

# INVESTIGATIONS INTO THE MICROSTRUCTURAL COMPOSITION OF CEMENT PASTE WITH CARBON DIOXIDE SEQUESTRATION.

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**Keywords:** CO<sub>2</sub> sequestration, Carbon Dioxide, Cement Paste, Dry Ice, Chemical Characterization, Calcite precipitation.

**Abstract:** The study examines the impact of different water-to-cement ratios on CO<sub>2</sub> sequestration in cement paste, crushed dry ice was added at 4% by weight of cement, to carbonate paste made with regular Portland cement and tap water. The second approach used bubbling CO<sub>2</sub> gas directly into the mixing vessel. Setting time and compressive strength experiments on 50mm cube specimens have been carried out to investigate the impact of early-age carbonation on physical attributes. Measurements of pH, X-ray Diffraction (XRD), and Thermogravimetric analysis (TGA) have all been used to analyze modifications in the chemical structure of the hardened cement paste brought on by the procedure employed to capture CO<sub>2</sub>. Scanning Electron Microscopy (SEM) has been used to analyze the morphological and chemical differences between non-carbonated and carbonated samples.

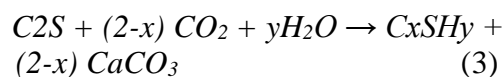
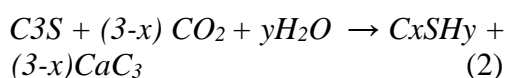
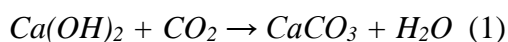
## 1 INTRODUCTION

Greenhouse gas emissions that cause global warming have led to rising sea levels, abnormal temperatures, and increased natural disasters [1]. Among the greenhouse gases, CO<sub>2</sub> has been the most significant contributor. Industries such as chemical, cement, refining, thermal power plant, and steel are responsible for 50% of the emissions globally. Consequently, research aimed at reducing CO<sub>2</sub> emissions is being conducted in these industries, including carbon capture, utilization, and storage (CCUS) technology, which remains the primary method for reducing CO<sub>2</sub> emissions. This technology recognizes captured CO<sub>2</sub> as a reusable entity and recycles it. A typical CCUS method is mineral carbonation, which traps and stores greenhouse gases in the crystal structures of carbonate minerals like CaCO<sub>3</sub>.

Natural minerals or inorganic industrial waste products can interact with CO<sub>2</sub> that has

been gathered from emission sources thanks to technology. Since carbonates, which are by-products of the carbonation reaction of CO<sub>2</sub>, are thermodynamically stable and insoluble, and permit long-term CO<sub>2</sub> fixation. Thus, mineral carbonation technology provides many advantages [2].

Although carbonation can occur naturally during the production of concrete and aid in the absorption of CO<sub>2</sub> emissions, the process is too slow. It may take hundreds of years to fully absorb all emissions. It can also lead to the corrosion of steel reinforcements, ultimately harming the structure. While early-age cement carbonation using CO<sub>2</sub> can strengthen concrete and decrease porosity. Following are the basic chemical reactions (Eqn. (1-3)) occurring in early-age carbonation for permanent CO<sub>2</sub> fixation in concrete [3,4].



Various studies have been conducted to explore the effects of CO<sub>2</sub> on cement and concrete. Pan et al. (2017) have shown increased compressive strength, improved impermeability, and reduced water absorption by 15-30% in CO<sub>2</sub> gas surface-treated cement mortar [5]. Kou et al. (2014) have found that recycled concrete aggregates exposed to CO<sub>2</sub> gas pressurized curing have improved physical properties and a better degree of carbonation [6]. Kunther et al. (2013) have reported significantly reduced mortar swelling in the presence of bicarbonate ions [7]. Jang et al. (2015) have investigated the performance of cement slurry under the action of sodium bicarbonate and have observed improved compressive strength up to 5% NaHCO<sub>3</sub> [8]. Wang et al. (2018) have studied the effect of dry ice on cement hydration and have reported a 30% increase in compressive strength with the addition of 0.6% dry ice [9]. Kwasny et al. (2014) have attempted CO<sub>2</sub> sequestration by directly mixing carbonated water in cement and have observed an increase in the rate of initial hydration of carbonated pastes [10].

