Effects of accelerated carbonation curing on CO₂ sequestration and on the compressive strength of concrete masonry units

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ABSTRACT: The global consumption of Portland cement has risen to over 4 billion tonnes per annum. Its manufacture is energy and carbon intensive and approximately 900 kg of CO₂ is emitted into the atmosphere for each tonne of Portland cement produced. The International Energy Agency (IEA) roadmap sets out a goal to reduce emissions due to cement production to 18% below 2006 levels by 2050.

Concrete has the potential to re-absorb CO₂ by the process of carbonation, where it reacts with CaO in the concrete to form calcium carbonate. Accelerated carbonation curing (ACC) is a technique for curing fresh concrete that can sequester CO₂. ACC of concrete masonry units (CMU’s) can reduce the embodied carbon footprint and play a major role in sustainability by reducing global CO₂ emissions due to cement production to 18% below 2006 levels by 2050.

Experimental work was carried out which involved the ACC of CMU’s at a CO₂ concentration of 50% over various time intervals and exposure conditions. It was calculated that the maximum possible CO₂ uptake potential of the cement was approximately 49.5%. A CO₂ uptake of 23% per mass of cement was achieved after 7 days of ACC along with compressive strength increases of 15.4% and 28% for ACC samples at 7 and 28 days respectively. The study found that the greatest compressive strength increase occurred between 4 and 24 hours. After 24 hours the ACC process showed a similar proportional rate of strength gain over time when compared to the control.

The study shows that ACC is different from weathering carbonation as it accelerates the hydration reaction of the unhydrated cement phases C₃S and C₄S producing rapid strength gains. Weathering carbonation occurs in concrete after the hydration process has been predominately completed and results in the decalcification of C-S-H and the formation of silica gel which is detrimental to the cement paste.

KEY WORDS: CO₂, sequestration, uptake, cement, accelerated carbonation curing, ACC, concrete masonry units, CMU’s, carbon capture and storage, CCS.

1 INTRODUCTION

Due to production of over 4 billion tonnes of Portland cement per year, the global cement industry is responsible for c. 5% of anthropogenic CO₂ emissions [1,2]. Global CO₂ emissions have been increasing significantly over the past two hundred years, reaching 32.5Gt of CO₂ in 2017 with atmospheric concentrations surpassing 400ppm [3,4]. Approximately 900kg of CO₂ is emitted into the atmosphere for each tonne of Portland cement produced [5]. The calcination process and the combustion of fossil fuels account for approximately 60% and 40% of these emissions respectively [6]. The International Energy Agency (IEA) roadmap sets out a goal to reduce emissions due to cement production to 18% below 2006 levels by 2050 [7]. The main areas of focus for achieving the necessary emissions reductions in the cement industry are by clinker substitution, alternative fuels, thermal and electric efficiencies, and carbon capture and storage (CCS) [7]. CCS could provide 50% of the needed reduction in global CO₂ emissions by 2050 [7–9]. When captured, suitable storage of the CO₂ is critical to the CCS chain and one potential storage method is to upcycle carbon dioxide into concrete products by curing them with CO₂.

Accelerated Carbonation Curing (ACC) is the term used to describe the exposure of young concrete to high concentrations of CO₂ for a limited time [10]. Early carbonation curing of concrete differs from weathering carbonation in that early carbonation curing promotes the formation of more hydration products which surround carbonation products, resulting in enhanced properties such as compressive strength, durability and dimensional stability [11–14]. CO₂ captured from CCS and utilised in an ACC process has the potential to reduce CO₂ emissions from major point sources while simultaneously developing a value-added product. ACC has the potential to offer a carbon sequestration process that combines technical, economic and financial benefits.

Concrete Masonry Units (CMU’s) were selected for this study as a potential suitable candidate product for CO₂ sequestration using accelerated methods as they do not contain steel reinforcement. There is currently a high demand for CMU’s in the construction industry and therefore ACC CMU’s may provide a viable option for future construction and offer a more environmentally sustainable construction product. The study aims to assess the potential to recycle CO₂ back into concrete products whilst simultaneously promoting strength.
gain. If achievable, this would provide an opportunity for the adoption of ACC as technology in the manufacturing process.

2 EXPERIMENTAL INVESTIGATIONS

2.1 Constituent Materials

Standard 7.5MPa concrete masonry units, of nominal dimensions 440x215x100mm were chosen for this study. These units were chosen since they are currently in production in a manufacturing plant. Cement conforming to IS EN 197-1 [15] with the designation CEM II/A-L 42.5 N was used to manufacture the CMU’s. The chemical oxide composition of the cement is given in Table 1. A crushed rock fines (CRF) was the predominant aggregate used and this was manufactured from crushed limestone. The second aggregate constituent was a siliceous washed natural sand. The proportions of the materials used in the concrete mix are given in Table 2.

