Early age impacts of CO₂ activation on the tricalcium silicate and cement systems

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Abstract

The early-age impacts of CO₂ activation (using a dose of 0.3% CO₂ by weight of cement) on two binder systems (tricalcium silicate and cement) were studied, principally across the first 3 h of hydration. The investigation included calorimetry, ICP-OES, TGA, and SEM. The in-situ mineralization of CO₂ accelerated the hydration of both the systems, with the effect being more pronounced in cement. During the first 30 min of hydration, the CO₂ addition impacted the solution phase pH and certain elemental concentrations (Ca, Mg, S). At later times of observation, the values were comparable to the level of the reference sample. Thermodynamic modeling revealed that the presence of CO₂ resulted in stronger undersaturation with respect to the binder phases, which implies a strong driving force for their dissolution. The carbonates were observed in SEM micrographs as a multitude of rhombohedral-shaped calcite crystals while TGA confirmed an increased quantity of carbonates in both binder systems.

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1. Introduction

Amid rising recognition of the impacts of anthropogenic global climate change and the related efforts towards implementing carbon emissions reductions, the cement and concrete industries, the source of around 7% of annual global CO₂ emissions, face the challenge of meeting a lower carbon future [1,2]. In recent years, a target of Net-Zero by 2050 [3] has inspired the industry and stakeholders to develop carbon neutrality roadmaps identifying necessary actions and potential impacts. Common among publications from ETH Zurich [4], Cembureau [5], the Portland Cement Association (PCA) [6], and the Global Cement and Concrete Association (GCCA) [7] is a recognition that action must come from across the cement-concrete value chain and that innovative technologies are needed. In the GCCA estimate, the improvements to business-as-usual approaches (increased efficiencies in cement manufacturing, concrete production, design, and construction; decarbonization of electricity; increased SCMs usage) still require carbon capture and utilization and storage (CCUS) technologies to make the largest contribution (36% of the total reduction) to reach industry net-zero goals by 2050.

The quantity of CO₂ emitted at individual cement plants suggest they hold potential as integrated links within the CCUS chain [8]. Utilization as a part of concrete production takes advantage of the mineralization pathway that it is thermodynamically favoured and offers permanent CO₂ conversion [9,10]. In contrast to other approaches for using CO₂ (e.g., conversion to fuels and chemicals, production of materials like carbon nanotubes, production of polymers), the construction materials pathway offers the greatest likelihood to make a climate impact both due to the scale of the opportunity and the advantageous energy and CO₂ footprint considerations [11].

One concept has examined the use of CO₂ as an admixture in ready mixed concrete production. Technology to add carbon dioxide into fresh concrete as part of the batching and mixing step has been developed and industrialized [12]. An optimal dose of liquid carbon dioxide is portioned and delivered according to the cement content of the batch. The CO₂, mixed into the concrete as a mixture of solid and gas, reacts with calcium ions in solution to develop calcium carbonate reaction products. Carbon dioxide reacts with
freshly hydrating cement to form calcium carbonate and calcium silicate hydrate gel,
expressed here as reactions with the main calcium silicate phases of tricalcium silicate
and dicalcium silicate [13]:

$$3\text{CaO} \cdot \text{SiO}_2 + (3-x)\text{CO}_2 + y\text{H}_2\text{O} \rightarrow x\text{CaO} \cdot \text{SiO}_3 \cdot y\text{H}_2\text{O} + (3-x)\text{CaCO}_3 \quad (1)$$

$$2\text{CaO} \cdot \text{SiO}_2 + (2-x)\text{CO}_2 + y\text{H}_2\text{O} \rightarrow x\text{CaO} \cdot \text{SiO}_3 \cdot y\text{H}_2\text{O} + (2-x)\text{CaCO}_3 \quad (2)$$

The carbonate reaction products that form are nanoscale and intermixed with calcium silicate hydrate (C-S-H) gel [13–15]. The product formation has been observed to impact the earliest stages of hydration, but an optimal dose does not prevent the subsequent formation of typical hydration products such as calcium hydroxide, ettringite, or calcium silicate hydrate gel [16].

Carbon dioxide used as a feedstock in concrete production can impart performance benefits on the concrete so produced while also achieving carbon removal and reduction. The in-situ nanoparticle development can improve the compressive strength of the concrete. The improved strength can support a redesign of the concrete mix to use less Portland cement; the approach can reduce the concrete’s carbon footprint and drive sustainable production [12,17]. The cement has a carbon footprint around 0.863 tonnes CO$_2$/tonne of cement [2]. Leveraging the CO$_2$ utilization to use cement more efficiently drives lower carbon concrete while also achieving an economic saving for the producer.

