The effect of combined carbonation and steam curing on the microstructural evolution and mechanical properties of Portland cement concrete

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Abstract. The present study investigated the effect of the combined carbonation and steam curing on the physicochemical properties and CO₂ uptake of the Portland cement concrete. Four different curing regimes were adopted during the initial 10 h of curing to evaluate the potential of carbonation curing as an alternative to conventional steam curing in the precast concrete industry from environmental and practical viewpoints. Four combinations of carbonation and steam curing conditions were applied as curing regimes to the samples at an early age. The test results indicated that the samples treated with the combined carbonation and steam curing exhibited higher early strength development compared to the other samples, signifying that carbonation curing can reduce the production time of precast concrete. Furthermore, the CO₂ uptake capacity of the samples was calculated and found to be as high as 18% with respect to the mass of the paste samples. Hence, the simultaneous utilization of steam and CO₂ for the fabrication of precast concrete members has the potential to make precast concrete greener and more cost-effective.

Keywords: Portland cement; carbonation; characterization; steam curing

1. Introduction

The emission of CO₂ from rapid industrialization given the heavy dependence on the use of fossil fuels for power generation is responsible for the current atmospheric crisis and hence has become a global concern (Annadurai et al. 2020, Jenkinson et al. 1991). The CO₂ emissions associated with the cement industry are considered to account for 5-8% of all man-made CO₂ emissions, a situation increasing the desire to reduce CO₂ emissions (Gartner and Hirao 2015, Goto et al. 2013). Numerous studies and attempts have attempted to reduce the CO₂ emissions associated with the production of ordinary Portland cement (OPC), including (1) the replacement of the volume of OPC in the concrete with supplementary cementitious materials (SCMs) (Al-Amoudi et al. 2019, Kumar and Prasad 2019, Lothenbach et al. 2011, Seo et al. 2021), (2) the use of alternative clinkers with sintering temperatures lower than that of OPC (Yoon et al. 2021), (3) the utilization of alkali-activated binders derived from industrial by-products (Bernardo et al. 2006, Duxson et al. 2007, Park et al. 2017, Park et al. 2016, Péra and Ambroise 2004), and (4) the widespread openness of carbon capture and storage (CCS) strategies by relevant industries (Gibbins and Chalmers 2008, Jang and Lee 2016). Accelerated carbonation curing (ACC) of OPC is a straightforward technique to actualize the CCS strategy in an effective manner (Kashef-Haghighi et al. 2015, Loo et al. 1994). Specifically, Xi et al. (2016) found that 43% of CO₂ emitted from the production of OPC can be offset by adopting ACC. Capturing CO₂ from the cement industry and reusing it for concrete curing in a cost-effective approach that can be considered as a potential large-scale component of the circular carbon economy concept (Lee et al. 2017).

ACC has attracted attention not only because it offers the potential to store a large amount of CO₂ in the OPC matrix but also because it can enhance the mechanical properties of OPC-based concrete through the formation of calcium carbonates (Jang et al. 2016, Jang and Lee 2016, Kashef-Haghighi et al. 2015). The steam curing of OPC is one of the conventionally used methods in the
manufacturing of precast concrete members to achieve high early strength values (Hu et al. 2020, Rostami et al. 2012). However, advancements in carbon capture technologies have led to CO₂ gas with high purity levels, enabling the ACC of OPC in a cost-effective manner with higher efficiency than that by conventional curing technology (Rostami et al. 2012). The mechanism of strength development upon carbonation curing is attributed to the formation of calcium silicate hydrate (C-S-H) and calcium carbonate (CaCO₃) caused by the carbonation of alite (Ca₃SiO₅), belite (Ca₂SiO₄), portlandite (Ca(OH)₂), and C-S-H (Jang and Lee 2016, Rostami et al. 2012).

