH)$_2$ solution drenching increases the density and compressive strength of concrete blocks [27].

The use of lime water as a curing water is recommended as the concrete curing method according to ASTM C511, as this approach can inhibit the elution of calcium ions from concrete. It has been reported and is also a well-known fact that lime water curing can improve the strength development of concrete [28]. Chougule et al. revealed the effects of
various curing techniques on the strength of concrete when cement is replaced with blast furnace slag at replacement rates of 50% to 60% [29]. Their experimental results showed that lime water curing can increase the maximum strength of the concrete in a comparison of four different curing methods, including underwater curing, steam curing, compound curing, and high-pressure steam curing [29]. Pan et al. placed mortar specimens in a chamber for CO\textsubscript{2} surface treatments lasting three and six hours and then immediately immersed them in saturated lime water for a specific curing period [28]. Their experimental results indicated that the curing method does not have a significant effect on the compressive strength but a significantly positive effect on the impermeability of cement mortar [28]. On the other hand, studies have also shown that the compressive strength of concrete samples cured in a tank containing lime water decreases compared to samples which undergo water curing. Yeih et al. investigated the effects of different types of cement and different curing conditions on the performance outcomes of pervious concrete, noting that applying lime water curing conditions to pervious concrete made with sulfoaluminate cement could seriously degrade the compressive strength of this type of concrete [30]. This shows that there is only limited information about the effects of the use of lime-saturated water during the carbonation curing of concrete. The main objective of the present study is to investigate the effect of hybrid carbonation curing with lime-saturated water and normal water at different levels of submergence on the carbonation efficiency of concrete. Five different curing environments were considered, and paste specimens cured for a certain period were used to analyze the strength development characteristics and phases of the hydration and carbonation products.

2. Materials and Methods

2.1. Materials and Sample Preparation

Ordinary Portland cement (Type 1) and belite-rich Portland cement (Type 4) produced in South Korea were used in this study. The classification of cement used in this study satisfies ASTM C150-20 standards. The chemical and mineral compositions of both types of cement are provided in Table 1. Jumunjin standard sand produced in South Korea, composed of quartz-based minerals, was used as a fine aggregate material to produce mortar specimens. The standard sand is the most commonly used in Korea for strength testing of cement. The granularity distribution of the standard sand is specified in KS L ISO 649, and its specific gravity is 2.65.

<table>
<thead>
<tr>
<th>Cement</th>
<th>Chemical Composition (wt.%)</th>
<th>Mineral Composition (^{1}) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO\textsubscript{2}</td>
</tr>
<tr>
<td>Ordinary Portland cement</td>
<td>62.5</td>
<td>21.0</td>
</tr>
<tr>
<td>Belite-rich cement</td>
<td>62.5</td>
<td>25.3</td>
</tr>
</tbody>
</table>

\(^{1}\) The mineral composition is calculated from Bogue’s equations.

The cement mortar specimens were prepared with a water-to-cement ratio of 0.5, with the ratio of cement to sand kept at 1:2. Simultaneously, cement paste samples with an identical water-to-cement ratio but without fine aggregate were also fabricated for physicochemical investigations. Cement paste was manufactured by mixing 50 g of tap water per 100 g of cement. Cement mortar was manufactured by mixing 100 g of sand and 50 g of tap water per 100 g of cement. For the mixing of all ingredients, the water was lastly added after sufficient mixing of cement and sand. The ingredients for the mortar/paste specimens were properly hand-mixed for five minutes to ensure consistency and uniformity. The mortar and paste specimens were cast in 50 mm cubic molds for the compressive strength and physicochemical analysis. All specimens were cast continuously from one batch throughout the entire process, from mixing to pouring, to secure the consistency of specimens. To measure the compressive strength of the cement mortar, three specimens were prepared for each curing condition and/or cement type.
2.2. Curing Conditions and Test Methods