Earlier work examined adding CO$_2$, as an admixture, to tricalcium silicate and identifying the rapid in-situ development of reaction products [14]. The present work focussed attention, for the first time, on the earliest stages of hydration where the mineralization of CO$_2$ is completed, and direct impacts are the most noticeable. Both C$_3$S (tricalcium silicate, in cement chemistry notation) and cement were examined. An initial experimental program was undertaken to determine the sensitivity of water-cementitious ratio and CO$_2$ dose on the calorimetric response. The samples prepared with the selected dose were thereafter analyzed for changes in hydration. A variety of characterization
techniques, including isothermal calorimetry, TGA, XRD, and SEM, were employed for this purpose. A novel examination of the pore solution pH and solution chemistry through ICP-OES identified the impacts of the CO₂ addition in both the simple C₃S system and the more complex cement system. The saturation indices of various reactant and product phases were determined using thermodynamic modeling. Quantities and morphologies of the CO₂ mineralization and hydration products were determined. The present work improves the physicochemical understanding, from the early moments of hydration, of using CO₂ as a concrete admixture and how it can impart performance benefits in ready mixed concrete production.

2. Materials and methods

2.1 Materials

The materials used in this study were calcium trisilicate (C₃S), cement, CO₂, and water. C₃S powder was obtained from CTL Group (Skokie, IL). The cement was a general use (GU) Portland cement (Table 1). The CO₂ gas (Coleman, Grade 4.0, purity 99.9%) used in the study was commercial grade and supplied by BOC gases. Ultrahigh purity water, ddH₂O (resistivity of 18.2 MOhm at 25 °C), was prepared in a Simplicity UV water purification system (EMD Millipore Sigma). Isopropanol (HPLC grade) and HNO₃ (15.8N, ACS grade) were obtained from Fisher Scientific. The flowmeter (Omega FMA1814A) was used to control the flow of gaseous CO₂. Analytical paste samples were prepared in 20 ml scintillation vials. The paste was premixed with a vortex vial mixer (Maxi Mix II, from Thermo Scientific, Pittsburgh, PA). A 50 ml plastic syringe with attached 0.45 μm filter unit and Durapore PVDF membrane (Millex HV) was used to extract pore solution aided by a pneumatic press.
Table 1: Chemical analyses of the cement used in the study (phases reported as weight percent, potential phase composition via calculation, cement compounds reported using cement chemistry notation)

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>61.9%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19.4%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.9%</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.9%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.3%</td>
</tr>
<tr>
<td>MgO</td>
<td>2.7%</td>
</tr>
<tr>
<td>Free CaO</td>
<td>1.1%</td>
</tr>
<tr>
<td>Insoluble residue</td>
<td>0.45%</td>
</tr>
<tr>
<td>Total alkali as Na₂O</td>
<td>0.64%</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>2.3%</td>
</tr>
<tr>
<td>C₃S (calculated)</td>
<td>56%</td>
</tr>
<tr>
<td>C₂S (calculated)</td>
<td>14%</td>
</tr>
<tr>
<td>C₃A (calculated)</td>
<td>7%</td>
</tr>
<tr>
<td>C₄AF (calculated)</td>
<td>10%</td>
</tr>
<tr>
<td>Blaine Fineness</td>
<td>364 m²/g</td>
</tr>
</tbody>
</table>

2.2 Sample preparation

Fig. 1 shows the experimental design adopted in this study. Additional details are included in Section 1 of the Supplemental Information. A preliminary study optimized the experimental conditions. Firstly, cement paste samples were prepared at different water-to-cement (w/c) ratios (0.5, 0.8, 1.0, 1.2, and 1.5). A series of tests were conducted to optimize the amount of pore solution extracted using the filter press. The work identified an optimum w/c of 1.2 (detailed information in Section 2 of the Supplemental Information) that was used for further sample preparation. Using a vortex mixer, paste samples activated with CO₂ were then prepared in the following fashion: (1) portioning water and cement into a vial and premixing for 30 s; (2) pause for 5 s; (3) restart mixing
and commence injection of the required amount of CO$_2$; and (4) complete CO$_2$ injection and continue mixing until a total elapsed time of 90 s beyond in the initial contact of the water and the C$_3$S or cement. The samples were then transferred to an isothermal calorimeter, and the gathered data was analyzed to select an optimum amount of CO$_2$ from various dosages used (0.1, 0.3, 0.5, 0.7, and 0.9% by weight of cement).

*Fig. 1. Experimental design used in this study*
At the determined optimums of w/c and CO₂ dose, the cement and C₃S paste samples were then prepared for further analysis according to the mixing procedure. The samples were let to hydrate, capped, in their vials until the required hydration arrest times. The CO₂ activated system was analyzed at 1, 3, 6, 10, 15, 30, 60, 120, 180 min after the conclusion of the mixing, while the control was examined at 6, 15, 30, 60, 120, and 180 min. At the intended time of hydration arrest, around 2 ml of paste (cement or C₃S dispersion) was pipetted and transferred to a glass vial filled with about 18 ml of isopropanol to arrest hydration. Solids were let to sediment for 2 to 3 min, after which the vial was filled with fresh isopropanol. The sedimentation and replenishing of isopropanol were repeated at least four more times to eliminate the water. The isopropanol was then decanted, and the sediment-containing vial was placed in a vacuum oven equipped with a liquid nitrogen trap and held at 40 - 50 °C (a temperature low enough to avoid decomposition of phases such as ettringite) to dry the material. The solid sediments thus obtained were used for TGA, XRD, and SEM analysis. For the ICP-OES and pH measurement, pore solution was extracted using the filter press assembly.