Numerous studies have investigated the effects of carbonation curing on the properties of concrete and the potential of carbonation curing as an alternative to conventional steam curing. Rostami et al. (2012) compared the effects of steam curing and carbonation curing on the production outcomes of precast concrete. They reported that the early carbonation curing of OPC concrete promoted strength development in concrete and densified its superficial layers, resulting in enhanced durability performance in comparison with that of steam-cured concrete (Rostami et al. 2012). Zhang and Shao (2016) reported that early carbonation curing with a high CO₂ concentration level can enhance the durability of precast reinforced concrete by forming a carbonate-rich surface layer. Other studies reported that the ACC of OPC concrete can enhance the mechanical properties of concrete at a level similar to that of steam curing (El-Hassan et al. 2013, Jang and Lee 2016, Rostami et al. 2011). However, the simultaneous application of carbonation and steam curing to OPC concrete at an early age and the corresponding microstructural behavior and CO₂ uptake, to the best of our knowledge, has not been attempted.

The present study, therefore, investigated the effect of a combination of carbonation and steam curing on the physicochemical properties and CO₂ uptake capacity of OPC concrete samples. Fresh-state samples were air-cured for 2 h and thereafter treated for 8 h using four different curing regimes combining carbonation and steam curing. The samples cured by the different curing regimes were characterized by means of X-ray diffraction (XRD), thermogravimetry (TG)/ derivative TG (DTG), mercury intrusion porosimetry (MIP), and compressive strength testing at 10 h, 7 days, and 28 days of curing. Furthermore, the CO₂ uptake capacity of the carbonated samples was evaluated to provide an indication in the context of the recent CCS campaign.

2. Experimental procedure

2.1 Materials and sample preparation

Type I Portland cement, supplied by Arabian Cement Co., was used as a binder material. The chemical and mineralogical compositions of the cement as obtained from an X-ray fluorescence method and by the XRD Rietveld refinement method, respectively, are shown in Table 1. Dune sand and limestone (particle size less than 20 mm), obtained from Khurais - Saudi Arabia, were used as fine and coarse aggregates, respectively. It should be noted that this paper uses standard cement abbreviations, where CaO is denoted as C, MgO as M, Al₂O₃ as A, SiO₂ as S, CO₂ as C, SO₃ as S, and H₂O as H.

Concrete samples were fabricated by mixing the dry constituents (cement and aggregates) for 5 min according to the mix proportion provided in Table 2. Water and a water-reducing agent were slowly added to the dry mixture and further mixed for 5 min. A sulfonated lignin-based water-reducing agent was used at the dosage level shown in Table 2, which was designed to achieve a slump value of the fresh mixture of 170 mm. The fresh mixture was cast into cylindrical molds (100 mm dia.×200 mm height). On the other hand, paste samples (samples without aggregates) were fabricated to exclude the unwanted contributions of the aggregates when they were characterized.

After casting, the samples initially underwent 2 h of air curing, followed by four different curing regimes for the subsequent 8 h. The carbonation curing process was introduced without demolding of the concrete samples. This method may result in the carbonation of the upper surface of the samples, yet this simulates the field condition of the precast factory. The curing regimes were air curing under ambient conditions (denoted as A-series), curing at 60°C and 60% R.H. (denoted as S-series), curing at room temperature with a 10% atmospheric CO₂ concentration (denoted as C-series), and curing at 60°C and 60% R.H. with a 10% atmospheric CO₂ concentration (denoted as SC-series). These curing conditions were maintained by a thermo-hygrostat sensor. The S-series curing regime simulates the steam curing condition typically employed in precast industries, while the SC-series curing regime merges the curing conditions of the S- and C-series regimes (Amr et al. 2019). After the curing treatments, the samples

