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CO₂ Diffusion and Carbonation in OPC/ γ -2CaO·SiO₂ Composite

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Abstract: Gamma dicalcium silicate (γ -2CaO·SiO₂, abbreviated as γ -C₂S) is considered a potential candidate as a construction material owing to its high carbonation reactivity and consequent CO₂ absorption. This study investigates the diffusion of CO₂, a physical process, into hardened cement paste and the resulting carbonation, a chemical process. CO₂ diffuses from a region of high concentration to one of a lower concentration, which is the inner core of the hardened cement. This study aimed to examine whether the diffusion of CO₂ into the ordinary Portland cement (OPC)/ γ -C₂S composite paste followed the conventional laws of diffusion. We also studied the diffusion of CaCO₃ to determine if carbonation products were formed in the pores and examined the capture of CO₂. The paste specimens were prepared and subjected to CO₂ in the carbonation chambers for varying periods. The results showed that the CaCO₃ deposited in the pores affected the rate of diffusion of CO₂ in the mortars and pastes, resulting in the densification of such bodies and a decreased rate of diffusion, leading to the shutdown of diffusion. The diffusion of CO₂ in hardened cement pastes made from OPC and γ -C₂S follows Fick's second law, wherein there is a change in the concentration of CO₂ diffusing at a particular distance with time.

Keywords: CO₂; carbonation; diffusion; γ -C₂S; Fick's laws



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1. Introduction

The increase in the atmospheric CO₂ concentration increases the potential of blanketing heat within the Earth's atmosphere, thereby increasing the Earth's atmospheric temperatures as well as those of land and water bodies. Higher than normal concentrations of carbon dioxide, together with other GHGs, are the major causes of environmental imbalances leading to global warming and climate change. The motivation for this research was to contribute to the measures taken to mitigate global warming caused by the cement industry. The production of OPC, a common binder used in the building and civil engineering sectors, is an anthropogenic source that significantly increases the amount of CO₂ in the atmosphere [1]. The cement industry is responsible for the generation of approximately 6% of anthropogenic CO₂ emissions worldwide. Therefore, there is a need to decrease the carbon footprint of the cement industry as it pertains to the production technology by decreasing the OPC clinker produced by itself without decreasing the cement output, considering this reduction in the quantity of OPC produced from the cement industry. In addition, it can significantly affect the reduction in CO₂ emissions and its attendant global warming effect. Furthermore, there is potential for OPC replacement materials to further enhance the reduction in CO₂; therefore, there is a need to increase the scope of the materials that can be admixed with OPC [2]. According to the Cement Chemist Notation (CCN), γ -C₂S is a candidate OPC replacement material in this context, which can further serve the purpose of CO₂ capture. To this end, it is necessary to verify the performance of CO₂ capture by the carbonation of γ -C₂S, and research on the rate of CO₂ diffusion and carbonation in cement is necessary.

This study focuses on the phenomenon of diffusion of CO_2 into hardened cement pastes and the resulting carbonation. The diffusion of CO_2 is a physical process, whereas carbonation is a chemical process. CO_2 is diffused from an area of high CO_2 concentration at the surface to the inside core of the cement mortar with a lower CO_2 concentration [3,4]. Therefore, this study examined whether the diffusion of CO_2 in OPC/ γ - C_2S composite paste specimens follows conventional laws of diffusion (Fick's laws) and how the carbonation products formed in the pores, CaCO_3 , affect the diffusion process and the extent of the CO_2 capture from such bodies. The experiment described below addressed both diffusion and carbonation.

2. Experiments

To examine the diffusion process of CO_2 in the OPC/ γ - C_2S mortar and paste bodies, two experiments were carried out: with mortars and with pastes. Owing to the high porosity of the mortars, the tests with mortar showed carbonation throughout the blocks in a few hours, and hence they were not considered. Instead, the tests with pastes were considered, as described below (Figure 1). The aim of these experiments was to determine the carbonation products formed during diffusion and the depth of carbonation. Four different paste specimens with binder compositions of OPC and γ - C_2S replacements of 0, 5, 15, and 25 wt.% were prepared and moist cured for 1 d. Then, the samples were cured under water for 28 d before being subjected to CO_2 in the carbonation chambers for varying periods. It was expected to vary all the conditions; however, owing to the limitations of the carbonation chamber size, only a temperature of 100 °C was used (leaving out 2 °C and 50 °C), and only a water-to-binder ratio of 0.5 was used (leaving out 0.4 and 0.6, respectively).

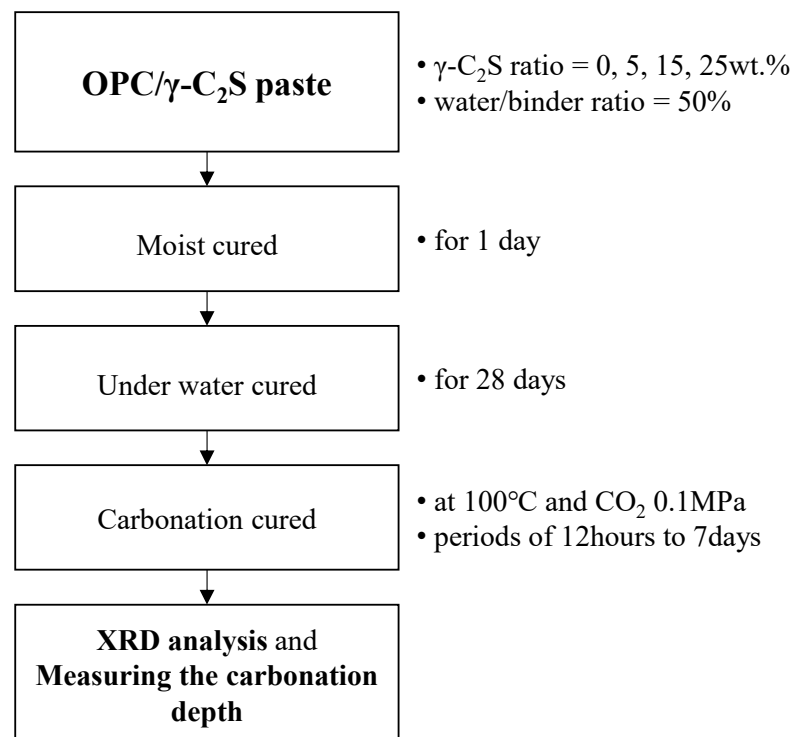


Figure 1. Flow chart of experimental procedure.