### 2.3 Test methods

#### 2.3.1 Isothermal calorimetry

Isothermal heat conduction calorimetry was performed with a TAM Air (Thermometric) calorimeter. Paste samples were placed in 20 ml plastic Wheaton vials. Each sample for calorimetry contained 8.8 g of paste (equivalent to 4 g of cement or C₃S). The test was run at 20 °C for 24 - 48 h.

#### 2.3.2 TGA

Thermal gravimetric analysis (TGA) was performed with SDT Q600 (TA instruments). Samples (33 - 37 mg) were placed in the alumina crucible and heated to 1000 °C at a rate of 10 °C/min in a nitrogen flow. Samples at the early stage of hydration showed very low weight loss, which can possibly result in high errors due to weight drifts occurring during the heating. Weight loss occurring during the decomposition of cement or C₃S components was quantified across defined temperature intervals as per the approach of
Bhatty [18]. The temperature intervals were selected according to the observed onset points of the calcium hydroxide and carbonate mass losses. Further analysis of the carbonate loss was completed using the derivative thermogravimetric (DTG) data (derivative weight (%/min) vs. temperature) to understand overlapping mass losses of amorphous and crystalline carbonate. The processing of the overlapping mass losses was performed with the peak fitting software Fityk [19].

2.3.3 XRD

Powder X-ray diffraction (XRD) was performed with Bruker D8 Advance diffractometer equipped with position-sensitive detector Vantec-1. Radiation was generated with an X-ray tube with a Cu anode (Kα radiation, λ=1.54184 Å) at 35 kV and 40 mA. The 2θ range was 10 - 50°, and the resolution was 0.035°, with 2 s averaging time per step. Phase analysis was performed using ICDD PDF-2 databases. The XRD did not elucidate significant differences between the samples over the analysed timeframe and is included in Section 7 of the Supplementary Information.

2.3.4 SEM

Scanning Electron Microscopy (SEM) was performed with a Hitachi S4800 field emission scanning electron microscope with embedded Oxford Inca X’sight Energy Dispersive Spectrometer (EDS) equipped with Si (Li) detector and ATW detector window. Before imaging, samples were attached with double-sided conductive glue tape on an aluminum sample holder without any further conductive coating. The imaging was performed in secondary electron (SE) mode at 1.0 - 2.0 kV accelerating voltage. EDS was performed at 8 kV accelerating voltage.

2.3.5 ICP-OES and pH

The extracted pore solution was analyzed to determine the solution phase composition. The pH was measured with combination pH electrode with built in automatic temperature compensation probe (Ag/AgCl reference, single junction), Accumet from Fisher Scientific. To stabilize the solution and prevent precipitation, 0.4 ml of HNO₃
(V_hno3:V_water = 1:2) was added to a 9 ml sample of pore solution. Elemental composition results were corrected to the amount of HNO3 according to: $C_{actual} = C_{laboratory} \times \frac{9.4}{9.0} = 1.044 \ C_{laboratory}$. The solution was subsequently analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES).

### 2.4 Thermodynamic modeling

The measured elemental concentration of extracted pore solution was used to calculate the saturation indexes for the anhydrous clinker and hydrate phases. The calculations were performed using the geochemical modeling program GEMS version 3.6.0 [20]. Thermodynamic data from the default PSI-GEMS database [21] and the cement-specific data from the CEMDATA18 database [22] were used. The C-S-H was simulated as an ideal solid solution between Jennite, Tobermorite, NaSH, and KSH, based on the CSHQ model originally proposed by Kulik [23]. The carbonate concentrations were estimated assuming saturation with respect to calcite. In addition, undersaturation with respect to C3S is calculated, using the experimental solubility product of C3S as suggested by Nicoleau et al. [24] and detailed in Schöler et al. [25]. Saturation index (SI) is an index that determines the equilibrium condition of a phase with the pore solution. In other words, it indicates whether the pore solution is saturated, undersaturated, or supersaturated with respect to a particular phase. SI is calculated as given in Eq. (3).

$$SI = \log_{10} \left( \frac{\text{IAP}}{K_{sp}} \right)$$

Where IAP is the ion activity product calculated from the measured concentration (from ICP-OES), and $K_{sp}$ is the (theoretical) solubility of the phase in question.

