CO₂ Sequestration in Cement-Based Materials During Mixing Process Using Carbonated Water and Gaseous CO₂

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ABSTRACT

This paper presents selected findings from a recently completed research project, aimed at the investigation of CO₂ sequestration in cement-based materials during the early stages of hydration when the cement paste is being mixed. Portland cement pastes were carbonated during the mixing process, using both carbonated water and gaseous CO₂, and their properties were compared to the control non-carbonated mix. All mixes were prepared in a purpose-designed chamber that permitted carbonated water and gaseous CO₂ to be mixed with the cement-based materials during the mixing process, without losses of CO₂ to the external environment. Temperature measurements taken of the samples during mixing were used to evaluate the influence of carbonation on the properties of fresh pastes and their early hydration. Changes in the composition of the hardened pastes, due to the above-mentioned processes, were studied using thermogravimetric (TG) analysis, X ray diffractometry (XRD), and Fourier transform infrared spectroscopy (FTIR). Scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDXS) were used to investigate physical (morphological) and chemical differences between non-carbonated and carbonated samples.

It was found that, when compared to the non-carbonated mixes, the rate of the initial hydration of carbonated pastes increased, but the later hydration rate was decreased dramatically. TG, XRD, and FTIR spectroscopy revealed a substantial increase in the CaCO₃ content and decrease in the Ca(OH)₂ content in carbonated pastes. SEM showed substantial differences in the microstructure of the carbonated mixes when compared to the non-carbonated ones; needle- and lichen-like hydrates, with a high content of CO₂, covered the surface of the fractured carbonated samples.

Keywords: carbonated water, carbonation, CO₂ sequestration, cement hydration, TG, XRD, FTIR, SEM.

1. INTRODUCTION

Concrete is the single most widely used construction material in the world. This drives the production of cement (in 2011, 3.6 Bt was produced globally which is more than three times the 1990 level; CEMBUREAU, 2011), a concrete binding medium, which in terms of embodied CO₂ is one of the “richest” concrete constituents (on average 870 kg of CO₂ is produced per tonne of cement; Damtoft, Lukasik, Herfort, Sorrentino, & Gartner, 2008). Consequently, cement production contributes to at least 5% of global anthropogenic CO₂ emissions, which is estimated to be 85% of the figure associated with building materials sector as a whole (Habert, Billard, Rossi, Chen, & Roussel, 2010). Therefore, reduced cement content through sequestration of CO₂ in concrete products should allow for a significant reduction of concrete carbon footprint.

Naturally occurring carbonation is a well-understood and extensively documented durability problem,

which mainly affects reinforced concrete. In the presence of moisture, CO₂ readily reacts with calcium phases within hydrated cementitious systems to form CaCO₃, a denser and bulkier mineral than the minerals it replaces, but it lowers pH of the hardened cement paste to approximately 9, which in turn can trigger the corrosion of reinforced steel (Papadakis, Vayenas, & Fardis, 1991). However, the mineralogical conversion of calcium phases to CaCO₃ leads to a significant improvement in density and to reduction in porosity and permeability of concrete, beneficially affecting its mechanical and durability properties. Thus, if carbonation is accelerated and occurs at the initial stages of hydration of Portland cement, as is in the case of concrete products cured in presence of CO₂, performance of the products is expected to improve.

Different accelerated carbonation techniques have been developed, mainly based on curing freshly molded or hardened concrete products in elevated

gaseous CO₂ atmosphere or using supercritical or near-to-supercritical CO₂ (Bertos, Simons, Hills, & Carey, 2004). However, these approaches have many drawbacks, for example, carbonation is limited only to the surface of the concrete product, relatively long time of concrete treatment is required, which slows the production, and the high cost of additional equipment. Therefore, alternative methods allowing for carbonation of the whole concrete volume have been recently investigated (Owens, 2010). This involved use of CO₂ dissolved in mixing water, either by dry ice dissolution or by passing CO₂ gas through the water until it was saturated. These strategies resulted only in a slight carbonation of cementitious materials (an increase in CaCO₃ and a reduction in Ca(OH)₂ contents), due to a relatively low solubility of CO₂ in water under atmospheric pressure (0.039 mol L⁻¹; Dodds, Stutzman, & Sollami, 1956). Therefore, one of the objectives of this study was to investigate the use of highly carbonated mixing water and gaseous CO₂ to sequester carbon dioxide in cement-based materials during mixing process.

2. EXPERIMENTAL PROGRAM

The focus of the work presented in this paper was to investigate the influence of early age carbonation on hydration, chemical composition, and microstructure of cement pastes. The control mix (A), prepared in air, was compared with the carbonated mix (B), which was made with carbonated mixing water (treated under 40 bar CO₂ pressure) and mixed in high (ca. 100%) CO₂ concentration.

