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Potential for carbon dioxide sequestration in wet concrete mixes

I.I. Milanova (1) and E. Kearsley (1)
(1) Department of Civil Engineering, University of Pretoria

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The novel concept of CO_2 sequestration in wet concrete mixes relies on permanent capture and storage of CO_2 in the form of solid limestone within the concrete matrix. This technology is designed to alleviate a portion of the carbon footprint while ensuring that the strength and integrity of the concrete is not impaired. Sequestration occurs when CO_2 is introduced into the freshly hydrating cement paste where it reacts with the main calcium silicate phases, forming calcite and silicate hydrate gel. In this study, CO_2 was added to fresh concrete and mortar mixes during mixing. Two forms of CO_2 addition were utilised: the first comprised carbonating the mix water and the second, CO_2 within its solid state, commonly referred to as dry ice. The effects of CO_2 absorption of mixes were physically and chemically investigated during a series of comparative tests. Results indicate a strong potential for concrete mixes treated with dry ice to reach acceptable flexural and compressive strengths after 28 days,

Keywords:concrete, carbon dioxide, carbonation.

Journal contact details:

Block D, Lone Creek, Waterfall Park, Bekker Road, Midrand, 1682
PO Box 168, Halfway House, 1685, South Africa
☎ +27 11 315 0300
✉ info@cemcon-sa.org.za
www.cemcon-sa.org.za

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ABSTRACT

The novel concept of CO_2 sequestration in wet concrete mixes relies on permanent capture and storage of CO_2 in the form of solid limestone within the concrete matrix. This technology is designed to alleviate a portion of the carbon footprint while ensuring that the strength and integrity of the concrete is not impaired. Sequestration occurs when CO_2 is introduced into the freshly hydrating cement paste where it reacts with the main calcium silicate phases, forming calcite and silicate hydrate gel. In this study, CO_2 was added to fresh concrete and mortar mixes during mixing. Two forms of CO_2 addition were utilised: the first comprised carbonating the mix water and the second, CO_2 within its solid state, commonly referred to as dry ice. The effects of CO_2 absorption of mixes were physically and chemically investigated during a series of comparative tests. Results indicate a strong potential for concrete mixes treated with dry ice to reach acceptable flexural and compressive strengths after 28 days,

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1. INTRODUCTION

The anthropogenic CO_2 load is an increasingly problematic secondary effect of the modern world. Cement production alone is responsible for nearly 7% of global CO_2 emissions [14]. In an attempt to combat this, Carbon Capture and Storage (CCS) has become a popular field of study in recent years [5]. As concrete is the most universal building material, storage of CO_2 within it offers massive promise, offering a 'greener' solution to current industrial practices. During the production of cement, a calcination process occurs wherein calcite ($CaCO_3$) is transformed into calcium oxide (CaO) as indicated in Equation 1.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{Equation (1)}$$

This reaction, along with the energy necessary to run the cement kiln, together comprise the CO_2 released into the atmosphere. The chemical makeup of concrete has a direct effect upon its strength and durability. During the carbonation of freshly hydrating cement paste, the main calcium silicate phases present in the cement and the added CO_2 react together to form calcite as well as silicate hydrate gel as shown in Equation 2 and 3 respectively.

$$3CaO{\cdot}SiO_2 + 3CO_2 + XH_2O \rightarrow SiO_3{\cdot}XH_2O + 3CaCO_3 \qquad \text{Equation (2)}$$

$$2CaO{\cdot}SiO_2 + 2CO_2 + XH_2O \rightarrow SiO_3{\cdot}XH_2O + 2CaCO_3 \qquad \text{Equation (3)}$$

This reaction begins during the hydration of the cementitious phases with the added CO_2. The products formed during these hydration reactions are calcium ions (Ca^+) and carbonate ions (CO_3^{-2}) respectively. When these ions bond together, they undergo an exothermic carbonation reaction in which calcite is produced as seen in Equation 4. This carbonation reaction is diffusion limited when it takes place in cement, responding with CaO individually as well as in the C-S-H phase [5].

