

A study of curing characteristics of CO₂-absorption calcium silicate cement with respect to CO₂ concentration

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CSC is an eco-friendly, low-energy cement-based material, the use of which can reduce CO₂ emissions by up to 70% over the entire course of the manufacturing and curing processes when compared to typical cement mixes. In the present study, the ability of CSC to realize its desired properties, i.e., being cured by the carbonation reaction, was examined. More specifically, CSC samples were cured at varying CO₂ concentrations (0, 5, 10, 20%), and their ability to implement their desired properties was studied at each curing time (5, 10, 24, 48, 96 h). In doing so, the potential for utilizing CSC in practice was assessed. The experimental results showed that with higher CO₂ concentration, the carbonation reaction of CSC became accordingly faster. The compressive strength was measured to be over 56 MPa at curing 7 days, indicating that these CSC samples provided excellent early-stage strength. Also, all samples subjected to carbonation curing exhibited a much higher curing 7 days compressive strength regardless of the CO₂ concentration in the curing atmosphere when compared to Type 1 cement in accordance with the Korean Industrial Standards. This indicates that these materials have a high potential for extended applications.

Keywords: CO₂ absorbing, Calcium silicate cement, CO₂ concentration, Carbonation, Curing condition.

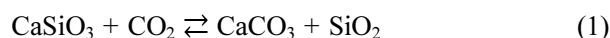
Introduction

In order to reduce greenhouse gas emissions in the industrial sector, it is necessary to reduce greenhouse gas emissions emitted during the production process. In the case of the cement industry, about 90% of the carbon dioxide generated in the manufacturing process is emitted from the clinker manufacturing process, and since high calcination temperature for the manufacture of clinker is essential, there is a limit to reducing greenhouse gas emissions from the manufacturing process.

Calcium silicate cement that cures by absorbing CO₂ (hereinafter referred to as "CSC") is defined as calcium silicate-based cement and lime calcium silicate cement types. In its manufacturing process, the sintering temperature is set to about 1,200°C, which is approximately 200°C lower than that of typical cement mixes, thereby leading to a reduction in energy consumption. Also, the ratio of its main mineral phases, Ca and Si, is set to 1:1 or 3:2 [1], and thus the CO₂ emissions are less when compared to ordinary portland cement [2]. In addition,

its ability to cure by absorbing CO₂ may allow for a roughly 30% reduction of CO₂ during the curing process. This means that, over the entire course of the manufacturing and application processes, up to 70% of CO₂ emissions can be cut when compared to ordinary portland cement [2, 3].

In theory, the main mineral phases of CSC include CS (CaO·SiO₂, pseudowollastonite) and C₃S₂ (3CaO·2SiO₂, rankinite). However, depending on the raw material mixing ratios and sintering characteristics, other cement mineral phases, such as C₂S and C₃S, may be included, along with the remaining unreacted SiO₂. Here, the mineral phases that react with CO₂ are CS and C₃S₂, and compressive strength of up to over 70 MPa may be achieved through reactions represented by Eqs. (1) and Eq. (2) below [1-4].



In the present study, CSC was fabricated using domestic raw materials and examined with regard to its ability to implement desired properties. In doing so, the potential for its commercialization was assessed.

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Experimental Methods

Characteristics of raw materials

In the present study, CSC clinker was produced using domestic limestone and siliceous raw materials, as shown in Fig. 1. It was then crushed into particles with a size of about 10 μm , which is similar to the particle size range of ordinary Portland cement. As a result, CSC samples were obtained, as shown in Fig. 2. The main mineral phases of these CSC samples included CS, C_3S_2 , C_2S , and unreacted SiO_2 , which largely coincided with the results of previous overseas studies that reported the mineral characteristics of CSC, as shown in Fig. 1 [2-4]. Also, the proportion of CS and C_3S_2 combined, which directly contributes to the carbonation reaction, was found to be 91.5%. This figure was considered to be high enough to achieve sufficient durability improvement. It was found that a small amount of SiO_2 was used when mixing raw materials remained. As reported in other similar studies, it was