However, the larger question of the quantum of CO<sub>2</sub> captured and its effect on the microstructure and chemical properties of hardened cement paste remains unanswered. Although many attempts have been made to sequester CO<sub>2</sub> in cement, sequestering CO<sub>2</sub> in fresh cement paste is not well studied and has served as motivation for the present study.

The current study focuses on the comparative evaluation of the effects of varying water-to-cement (w/c) ratios on microstructure, chemical characteristics, and mechanical properties of modified carbonated cement pastes prepared using dry ice and CO<sub>2</sub> gas bubbling. The dry ice percentage was fixed

to 4% by the weight of the cement. The microstructure and porosity have been verified through Scanning electron microscopy (SEM). Changes in chemical characteristics have been investigated by performing Fourier-transformed Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD). The thermogravimetric analysis (TGA) technique has been used to quantify the quantum of CO<sub>2</sub> sequestered. A compressive strength test (as per ASTM C109[13]), and an initial setting time test (as per ASTM C191-21[14]) have been performed.

## 2 EXPERIMENTAL PROGRAM

The current experimental study has been proposed to investigate the chemical composition, compressive strength, initial setting time, and microstructure of OPC(C), OPC mixed with 4% dry ice(D) by weight of cement, and OPC mixed with CO<sub>2</sub> bubbled(B) in a fresh state, which has been subjected to 10 minutes of treatment at an output pressure of 1.5 bar through a 6mm diameter tube.

### 2.1 Materials

The Ordinary Portland Cement CEM I 52.5N\*, conforming to the BS EN 197-1:2011 (BSI, 2011) [12] standards, has been used in this study, and its chemical composition and other properties are listed in Table 1. According to Bogue calculation (ASTM C150) [15], the cement contains 71.98% C3S, 1.75% C2S, 7.02% C3A, and 12.16% C4AF.

Crushed dry ice, with a CO<sub>2</sub> content of 99.99%, and CO<sub>2</sub> gas, with 99.99% purity, have been employed. All experimental procedures were performed using tap water.

### 2.2 Casting and sample preparations

Batches of cement pastes weighing 3 kilograms have been prepared with a water-to-cement ratio of 0.3, 0.35, 0.4, and 0.45, following ASTM C305[16]. To prepare the paste, cement, and water were weighed with a precision of 0.1 grams, and crushed dry ice was immediately added to prevent sublimation losses.

**Table 1:** Chemical constituents of cement grade CEM I 52.5 N\* [by weight%]

<b>Constituents</b>	<b>CaO</b>	<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>
<b>W%</b>	64.25	18.35	5.25
<b>Constituents</b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>SO<sub>3</sub></b>	<b>MgO</b>
<b>W%</b>	3.95	3.50	1.40
<b>Constituents</b>	<b>Na<sub>2</sub>O</b>	<b>K<sub>2</sub>O</b>	
<b>W%</b>	0.32	0.43	

\*Cement commonly used in India closely confirms to the above.

The dry ice was slowly mixed until fully mixed and sublimated to form a homogeneous paste. For CO<sub>2</sub> bubbling, cement and water were mixed for 5 minutes to form a smooth paste. CO<sub>2</sub> gas was injected for 15 minutes using a 6mm diameter pipe, and slow stirring was employed for proper mixing. Cubic samples measuring 50 mm × 50 mm × 50 mm were cast in both mixes.

After standard curing, hydration was terminated with anhydrous ethanol [9], and samples were dried in a vacuum drying oven at 40 °C, just before the compressive strength test. Microstructure characterization has been done by grinding samples taken from the edge of the crushed cubes with a stone grinder and passing powdered samples through a 75 mm sieve.

## 2.3 Testing methods

### 2.3.1 pH measurement

To ensure that the paste is not acidic pH measurement has been carried out on fresh cement paste using pH paper.