$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3 \qquad \text{Equation (4)}$$

Various experimentation with CCS in concrete have been undertaken, with adjustments made in the means and methods of CO_2 sequestration. From these, it was concluded that introducing CO_2 to wet concrete during the mixing stage would utilize CCS on a larger scale, as opposed to it being exposed to mature concrete. The addition of CO_2 to the concrete mix thus eventually accounts for the formation of calcite within the hardened concrete matrix. Moreover, the fresh properties of the mix are also said to experience an impact, such as accelerated drying times and decreased alkalinity. Further experiments [5] saw increased early-age compressive strengths of concrete cubes treated with varying concentrations of solid CO_2 during the mixing phase. This strength increase is attributed to the formation of calcite within the hardened concrete. When carbonation takes place within a concrete matrix, carbonic acid is formed during the reaction shown in Equation 5:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad \text{Equation (5)}$$

The creation of this acid results in a pH drop of the pore solution which is originally of a high alkalinity, usually a pH reading of above 12.5. Carbonation of hydrated Portland cement paste can reduce this value to as low as 8.3, which may be deemed problematic as the depassivation threshold of reinforcing steel is approximately 9.5 [7], thus potentially resulting in accelerated corrosion of reinforcement. However, this is said to be a possibility only when CO_2 is exposed to mature concrete and its hydration phases [6]. Furthermore, the porosity of carbonated cement paste may change. This change can be manifested as a decrease in the case of Portland cement and an increase in the case of blended cement paste [4]. The chemical changes arising in cement paste when it is carbonated can be analysed using X-ray powder diffraction (XRD) and Thermogravimetric analysis (TGA). XRD is a reliable method to use to identify the phases present in the cement, as well as trends in the production and consumption of secondary hydration products like portlandite and ettringite [2]. TGA portrays the change of mass of a material sample as a function of time over a temperature heating rate.

2. EXPERIMENTAL WORK

2.1 Preparation of Mortar

The mortar mix allowed for a comparative, small scale representation of the concrete mix which could be chemically analysed while disregarding chemically inert aggregates. The mix design for one batch of mortar consisting of a set of three prismatic specimens comprised of 450 g of CEM II with a 20 % fly ash content, 1350 g of ISO standard sand and 225 g of water and possessed a 0.5 water:binder ratio. Each prismatic specimen had dimensions of 40 mm x 40 mm x 160 mm. As the ultimate goal of this experiment was to test the structural suitability of a greener and more environmentally friendly building material, CEM II was chosen as it already contains fly ash as an admixture.

Originally, three test mixes were created: the reference mix (Mix T) with the standard mix design, Mix A wherein one litre of mix water was carbonated using approximately 3.3 litres of CO_2 and Mix B wherein one litre of mix water was carbonated using approximately 6 litres of CO_2. Mix water was carbonated one litre at a time using commercially available home carbonation equipment. Subsequently, it was decided to include two more mortar mixes, to which CO_2 was introduced during the mixing stage in the form of dry ice in additions of 200 g and 300 g respectively per litre of mix water.

Specimens from Mixes T, A and B were prepared for curing ages 1, 3, 7 and 14 days, while specimens from Mixes C and D were prepared for curing ages 1, 3, 7, 14 and 28 days. Directly following the mixing stage, the wet mortar from each mix was tested for its pH using an electronic pH probe and subsequently for its workability using the flow table test (ASTM C230). Mortar specimens were left to set for 24 hours in a humidity and temperature controlled room, whereafter they remained in a water bath until their respective curing ages were reached.

Flexural strength testing followed by compressive strength testing were performed on the mortar specimens at the stipulated curing ages (EN 196-1). Thermogravimetric analyses were performed on mortar samples at their various curing ages. Pieces from the mortar specimens were stored in an oven at 60 °C for a duration of 24 hours to expel any remaining water, and thereafter ground into powder and stored in sealed, clearly marked packets to be used during TGA. During the test, the sample was covered by the TGA furnace and heated to a temperature of 800 °C at a rate of 20 °C/min in the presence of Nitrogen gas to induce chemical decomposition of the material. XRD analysis was performed on samples from each of the five mortar mixes at a curing age of 14 days.

2.2 Preparation of Concrete

A simple concrete mix design, with a water:binder ratio of 0.5 was chosen. The mix design per cubic meter comprised of 400 kg CEM II (containing 20 % fly ash), 200 kg of water, 900 kg of dolomite sand and 900 kg of 10 mm dolomite aggregate. A reference mix (Mix 1) and a CO_2 treated mix (Mix 2) were produced in order to run comparative tests. The CO_2 for Mix 2 was added in the form of carbonated mix water, with approximately 3.3 litres of CO_2 used per litre of mix water. Directly following the mixing stage, both concrete mixes were tested for their pH level using an electronic pH probe. Thereafter slump tests were performed for each mix (SANS 5862-1) in the attempt to observe potential relationships between the added CO_2 and the resulting workability of the mix. Concrete specimens were cast into the required moulds and left to set for 24 hours in a humidity and temperature controlled room, whereafter they remained in a water bath until their respective curing ages were reached.