2.1. Materials

The materials used in these experiments were OPC, synthetic γ - C_2S , sand, water, and CO_2 . The OPC used was obtained from Sampyo Cement Company Ltd., Samcheok, Republic of Korea, (specific gravity = 3.15, specific surface area = 3300 cm^2/g), and the

synthetic γ -C₂S was a Magnesium Reduction Slag sourced from a local company. The chemical compositions of OPC and γ -C₂S are shown in Tables 1 and 2, respectively.

Table 1. Chemical composition of the OPC used.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Specific Gravity	Blaine (cm ² /g)
22.25	5.33	3.65	64.45	2.45	2.16	0.94	3.15	3300

Table 2. Chemical composition of synthetic γ -C₂S.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI	Density	γ -C ₂ S	Akermanite
51.1	3.70	1.70	47.60	7.20	0	4.10	2.68	91.4	8.6

2.2. Sample Preparation and Analysis

Four different specimen batches were prepared with the material ratios listed in Table 3 for the mortar specimens C₂S0, C₂S5, C₂S15, and C₂S25, and the corresponding ratios of γ -C₂S in the pastes.

Table 3. Experimental mixing ratios for the cement pastes.

Sample No.	Label	Binder		W/B Ratio
		OPC	γ -C ₂ S	Water/Binder
1	C ₂ S0	100	0	0.5
2	C ₂ S5	95	5	
3	C ₂ S15	85	15	
4	C ₂ S25	75	25	

2.3. Carbonation Conditions

The carbonation conditions are summarized in Table 4.

Table 4. Experimental conditions used in carbonation.

Parameter	Value
CO ₂ pressure (MPa)	0.1
Temperature (°C)	100
Relative humidity (% RH)	60

2.4. Diffusion of CO₂ in OPC/ γ -C₂S Specimens

The specimens were left to cure for 1 d in the molds. Then, the specimen was demolded and soaked in water for 28 d. After curing under water, the labeled specimens were carefully placed in the carbonation chamber in a vertical position to ensure the chamber accommodated as many specimens as possible. Then, the chamber was sealed. The CO₂ gas fed from the cylinder was injected into the chamber and the vent valve was opened for approximately 3 min to ensure the chamber was saturated with CO₂. The vent valve was then closed, and the inlet valve was controlled to maintain the build-up of pressure in the chamber. Over the course of the experiment, the pressure in the chamber was regulated to remain constant. The carbonation conditions used were a temperature of 100 °C and relative humidity of 60%, as listed in Table 4. The chamber was opened to withdraw the treated specimens for testing at the end of 12 h, 1 d, 3 d, and 7 d, following the same procedure of venting off CO₂ gas and closing repeated every time carbonation was restarted. Figure 2 shows a schematic of the CO₂ diffusion chambers used in this experiment.

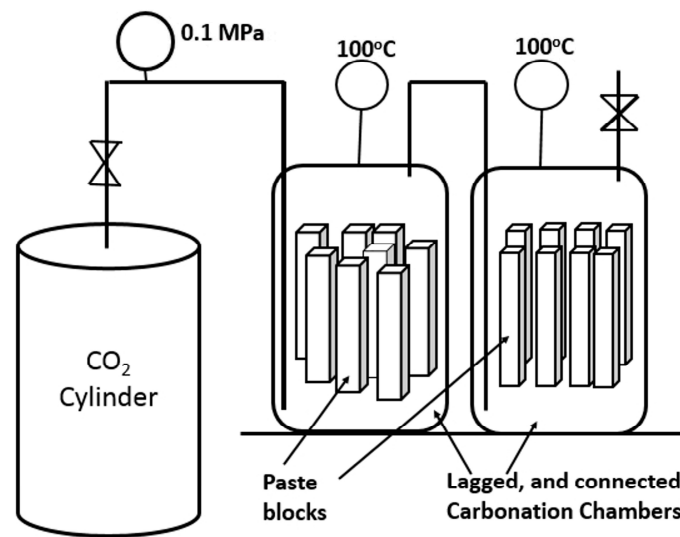


Figure 2. Experimental schematic of diffusion of CO₂.

2.5. Testing Method for Carbonation Depth in Paste Blocks

Each carbonated paste block was broken transversally, and a 2% phenolphthalein solution was sprayed onto freshly broken paste blocks [5–8]. The colorless region indicated the depletion of hydroxyl ions in the pore solution when Ca(OH)₂ reacts with CO₂ to be converted to CaCO₃, whereas the purple regions indicated non-carbonation owing to an abundance of hydroxyl ions.