### 2.3.2 Initial Setting Time

The initial setting time has been tested in accordance with ASTM C191[14] using the Vicat's needle apparatus to evaluate the effect of carbonation on the initial setting time of modified carbonated cement paste.

### 2.3.3 X-Ray Diffraction (XRD)

Fractured pieces of cement paste located within 10 mm from the edge have been collected and examined by XRD after the compressive strength test.

The crystallographic texture of normal hydrated and early-age carbonated cement paste has been evaluated using an analytical X'Pert PRO diffractometer equipped with a Cu K $\alpha$  radiation source.

### 2.3.4 Thermogravimetric analysis (TGA)

To compare the thermal decomposition of hydrated cement products from dry ice and direct CO<sub>2</sub> gas bubbling, powders from representative batches have been tested using TGA after 1, 7, and 28 days of casting. The Simultaneous Thermal Analyser 8000 from PerkinElmer has been used to measure weight changes as a function of temperature to estimate the amount of hydration product formed, specifically Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>. The TGA test uses powdered samples of 20 mg heated in open alumina crucibles with a heating rate of 10°C per minute up to 890°C in an inert nitrogen gas atmosphere.

### 2.3.5 Fourier Transform Infrared Spectroscopy (FTIR)

The vibrational bands of cement paste have been investigated using FTIR with the same powdered samples used for previous tests. The FTIR measurements have been conducted using a PerkinElmer Mid-IR and a KBr beam splitter after 1, 7, and 28 days of casting. Spectra have been recorded using a crystal (ZnSe or diamond) in contact with the samples. The data has been analyzed using the Portland Cement Associations (PCA) library.

### 2.3.6 CO<sub>2</sub> Uptake

The mass loss in TGA analysis in the range of 400 °C - 540°C can be attributed to the dehydroxylation of calcium hydroxide [11], which is an indirect measure of the degree of hydration that has been calculated using eqn. (4)

$$CHloss(\%) = \frac{W_{540} - W_{400}}{W_{105}} \quad (4)$$

Where,

W540 = mass loss in TGA at 540 °C,  
W400 = mass loss in TGA at 400 °C, and  
W105 = mass loss in TGA at 105 °C.

The mass loss in TGA analysis in the range of 550 °C - 950 °C is attributed to the dissociation of calcium carbonate, which can be directly attributed to CO<sub>2</sub> captured [11] and has been calculated by eqn. (5)

$$CCloss(\%) = \frac{W_{950} - W_{550}}{W_{105}} \quad (5)$$

Where,

W950 = mass loss in TGA at 950 °C, and  
W550 = mass loss in TGA at 550 °C.

### 2.3.7 Compressive strength

From each group, six specimens of dimensions 50mm x 50 mm x 50 mm were tested at 1, 7, and 28 days after casting following ASTM C109[11] using a 300KN capacity servo-controlled hydraulic Universal Testing Machine.

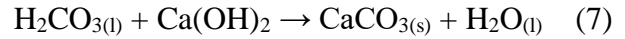
### 2.3.8 Scanning Electron Microscopy (SEM)

Produced hydrated cement pastes have been studied for their microstructure and morphology using Scanning electron microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDXS) to study the effect of carbonation. The JEOL SEM-IT 300 has been used for this purpose, with powdered samples placed on carbon tape and coated with Gold (Au) to minimize charging.

## 3 RESULTS AND DISCUSSIONS

### 3.1 pH measurement

Current experimental studies involve the dissolution of CO<sub>2</sub> in the cement paste using physiochemical processes such as:



The intermediate product H<sub>2</sub>CO<sub>3</sub> so formed is acidic. Thus, to ensure that the above method is not harmful to reinforcing steel during upscaling. pH measurement has been performed on all samples using pH paper. It has been observed that the pH of all the paste samples was above 11, including samples of different water-to-cement ratios tested just after carbonation, as shown in Figure 1. Thereafter the pH value was observed to increase for carbonated specimens. The results were in accordance with the amount of calcium hydroxide observed in the TGA analysis.