### 3. Results and discussions

#### 3.1 Calorimetry

##### 3.1.1 Preliminary dosage study

A summary of the isothermal calorimetry results of cement paste produced with increasing dosages of CO2 is shown in Fig. 2. The most pronounced effect on hydration (primarily in terms of an increase in the total heat release) was obtained at 0.5% of CO2 where there was
a 23% increase in the total heat at 48 hours. Detailed quantitative analyses of the calorimetry are included in Section 3 of the Supplementary Information. A dose at 0.3% CO₂ had a similar response as the 0.5% dose; it is within the typical dosage range (0.1 - 0.3%) of the industrial use of the technology and was selected as the dosage of interest for further investigation.

Fig. 2. Calorimetry curves of cement dispersions prepared with different percentages of CO₂

3.1.2 Comparison of two binder systems

The isothermal calorimetry results through 48 h of hydration in cement and tricalcium silicate systems (control condition and dosed with 0.3% CO₂ by weight of binder) are presented in Fig. 3 with analytical observations reported in Table 2. The addition of CO₂ imparted an acceleration (shift of the power curve to earlier times) in both systems. The
ASTM C1679 thermal indicator of setting time [26] was calculated to be 11.6 h in the control tricalcium silicate system. The CO₂ imparted a 4.7 h decrease to 6.9 h. The time at peak power decreased from 20.5 h in control to 10.6 h in the CO₂ sample. The heat flow at the peak increased by 18% due to CO₂ addition. In the cement system, the control set time by calorimetry was 4.5 h, reducing to 4.1 h under influence of CO₂. The CO₂ addition changed the time at peak power from 6.9 to 5.4 h and increased the corresponding heat flow by 26%.

Fig. 3. Isothermal calorimetry (power and energy and energy relative to the control) from cement (left) and tricalcium silicate (right) in the control and 0.3% CO₂ addition conditions
Table 2: Calorimetry curve analysis

<table>
<thead>
<tr>
<th>Metric</th>
<th>C₃S Reference</th>
<th>C₃S CO₂</th>
<th>Cement Reference</th>
<th>Cement CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal indicator of set (h)</td>
<td>11.6</td>
<td>6.9</td>
<td>4.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Acceleration slope (mW·g⁻¹·h⁻¹)</td>
<td>0.11</td>
<td>0.20</td>
<td>0.48</td>
<td>0.70</td>
</tr>
<tr>
<td>Time at peak heat flow (h)</td>
<td>20.5</td>
<td>10.6</td>
<td>6.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Heat flow at peak (mW/gₗₐₚₚ)</td>
<td>1.80</td>
<td>2.13</td>
<td>2.88</td>
<td>3.63</td>
</tr>
<tr>
<td>Total heat at 24 hours (J/gₗₐₚₚ)</td>
<td>109</td>
<td>129</td>
<td>145</td>
<td>182</td>
</tr>
<tr>
<td>Relative total heat at 24 hours</td>
<td>100%</td>
<td>119%</td>
<td>100%</td>
<td>125%</td>
</tr>
<tr>
<td>Total heat at 48 hours (J/gₗₐₚₚ)</td>
<td>197</td>
<td>165</td>
<td>195</td>
<td>234</td>
</tr>
<tr>
<td>Relative total heat at 48 hours</td>
<td>100%</td>
<td>84%</td>
<td>100%</td>
<td>120%</td>
</tr>
</tbody>
</table>

An increased heat of hydration (upward shift of energy curve) was observed across the observation period in the C₃S system through the first 24 h (19% increase) before becoming equivalent to the control at around 30 h and 16% less at 48 h. In the cement system, the CO₂ increased the energy at all times of observation with an increase of 25% at 24 h and 20% at 48 h.

3.2 pH changes

The changes in pH of the pore solutions extracted from C₃S and cement systems with and without CO₂ are shown in Fig. 4. The pH of control C₃S samples varied over a narrow range (between 12.64 and 12.74), while the pH of samples with injected CO₂ was slightly lower at the initial stages (initial observation of 12.40 at 1 min and 12.48 at 6 min), before becoming comparable to the control samples at 60 min and beyond. The cement system exhibited a similar pH response. The pH of control samples was around 12.80 throughout the test period of 180 min of hydration. The samples with injected CO₂ showed a slight reduction in the pH at the start of hydration (12.26) that was maintained through 6 min (pH = 12.28), which was the first common time of comparison to the
control system (pH = 12.79). The pH in the CO2 system increased monotonically during
the first 30 min of hydration to settle at values comparable to that of control samples. In
both case the CO2 addition acidified the pore solution temporarily with a full recovery
within 60 min.

![Graph showing pH changes over time for C3S and cement pastes with and without CO2 addition.]