Table 1 Chemical composition of the CEM II/A-L cement used in this study

<table>
<thead>
<tr>
<th>Constituent</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>SO₃</th>
<th>Na₂O Eq</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.96</td>
<td>5.06</td>
<td>2.84</td>
<td>63.6</td>
<td>2.57</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 2 Mix Proportions for the 7.5MPa CMU’s

<table>
<thead>
<tr>
<th>Constituent Material</th>
<th>kg/m³</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregate</td>
<td>1,925</td>
<td>Crushed Rock Fines</td>
</tr>
<tr>
<td>Sand</td>
<td>240</td>
<td>Washed Sand</td>
</tr>
<tr>
<td>Water</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td>120</td>
<td>CEM II/A-L</td>
</tr>
<tr>
<td>Total</td>
<td>2,413</td>
<td></td>
</tr>
</tbody>
</table>

2.2 Sample Preparation

The preferred option for the experiment was to remove CMU’s directly from the production line and to use these as test specimens in the study. However, this was not a practical option as the CMU’s were too fragile immediately after manufacture and had not developed adequate strength to allow them to be removed from the production belt without disintegrating when handled. Therefore, CMU’s were removed from the manufacturing line and the material was used to produce 100mm cube specimens using a vibrating hammer to a target wet density of 100%. The CMU’s manufactured in the production plant have a target density of 2,000 kg/m³. Since this was too low to yield units that could be handled in their fresh state, the laboratory compaction process facilitated the manufacture of test specimens which could be handled at early ages. The average density of the test specimens was 2,515kg/m³, approximately 25% greater than the standard CMU’s in the production plant. The CMU’s recovered from the production line in both phases were then transported to a mixing area where they were combined and remixed prior to the manufacture of the test specimens. The time taken to manufacture and transport the samples to the test laboratory was approximately 3.5 hours.

2.3 Curing Process

A carbonation chamber was developed and commissioned to facilitate the accelerated carbonation curing of the CMU’s (Figure 1). The carbonation chamber provided a storage facility for the test specimens where they could be subjected to a controlled concentration of CO₂ with a 99.9% purity, verified by a bespoke data logging setup, and connected to the regulator. To control the level of CO₂ in the chamber, a sensor was connected to a data logger and voltmeter which controlled the regulator. This in turn controlled the level of CO₂ being released into the chamber to maintain the required concentration. To control the relative humidity (RH) in the chamber, a glass beaker containing a saturated aqueous sodium nitrite (NaNO₂) solution was placed in the bottom of the chamber. The saturated salt solution maintained the RH in the chamber by absorbing water without altering the equilibrium vapour pressure. This arrangement provided a steady 65% RH at 20°C, which is considered as optimal for carbonation [16,17]. Two fans powered by a 12V power supply were placed within the carbonation chamber to facilitate a uniform circulation of CO₂ in the chamber. A software program was written to monitor the CO₂ level within the chamber every 60 seconds by means of the analogue probe sensor. The program controlled the release of a 30 second burst of CO₂ into the chamber by opening the solenoid when it fell below the target concentration. This 60 second process loop maintained the required CO₂ concentration in the chamber.

2.4 CO₂ Exposure Timeframe

The timeframes of the initial exposure were divided into five categories as outlined in Table 3. Most of the analysis was performed over the first 7 days and this was chosen to correlate to CMU’s in production, where the general minimum storage period is 7 days in the manufacturing plant before being sold for use in construction projects. A further extended period trial for 28 days was conducted to evaluate the impact of extended periods of CO₂ curing. The aim of the experiment was to identify if there is an optimal timeframe for ACC for the CMU’s, with focus on early ages, as a shorter CO₂ curing regime would be considered preferable. A control set of samples that were not subjected to CO₂ curing were used as a reference and these samples provided a baseline for each scenario to allow a comparison of each of the curing regimes.

The second exposure tests were divided into six categories (Table 3), ranging from 4 hours to 7 days. The Phase II study concentrated on assessing the compressive strength of the ACC CMU’s specimens against control air cured samples at early ages up to 7 days. An assessment of the CO₂ uptake of the ACC CMU’s based on percentage increase compared to the control samples was also conducted in this phase of analysis.