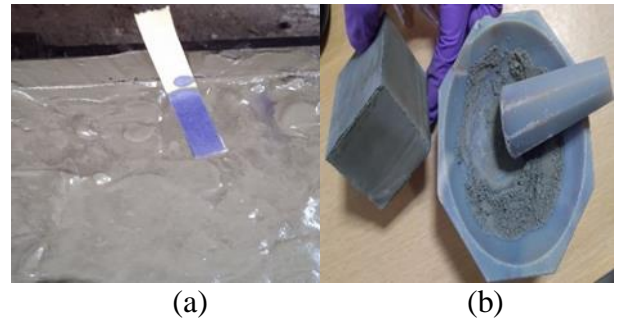


Figure 1. (a) the pH test performed using pH paper on fresh cement paste. (b) shows the powdered sample preparation using a stone pestle and a 50mm cube specimen used for the compressive strength test.

### 3.2 Initial setting time

To study the changes in the initial setting time due to carbonation, an initial setting time test (as per ASTM c191[14]) was performed on all samples for 4% dry ice, bubbled co<sub>2</sub> gas, and control specimens, for varying water-to-cement ratios.

It has been observed that specimens manufactured with bubbled co<sub>2</sub> gas showed an average increase of 10,8% in the initial setting time compared to control specimens. For specimens made with dry ice, the initial setting time decreased by 12% compared to the control specimen. This decrease in setting time can be attributed to the change in temperature

caused by dry ice addition.

The setting time for carbonated specimens with varying water-to-cement ratios also showed a similar trend as that of the control specimens of respective w/c ratios, as shown in Figure 2. The initial setting time for dry ice mixed samples corresponding to different w/c ratios showed a decreasing trend, that is setting time for dry ice mixed specimen with a w/c ratio of 0.3 was the lowest and the setting time for dry ice mixed specimen with w/c ratio 0.45 was highest among all dry ice mixed specimen, but lower than that of control specimen of respective w/c ratio.

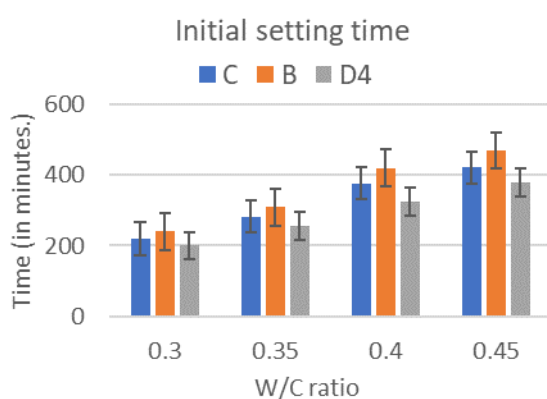


Figure 2. Variation of initial setting time for control (C), bubbled CO<sub>2</sub> gas(B), and 4% dry ice by weight of cement specimens, with respect to water-to-cement ratios.

### 3.4 Compressive strength

To study the effect of the degree of carbonation on compressive strength, a compressive strength test has been performed on specimens of size 50 mm cube (as per ASTM C109[13]).

Bubbled CO<sub>2</sub> gas specimen showed the highest compressive strength compared to dry ice and control cement paste for respective water-to-cement ratios at the end of 28 days. The dry ice specimen also showed a higher compressive strength compared to the control specimen but lesser than the bubbled specimen at the end of 28 days. The 1-day compressive strength of the bubbled specimen was higher than the control specimen. The dry ice gave a

comparable strength to that of the control specimens at the end of day 1.

The compressive strength of bubbled CO<sub>2</sub> gas specimen was 8-10% higher than the control specimen, whereas the dry ice specimen was 6-8% higher than the control specimen of respective w/c ratio at the end of 28 days. With the increase in the w/c ratio, both bubbled and dry ice specimens showed a similar decrease in strength as that of the control cement paste.