3. Results and Discussion

3.1. Testing the Carbonation Products Formed in the Pastes

The XRD analyses were conducted on the samples extracted from the colorless and purple regions of the pastes. Figure 3a,b at 24 h and 72 h and Figure 4a,b at 24 h and 72 h, respectively, show the XRD results for the non-carbonated (purple) inner regions and the carbonated (colorless) outer side regions of the blocks. For the sample with no γ -C₂S supplementation, C₂S0, the principal phase reacting in the carbonation of the pastes was portlandite (Ca(OH)₂) and, to a lesser extent, alite (C₃S) and belite (C₂S). The presence of portlandite (Ca(OH)₂) in all the paste blocks was mainly indicated by the characteristic XRD 2-theta-degrees peaks at $2\theta = 18.09^\circ, 28.76^\circ, 32.2^\circ, 47.23^\circ, 50.89^\circ, 54.45^\circ, \text{ and } 71.93^\circ$ [5]. From Figure 3a at 24 h and Figure 3b at 72 h, 3 out of the 6 possible (because the 2θ reading stopped at 60°) peaks at $2\theta = 18.09^\circ, 28.76^\circ, \text{ and } 47.23^\circ$ were clearly visible, thereby representing the Ca(OH)₂ content inside the paste blocks. The presence of CaCO₃ in the paste blocks in Figure 3a,b was indicated by the characteristic peaks of calcite (CaCO₃) at $2\theta = 23.08^\circ, 29.39^\circ, 36.04^\circ, 39.46^\circ, 42.23^\circ, 47.42^\circ, 48.5^\circ, 57.51^\circ, 60.76^\circ, \text{ and } 64.8^\circ$ [9,10]. However, despite the range of 2θ having stopped at 60° and excluding 1 peak, only 2 peaks were visible out of the possible 6 peaks, at $2\theta = 23.08^\circ$ and 48.5° . Notably, the XRD intensities for both Ca(OH)₂ and CaCO₃ for their clear peaks at 24 h were not significantly higher than their corresponding peaks at 72 h after carbonation, thereby indicating that the portlandite in the purple regions of the blocks barely reacted with the CO₂ from the onset of carbonation, through the 24 h to 72 h test times, and hence the near equality of the intensities at the characteristic 2θ peaks. The same observation was made for the alite and belite phases in all the purple-colored parts of the specimens (inner regions), as their peaks at 2θ degrees of approximately 32 to 33 barely changed in intensity between the test periods of 24 and 72 h. This indicates that 72 h was not sufficient for the CO₂ to diffuse to the inner parts of the paste specimens. However, most of the inner regions of the discarded mortar test samples were carbonated for 72 h.

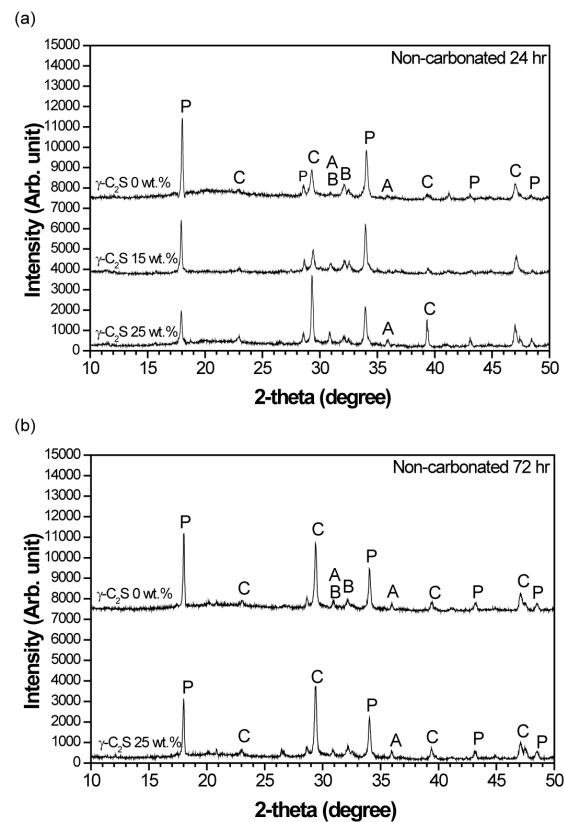


Figure 3. XRD results on the non-carbonated (purple) inner regions of the blocks (a) at 24 h and (b) 72 h. P = portlandite (Ca(OH)₂); C = calcite (CaCO₃); B = belite (C₂S); A = alite (C₃S).

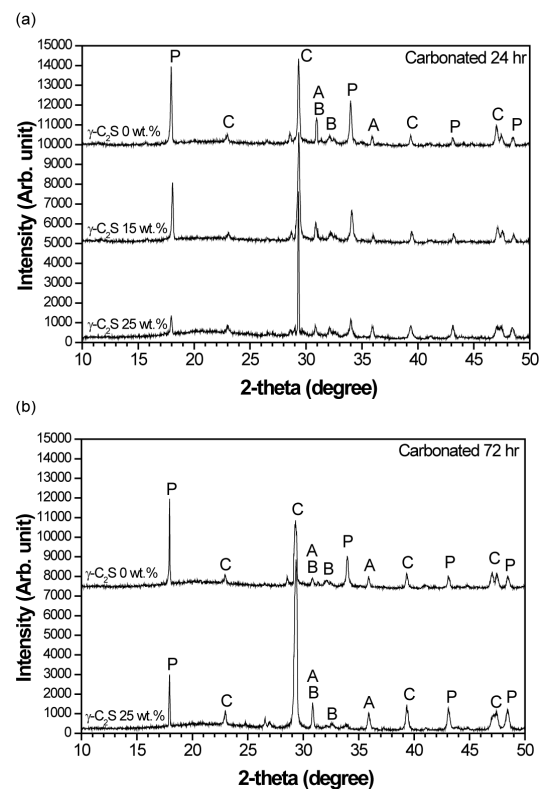
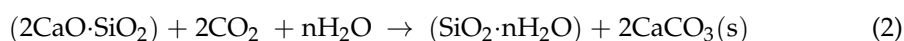
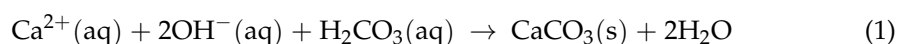


Figure 4. XRD results on the carbonated (colorless) outer regions of the blocks (a) at 24 h and (b) 72 h. P = portlandite (Ca(OH)₂); C = calcite (CaCO₃); B = belite (C₂S); A = alite (C₃S).