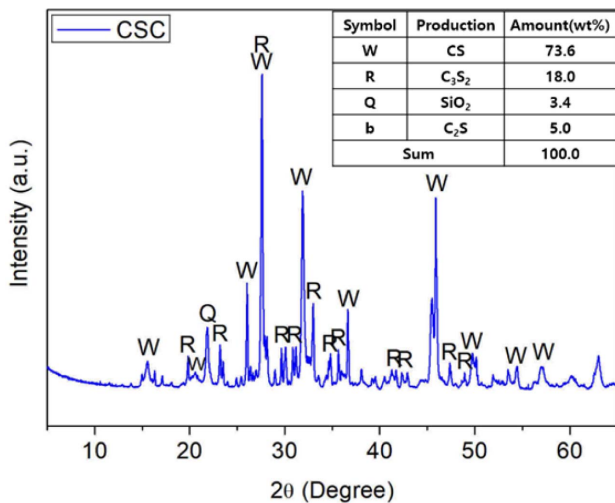


Fig. 1. XRD pattern of CSC.

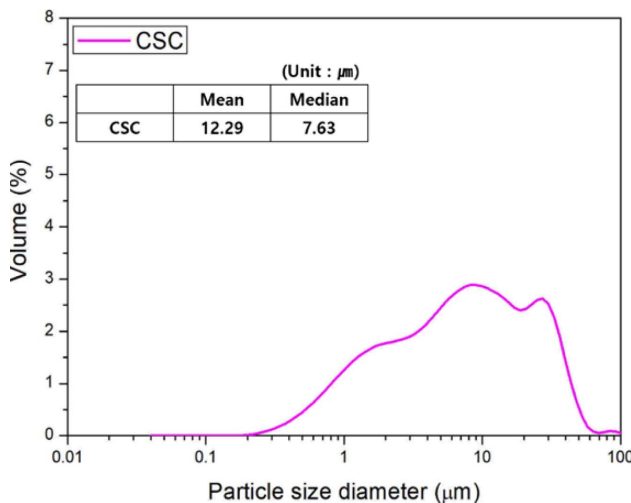


Fig. 2. Particle size diameter of CSC.

less likely that SiO_2 could be fully used up during the manufacturing process despite attempting to adjust the mixing molar ratio of raw materials [4-6]. Also, it was confirmed that its presence did not negatively affect CSC realizing its properties.

Experimental methods

CSC paste was prepared to examine its ability to realize desired properties with respect to the curing conditions. Subsequently, it was subjected to carbonation curing while varying the CO_2 concentration. The test conditions are summarized in Table 1. When preparing this CSC paste, the water ratio was set to 40%, which is the level that allows for the fabrication of samples in the form of a paste. Immediately after the mixing process, these samples were put on each reagent plate and spread widely with a thickness of about 100 mm and then subjected to curing in a carbonation chamber. This carbonation chamber operated at a temperature of 20°C and a humidity of 70%, and the CO_2 concentration was set to 0, 5, 10, and 20%. At each curing time, samples were withdrawn from the chamber and pretreated, and their physical characteristics were examined using XRD, DSC, SEM, and porosity measurement.

Compressive strength test specimens were molded in a cement specimen mold with width, length, and height of 40 mm, 40 mm, and 160 mm, respectively. It was impossible to de-mold the molded samples right after the molding process was complete, and thus they were dried and cured in the atmosphere for about 24 h and then de-molded to be cured inside the carbonation chamber. Here, the operating conditions of the carbonation chamber were set to be the same as the curing conditions of the paste. At curing 7 days, the compressive strength was measured at a loading rate of 144 kN/min in accordance with KS L ISO 679.

Experimental Results

The mineral phases of the CSC paste were analyzed according to the curing conditions, as shown in Fig. 3. As the CO_2 concentration increased, the CaCO_3 peak near 30° was found to increase in size. This was considered to be due to the increased contribution of C_3S_2 and CS to the carbonation reaction caused by the increasing CO_2 concentration. This was also likely

Table 1. Experimental conditions of CSC paste

Sample	CSC
Water ratio	40 %
Curing condition	Temperature 20°C, Relative humidity 70%
Accelerated carbonation condition	Temperature 20°C, Relative humidity 70%, CO_2 concentration (0, 5, 10, 20)%
Curing time	(5, 10, 24, 48, 72, 96)h
Instrument analysis item	XRD, DSC, Porosimeter, SEM
Mechanical properties	Compressive strength

related to the time of formation of CaCO₃, which might vary according to the CO₂ concentration. However, as shown in the mineral phase analysis results, it was impossible to ascertain how changes in the C₃S₂ and CS peak sizes are related to their contribution to the carbonation reaction. Also, the formation of amorphous SiO₂, one of the reaction products of the carbonation reaction, was not clearly identified.