### 3.5 FTIR & SEM

FTIR test's peaks were identified and assigned to various bond stretching and vibrations in accordance with Portland Cement Associations (PCA) library.

The O-H bond peak observed at 3629 cm<sup>-1</sup> in Ca(OH)<sub>2</sub> has been attributed to hydration progress, with the peak shifting to 3642 cm<sup>-1</sup> for bubbling and dry ice, and to 3645 cm<sup>-1</sup> for all samples after 1, 7, and 28 days. Other hydroxyl compounds have exhibited strong O-H stretching of the free water. The peak observed at 1643 cm<sup>-1</sup> for the H-O-H bond bending vibration has remained unchanged over time, indicating the presence of unbound water in all the specimens. The peaks observed at 1416 cm<sup>-1</sup>, 1114 cm<sup>-1</sup>, 872 cm<sup>-1</sup>, and 817 cm<sup>-1</sup>, corresponding to the in-plane bending and asymmetric, symmetric, and stretching/bending vibrations of the carbonate ion, have shifted towards 1410 cm<sup>-1</sup> in carbonated mixes over time. The peak around 940 cm<sup>-1</sup>, associated with the Si-O-Ca vibrational stretching of the C-S-H gel, has shifted to 948 cm<sup>-1</sup> on day 1 for bubbled specimens.

Higher calcite peaks observed in FTIR were attributed to early calcite ion precipitation in carbonated specimens, which also act as deposition sites for hydration products. These results have also been confirmed through sem imaging.

### 3.6 TGA & CO<sub>2</sub> uptake

The mass loss in TGA analysis between the temperature range of 400 °C – 540 °C has been

attributed to the decomposition of calcium hydroxide, which can be directly correlated to the progress in the degree of hydration. Similarly, the mass loss in the temperature range of 550 °C – 950 °C has been attributed to the decomposition of calcium carbonate, which can be taken as a measure of CO<sub>2</sub> sequestered in specimen [11].

The maximum amount of mass loss due to calcium carbonate decomposition was observed in dry ice specimens for all w/c ratios. This indicates that the maximum amount of CO<sub>2</sub> sequestered was using dry ice. The TGA analysis of bubbled CO<sub>2</sub> gas specimen also showed a higher amount of carbonate loss compared to the control specimen, indicating that both methods can be used to sequester CO<sub>2</sub> in cement paste.

The mass loss due to carbonate increased with an increase in the w/c ratio, indicating that increasing the water content helps in the dissolution of larger amounts of CO<sub>2</sub> into the paste, eventually leading to higher calcite precipitation.

Non-carbonated control specimens also showed mass loss due to calcium carbonate, which was attributed to the presence of residual calcium carbonate during the cement manufacturing process.

## 8 CONCLUSIONS

The effect of change in water-to-cement ratio on carbon dioxide sequestration potential using 4% dry ice by weight of cement in the mix and by bubbling CO<sub>2</sub> gas in fresh cement paste has been studied through the current experimental work, and the following conclusions have been made:

1. Increasing the w/c ratio increases the amount of CO<sub>2</sub> sequestered in both methods for the same degree of carbonation, that is, by keeping the amount of dry ice and CO<sub>2</sub> gas constant.
2. The amount of CaCO<sub>3</sub> produced is 4-6% higher for bubbled CO<sub>2</sub> gas specimen with respect to the control corresponding specimen and for the dry ice specimen 3- 5% higher

compared to the corresponding control specimen. Calcite precipitation increases with the increase in the w/c ratio.

3. The compressive strength of bubbled CO<sub>2</sub> gas carbonated specimens is 8-10% higher than that of non-carbonated specimens and the percentage increases with a decrease in the w/c ratio as compared to the control specimen.
4. The compressive strength of dry ice mixed specimens is 6-8 % higher as compared to the control specimen at the end of 28 days.
5. The initial setting time for bubbled CO<sub>2</sub> gas specimen is higher than the control specimen, and that of the dry ice mixed specimen is lower than the control specimen. The trend remains similar for varying w/c ratios.

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