The cast specimens were wrapped to prevent evaporation loss and were then pre-cured at 20 °C and 60% R.H. for 24 h. After demolding, five different types of curing immediately followed. Table 2 and Figure 1 present the details and an outline of the curing conditions. It can be noted from Figure 1 that four conditions were carried out inside a carbonation chamber with maintained conditions of a CO₂ concentration of 10%, a temperature of 20 °C and 60% R.H., whereas one condition was carried out in a laboratory environment as a control group. Moreover, for three hybrid conditions, the specimens under curing in the carbonation chamber were also submerged at various depths under a permeating liquid, in this case tap water or lime-saturated water. The nomenclatures utilized in the present study are as follows: for condition 1, “CC-40L” indicates a carbonation-cured specimen submerged at 40 mm in lime-saturated water; for condition 2, “CC-10L” indicates a carbonation-cured specimen submerged at 10 mm in lime-saturated water; for condition 3, “CC-10N” indicates a carbonation-cured specimen submerged at 10 mm under water; for condition 4, “CC” indicates a specimen carbonation-cured in the chamber environment; and for condition 5, “NC” indicates a specimen completely submerged under water in the laboratory conditions. For conditions 1–3, specific care was taken to maintain the level of submergence and to ensure that CO₂ remains in contact with the non-submerged part of the specimen. It should be noted that the specimens prepared from both types of cement were cured under all five of the curing conditions used here. The tap water or lime-saturated water level in conditions 1–3 was renewed every two days to maintain a constant depth. Furthermore, as shown in Figure 1, the bottom of the test specimens was shored up in each case to maximize the curing contact area of the specimen. In this study, the lime saturation solution was produced by dissolving calcium hydroxide in tap water, and tap water was also used to cure the mortar and paste specimens. The curing of the specimens was carried out for 7, 14, and 28 days for the compressive strength test and for 28 days for the physicochemical analysis.

Table 2. Summary of the curing conditions and specimen codes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Code</th>
<th>Curing Method</th>
<th>Permeating Liquid</th>
<th>Depth ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CC-40L</td>
<td>Carbonation curing ¹</td>
<td>Lime-saturated water</td>
<td>40 mm</td>
</tr>
<tr>
<td>2</td>
<td>CC-10L</td>
<td>Carbonation curing</td>
<td>Lime-saturated water</td>
<td>10 mm</td>
</tr>
<tr>
<td>3</td>
<td>CC-10N</td>
<td>Carbonation curing</td>
<td>Water</td>
<td>10 mm</td>
</tr>
<tr>
<td>4</td>
<td>CC</td>
<td>Carbonation curing</td>
<td>Water</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>NC</td>
<td>Water curing</td>
<td>Water</td>
<td>&gt;50 mm</td>
</tr>
</tbody>
</table>

¹ Condition of the carbonation curing: 20 °C, 60 R.H.% and 10% CO₂; ² Depth = depth from bottom of 50 mm cubic specimen to surface of permeating liquid.

Figure 1. Five curing conditions tested in this study.
The compressive strength test is performed using a universal testing machine according to ASTM C109/109M-20b. The compressive strength of mortar specimens was measured using three cubes for each condition, and the average of the three measurements was plotted on the graphs. The physicochemical properties of the cement paste samples were investigated by X-ray diffractometry (XRD), thermogravimetric analysis (TG), and derivative thermogravimetry (DTG) analysis. The XRD analysis was carried out on a PANalytical 640C instrument at a scan range of 5–60° with a scan speed of 0.2°/min. The TG/DTG analysis was carried out from 30 °C to 900 °C at a heating rate of 10 °C/min on an EA 1108 CHNS-O/FISONS device. The samples used in the physicochemical analysis were dried using a desiccator to stop the hydration reaction process and then ground to allow them to pass through a 150 µm sieve. It should be noted that the cement paste samples were extracted from the central part of the test specimens.

3. Results and Discussion

3.1. Compressive Strength

Figure 2 shows the results of the compressive strength of the mortar specimens manufactured with ordinary Portland cement or belite-rich cement. This figure shows that the two cement types present different behaviors depending on the curing condition. However, the results after standard water curing (NC) and carbonation curing (CC) for the ordinary Portland cement and belite-rich cement mixes are consistent with those in previous studies [15,21].

![Figure 2. Compressive strength of cement mortar: (a) manufactured using ordinary Portland cement; (b) manufactured using belite-rich cement.](image)

It can be seen in Figure 2a that for the ordinary Portland cement mixes, the NC- and CC-cured samples present similar compressive strength levels (around 56 MPa). This indicates that the effect of carbonation curing on ordinary Portland cement concrete is not significant. On the other hand, interesting observations can be drawn from the compressive strength of the three hybrid-cured samples. It can be seen that the CC-10N samples registered the highest compressive strength (63.87 MPa) among all samples. However, the lowest compressive strength was obtained from the CC-40L and CC-10L samples. The dual action of carbonation and hydration resulted in higher compressive strength of the CC-10N samples. The compressive strength of CC-10L samples is approximately 10 MPa higher than that of other samples.