The CO_2 treated concrete was examined in order to determine whether its transformed chemical composition would impact its durability in any way. Test specimens comprised of circular disks, approximately 70 mm in diameter and 30 mm in thickness, cored and cut from previously cast cubes. Specimens were left in an oven for 7 days at a temperature of 50 °C in order to remove an excess moisture within the sample. The same set of specimens were used first in the oxygen permeability test, and later in the water sorptivity test.

An investigation of the impact of carbonation on the concrete's pH level was conducted through an experiment in which 300 mm x 300 mm x 200 mm concrete specimens were cast from Mix 1 and Mix 2 and reinforcing was positioned within each specimen such as to create a voltaic cell. Sodium Chloride (NaCl) solution was periodically poured on the top surface of each specimen so as to accelerate the natural rusting process by inducing cyclic wetting and drying of the concrete. This corrosion experiment continued for 28 days, after which both specimens were broken in half and the exposed inner surface sprayed with a phenolphthalein solution to give an indication of the concrete's pH level. Thereafter, the reinforcement bars were cleaned from rust and weighed to determine the degree of corrosion suffered.

3. ANALYSIS OF RESULTS

3.1 Mortar Results

Analysis of the mortar results suggest a higher rate of CO_2 sequestration taking place in Mix C and Mix D. This is indicated in Table 1 by lower pH values and workability as well as greater amounts of calcite within the samples as predicted.

Flexural and compressive strength of the prismatic specimens from each mix are portrayed in Figure 1 and Figure 2 respectively. Prisms from the reference mix appear to have the highest strengths, followed by those from Mix A and Mix B, which increase in relative flexural and compressive strength with time. Mixes C and D indicate an even smaller retention of the reference mix's flexural and compressive strength at early age. The general decline in strengths between prism of the reference mix and those of Mixes A, B, C and D can be attributed to the previous exposure to CO_2. However, their steady increase in percentage flexural and compressive strength of the reference mix suggests the possibility of minimal strength differences between these mixes and the reference mix at later ages.

Results thus imply that the addition of solid CO_2 offers a more efficient sequestration method compared to the carbonation of mix water.

TGA curves relating percentage weight loss of the five samples at 14 days curing age as a function of temperature are indicated in Figure 3. A distinct dip is visible in every curve between 600 °C and 800 °C, indicating the temperature region of calcite decomposition (decarbonation). The varying amounts of

Table 1: Summary of mortar results.

	Mix T	Mix A	Mix B	Mix C	Mix D
pH value	12.96	12.53	12.50	11.35	11.02
Flow (%)	183	186	195	138	115
Weight of calcite within sample at 14 days (%)	1.48	1.79	1.84	1.99	2.38