Fig. 4. Evolution of pore solution pH in C3S and cement pastes in the absence or
inclusion of an addition at 0.3% CO2 by weight of the binder during the sample mixing

It is suggested that the action of the CO2 led to a rapid decrease of pH of the solution at
initial times of hydration through a multi-step dissociation reaction:

\begin{align*}
\text{CO}_2 \ (g) & = \text{CO}_2 \ (aq) \\
\text{CO}_2 \ (aq) + \text{H}_2\text{O} & = \text{H}_2\text{CO}_3 \ (aq) \\
\text{H}_2\text{CO}_3 \ (aq) & = \text{HCO}_3^- \ (aq) + \text{H}^+ \\
\text{HCO}_3^- \ (aq) & \leftrightarrow \text{CO}_3^{2-} \ (aq) + \text{H}^+
\end{align*}

Over the subsequent 30 to 60 min, the pH increased though the reaction of Ca(OH)$_2$ and
precipitation of CaCO$_3$ and the production of OH- to neutralize the acid.

\[ \text{Ca(OH)}_2 + \text{CO}_3^{2-} = \text{CaCO}_3 + 2\text{OH}^- \]
It was observed that CO₂ caused a greater decrease in the pH of the cement pore solution compared to that of the C₃S pore solution. As presented later (Fig. 7), the reduction in the Ca/Si ratio of cement pore solution upon CO₂ injection was higher than observed in the corresponding C₃S pore solution. C-S-H with a lower Ca/Si ratio generally leads to an increase in alkali uptake by C-S-H, which reduces the pH of the pore solution [27–29]. A high initial concentration (50-75 mmol/L) of sulfur (present as SO₃²⁻) in cement pore solution (Fig. 6) would also have lowered the dissolved hydroxide concentration, thereby lowering the pH significantly as the electroneutrality of the solution had to be maintained [27].

3.3 Pore solution chemistry

The elemental molar concentrations (measured by ICP-OES) present in C₃S and cement pore solutions are presented in Fig. 5 and Fig. 6, respectively. Additional analysis is presented in Section 4 of the Supplementary Information. The precision of the equipment/technique was described as 1-2%. Differences are identified where the compared results are more than 5% different thereby being conservatively outside of the expected reproducibility of the measurements. Effects (increases or decreases) observed in the CO₂ activated systems at the earliest times of common observation (6 min) but diminishing at subsequent ages are understood as valid observations according to alignment with trends established at 1, 3 and 10 min observations that were not made in the control systems.

Pore solutions of C₃S samples contained a high concentration of Ca (around 20 mmol/L), followed by those of the alkalis (Na and K). The concentrations of other elements (Si, Al, Mg, and Fe) were less than 0.1 mmol/L for the entire tested duration. Differences observed between the control and the CO₂ cases were evident in the Ca and alkalis. At the first observation of CO₂ system, the Ca concentration was about half that of the average reference concentration across the analytical period. At times of common observations, the Ca was reduced 24% at 6 min before recovering to 13% less at 60 min and within 7% at 180 min. The concentration of Si was elevated an average of 6% across the observation period. The other elements were present in trace quantities in the starting
material. The concentration of Al was an average 20% lower through the first 60 min and comparable thereafter. The alkalis, Na and K, was 15% and 8% lower in the CO₂ activated solution across the observation period. The Mg concentration increased 16% at 6 min, remained 10% greater through 60 min and was comparable thereafter. The S concentration increased 25% at 6 and 10 min, was 10% greater through 120 min, and comparable thereafter. The Fe concentration was not changed by the CO₂ activation.

Fig. 5. Measured molar concentrations present in pore solution of C₃S pastes in the absence or inclusion of an addition at 0.3% CO₂ by weight of the binder during the sample mixing
The level of the Ca concentration in the cement pore solution was slightly lower than that in the C₃S pore solution (around 17 mmol/L). At the first observation of CO₂ system, the Ca concentration was about 60% greater than what the average reference concentration was across the analytical period. At times of common observations, the Ca was increased 40% at 6 min and comparable to the control thereafter. The concentration of Si was lower across the observation period with a reduction of 29% at 6 min and 7 - 12% at later times. Al, Fe, Na and K were not changed significantly by the CO₂. The Mg concentration was about double what the average reference concentration was across the analytical period at the first observation, about 30% greater at 6 min, and close to the control thereafter. The S concentration was 19% greater than the control at 6 min and comparable thereafter.

**Fig. 6. Measured molar concentrations present in pore solution of cement pastes in the absence or inclusion of an addition at 0.3% CO₂ by weight of the binder during the sample mixing**
The ratios of Ca/Si in solution with time for the two binder systems are shown in Fig. 7. The Ca/Si in the solution phase can influence Ca/Si within, and thus the mechanical properties of, C-S-H gel that would be forming [30,31]. The activated C₃S showed a much lower ratio initially compared to later ages, whereas in the activated cement the initial ratio was much higher than it was at later ages. Within the common time comparisons, the Ca/Si of solution at 6 min for the CO₂ activated C₃S was 31% lower than in the control. The ratio increased over time, as it did in the control, but it remained on average 17% lower than the control across the remainder of the observation period. The Ca/Si ratio of the solution phase in the CO₂-activated cement paste was 97% higher than in the control at 6 min and reduced to 13% higher at 15 min. It was thereafter equivalent to, or slightly greater than, the control through to 180 min. The impact in the cement system appeared to be temporary with the Ca/Si development of both systems matching at 10 min and beyond. As supported by the data in Fig. 8, the initial response in the C₃S is for the CO₂ to decrease the Ca in solution and increase the Si, whereas in cement, it acted to increase the Ca and decrease the Si.