In the case of the samples cured under typical moist curing conditions without any CO₂ supply, as shown in Fig. 3(a), there were no noticeable changes in the mineral phases at varying curing days, unlike in the samples subjected to carbonation curing, as shown in Figs. 3(b), (c), and (d). Also, no products of the carbonation reaction were found. This suggests that carbonation curing is critical to CSC being able to realize its desired properties. It is thus necessary to determine the optimal curing conditions that will allow CSC to realize its desired properties [7, 8].

For the relative quantification of products of the

carbonation reaction, differential scanning calorimetry (DSC) was performed, as shown in Fig. 4. It was found that the CaCO₃ peak around 800°C increased in size with increasing CO₂ concentration and curing time [7]. Also, the onset of CaCO₃ formation was earlier when the CO₂ concentration was higher, which suggested the relationship between the CO₂ concentration and the kinetics of the carbonation reaction [8].

For the samples subjected to carbonation curing, as shown in Figs. 4(b), (c), and (d), it was expected that the final amount of the reaction products might vary according to the curing atmosphere where the CO₂ concentration varied. However, the volume of reaction products was found to be not significantly affected by CO₂ concentration. In general, the carbonation reaction starts from the sample surface, where any surfaces in contact with CO₂ are preferentially subjected to densification caused by the crystalline growth of mineral phases. However, when the reaction proceeds to some extent, it becomes difficult for CO₂ to enter the inside