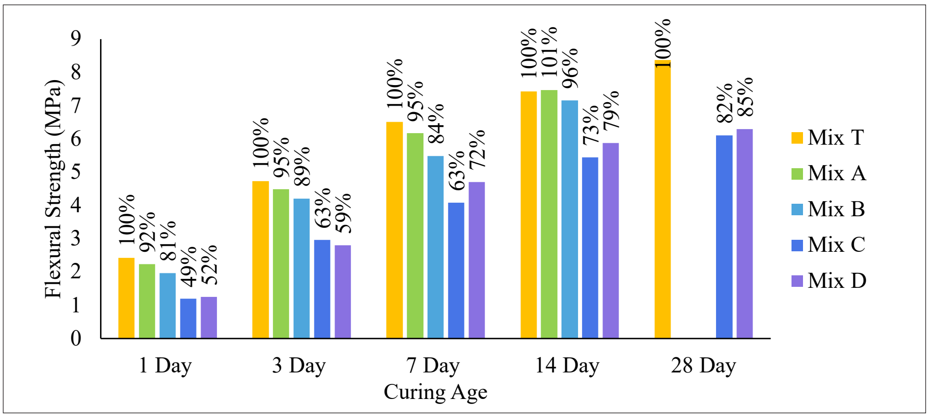


Figure 1: Flexural strength of mortar prisms

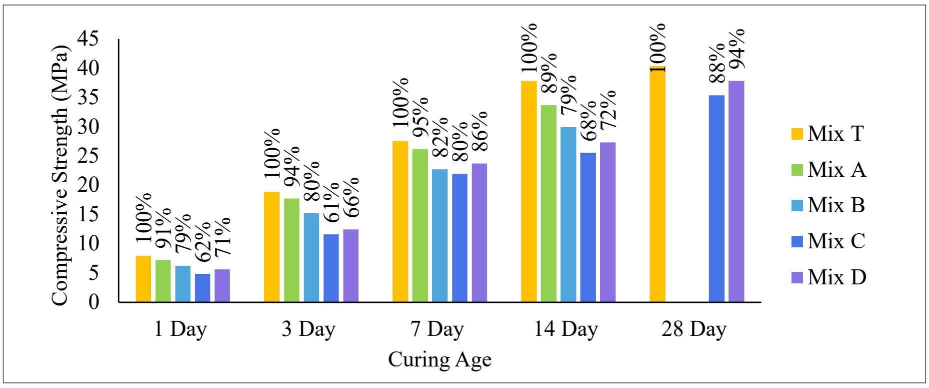


Figure 2: Compressive strength of mortar prisms.

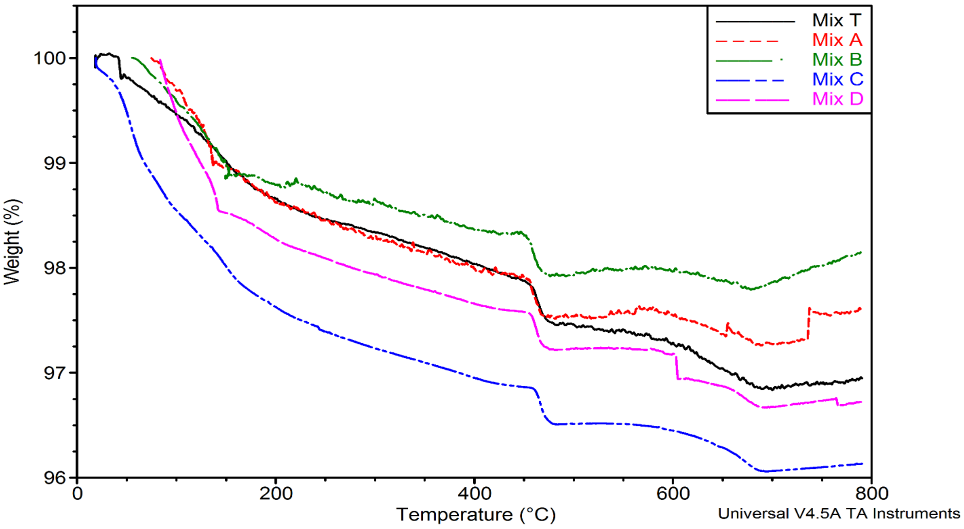


Table 2: Summary of results from oxygen permeability and water sorptivity testing.

	Mix 1	Mix 2
Oxygen Permeability Index	10.53	10.50
Water Sorptivity Index (mm/hr$^{0.5}$)	8.68	9.95
Porosity (%)	9.49	10.62

calcite within the mortar, most prominent in the case of Mix C and Mix D, within the mortar allude to the fact that CO_2 has been captured inside the mortar as anticipated. The percentage mass loss due to decarbonation can be further deduced as a result of this.

3.2 Concrete Results

Comparison of the concrete results revealed a certain difference in performance between the CO_2 treated mix and the reference one. The pH readings for Mix 1 and Mix 2 were 13.30 and 12.68 respectively. This discrepancy in values indicate a change in original concrete alkalinity which can only be attributed to the CO_2 addition. While the lower value remains higher than the depassivation threshold of reinforcing, problems may arise when the concrete sets and hardens as the drop in alkalinity may potentially continue as a result of the hydration of products inside the concrete matrix. The slump was determined as an indication of the workability of the fresh concrete. The slump was measured as 90 mm for Mix 1 and 105 mm for Mix 2. The CO_2 addition in Mix 2 thus increased the workability with more than 15 %. This may be attributed to improved lubrication of the mix as a result of the entrained air present from carbonation of the mix water. The results for oxygen permeability and water sorptivity testing are summarised in Table 2. General observation of these values indicates good durability characteristics in both mixes. The permeability of concrete defines its ability to resist flow of a fluid within its hardened matrix. Permeability of Mixes 1 and 2 appears to be practically equivalent, with no significant variance which may be linked to the CO_2 addition.