Fig. 7. Evolution of Ca to Si ratio in pore solution of C₃S and cement pastes in the absence or inclusion of an addition at 0.3% CO₂ by weight of the binder during the sample mixing.
Fig. 8. Molar concentrations in pore solution relative to the control at common times of comparison for C3S and cement pastes including an addition at 0.3% CO2 by weight of the binder during the sample mixing.

3.4 Saturation indices

Cement hydration is a dissolution-precipitation process wherein the anhydrous material dissolves in the solution, and the hydrates precipitate from the solution [32]. Saturation index (SI), calculated as per Eq. (3), provides the possibility of the two processes occurring vis-à-vis an anhydrous or hydrate phase. SI can either be positive, negative, or zero (equilibrium). A positive value implies oversaturation, suggesting the probability of the precipitation of a phase, while a negative SI implies undersaturation, meaning thereby that the phase is not in equilibrium with the pore solution and is likely to dissolve.
Fig. 9 shows the calculated SIs corresponding to the main phases of concern (C₃S, C-S-H gel, portlandite) in the C₃S and cement systems. Concerning the main hydrate phase C-S-H, the reference C₃S system was supersaturated right from the start of hydration (SI = 0 - 0.2), while the cement system remained mostly undersaturated (SI = -0.3 to 0). On the other hand, both reference systems were undersaturated (in general) with respect to portlandite for the first 30 min of hydration, suggesting a lesser chance of its precipitation, after which SIs became positive, supporting likely precipitation. The saturations with respect to C-S-H and portlandite were affected similarly upon CO₂ injection. In sync with earlier observed effects of CO₂ on chemistry and pH of pore solution (sections 3.2 and 3.3), the over/under-saturation (w.r.t C-S-H and portlandite) of the CO₂-injected system was lower than that of control during the first 30 min of hydration but the differences were reduced at later times. This observed effect can be attributable to the initial pH values in the presence of CO₂.
Fig. 9. Saturation indices of C₃S, CSH, and Portlandite
The addition of CO₂ in both cases (C₃S and cement) increased the undersaturation with respect to C₃S; the impact was stronger in the case of C₃S paste, where the calcium concentrations were clearly decreased in the presence of CO₂. This stronger undersaturation persisted up to 3 h (and possibly longer), which could explain the faster reaction of C₃S in the presence of CO₂ observed by isothermal calorimetry (see Fig. 3). The undersaturation with respect to C₃S is much stronger in the case of the cement as compared to the C₃S binder.

The dissolution of C₃S and the corresponding precipitation of C-S-H and portlandite are linked in series. If either of the two processes is near equilibrium, the other controls the hydration kinetics [33]. SI values of the two hydrates (Fig. 9; close to zero) indicated them to be near-equilibrium conditions, implying that the constraints pertaining to C₃S dissolution were more critical than those corresponding to hydrate precipitation, which could be related to the relatively high sulfate concentrations of 50 mM and more observed in the presence of PC. Nicoleau et al. [34] concluded that sulfate (in addition to Al) has an inhibiting effect on C₃S dissolution. Therefore, it can be postulated that the high sulfate concentrations limits C₃S dissolution in the PC system. Overall, the calculated SIs and the underlying mechanisms elucidated that the effect of CO₂ on the precipitation of main hydrate phases was limited to the initial stages of hydration.

For the entire tested duration, both the systems remained supersaturated with respect to ettringite, monosulfate and hydrotalcite; however, the supersaturation was much lower for the C₃S system. The reason being that those phases require sulfate and Mg, respectively, to precipitate, and since those are trace elements in tricalcium silicate, their elemental concentrations in C₃S as compared to cement pore solution were very low, as also observed experimentally (Fig. 5). No significant effect of CO₂ injection on the saturation indices regarding those phases was observed.
3.5 TGA

The mass loss TGA curves of all samples are included in Section 5 of the Supplementary Information. For purposes of the present analysis, mass losses in the ranges of 105 - 350 °C (taken as loss of bound water from C-S-H gel), 350 - 550 °C (the dehydroxylation of portlandite), and 550°C - 1000 °C (the decomposition of carbonates) were quantified. Further quantitative analysis of the weight losses was made with the derivative of the weight loss plot (derivative thermal gravimetry or DTG) to better characterize the carbonate mass loss in terms of amorphous and crystalline carbonates.