2.5 Carbon Uptake Estimation

In order to concurrently analyse the CO₂ uptake of multiple samples under varying exposure conditions and to facilitate the introduction and removal of specimens from the closed system, a method called the “mass loss difference method” was devised. This method involved comparing the masses of ACC and control non-ACC cured samples to their dry mass. The drying process involved vacuum drying for 30mins followed by oven drying at 50°C for 48 hours to constant mass.
By comparing the difference in the dry mass between the curing regimes, the CO$_2$ uptake is calculated. As the samples are dried to a constant mass, the effects of bound moisture on the mass calculation are eliminated.

### 3 EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1 Carbon Uptake Estimation

According to Steinour’s formula [18], the cement described in Table 1 has a theoretical capacity to sequester CO$_2$ up to approximately 49.5% of the cement mass. Using the above procedure, the increase in mass of ACC specimens compared to the control at each time interval is in Table 4. As shown, the percentage gain in mass increased with exposure time with a 1.15% increase achieved after 7 days of ACC.

Based on the mix proportions in Table 2, the calculated cement content of the concrete was 5% by mass. This infers that the concrete had sequestered 23% CO$_2$ by mass of cement after 7 days of ACC. After 24 hours of ACC, a 1.04% increase in mass was observed. This suggests that each standard 7.5MPa CMU’s with a mass of 20kg can sequester up to 0.21kg of CO$_2$ under similar curing conditions. It should be noted that the CMU’s in production have a lower density than the specimens tested with full compaction. Also, CMU’s produced in the production plant will have a more open texture. These factors are likely to be favourable in assisting greater ingress of CO$_2$ and uptake in CMU’s, so these findings could be conservative.

### 4 EFFECT OF CO$_2$ UPTAKE ON COMPRESSIVE STRENGTH

#### 4.1 Early age compressive strength

Samples cured at 50% CO$_2$ were compared to air cured control samples over time, as indicated in Table 5. A set of three cubes were made for each time interval and the average values determined.

Carbonation curing significantly accelerated early strength gain at each time interval compared to air cured samples. A minimum recorded comparative strength increase of 7.1% was recorded after 4 hours. A maximum comparative compressive strength increase of 15.5% was recorded after 24 hours. The CO$_2$ cured CMU’s achieved an average strength of 27.8MPa after 72 hours curing which exceeded the 26.9MPa strength achieved by the reference air cured specimens after 7 days.
The increase in compressive strength of the ACC samples was 11.3% on average compared to the control samples. As can be seen in Figure 2, the proportional strength gains in the ACC concrete compared to the control indicate that more reaction products were produced during early carbonation, and as can be seen after 24 hours ACC, there is a reduction in the rate of strength gain over time. This reduced rate of compressive strength increase is due to the different curing processes. In the ACC process, the addition of CO₂ accelerates the hydration reaction of C₃S and C₅S and results in the rapid strength gain [19]. This carbonation process results in the production of CaCO₃ which fills the narrow pores thereby limiting the further mass transport of CO₂ to reactive cement materials. This leads to delayed reactions which reduce carbonation efficiency over time [20]. As the concrete matures the microstructure becomes denser limiting the CO₂ penetration by slowing down the diffusion rate of the CO₂. This densification delays the reactions of CO₂ with C₃S and C₅S and with the early hydration products Ca(OH)₂ and C-S-H [19].

The carbonation process is also dependent on the water content. Water will dissolve calcium ions in the anhydrous cement phases, which react to form CaCO₃. The ACC process accelerates the hydration reactions of the un-hydrated cement compounds and, in turn, lowers the water content. This lower water content can inhibit the formation of carbonic acid which limits the dissolution of Ca(OH)₂. This contributes to the reduction in the ACC samples rate of strength increase after the initial 24 hour curing period as the available water was consumed. A similar reduction in the rate of strength gain after 24 hours was noted for the control air-cured samples. As the rate of strength gain after this point was comparable to the ACC samples, this suggests that CO₂ curing has the greatest effect in terms of strength gain for early age compressive strength. Exposures after 24 hours showed less of an effect on increasing the rate of compressive strength gain.

### 4.2 7-day compressive strength

Five curing conditions were selected for analysis of compressive strength at 7 days. The time intervals were such to represent those that could be replicated in the production process during normal working hours with minimum disruption. The time intervals, curing conditions and compressive strength results are summarised in Table 6. As shown, ACC has led to increased compressive strengths. Samples exposed to CO₂ for 4, 24 and 48 hours and left to air cure up to 7 days, had compressive strengths of 27.7, 29.1 and 30.2MPa respectively, compared to the air-cured control samples, which achieved a 7-day compressive strength of 27.1MPa. Longer exposure to CO₂ led to greater strengths, with samples initially exposed for 48 hours showing an increase of 11.4% compared to the control. Since the samples only differed in their CO₂ duration, the differences must be due to this, with longer exposures promoting the early age hydration of the cement plus the conversion of portlandite to calcite and C-S-H produced through hydration.