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Mineralogical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>C₃S</td>
</tr>
<tr>
<td>SiO₂</td>
<td>C₂S</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>C₃A</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>C₅AF</td>
</tr>
<tr>
<td>SO₃</td>
<td>Ce</td>
</tr>
<tr>
<td>MgO</td>
<td>CS₂H</td>
</tr>
<tr>
<td>Na₂O</td>
<td>C₆S.5H</td>
</tr>
<tr>
<td>K₂O</td>
<td>M</td>
</tr>
<tr>
<td>TiO₂</td>
<td>NS</td>
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<tr>
<td>P₂O₅</td>
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</tr>
<tr>
<td>Mn₃O₄</td>
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<tr>
<td>SrO</td>
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<tr>
<td>LOI*</td>
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</table>

*Loss on ignition

<table>
<thead>
<tr>
<th>Cement</th>
<th>Fine aggregate</th>
<th>Coarse aggregate</th>
<th>Water</th>
<th>Water-reducing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>584</td>
<td>1211</td>
<td>158</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 1 Chemical and mineralogical compositions of the Portland cement used in this study

Table 2 Mix proportion of the concrete specimens (kg/m³)
were allowed to be cured in open air until the designated test day.

2.2 Test methods

Paste samples were solvent-exchanged using acetone to arrest the hydration at 10 h, 7 days, and 28 days of curing. The paste samples were thereafter pulverized to pass a 75 μm-sieve for the XRD and TG/DTG analyses or crushed into a few millimeters in size for the MIP analysis. XRD was conducted using an Empyrean PANalytical X-ray diffractometer with CuKα at 40 kV and 30 mA. The samples were scanned in a range of 5° to 45° 2θ with a step size of 0.026° 2θ for one hour. The X-ray fluorescence was carried out by means of an X-ray fluorescence spectrometer (Axios FAST manufactured by Malvern PANalytical). The Rietveld analysis results of the raw cement were obtained from the XRD pattern of the cement. The test results of the Rietveld analysis were normalized to the entire crystalline phases, assuming the absence of an amorphous phase in the raw cement. The TG/DTG assessment was carried out using a Labsys Evo device manufactured by SETARAM at a heating rate of 10°C/min with a temperature range of 40–1000°C under an N₂ environment. The MIP test was conducted using an Autopore VI 9500 device. The pressure for the MIP analysis ranged from 0.00069 to 413.7 MPa (0.1 to 60,000 psia). Meanwhile, the compressive strength values of the concrete samples were measured at 10 h, 7 days, and 28 days of curing to investigate the effect of carbonation curing on the strength development of concrete. The compressive strength test was carried out using a 2,500 kN universal testing machine under a constant loading rate of 0.02 mm/s.

3. Results and discussion

3.1 X-ray diffraction

The XRD patterns of the paste samples are shown in Fig. 1. Peaks corresponding to the presence of CS2H and CS0.5H were observed in the patterns of the C- and SC-series samples regardless of the curing age, unlike in those of the A- and S-series, implying that sulfate depletion in the pore solution is hindered by the dissolved carbonates under the carbonation curing condition (Vollpracht et al. 2016).

Notable differences were observed with the peaks corresponding to the presence of CH and Cc. Peaks due to CH were observable in the samples cured in a CO₂-free condition, while the C- and SC-series samples showed particularly notable peaks corresponding to the presence of Cc. These observations stemmed from the consumption of CH during carbonation curing leading to the formation of the Cc.

The phase assemblage of the hydrated samples in this work varied according to the applied curing regime during the 10 h of initial curing. Ettringite was observed to have precipitated in the samples cured in an ambient temperature range (i.e., A- and C-series samples), while it may have coexisted with Cc in the carbonation-cured samples cured at an ambient temperature. Nevertheless, sulfate consumption upon hydration was greatly hindered, implying that anionic species in the interlayer of AFt and AFm can be dominated by carbonates (Seo et al. 2019). The XRD patterns of the C- and SC-series samples also suggested that CH was rapidly carbonated to form Cc under the carbonation curing condition.