Only times of common comparison between the two conditions are included in the analysis. A summary of the evolution with hydration time of the total mass loss and specific mass losses (carbonates, total bound water, bound water in C-S-H gel and bound water in calcium hydroxide) for both the C3S and cement systems, including the anhydrous condition, is shown in Fig. 10. The mass losses for each binder were normalized to the final mass (after heating to 1000 °C) of the anhydrous binder to allow all mass losses to be expressed on the same basis as the dosage of the CO₂, i.e., as percentages by weight of the anhydrous binder.
Fig. 10. Weight losses (by % of original cement) as measured by TGA. Reported as the total loss, loss associated with carbonates, total loss associated with bound water, loss of bound water from C-S-H gel, and loss of bound water from portlandite.

The anhydrous C₃S had a total mass loss of 0.42%. The total mass was greater (about 1%) than the initial state in both conditions (reference or CO₂) but it did not show an
increasing trend with hydration time. An increased total mass loss observation in both
conditions at 15 and 30 was likely an aberrant result since the solution phase analysis and
thermodynamic modelling did not identify any temporally synchronous anomalies. The
total mass loss on the cement increased with time. The anhydrous cement had a total
mass loss of 1.28% whereas for the initial states of the analyzed samples it was around
2.4% and then increased to around 3.4% by the end of the observation period. The total
mass loss includes loss of water from C-S-H, water from calcium hydroxide, and CO₂
from carbonates. The CO₂ systems had lower amounts of calcium hydroxide and CSH,
and greater amounts of carbonate. The average amount of calcium hydroxide formed in
the CO₂ activated C₃S was about 40% less across the observation period although the gap
closed to 30% less in the final two observations. Likewise, the cement averaged about
30% less calcium hydroxide than in the reference but was within 20% at three hours
hydration. The gel mass loss was about 15% less than the reference in the C₃S system and
10% less in the cement system

Quantitatively, the C₃S samples activated with CO₂ showed an average total net
carbonate gain of 0.21% (excluding comparisons to the anomalously elevated carbonate
content in the control at 15 and 30 min). The cement system with injected CO₂ showed an
average 0.27 wt.% higher carbonate weight loss than the corresponding control sample.
The net carbonate increase in the cement system is very close to the amount of CO₂ dosed
to the system (0.3% by weight of cement). The data from the cement system implied a
90% mineralization efficiency, while in the C₄S system, it was closer to 75%.

Analysis of the DTG mass loss peak attributable to the carbonate (data considered over
the span 450°C to 750 °C) allowed a deconvolution of the overlapping peaks of
amorphous carbonate and crystalline carbonate (examples and results summary provided
in Section 6 of the Supplementary Information). Amorphous carbonate was identified
(with an average observed onset of 550 °C and peak at 605 °C) as a mass loss
abutting/adjacent to the main carbonate mass loss (average peak of 650 °C). The
conclusion is consistent with the work of Thiery et. al. [35] who identified amorphous
carbonate decomposition starting at 550 °C and crystalline carbonate decomposition at
higher temperatures. The two carbonate forms suggest differing degrees of crystallinity and modes of formation [36,37].

Increases to the carbonate content of the hydrated system were only of amorphous carbonate (an average net 0.12% if excluding the anomalously high carbonate data at 15 and 30 min). It is likely that the carbonates in these cases were attributable to environmental exposure. The addition of the CO₂ in the C₃S system resulted in an greater total carbonate content (average 0.21% mass loss) that was representative of crystalline calcium carbonate.

The anhydrous cement sample contained a small amount CO₂ bound in amorphous carbonate (0.08% mass loss) and a larger amount of bound CO₂ within crystalline carbonate (0.58%). The crystalline carbonate would have come from the raw materials for the cement. The addition of the CO₂ to the cement system caused a net increase in total carbonate of 0.27% of which 48% was amorphous.

3.6 SEM

The hydration product formation in the hydrating C₃S and cement systems was evaluated through SEM. As a baseline condition, the micrographs of as-received anhydrous C₃S and cement were captured (see Section 8 of the Supplementary Information). The surfaces of anhydrous particles can be observed to be bare, with some flecks of irregularly shaped debris. An unreacted surface was understood as the baseline condition for subsequent further analysis of hydrated systems.