Since conventional carbonation is dependent on the transport of CO₂ through the cement pore structure, there is a well-known dependence of carbonation rate [21] on the RH, with the maximum rate occurring at approximately 60%. At this RH, there is a sufficiently open pore structure to allow the ingress of CO₂, with enough water present to allow the dissolution of CO₂ to form carbonic acid. Consequently, many standards for accelerated carbonation studies stipulate a period of preconditioning between curing and exposure to CO₂ to reduce the free water in the concrete and allow partial evaporation of from the pores [21]. With the rate of CO₂ transport through water being ~10³ times less than through air, previous studies have found that excessive free water prevents CO₂ diffusing into the concrete by blocking capillary pores [14]. For this reason, an additional set of samples were prepared and air cured for 24 hours before ACC, with a final air-curing step to 7 days. These samples achieved an average compressive strength of

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### Table 5 Compressive strength of CMU specimens

<table>
<thead>
<tr>
<th>Age (hrs)</th>
<th>Air Cured Compressive Strength (MPa)</th>
<th>50% CO₂ Cured Compressive Strength (MPa)</th>
<th>Increase in Compressive Strength (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>10.5</td>
<td>11.3</td>
<td>7.1</td>
</tr>
<tr>
<td>24</td>
<td>18.6</td>
<td>22.0</td>
<td>15.5</td>
</tr>
<tr>
<td>48</td>
<td>22.8</td>
<td>25.2</td>
<td>9.5</td>
</tr>
<tr>
<td>72</td>
<td>25.3</td>
<td>27.8</td>
<td>9.0</td>
</tr>
<tr>
<td>96</td>
<td>26.6</td>
<td>30.0</td>
<td>11.3</td>
</tr>
<tr>
<td>168</td>
<td>26.9</td>
<td>31.8</td>
<td>15.4</td>
</tr>
</tbody>
</table>

### Table 6 7-day compressive strength of CMU specimens

<table>
<thead>
<tr>
<th>Curing Conditions</th>
<th>50% CO₂ Cured Compressive Strength (MPa)</th>
<th>7 Days Air Cured Compressive Strength (MPa)</th>
<th>Increase in Compressive Strength (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 hrs CO₂ cured &amp; 164 hrs air cured</td>
<td>27.7</td>
<td>27.1</td>
<td>2.2</td>
</tr>
<tr>
<td>24 hrs CO₂ cured &amp; 144 hrs Air Cured</td>
<td>29.1</td>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td>48 hrs CO₂ cured &amp; 120 hrs Air Cured</td>
<td>30.2</td>
<td></td>
<td>11.4</td>
</tr>
<tr>
<td>24 hrs Air cured &amp; 24 hrs CO₂ Cured &amp; 120 hrs Air Cured</td>
<td>27.5</td>
<td></td>
<td>1.5</td>
</tr>
</tbody>
</table>
27.5MPa. This was slightly higher than the control sample (~1.5%). Despite the same duration of exposure to CO2, these samples developed strengths 5.5% lower than those initially exposed to CO2 for 24 hours.

The 24-hour preconditioning period did not enhance the compressive strength. This suggests that at the commencement of ACC, the water content in the samples was close to optimal. The preconditioning step led to loss of water from the samples which was available to dissolve the calcium ions in the anhydrous C3S and C2S. Although the water content of the concrete will have an effect on the CO2 uptake, the study shows that it is the early exposure to CO2 curing that is most critical when it comes to strength development. At this early stage, C3S and C2S have not been fully hydrated by the water and the CO2 in early carbonation curing accelerates the hydration reaction.

4.3 28-day compressive strength

The longer-term effects of CO2 curing were assessed by subjecting concrete samples to curing at various time intervals and testing for compressive strength at 28 days. The results are summarised in Table 7. The minor difference between the results (0.5MPa) is most likely due to the repeatability and reproducibility of the samples and their testing.

Eight curing conditions were chosen for the CMU mix for analysis of compressive strength at 28 days. As with the 7 day strengths, carbonation curing led to increased compressive strengths, with longer exposure to CO2 leading to higher strengths. Indeed, it was the sample cured for the entire 28 days in a CO2-rich environment which showed the greatest strength, 28% greater than the reference sample. Again, the point at which samples were exposed to CO2 was found to be critical. Three different samples were exposed to CO2 for 24 hours out of the 28-day curing period; at the onset, after conditioning for 24 hours, and during the last 24 hours of the 28 days. But these three samples all showed very different behaviour. Exposure to CO2 for the first 24 hours led to an 18.9% increase in strength. Conditioning for 24 hours prior to CO2 exposure led, as with the 7-day old sample, to a slight strength increase (2.1%), similar to that observed after 7 days. However, when the sample was exposed to CO2 for the last 24 hours of the 28-day curing period, there was a slight decrease in strength. As for the samples tested at 7 days, it was early carbonation curing which had the greatest impact on compressive strength, as the CO2 accelerates the hydration reaction of the unhydrated C3S and C2S resulting in rapid strength gain.