When the XRD analyses for the outer parts of the paste specimens were examined in Figure 4a at 24 h and Figure 4b at 72 h, the characteristic peaks for portlandite (2θ degrees of about 18.09° , 28.76° , and 34.23°) significantly decreased from the test time of 24 h to 72 h, and the peaks characteristic of the alite and belite phases (2θ degrees between 32° and 33°) decreased; however, in the same figure and time interval, the characteristic peaks for calcite (CaCO_3) at $2\theta = 29.39^\circ$ were enhanced significantly, whereas its peaks at $2\theta = 23.08^\circ$ and 39.46° appreciably increased, thereby indicating the carbonation reactions occurring on both the portlandite on one part and on the alite and belite phases on the other, from the outer regions of the blocks going inward. The reaction of portlandite with CO_2 after hydration is given in Equation (1) and results in the formation of CaCO_3 , whereas that for alite carbonates is given in Equation (2) and that for belite is given in Equation (3) or Equation (4).



However, the high intensity of the CaCO_3 observed at $2\theta = 29.39^\circ$ indicates that another compound (or phase) other than portlandite, alite, or belite must have contributed to this high intensity. The only other source of CaCO_3 apart from the portlandite, belite, and alite was $\gamma\text{-C}_2\text{S}$; the highest intensity for CaCO_3 at $2\theta = 29.39^\circ$ occurred when the specimen under test was that with the highest ratio of replacement used, 25 wt.% $\gamma\text{-C}_2\text{S}$, thereby proving that $\gamma\text{-C}_2\text{S}$ was responsible for the generation of the additional CaCO_3 in the carbonated regions. Similar observations have been reported in the literature [9,11].

The CaCO_3 formed from all four sources was rendered in the solid state owing to its low solubility. The decreasing XRD intensity for portlandite in the specimen from $\text{C}_2\text{S}0$ to $\text{C}_2\text{S}15$ to $\text{C}_2\text{S}25$ at 24 h shown in Figure 3a shows that most of it was sourced from OPC, and this observation was given credence because its content was lowest in $\text{C}_2\text{S}25$. Additionally, the low intensity of calcite after 24 h of carbonation for the wholly OPC-constituted specimens ($\text{C}_2\text{S}0$) compared to the $\text{C}_2\text{S}15$ and $\text{C}_2\text{S}25$ specimens indicated that the formation of CaCO_3 occurred more in these specimens than in the $\text{C}_2\text{S}0$ specimens at 24 h. Figure 4b shows that the highest amount of calcite was formed at 72 h, and that this was in the $\text{C}_2\text{S}25$ specimen with the highest substitution amount of $\gamma\text{-C}_2\text{S}$ for OPC. Therefore, most of the CaCO_3 was not formed from $\gamma\text{-C}_2\text{S}$ and not portlandite, indicating that portlandite is the main source of CaCO_3 during the carbonation of OPC mortars. In mortars whose OPC has been substituted with $\gamma\text{-C}_2\text{S}$, additional CaCO_3 is formed, indicating that when $\gamma\text{-C}_2\text{S}$ is exposed to CO_2 in moist conditions, CaCO_3 is formed [12,13]. Although supplementary proof for the formation of CaCO_3 from $\gamma\text{-C}_2\text{S}$ is needed in the form of porosity measurements of both the uncarbonated and carbonated regions of the specimens, it was not available.

3.2. Measuring the Carbonation Depth of the Specimen

The carbonated specimens were broken and sprayed with the phenolphthalein indicator, which turned some regions colorless and some purple. The colorless regions indicated that carbonation occurred in these regions owing to the depletion of hydroxyl ions when $\text{Ca}(\text{OH})_2$ reacted with CO_2 to form carbonates (CaCO_3). The regions that turned purple indicated the presence of hydroxyl ions that did not react with CO_2 , thereby indicating that the carbonation reaction had not yet taken place. The measurements of the colorless regions of the paste were performed on all four sides, and the average, $\bar{x}^1$, was taken as

the diffusion depth, as shown in Figure 5. The colorless regions near the surface were carbonated regions, whereas the purple regions were not carbonated. The measurements of the thicknesses of these colored regions that were performed for the collection of all the block specimens are shown in Figure 6, and the averages are listed in Table 5.

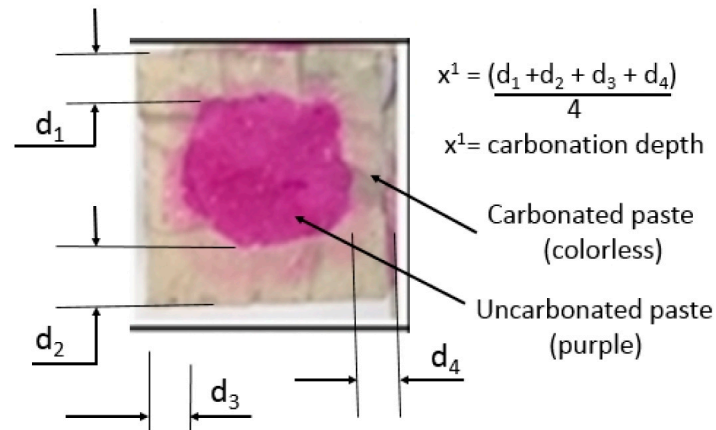


Figure 5. Measuring the carbonation depth of paste blocks.