Fig. 11 presents the micrographs of C₃S paste (control and CO₂) at different hydration times. The surfaces of all hydrated C₃S samples were covered with hydration products (as assessed in comparison to view of the anhydrous starting condition). Rhombohedral-shaped formations with a characteristic dimension of 0.4 - 0.7 µm were present on the surfaces of CO₂-activated samples right from the first observation (one minute after the end of the mixing under the CO₂ injection) up until 60 min. The rhombohedral shape is typical of a crystalline calcite form of calcium carbonate [38–41], which pointed towards
the development of calcite through the mineralization of CO$_2$. This was confirmed by performing EDS on a rhombohedral site of interest identified in the CO$_2$-activated C$_3$S sample hydrated for 3 min (see Section 8 of the Supplemental Information). The EDS spectrum (Fig. 12) showed the presence of Ca, O, and C. While detection of carbon is very common for EDS since even the smallest contamination with organic materials can show the presence of C (e.g., from conductive carbon glue tape used to place the sample), the morphology and absence of a signal from Si indicated that the rhombohedral formations were not a silicate but rather a carbonate particle.
Fig. 11. SEM micrographs showing the formation of hydration products (with time) in C₃S, control and CO₂ activated paste (Cc: Calcium carbonate; CH: Portlandite)
The micrographs of cement paste (control and CO2-activated) at different hydration times are shown in Fig. 13. There is a notable abundance of hydration products in all cement samples starting from time zero (the conclusion of 90 s of mixing) through to 180 min of hydration. Samples at 0 min (both control and with injected CO2) show the development of C-S-H. A few hexagonal crystals of Ca(OH)$_2$, approximately 100 to 300 nm in size, can also be spotted.

**Fig. 12.** EDS spectrum (left) of rhombohedral products observed in C$_3$S sample activated with CO$_2$ at 3 min (right). Analyzed particle indicated with an $\times$
Fig. 13. SEM micrographs showing the formation of hydration products (with time) in cement, control and CO$_2$ activated paste (Cc: Calcium carbonate; CH: Portlandite)
In the case of cement samples with injected CO₂, calcium carbonate crystals were not clearly observed, despite a considerable increase of carbonate content according to TGA. This can be due to either covering of carbonate crystals by other hydration products or a possible formation of amorphous CaCO₃ or a difficulty associated with increased heterogeneity of the cement with respect to the C₃S.

### 4. Conclusions

The early-age changes (up to 3 h) occurring in the C₃S and cement systems activated with 0.3% CO₂ by mass of binder were analyzed through multiple characterization techniques such as calorimetry, ICP-OES, TGA, XRD, and SEM. The observations add to the knowledge base of using CO₂ as a concrete admixture and improves understanding of the associated performance benefits in ready mixed concrete production. Specific conclusions from this study are as follows:

- CO₂ activation caused an acceleration of hydration of C₃S and cement as demonstrated through decreased time to thermal set, increased slope of the main hydration peak, and increased maximum energy release at the hydration peak. In cement, the CO₂ led to greater energy release across the 48 h observation period, with a 20% increase over the control at the conclusion. In C₃S, the total energy release was 19% more than the control at 24 h, equivalent at 30 h, and 16% lower at 48 h.

- Consumption of Ca(OH)₂ in the CO₂ mineralization process reduced the pH of both the binder systems during the first 30 to 60 min of hydration. However, at later times it had rebounded to the level of control sample pH.

- CO₂ mineralization also affected the elemental concentrations observed in the C₃S and cement pore solutions. Compared to control, the CO₂-activated C₃S solution showed slightly but consistently lower concentrations of calcium and alkalis (Na and K). On the other hand, the CO₂-activated cement solution contained higher concentrations of calcium and sulfur (compared to control) only during the first few min of hydration. No significant change in the alkali concentration was observed.

- The Ca/Si ratio of the C₃S and cement pore solutions were impacted differently upon CO₂ activation. Compared to their control counterparts, CO₂ led to lower ratios in the
C₃S system, while the ratios were higher in the cement system during the first 10 min of hydration. Thereafter, ratios equivalent to control were maintained in the cement system, while it remained lower than the control in the C₃S system.

- The observed formation of calcium carbonate in both the CO₂-activated binder systems indicate a strong driving force for the precipitation of carbonates upon CO₂ activation.

- The total amount of reaction products, as detected by TGA in terms of bound water and CO₂, was similar between the two conditions, for both binders, across the first 180 min of hydration. The CO₂-activated systems had an increase in the amount of carbonate and a corresponding decrease in the amount of C-S-H and CH formed.

- SEM micrographs exhibited a multitude of rhombohedral-shaped calcite (confirmed through EDS) crystals in the CO₂-activated C₃S system up until one hour of hydration, while only a few such crystals were spotted in the cement system.
CRediT authorship contribution statement

Sean Monkman: Conceptualization, Methodology, Formal analysis, Writing - review and editing, Funding acquisition.

Yogiraj Sargam: Formal analysis, Writing - original draft, Writing - review and editing.

Olga Naboka: Methodology, Investigation, Supervision, Initial analysis, Writing - original draft, Writing - review and editing.

Barbara Lothenbach: Formal analysis, Writing - review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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References


[38] H. Cheng, X. Zhang, H. Song, Morphological Investigation of Calcium Carbonate during Ammonification-Carbonization Process of Low Concentration Calcium
Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2022.102254.

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