3.2 Thermogravimetric analysis and CO₂ uptake

The TG analysis results of the paste samples are shown in Fig. 2. At 10 h of curing, the samples commonly showed weight loss in the temperature range of 50–200°C associated with the evaporation of interlayered water in the C-S-H and the dehydration of the AFt and AFm phases (Kim et al.
It should be noted that the weight loss in this temperature region may include the free water in the samples, the presence of which is due to the insufficient curing period. Carbonation resulted in a reduction in the weight loss in this temperature region. The S-series sample at 10 h of curing exhibited weight loss in the temperature range of 400-480°C, corresponding to the dehydroxylation of CH (Kim et al. 2021, Seo et al. 2018, Silva et al. 2002), while the C- and SC-series samples showed weight loss in the temperature region of 640-760°C, where the decarbonation of Cc appears (Borges et al. 2010, Rostami et al. 2012). This observation indicates that the formation of Cc was favored at the expense of CH by early carbonation. In addition, the SC-series sample was found to generate more Cc than the C-series sample, meaning that the high-temperature and high-humidity condition is preferred to achieve high CO₂ uptake at an early age.

The weight loss due to decarbonation of Cc in the C- and SC-series sample was vastly increased at 7 and 28 days of curing as compared to that observed at 10 h of curing, demonstrating the diffusion of CO₂ into the matrix after the initial carbonation curing. The diffusion of CO₂ in the matrix was also evidenced by the absence of weight loss due to the dihydroxylation of CH in the C- and SC-series samples, even at 28 days of curing. Weight loss below 200°C in the C- and SC-series samples barely developed at 7 days of curing. At 28 days of curing, the C-series sample showed a notable increase in the weight loss below 200°C, likely to be related to the delayed hydration of cement.
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Fig. 3 CO₂ uptake of the paste samples after 10 h, 7 days, and 28 days of curing as calculated from thermogravimetry analysis results.

Carbonation curing indeed enhanced the CO₂ uptake capacity of the samples in comparison with that of uncarbonated samples (i.e., A- and S-series samples). The CO₂ uptake capacity of the SC-series sample in this temperature region was observed to be similar regardless of the curing age.

The CO₂ uptake values of the paste samples as calculated from the TG analysis results are displayed in Fig. 3. Eq. (1) (Jang and Lee 2016) was used to estimate the amounts of Cc formed in the samples quantitatively.

\[
\text{CO}_2 \text{ uptake capacity (\%) } = \frac{M_{\text{CO}_2}}{M_{\text{cement}}} \times 100 \quad (1)
\]

Note that the weight loss occurred at 640–760°C, presented as the CO₂ uptake capacity in this study, did not take the limestone content and unreacted clinker in the raw cement into account.

Fig. 4 Mercury intrusion porosimetry analysis results of the samples after (a) 10 h, (b) 7 days, and (c) 28 days of curing.
CO₂ uptake of the S-series samples was slightly higher than that of the A-series samples, though it was much lower than that of the C- and SC-series samples. The CO₂ uptake of the SC-series samples was approximately two-fold higher than that of the C-series samples regardless of the curing age. Also, the SC-series sample reached the highest CO₂ uptake rate of 18.4% at 28 days of curing, which was significantly higher than the S-series sample by more than four times. The increase in the CO₂ uptake in the carbonated samples after carbonation curing reflects the diffusion of penetrated CO₂ during the early stage of carbonation curing. This observation indicates that the application of carbonation curing to the conventional steam curing process can significantly enhance the CO₂ uptake of the Portland cement-based materials.

### 3.3 Mercury intrusion porosimetry

The MIP analysis results of the samples are shown in Fig. 4. The most notable pore population region is 20-200 nm, associated with the formation of AFt and C-S-H (Jang and Lee 2016, Mehta and Monteiro 2017). The A- and S-series samples showed an outstanding pore population in this region at 10 h of curing, unlike the C- and SC-series samples, which exhibited predominant pores with diameters between 200 and 2000 nm. The A- and S-series samples at 7 days of curing underwent pore size refinement, as indicated by the development of pores with diameters of less than 10 nm, while the C- and SC-series samples scarcely showed pore size modifications at 7 days of curing due to the retardation of hydration by early carbonation curing. Since a significant amount of water was consumed during the early carbonation, the retardation of hydration had occurred in the C- and SC-series samples.