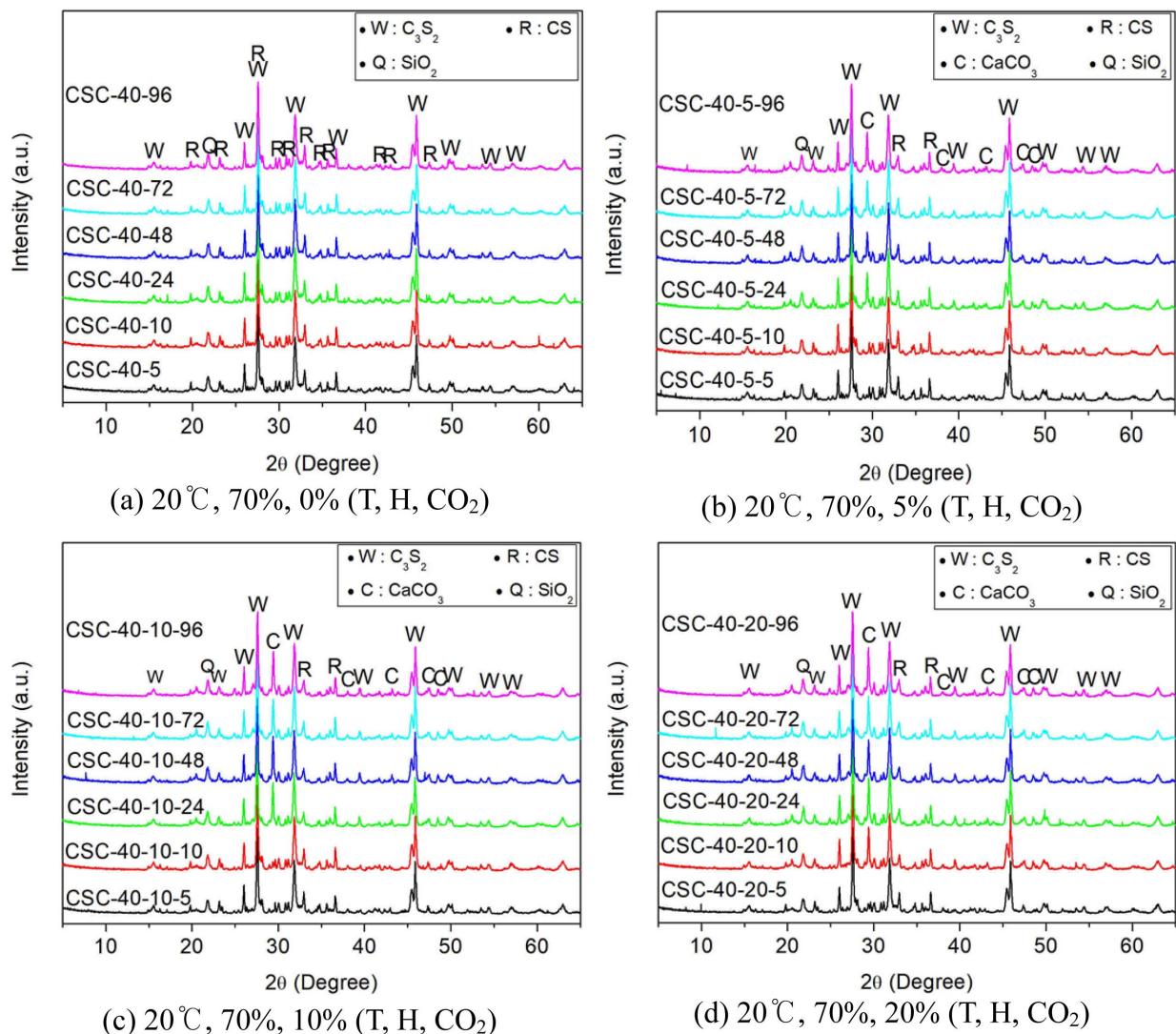


Fig. 3. XRD patterns of CSC paste with CO₂ concentration.