For the belite-rich cement mixes, the highest compressive strength was observed for the CC mix, as shown in Figure 2b. The sluggish hydration reaction rate of belite-rich cement...
can lead to lower compressive strength compared to that of ordinary Portland cement [31]. However, the carbonation reaction rate of belite-rich cement is higher than that of ordinary Portland cement, which leads to the densification of the cement matrix due to the formation of carbonation reaction products [15,21]. Accordingly, the compressive strength of the NC sample was nearly 44% lower when compared to that of the CC sample. In addition, when comparing the CC-cured samples of belite-rich cement and ordinary Portland cement, similar compressive strength was developed until the 7 days age. However, there was a significant difference between the 14 and 28 days age. In contrast to the results obtained for the ordinary Portland cement samples, the hybrid-cured belite-rich cement samples recorded lower compressive strength levels for all three hybrid curing conditions.

The dual action in the three hybrid conditions presents several interesting scenarios. Capillary action in the cement samples played an important role in the development of hydration or carbonation reaction products. The absorption of water or lime-saturated water due to the capillary action of cement samples can hinder the penetration of CO₂ into the cement matrix, thereby reducing the influence of the carbonation reaction relative to the hydration reaction. This phenomenon in the case of belite-rich cement severely compromises the development of compressive strength of hybrid-cured belite-rich cement samples.

### 3.2. X-ray Diffraction

Figure 3 shows the XRD spectra of cement paste samples subjected to the five different curing conditions. Figure 3a shows the XRD spectra of cement paste produced from ordinary Portland cement. The XRD spectra of belite-rich cement paste are presented in Figure 3b. For the ordinary Portland cement, the XRD spectra of NC and CC show the formation of calcite as well as portlandite. However, the intensity of the portlandite peaks in the NC sample is higher, whereas CC shows a higher peak intensity level of calcite. This shows that with regard to ordinary Portland cement, microstructural densification due to the formation of hydration products or carbonation products leads to a similar compressive strength outcome. For the CC-10N sample, the similar intensity peaks for both calcite and portlandite can lead to remarkable microstructural densification, which results in higher compressive strength. Furthermore, for the CC-10L and CC-40L samples, the lower peaks of calcite indicate that the hydration reaction takes precedence over the carbonation reaction.

![XRD spectra](image)

Figure 3. Cont.
For the belite-rich cement samples, the CC mix showed the highest calcite peak and the lowest belite peak, an outcome that indicates a higher carbonation reaction rate of the belite phase. However, the NC mix showed higher peaks for both portlandite and belite. This may be due to the slower reaction rate of the belite phase [31]. The slower hydration progress in the carbonation-cured sample may also be due to the build-up of carbonates, which restricts the exposure of unreacted cement clinker particles to water. An interesting observation can be drawn with regard to the formation of an ettringite phase in the belite-rich cement samples. It was noted that the carbonation-cured CC samples showed no presence of ettringite. This may be due to the decomposition of ettringite to calcite upon carbonation [32]. In the hybrid-cured samples, it was found that partial immersion of the samples in water or the lime solution severely compromised the carbonation capacity as well as the hydration capacity of the belite-rich cement.

3.3. Thermogravimetric Analysis

Figure 4 shows the TG/DTG results of the cement paste samples cured for 28 days in the five different environments. Figure 4a,c are the results of cement paste manufactured using ordinary Portland cement, while Figure 4b,d are the results of cement paste manufactured using belite-rich cement. In the TG curve, the weight loss occurring in the range of 50–120 °C is caused by the evaporation of free water and the decomposition of C-S-H and AFt [15,33]. The AFm phase decomposes near 170 °C, resulting in a weight loss peak [15,33,34]. In previous studies, peaks around 430–490 °C are accredited to the decomposition of Ca(OH)₂ [15,33,34]. However, if most of the Ca(OH)₂ is consumed through the carbonation process, the corresponding peak may not appear [15]. When the degree of carbonation of a cement paste sample increases, the intensity of the weight loss peak in the range of 720–810 °C, accredited to calcite, increases [15,34]. Furthermore, in this study, the weight percentages of Ca(OH)₂ (abbreviated to CH) and CaCO₃ (abbreviated to CC) contained in each sample were calculated using the change in the weight loss in specific decomposition temperature ranges (CH: 430–490 °C and CC: 710–820 °C).
Figure 4. TG results of cement paste samples at the 28 days age cured in 5 different conditions: (a) DTG curve for ordinary Portland cement paste; (b) DTG curve for belite-rich cement paste; (c) TG curve for ordinary Portland cement paste; (d) TG curve for belite-rich cement paste.