At 28 days of curing, the C-series sample showed a certain increase in the pore population with diameters of 20-200 nm, indicating that AFt and C-S-H had formed by delayed hydration (Gallé 2001). These observations coincide with the XRD and TG analyses results of the samples at 28 days of curing, which correspondingly indicated the presence of ettringite and an increase in the weight loss in the temperature range of 50-200°C in the C-series samples. Meanwhile, alteration of the pore population with diameters of 20-200 nm in the SC-series sample at 28 days of curing was mostly negligible, while the SC-series samples showed a decrease in the number of pores with diameters between 200 and 2000 nm.

### 3.4 Compressive strength

The compressive strength development of the concrete samples is shown in Fig. 5. The S- and SC-series samples showed higher early strength development than the other samples, indicating accelerated hydration due to the high temperature and high relative humidity conditions. Moreover, the SC-series samples showed higher early strength development than the C-series samples, indicating that carbonation curing further promoted the development of strength under the high temperature and relative humidity conditions. At 28 days of curing, the C-, S-, and SC-series samples exhibited similar compressive strength levels.

Meanwhile, the SC-series sample showed similar compressive strength values at 7 and 28 days of curing. From an industrial standpoint, the precast concrete mixture (Table 2) used here is predicted to have a target compressive strength of 35 MPa at 28 days of curing. The precast concrete manufacturer would demold the precast concrete members once the members achieve 65-68% of the target strength. The SC-series sample exceeded 22.75 MPa in just 10 h of curing, while similar strength development can be achieved after 24-72 h when using the conventional precast concrete procedure, meaning that the curing regime adopted for the SC-series samples can reduce the precast production time significantly.

The mechanical strength of concrete has high affinity with the porosity of the cement matrix. The porosity and AFT formation both have a momentous effect on the early development of strength in these materials (Chen et al. 2013, Poon et al. 2001, Rößler and Odler 1985). However, the C- and SC-series samples, with higher porosity, showed more outstanding strength development than the A- and S-series samples at 10 h of curing. This is likely due to the formation of Cc in the C- and SC-series samples at an early age, as quantitatively evidenced by the XRD and TG analyses results, indicated that the amount of Cc was much higher in the C- and SC-series samples than those in the A- and S-series samples. Consequently, the effect of carbonation curing can be described as allowing early strength development to an extent comparable to that by ordinary steam curing.

### 4. Conclusions

The present study investigated the effect of a combination of carbonation and steam curing on the physicochemical properties and CO₂ uptake capacity of Portland cement concrete. Four different combinations of carbonation and steam curing regimes were utilized with the samples here during the initial 10 h of curing. The characterization of the samples was performed by means of XRD, TG/DTG, MIP, and compressive strength tests at 10 h, 7 days, and 28 days of curing. In addition, CO₂ uptake of
the samples was evaluated to assess the potential of producing green precast concrete members that exhibit high early strength development. The findings obtained from this study are listed below.

- The XRD and TG/DTG results of the samples showed that early carbonation curing can contribute to the formation of Cc and can delay hydration to some extent and early steam curing can promote the hydration resulting in an increase in the amount of CH.
- The SC-series samples showed considerably higher CO₂ uptake than the other series of samples tested here, indicating that the application of high temperature and high relative humidity levels can further enhance the CO₂ uptake of carbonation-cured samples.
- Early carbonation curing retarded hydration, resulting in rare pore size refinement of the carbonation-cured samples.
- An outstanding enhancement in the early strength development was observed in the SC-series samples. Carbonation curing of these samples at a high temperature was found to be a more tailored strategy than ordinary steam curing from the standpoint of early strength development. This curing regime can potentially lead to a reduction in both the production time and the cost of precast concrete.

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References


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