The 28 day compressive strengths demonstrated that strength gains observed in the ACC samples increased with longer exposure to CO2 compared to the control. Although the actual increase in compressive strengths compared to the control were greater than for those achieved at 7 days, a similar rate of strength gain was noted for the comparable samples at 7 days and 28 days. The continued strength development for the ACC samples exposed to CO2 for longer concentrations showed a continued increase in compressive strength over the reference.

This may be partly due to the continued secondary reactions between the C-S-H and Ca(OH)2 which form as the hydration continues. While calcium carbonate is the predominant product resulting from the ACC process, portlandite is produced in the later stages as the concrete matures.

<table>
<thead>
<tr>
<th>Curing Conditions</th>
<th>50% CO2 Cured Compressive Strength (MPa)</th>
<th>28 Days Air Cured Compressive Strength (MPa)</th>
<th>Increase in Compressive Strength (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 hrs CO2 cured &amp; 27 days 20 hrs Air Cured</td>
<td>33.9</td>
<td>33.5</td>
<td>18.9</td>
</tr>
<tr>
<td>24 hrs CO2 cured &amp; 27 days Air Cured</td>
<td>39.0</td>
<td>40.1</td>
<td>22.2</td>
</tr>
<tr>
<td>48 hrs CO2 cured &amp; 26 days Air Cured</td>
<td>41.6</td>
<td>42.0</td>
<td>26.7</td>
</tr>
<tr>
<td>7 days CO2 cured &amp; 21 days Air Cured</td>
<td>32.8</td>
<td>34.5</td>
<td>28.0</td>
</tr>
<tr>
<td>28 days CO2 Cured</td>
<td>32.3</td>
<td>33.5</td>
<td>21.1</td>
</tr>
<tr>
<td>24 hrs Air, 24 hrs CO2 &amp; 26 days Air Cured</td>
<td>32.3</td>
<td>39.0</td>
<td>1.5</td>
</tr>
<tr>
<td>27 days Air Cured &amp; 24 hrs CO2 Cured</td>
<td>32.3</td>
<td>33.5</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

The increase in compressive strength with CO2 curing time has been demonstrated in previous studies [11,13]. These studies also found that the highest carbonation efficiencies were achieved at early ages, with the greatest uptake recorded within the first hour of ACC. It was similarly found that the compressive strength increases over time but at reducing rates.

5 CONCLUSIONS

Accelerated carbonation cured samples demonstrated significant increases in mass compared to the control air cured samples. A maximum CO2 uptake per mass of cement of 23% was achieved after 7 days of ACC at 50% CO2.

Accelerated carbonation curing resulted in an increase in early age compressive strength with an 11.3% increase achieved over 7 days compared to the control. The study found that the greatest increase in compressive strength occurred between 4 and 24 hours and after this point, ACC showed a similar proportional rate of strength gain over time as normal hydration of the control sample.

Substantial 28-day compressive strength increases were also achieved for samples that were accelerated carbonation cured. Samples cured under CO2 for 28 days recorded the greatest strength increase, of 28%, compared to the control. The rate of strength gain for samples exposed to CO2 reduced over time and the results prove that it is the early carbonation curing which has the greatest impact on compressive strength.

Concrete samples preconditioned by air curing for periods of 24 hours or greater before CO2 curing achieved lower compressive strengths at 7 and 28 days when compared to early carbonation cured samples. Samples preconditioned for 24 hours subjected to CO2 curing for 24 hours followed by air curing, achieved a 2.1% compressive strength increase. Samples initially cured with CO2 for 24 hours achieved a strength increase of 18.9% at 28 days.
CMU’s were studied as a potential suitable candidate for ACC as they do not contain reinforcement so the potential of detrimental effects due to carbonation are minimised. The study found no evidence of significant carbonation for the early CO₂ cured concrete which suggests that ACC may also be suitable for reinforced samples provided the exposure to CO₂ is kept to shorter timeframes.

It has been demonstrated that the 95 million CMU’s produced in Ireland in 2016 have the potential to sequester approximately 20,000 tonnes of CO₂ had they been subjected to ACC at a 50% concentration for 24 hours.

REFERENCES