For Portland cement mixes, the NC samples presented the highest peaks of C-S-H and calcium hydroxide phase and the lowest peaks of calcite as compared to other samples. For the carbonation-cured CC sample, the calcite peak registered the highest peak as compared to other samples. The samples which underwent hybrid curing presented intriguing observations; it can be seen that the ordinary Portland cement samples of CC-10N registered peaks of calcite and C-S-H, which indicate that both carbonation and hydration occur concurrently, contributing to higher compressive strength. However, the samples which underwent hybrid lime water curing presented similar peaks despite the different levels of submergence.

In the belite-rich cement samples, the CC sample registered the highest concentration of calcite. However, all hybrid-cured samples presented similar calcite peaks compared to the NC sample. It can be theorized that the submergence of samples in a solution can restrict the carbonation of belite-rich cement. Furthermore, the sluggish hydration reaction rate of belite-rich cement was well documented in previous studies [35,36]. These phenomena resulted in less compressive strength development, as indicated by the poor development of the hydration products as well as the carbonation products in this study.
3.4. Discussion

The hybrid curing parameters of different types of cement presented new insights into the carbonation curing efficiency of cement products. Samples in this study were exposed to normal water curing, carbonation curing and three different types of hybrid curing with different levels of submergence in a water or lime solution. It was observed that ordinary Portland cement and belite-rich cement presented quite different behaviors depending on the type of curing.

The ordinary Portland cement mixes here indicated that hybrid curing can be beneficial in terms of the strength development of samples. The XRD spectra of the ordinary Portland cement which underwent hybrid curing showed that these samples exhibited the formation of both hydration and carbonation products. This indicates that ordinary Portland cement is simultaneously involved in both hydration and carbonation reactions. Additionally, the type of liquid used during the hybrid curing process also plays a significant role; it was found that as compared to the lime solution, the water-submergence-based hybrid curing process led to higher compressive strength as well as a higher level of the formation of reaction products. In the belite-rich cement samples, the normal and carbonation-cured samples indicated well-defined strength development, as indicated also in previous studies [15,21]. However, the samples which underwent hybrid curing presented a reduction in compressive strength of nearly 65% when compared to that of the carbonation-cured samples. For belite-rich cement, hybrid curing restricts the penetration of CO\textsubscript{2} into the cement matrix, resulting in a slower carbonation reaction.

The presence of a solution during hybrid curing increases the humidity level, which results in a slower carbonation reaction. Furthermore, for lime-solution-based hybrid curing, dissolved CO\textsubscript{2} can react with the lime water to form a weak layer of CaCO\textsubscript{3}, which also acts as a barrier restricting the penetration of CO\textsubscript{2} into the cement paste matrix.

4. Conclusions

The effects of hybrid curing along with normal and carbonation curing on ordinary Portland cement and belite-rich cement mixes were investigated. The results provide qualitative and quantitative information about the formation of hydration and carbonation products along with the development of compressive strength. The main conclusions extracted from this work are as follows.

(1) In the belite-rich cement samples, the lime solution formed weak precipitates of calcium carbonate, which restricted the percolation of CO\textsubscript{2} into the cement matrix. Furthermore, the capillary rise of the lime solution or water acted as a barrier that prevented both CO\textsubscript{2} penetration and the carbonation reaction.

(2) Due to the lower hydraulic reactivity, the hybrid-cured belite-rich cement mixes displayed significantly lower compressive strength levels as compared to the carbonation-cured samples. XRD and TGA observations also showed that the hybrid-cured samples of belite-rich cement registered poor development of hydration as well as carbonation products.

(3) In the ordinary Portland cement samples, the highest compressive strength was obtained for the water-submerged hybrid sample. This shows that in ordinary Portland cement samples, hybrid curing can be beneficial as the hydration reaction proceeds efficiently along with the carbonation reaction, leading to higher compressive strength.

(4) The type of cement along with the type of hybrid curing used can be instrumental with regard to the strength development of carbonation-cured cement products. Therefore, it is important to understand the effect of the interaction of the two factors on the compressive strength and to apply them appropriately to satisfy required performances of products.

Author Contributions: Conceptualization, J.-G.J.; methodology, J.-G.J.; validation, H.K. and J.P.; investigation, H.K. and J.P.; writing—original draft preparation, H.K., J.P. and S.S.; writing—review and editing, S.S. and J.-G.J.; supervision, J.-G.J.; funding acquisition, J.-G.J. All authors have read and agreed to the published version of the manuscript.
**Funding:** This study was supported by Incheon National University (International Cooperative) Research Grant in 2020.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available from the corresponding author upon a reasonable request.

**Conflicts of Interest:** The authors declare no conflict of interest.

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