Considering the data, sorptivity and porosity are depicted to be higher in the case of Mix 2. This behaviour is in line with the findings of [4], which states that carbonation may induce an increase in the pore structure of concrete produced with blended cements. While a rise in sorptivity and porosity in concrete are not ideal, the results of Mix 2 are still within the limits of good practice. However, care should be taken in cases where reinforcement is present or higher CO_2 dosages are desired in the mix design.During the wetting-dry cycles of the accelerated corrosion test, qualitative changes were observed as a rust stain on the surface of the Mix 2 specimen (significantly larger than that on the surface of the Mix 1 specimen) began to appear. Figure 4 depicts, the specimens when they were halved d sprayed with phenolphthalein solution.

Considering the specimen of Mix 1, there is a very fine colourless strip at the top right-hand surface which signifies a small reduction in pH in this region. A pH drop was only experienced near the top of the specimen, and any potential corrosion of reinforcement is limited to that region. The previously CO_2 treated specimen of Mix 2, in contrast, displays an acidic region of substantial size near the top of its cross-section, entirely surrounding the first reinforcement bar. The drop in alkalinity caused by the extraction of sodium chloride ions within the NaCl solution into the concrete, further resulted in corrosion induced mass loss of the fixed reinforcement bars. The

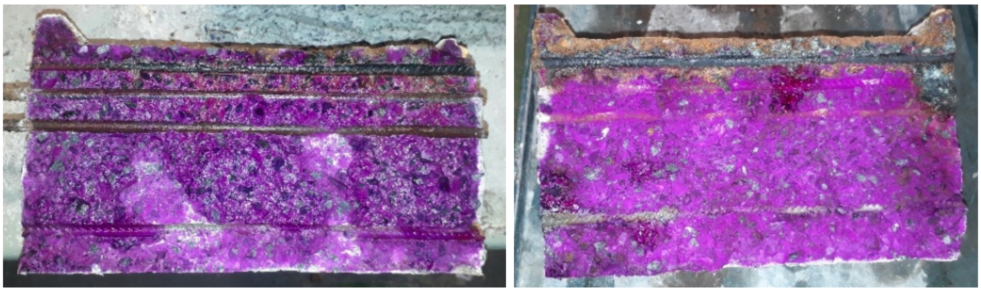
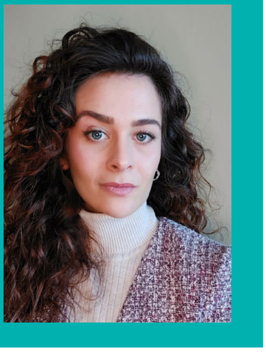


Figure 4: Inner surface of Mix 1 (left) and Mix 2 (right) specimens.

top reinforcement bar of Mix 1 experienced a mass loss of 2.07 % as opposed to that of Mix 2 which experienced a 6.41 % mass loss. Acidity was thus able to diffuse through a greater distance from the top surface of the Mix 2 specimen, similarly affecting the rest of the reinforcement bars, albeit to a lesser degree. This creates cause for concern as any reinforcing within CO_2 treated cement is at a greater risk for corrosion.

ELSABE KEARSLEY is Professor in Civil Engineering at the University of Pretoria. She is a registered Professional Engineer, and she holds a PhD from Leeds University. For the last 25 years her research has focused on reducing the environmental impact of the cement and concrete industry.

IVONA MILANOVA is a civil engineering graduate from UP and is currently enrolled at UP for a part-time BEng Honours in water resources engineering. She works as project manager at Aquaplan Water Treatment Services. She is a ardent environmentalist with a high regard for nature and green technologies.



4. CONCLUSIONS

Treating mortar and concrete with CO_2 during mixing results in carbonation of the cement and alters the chemical composition of the mix on an elemental level. TGA results exhibited a considerable mass percentage of the anticipated calcite within samples of mortar mixed with dry ice during decarbonation of the sample. From XRD analyses calcite was found to exist in the least amounts within the reference mix, with increasing dosages present in Mixes A to D, correlating to the sequestration method used and difference in carbon content. Better CO_2 sequestration appears to have taken place in Mixes C and D where it was added as dry ice.

The strengths of mortar prisms from Mixes C and D showed substantially weaker results for early-age strength gain, however, a prominent increase in strength was noticed toward the 28-day mark. This shows potential when considering strength development at later ages. In terms of durability aspects, it was found that sorptivity and porosity increased in the case of the CO_2 treated concrete mix, suggesting potential problems in the long-term durability of the concrete. This was further supported when results showed corrosion occurred at a faster rate in the CO_2 treated mix due to decreased alkalinity within it. Outcomes of the investigation prove that it is possible to sequestrate CO_2 into mortar and concrete during mixing without significant negative consequences on the material properties, especially in their later age. This, however, is only true on condition that no steel reinforcement is present in CO_2 sequestrated concrete. **CB**

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