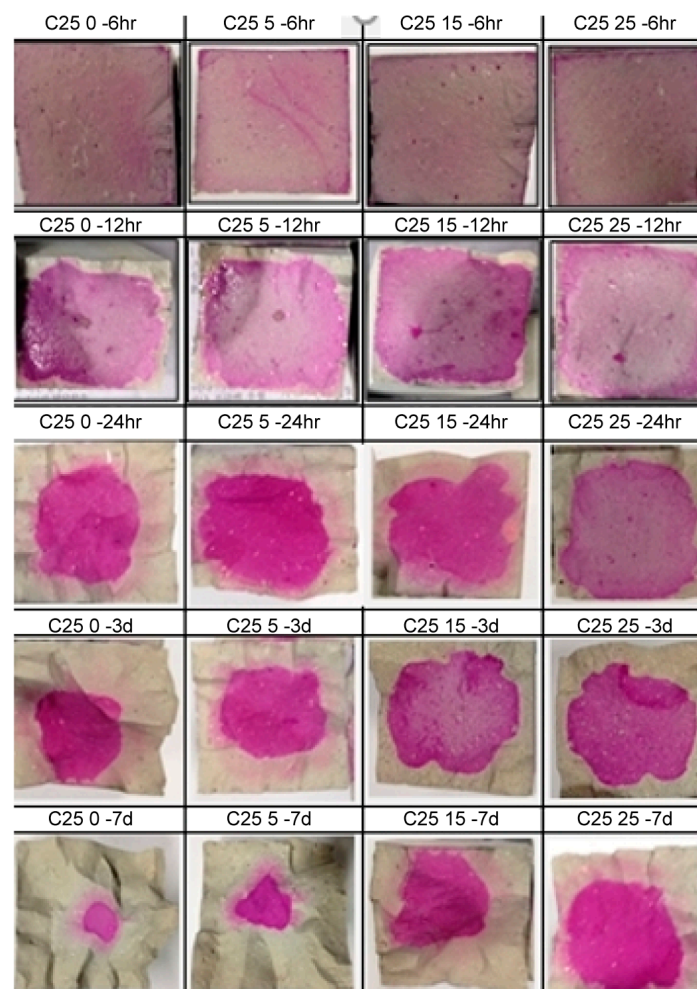


Figure 6. Collection of carbonated specimens sprayed with phenolphthalein indicator, carbonated regions (colorless), and not carbonated regions (purple).

Table 5. Average carbonation depths measured from the specimens.

Type	Average Measured Carbonation Depth x^1 , (mm)			
	12 h	24 h	72 h	7 h
C ₂ S0	3.952	8.916	10.903	14.324
C ₂ S5	3.204	7.552	10.322	10.871
C ₂ S15	2.543	5.236	6.716	9.406
C ₂ S25	2.602	4.554	4.854	7.225

3.3. Calculation of Diffusion Coefficient in Cement Bodies with γ -C₂S

It was difficult to measure the concentration of CO₂ in the paste blocks at the carbonation front using the error function (erf) solution given in Equation (6) derived from Fick's second law, Equation (7). Because the measurements of the CO₂ concentration at the carbonation front were not possible experimentally, the solution using the error function was not used to calculate the CO₂ diffusion coefficient and verify Fick's second law. Many researchers have simplified this difficulty by using Equation (5), such that the diffusivity constant, k , was calculated from the depth of carbonation, x^1 , in addition to the carbonation coefficient using Equation (5) [14–18].

$$x^1 = k\sqrt{t} \quad (5)$$

$$C_{(x,t)} = C_s \left[\operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (6)$$

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (7)$$

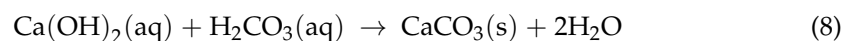
where

C = concentration in dimensions (quantity/volume), e.g., (mol. m⁻³);

t = time in seconds;

x = longitudinal separation distance from uphill to downhill position, e.g., (m);

D = coefficient of diffusion.



Fick's second law states that concentration in the body is a function of both position and time. In other words, an increase in concentration in a cross-section of a unit area with time is simply the difference between the flux in and out of the volume.

Fick's second law implies that the flux of CO₂ into the paste is equal to the flux of CO₂ out plus accumulation, Equation (9).

$$F_{\text{in}} = F_{\text{out}} + \Delta C \quad (9)$$

where Flux in = mass of CO₂ flowing in (kg. m⁻² s⁻¹); flux out = mass of CO₂ flowing out (kg. m⁻² s⁻¹). The accumulation quantity, ΔC , is the amount of CaCO₃ minus the CaO combined during carbonation.

Fick's second law can be proved considering the flux of CO₂ in and out of the paste specimen are not equal if the direction of flow is considered to be unidirectional. On comparing the chemical contents of the uncarbonated pastes in Figure 3a,b with those of the carbonated pastes in Figure 4a,b, it was clear that the carbonation ingress in the paste caused the deposition of CaCO₃ in the pore structure, as shown in Figures 7 and 8, resulting in densification in the carbonated regions. Therefore, because CaCO₃ was proved to have

been formed owing to the carbonation reactions in the OPC and γ -C₂S composite pastes, it indicated that the fluxes in and out of the pastes were not equal.

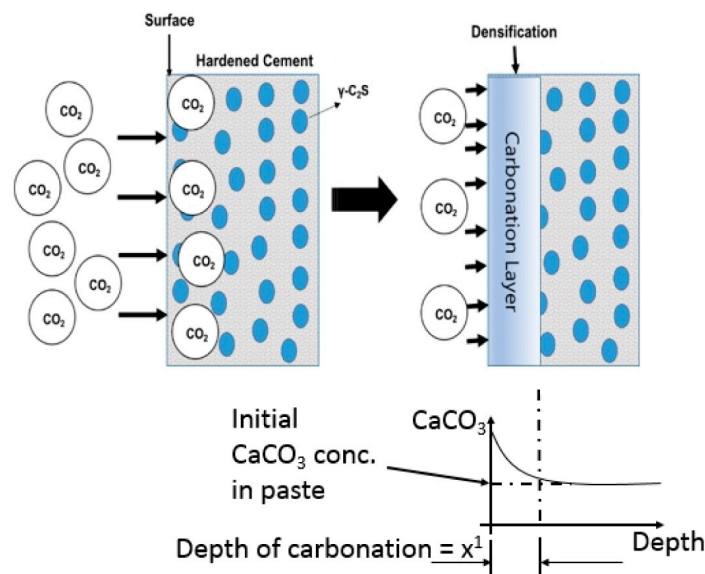


Figure 7. Densification on the surface of the pastes due to carbonation.