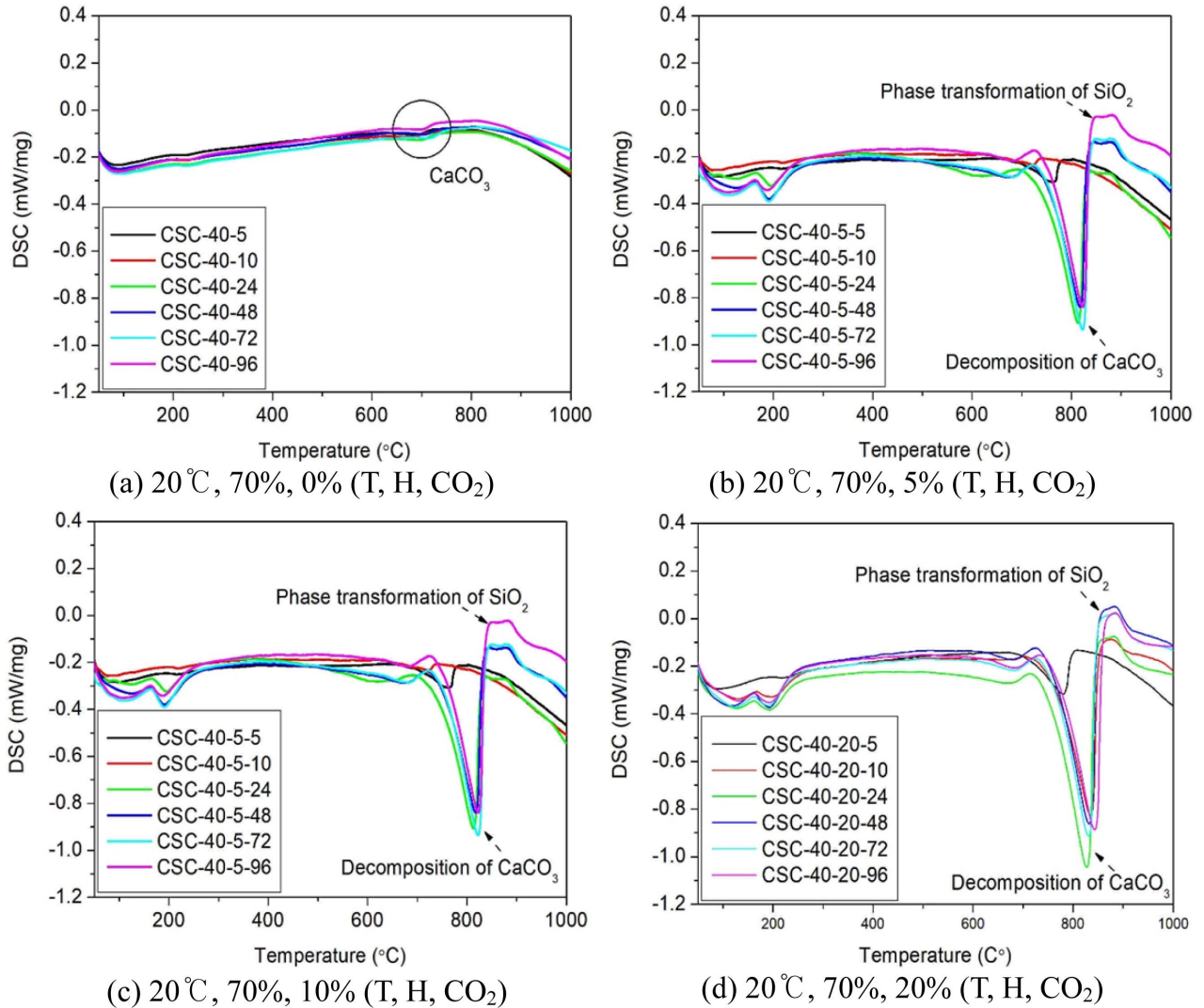


Fig. 4. DSC curves of CSC paste with CO₂ concentration.

of the sample because its crystalline structure has been densified [2, 9, 10]. Therefore, it is difficult to confirm the immediate effect of the CO₂ concentration on the reaction results. In light of this nature of the carbonation reaction, in the present study as well, the intensity and kinetics of the reaction could be confirmed in a macroscopic manner with respect to the CO₂ concentration at the early stage of curing (24 h). At the later curing stage, however, the total amount of reaction products remained at similar levels, understandably, because the reactivity was no longer affected by the CO₂ concentration.

A hyperbolic peak near 100-200°C was considered to be due to 2H₄SiO₄, an intermediate compound that was generated during the formation of SiO₂, one of the reaction products of the carbonation reaction of CS and C₃S₂ [2, 4].

In an attempt to observe the crystalline growth of CaCO₃, the samples cured at a CO₂ concentration of 20% were examined with respect to the curing time using SEM, as shown in Fig. 5. It was found that the

carbonation reaction proceeded somewhat faster in the samples cured at a CO₂ concentration of 20% than in those cured at the other conditions. Even at the early stage of curing, i.e., 10 h, the formation of CaCO₃ was identified. Similarly, SEM analysis results confirmed the crystallinity of CaCO₃ at curing 10 hours. At the early stage of curing, the degree of crystallinity appeared to be low, but as the curing time increased, the crystallinity became more evident, and the cured microstructure became increasingly densified. This was a macroscopic confirmation of durability improvement achieved in the cured CSC body by the carbonation reaction.

Fig. 6 shows the results of compressive strength measurement at curing 7 days with respect to the CO₂ concentration. When the CO₂ concentration was 5, 10, and 20%, the compressive strength was measured to be 28, 37, and 56 MPa, respectively, which indicated that the compressive strength increased with increasing CO₂ concentration. For Type 1 (typically referring to Portland cement) in accordance with the Korean Industrial

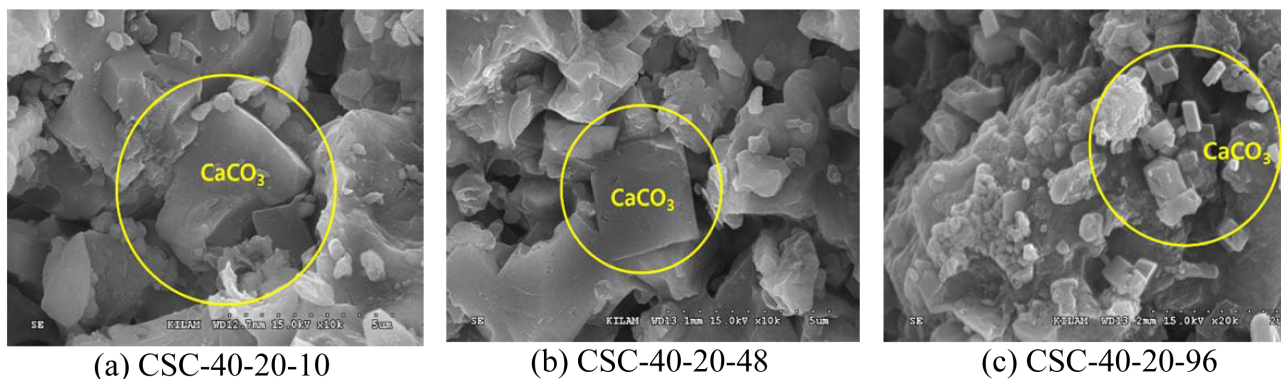


Fig. 5. DSC curves of CSC paste with curing at CO₂ concentration 20%.