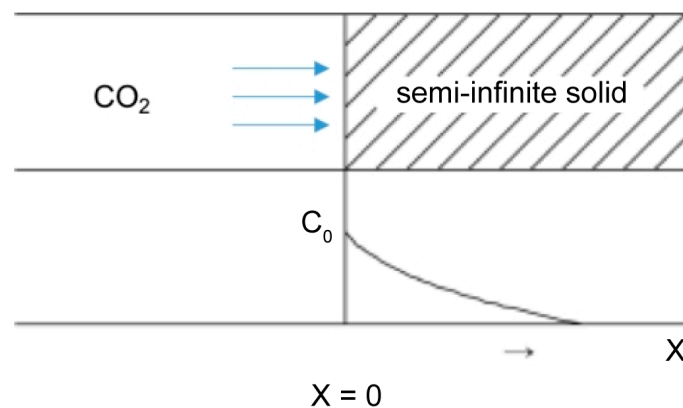


Figure 8. Carbonation in an OPC/ γ -C₂S paste specimen.

If a paste sample under carbonation was considered, as shown in Figure 7, making a material balance and applying the law of conservation of matter to Equation (9) results in Fick's second law, Equation (10).

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad (10)$$

Setting boundary conditions (BC) for the diffusion above,

$$C : t = 0, 0 < x < \infty, C_x = 0 \quad (11)$$

$$C : x = 0, 0 < t < \infty, C_x = C_0 \quad (12)$$

The general solution to such an equation is the error function, Equation (13).

$$\frac{C_x}{C_0} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{2Dt}}\right) \quad (13)$$

Using Equation (13), knowing the surface concentration C_0 and the concentration at distance x , C_x , the diffusion coefficient is calculated as D . However, because not all the data are available, Equation (14), which is a modification of Equation (5), can be used.

$$x^1 = k\sqrt{Dt} \quad (14)$$

This simplifies the calculations because although the concentrations at the carbonation front are not known, the diffusion depth x^1 (mm) and time t (years) are known; therefore, D can be calculated.

Using Equation (14), the diffusion coefficient can be calculated using the time of diffusion and depth of diffusion. The diffusion coefficients calculated for the different paste specimens in the experiment are shown in Figure 9. The diffusion coefficient shows a tendency to increase until the reaction time of 1 day and then decreases. As the substitution rate of γ -C₂S increases, the diffusion coefficient tends to decrease. This is due to CaCO₃, a carbonation product formed in the pores, reducing the porosity of the hardened cement paste, lowering the diffusion coefficient.

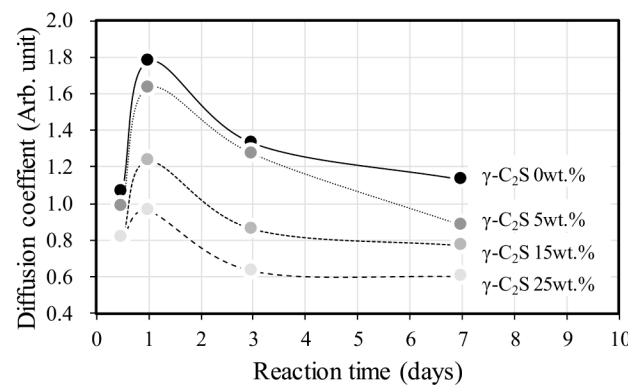


Figure 9. Diffusion coefficients of specimens from measurements taken.

4. Carbon Dioxide Capture by OPC/ γ -C₂S Cementitious Materials

The CO₂ released from cement manufacture mostly comes from burning limestone.



Some of the reported CO₂ emissions from the cement industry come from the transportation of materials (especially raw materials) and power generation. However, when cement is used in construction, it reverses the reaction in Equation (15), such that CaO reacts with CO₂ after a very long time to eventually produce CaCO₃, as given in Equation (16) [19].



Concrete takes up CO₂ when constructing normal houses, infrastructure works such as bridges and roads, and in demolished buildings. The rate of carbonation is difficult to calculate because it depends on several factors. However, because the coefficient D in Equation (14) changes over time, a number of researchers have simplified this by using Equation (17), which is based on a simplification of Fick's second law to obtain the carbonation depth in concrete [19].

$$x = K\sqrt{t} \quad (17)$$

where x is the depth of carbonation (mm), t is the carbonation time (years), and k is the carbonation rate factor.

Different situations require different values of K , that is, for the environment in which the concrete is carbonated, whether it is indoors or outdoors, covered/sheltered or open, and whether it is buried or under water; therefore, there is a need for correction factors,

k , involved in the different cases, all of which contribute to the value of K , such that $K = k_1 \times k_2 \times k_3 \times k_4$.

Different correction values of k were proposed by Lagerblad for a systematic method of calculating CO_2 uptake [19–21].

$$K = k_1 \times k_2 \times k_3 \times k_4 \quad (18)$$

It is sometimes convenient to combine some k values such that $K = k_1 \times k_2 \times k_3$. CO_2 capture can be calculated using Equation (18) [19,21].

$$\text{CO}_2 \text{ capture} = \text{vol of concrete carbonated (m}^3\text{)} \times 0.75 \times C \left(\frac{\text{kg}}{\text{m}^3} \right) \times \text{CaO}(\%) \times \text{mole fraction (CO}_2 / \text{CaO)} \times (K \sqrt{\text{time}(\text{year})}) \quad (19)$$

This method considers the factors that affect carbonation, considering it is a surface process. These factors include the strength class of concrete, environmental classes, factors to correct for the surface treatment of the concrete structure (e.g., paint), and a correction factor for the type of binder used. The 0.75 Equation (18) is owing to the general consideration that only 75% of the CaO in concrete in Equation (16) is capable of carbonation [19,21].

4.1. Correction Factors Used for CO_2 Uptake

The coefficient used to calculate the CO_2 uptake should be corrected because of the different variations encountered in the diffusion, such as the type of cement used, surface treatment (painted walls or not), and whether the concrete is sheltered indoors or outdoors.

4.1.1. Strength Classes Involved

Considering the concrete strength class or category depends on its porosity, four classes of strength have been proposed as follows: concrete structures of low strength, less than 15 MPa; concrete structures of strengths between 15 and 20 MPa, including old houses; concrete structures such as most new homes with strengths of 25–35 MPa; and concrete structures used for infrastructure works such as bridges with strength over 35 MPa. Each of these classes was assigned a factor for calculating the CO_2 uptake.

4.1.2. Environmental Classes Involved

Because carbonation is affected differently when it is either open or under a shelter, factors have also been assigned to the following classes: submerged or wet concrete, indoor concrete, outdoor concrete, sheltered concrete, and buried concrete. Table 6 provides the suggested values for k when using CEM I for different situations [19]. The k values are estimations derived from empirical data; therefore, they are considered when estimating k . This is true considering carbonation increases as the temperature increases, or the indoor walls in countries that receive snow are hotter than their corresponding outdoors; therefore, they have a higher value of k .

Table 6. Suggested k values for concrete surfaces made from CEM I and exposed.

Strength	<15 MPa	15–20 MPa	25–35 MPa	>35 MPa
Wet/submerged	2 mm/ $\sqrt{\text{year}}$	1.0 mm/ $\sqrt{\text{year}}$	0.7 mm/ $\sqrt{\text{year}}$	0.5 mm/ $\sqrt{\text{year}}$
Buried	3 mm/ $\sqrt{\text{year}}$	1.5 mm/ $\sqrt{\text{year}}$	1.0 mm/ $\sqrt{\text{year}}$	0.75 mm/ $\sqrt{\text{year}}$
Exposed	5 mm/ $\sqrt{\text{year}}$	2.5 mm/ $\sqrt{\text{year}}$	1.5 mm/ $\sqrt{\text{year}}$	1 mm/ $\sqrt{\text{year}}$
Sheltered	10 mm/ $\sqrt{\text{year}}$	6 mm/ $\sqrt{\text{year}}$	4 mm/ $\sqrt{\text{year}}$	2.5 mm/ $\sqrt{\text{year}}$
Indoors	15 mm/ $\sqrt{\text{year}}$	9 mm/ $\sqrt{\text{year}}$	6 mm/ $\sqrt{\text{year}}$	3.5 mm/ $\sqrt{\text{year}}$

4.1.3. Correction Factor for Surface Treatment

A correction factor is introduced to cater to concrete that is not bare, such as painted or covered walls. These correction factors are credible because painted surfaces exhibit lower carbonation than bare surfaces. Table 7 lists the values [19].

Table 7. Correction factors for surface treatment.

No	Surface Class	Correction Factor
1	Indoor house concrete	$k \times 0.7$
2	Outdoors house concrete	$k \times 0.9$
3	Infrastructure concrete when painted	$k \times 1.0$

4.1.4. Correction Factor for Type of Binder

The composition of CEM I was that of OPC, and the above values were for this type of cement. Other cements, such as those with higher ratios of fly ash or silica fumes, usually develop a lower porosity than OPC, which can be attributed to the microstructure that accrues. The suggested values are listed in Table 8 [19].

Table 8. Suggested correction factors dependent on the type of cement.

Amount wt. %	<10	10–20	20–30	30–40	40–60	60–80
Limestone		$K \times 1.05$	$K \times 1.10$			
Silica fume	$K \times 1.05$	$K \times 1.10$				
Fly ash		$K \times 1.05$		$K \times 1.10$		
GBFS	1.05	$K \times 1.10$	$K \times 1.15$	$K \times 1.20$	$K \times 1.25$	$K \times 1.30$

4.2. Calculating the CO₂ Uptake in a Concrete Structure

Applicable factors are considered when calculating the CO₂ uptake of a concrete structure. The calculations were supposed to provide the carbonation depth at a given time. It is also assumed that the maximum amount of CaO that can be carbonated in OPC is approximately 75% [19–21]. If the data for the cement paste or cement used are known, the amount of CO₂ uptake is calculated using Equation (18).

$$\text{CO}_2 \text{ uptake} = 0.75 \times C \times \text{CaO} \times (\text{MCO}_2/\text{MCAO}) \times (K/\sqrt{\text{time in years}}) \text{ m}$$

where C = amount of OPC in the concrete kg per m³.

CaO = amount of CaO in cement (wt.%).

MCO₂ = Molar weight of CO₂.

MCAO = Molar weight of CaO

4.3. Calculating the CO₂ Uptake in a Concrete Structure

Calculate the 50-years amount of CO₂ captured by a block of concrete slab (binder is OPC with 10 wt.% γ -C₂S), erected with the following dimensions, 2 m wide, 3 m height, and 0.2 m thickness, standing in the open (un-sheltered). Using Equation (18), the estimated carbonation depth was calculated from the corrected k values in Tables 6–8, while also considering that k₁ is a combined correction factor for the strength and environment:

$K = k_1$ (exposed, (Table 6)) $\times k_2$ (outdoors, (Table 7)) $\times k_3$ (type of cement, (Table 8)).