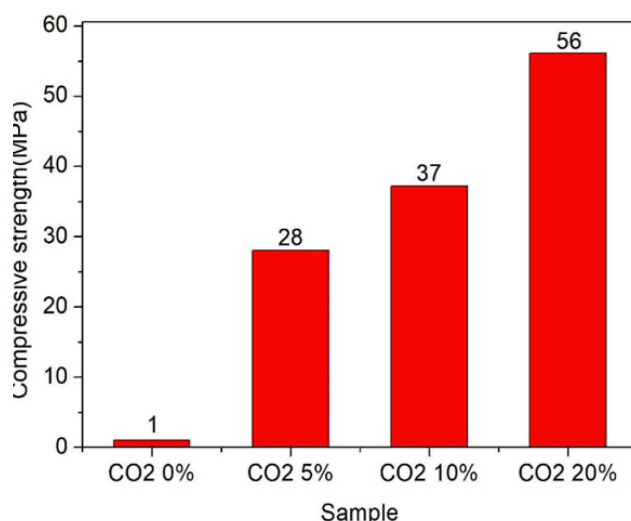


Fig. 6. Compressive strength of CSC with CO₂ concentration at curing of 7 days.

Standards (KS), the curing 7 days compressive strength and curing 28 day compressive strength are required to be 22.5 MPa and 42.5 MPa [11], respectively. In the present study, the CSC samples subjected to carbonation curing exhibited a higher curing 7 days compressive strength than Type 1 cement under the KS regardless of the curing conditions. Also, the samples cured at a CO₂ concentration of 20% showed a much higher compressive strength at curing 28 days than Type 1 cement under the KS. However, the curing 7 days compressive strength of the samples subjected to moist curing, where the CO₂ concentration was 0%, was measured to be 1 MPa or lower, which caused difficulty in measuring compressive strength in practice. These results indicated that carbonation curing was critical to CSC being able to implement their desired properties [7, 8]. Based on this nature, it will be possible to design the properties of CSC by adjusting the curing conditions. Also, it was found that these CSC samples were able to provide mechanical properties that were equivalent to or higher than those of Type 1 cement under the KS. Therefore, these materials are considered to have a high potential

for extended applications, such as blocks, ACL, panels, and rapid-hardening cement.

Discussion

In the present study, CSC was fabricated using domestic raw materials, and its physical behavior was observed while varying the CO₂ concentration in the curing atmosphere.

1) In the samples subjected to moist curing where the CO₂ concentration was 0%, almost no reaction products were found regardless of the curing time. Also, the compressive strength at curing 7 days was measured to be 1 MPa, which indicated that those samples had practically failed to implement their desired properties.

2) The mineral phases of CSC were analyzed according to the CO₂ concentration. It was found that the CaCO₃ peak increased in size with increasing CO₂ concentration. Here, CaCO₃ was a reaction product of the carbonation reaction. However, it was difficult to clearly confirm the formation of amorphous SiO₂.

3) Differential scanning calorimetry results showed that for the samples cured at a CO₂ concentration of 5% and 10%, the CaCO₃ peak was observed when the curing time was 24 h or longer. However, when the CO₂ concentration was 20%, the onset of CaCO₃ formation was earlier, i.e., when the curing time was 10 hours. These results suggested that the carbonation reaction accelerated with increasing CO₂ concentration, thereby increasing the pace at which its properties were implemented. However, there was no significant difference in the total amount of CaCO₃ formed regardless of the curing conditions.

4) Differential scanning calorimetry results showed that there was a peak near 100-200°C arising from 2H₄SiO₄, an intermediate compound generated during the formation of amorphous SiO₂. This was indicative of the ongoing formation of amorphous SiO₂ while implying that the carbonation reaction was continuing.

5) For the samples cured at a concentration of 5, 10, and 20%, curing 7 days compressive strength was 28, 37, 56 MPa, respectively. All samples subjected to

carbonation curing exhibited curing 7 days compressive strength equivalent to or higher than Type 1 cement under the KS. Also, the samples cured at a CO₂ concentration of 20% showed a higher compressive strength at curing 28 days age than Type 1 cement under the KS. These results suggested that the CSC samples fabricated in the present study provided excellent early-stage strength.

6) The major findings of the present study suggest that CSC requires a carbonation reaction to function properly. Based on this nature, it will be possible to design the properties of CSC by adjusting the CO₂ concentration in the curing atmosphere. Thus, these materials are considered to have a high potential for extended applications as eco-friendly construction materials, such as blocks, ACL, panels, and rapid-hardening cement.

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