The values of k₁, k₂, and k₃ were k₁ = 5 mm/ $\sqrt{t}$ (years), k₂ = 0.9, and k₃ = 1.05.

Then, the carbonation depth for 50 years, x₁ = (5 mm/ $\sqrt{50}$ years) $\times$ (0.9) $\times$ (1.05).

The carbonation depth = 33.41 mm in 50 years.

The carbonation depth on both sides of the slab was 33.41 $\times$ 2 = 66.82 mm.

Surface area of slab = $2 \text{ m} \times 3 \text{ m} = 6 \text{ m}^2$.

Therefore, the carbonated volume after 50 years = $(66.82 \text{ mm} \times 1 \text{ m}/1000 \text{ mm}) \times 6 \text{ m}^2 = 0.4 \text{ m}^3$ of carbonated concrete was used.

In mixing 0.4 m^3 of concrete, using the mixing ratios of cement mortar,

Cement: sand: water = 100:300:50.

Amount of cement in 0.4 m^3 concrete = $100/(100 + 300 + 50)$

$0.4 \times 100/450 = 0.089 \text{ m}^3$ cement.

The specific gravity of OPC (Table 1) was 3.15; therefore, the mass of the OPC mixture was $0.089 \text{ m}^3 \times 3150 \text{ Kg}/\text{m}^3 = 280.35 \text{ kg}$ of cement used (and carbonated).

Therefore, the CO_2 captured by concrete of $2 \text{ m} \times 3 \text{ m} \times 0.2 \text{ m}$ with OPC and 10 wt.% $\gamma\text{-C}_2\text{S}$ over 50 years, using Equation (18):

$= 0.75 \times \text{concrete carbonated} \times \text{cement (\%)} \times \text{CaO\%} \times \text{mole ratio } (\text{CO}_2/\text{CaO})$

$= 0.75 \times 0.4 \text{ m}^3 \times 280.35 \text{ kg}/\text{m}^3 \times (0.9) \times 0.66 \times (44/56)$

$= 39.25 \text{ kg}$ of CO_2 captured

Out of a slab volume of $= 2 \text{ m} \times 3 \text{ m} \times 0.2 \text{ m} = 1.2 \text{ m}^3$, only $66.82/\text{mm} \times 1 \text{ m}/1000 \text{ mm} \times 6 \text{ m}^2 = 0.4 \text{ m}^3$. However, the volume of the whole slab $= 2 \text{ m} \times 3 \text{ m} \times 0.2 \text{ m} = 1.2 \text{ m}^3$. Therefore, 0.3341 of the original concrete will have carbonated after 50 years.

The above example calculation assumes that (i) the water of the mixing is only sufficient for hydration and no excess water is available, thereby indicating that no evaporation of water will occur; (ii) the 10 wt.% $\gamma\text{-C}_2\text{S}$ was equivalent to 10 wt.% limestone in the cement to calculate the k^3 ; and (iii) the carbonation on the sides of the slab was negligible.

5. Conclusions

Cement mortars are porous bodies whose pore voids are regarded as interconnected, which can affect the rate of diffusion. Additionally, there are regions in the dry mortar body where fissures exist, such as the interfaces between the sand or aggregate and the mixed binder (cement) when it dries, and these fissures could be connected. All factors have a bearing on the diffusion of gases in the mortar; however, there could be a resistance to diffusion by the solids in the mortar, and the fissures and interconnected pores could allow the flow of gaseous (as well as liquid) substances at the depth of these mortars, resulting in deeper solutes in the gas in the mortar, which increases the penetration depth of the gas and reduces the directional distance for solutes to diffuse from the gas to the mortar solid body. In contrast, OPC mortars with replacement ratios of $\gamma\text{-C}_2\text{S}$ fall under this category of porous mortars, and the fact that the binder mixture contains OPC, which is a hydraulic substance, and $\gamma\text{-C}_2\text{S}$, which is not hydraulic, can complicate diffusion. This questions the behavior of such mortars to diffusion, especially when the gas diffusing is CO_2 , which reacts with the phases in the OPC/ $\gamma\text{-C}_2\text{S}$ mortars, causing densification.

This study is the first to test the conventional laws of diffusion (Fick's laws) for OPC/ $\gamma\text{-C}_2\text{S}$ paste specimens. It was confirmed that the cement concrete with $\gamma\text{-C}_2\text{S}$ can absorb a certain amount of CO_2 for a long time. The following conclusions were drawn from the phenomenon of diffusion of CO_2 into the pastes and the carbonation process:

1. The diffusion of CO_2 in mortars and pastes whose binders are made from OPC and $\gamma\text{-C}_2\text{S}$ generates more calcite (CaCO_3) than that generated by the carbonation of mortars and pastes, whose binder is only OPC.
2. The source of Ca in the above carbonation is CH, C_3S , C_2S , C-S-H, and $\gamma\text{-C}_2\text{S}$, as a higher intensity of calcite was observed when the ratios of $\gamma\text{-C}_2\text{S}$ were varied in the experiments.
3. The generated CaCO_3 deposits in the pore structures of the mortars and pastes result in densification.
4. The deposited CaCO_3 in the pores affects the rates of diffusion of CO_2 in the mortars and pastes, resulting in the densification of such bodies and a decrease in the rate of diffusion, leading to the shutdown of the diffusion process.

5. The diffusion of CO₂ in hardened cement pastes made from OPC and γ -C₂S follows Fick's second law, wherein there is a change in the concentration of CO₂ diffusing at a particular distance with time.
6. OPC with γ -C₂S has the capacity to capture CO₂.

In future work, we will study the CO₂ absorption in a hardened cement body with γ -C₂S according to the change in time and CO₂ concentration. We suggest a mechanism for CO₂ absorption and CO₂ storage in hardened cement bodies according to the long-term hydration progress of the cement body.

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