2.1 Materials

Portland cement CEM I 42.5N with a specific gravity of 3.13 [tested according to ASTM C188-95 (ASTM, 1995)], conforming to BS EN 197-1:2000 (BSI, 2000), was used. The chemical composition of cement was as follows: SiO₂ = 23.43%, Al₂O₃ = 6.54%, Fe₂O₃ = 2.97%, CaO = 59.79%, MgO = 1.85%, Na₂O = 0.23%, K₂O = 0.76%, SO₃ = 2.36%, LOI = 0.90%. The mixing water was from the water mains supply. Carbon dioxide was obtained from Air Products Ltd. at 99.995% purity.

2.2 Preparation of carbonated water

A galvanized steel pressure vessel, shown in Figure 1, was filled with desired amount of water. Afterwards, the vessel was closed and the pressure was raised to 41 bars above atmospheric by filling the vessel with CO₂ from a pressurized cylinder. Pressure inside the vessel was periodically monitored and if dropped below 40 bar, additional CO₂ was admitted. This process was considered to be finished once the pressure inside the vessel did not drop below 40 bar within a 24-h period. This ensured that desired content of CO₂ was

dissolved in the mixing water (ca. 1.090 mol of CO₂ L⁻¹ of water; Dodds et al., 1956).

Figure 1. The pressure vessel (used for the carbonation of the mixing water) connected to the environmental chamber.

2.3 Mix preparation

The pastes were prepared in a 5-L Hobart mixer in 1.7-L batches. The mixer was inside the environmental chamber, as shown in Figure 2. A sample of cement was placed in a mixing bowl and the environmental chamber was closed and sealed. The outlet valve was left open.

Prior to mixing of paste A, the environmental chamber was purged for 10 min with compressed air. Afterwards, the mixer was switched on at a low speed (140 rpm) followed by the direct introduction of designed amount of the non-carbonated mixing water (± 1 g), at temperature of $17 \pm 1^\circ\text{C}$, to the mixing bowl. After the water was added to the mixing bowl, the outlet valve of the environmental chamber was closed. The paste was continuously mixed for a duration of 25 min, counting from the moment when water first touched cement.

Prior to mixing of the mix B gaseous CO₂ was admitted to the sealed environmental chamber until the CO₂ concentration reached 95–100%. Then, the CO₂ inlet valve was closed. The rest of the procedure was the same as for mix A with the exception that this

time carbonated water, prepared under 40 bar CO_2 pressure, was used.

Figure 2. Schematic of setup used for paste mixing.

2.4 Sample collection and preparation

Samples were collected at 0.5, 10, and 25 h after beginning of mixing, as specified below:

- At 0.5 h a fresh sample of the paste was placed in a plastic bottle. Acetone was added to the sample bottle to enable the unreacted water to be removed from the cement paste. The mixture was centrifuged and decanted five times within a 1-h period after sample collection (each time the bottle was refilled with fresh portion of acetone). Afterwards the bottle was again filled with acetone, air-tight closed, and stored for future testing.
- At 10 and 25 h, the hardened cement paste was crushed and pieces obtained from the inner part of the 50 mm size cubes were placed in acetone filled plastic bottles that were subsequently sealed.

After 7 days, the acetone was removed from the bottle and the bottle was immediately transferred to a desiccator and stored for ca. 24 h under vacuum. To facilitate testing, dried samples were divided into two portions. Samples for thermogravimetric (TG), X ray diffractometry (XRD), and Fourier transform infrared spectroscopy (FTIR) studies were powdered using mortar and pestle to obtain a powder passing a 63- μm sieve. Immediately after grinding, powdered samples were placed in sealable plastic bags and stored in the desiccator under vacuum until testing. SEM analysis was carried out on fractured fragments. These samples were transferred to an air-tight plastic bottle for storage.

2.5 Testing methods

Conditions in the environmental chamber were measured with several sensing devices to determine apparent gaseous CO_2 concentration, relative

humidity, and temperature within the chamber (all at 10 s intervals). In addition, a novel temperature sensor was utilized to continuously measure, at 5 s intervals, the temperature development of the paste during the mixing process. Details are provided below.

CO_2 concentration in the environmental chamber was measured, at 10 s intervals, with a commercially available CO_2 sensor which uses non-dispersive infrared technology to sense, as a function of transmitted light, the concentration of CO_2 in air (measurement range of 0–100% CO_2 concentration, resolution of 0.01% and accuracy of $\pm 0.5\%$).

Paste temperature during mixing process was measured with a commercially available self-sufficient temperature logger (measurement range of -40 to 85°C , resolution of 0.06°C and accuracy of $\pm 0.5^\circ\text{C}$). The sensor, which was attached to the mixing blade, recorded measurements at 5 s intervals.

Heat of cement hydration was measured using isothermal calorimetry method (the reaction heat rate was measured at constant temperature of 20°C), using TAM Air Isothermal Conduction Calorimeter. Paste samples (5 ± 0.5 g) were collected straight after mixing and transferred to a plastic ampoule, which was immediately placed in a cell of the calibrated calorimeter. Data collection was started exactly 1 h after beginning of paste mixing (ca. 30 min after the placement of the ampoule in the cell).

Thermogravimetric analysis was used to confirm the type and quantify of hydrates developed in the paste samples. Powdered samples of 50 ± 3 mg were examined using Netzsch's STA 449C Jupiter. The temperature was ramped from 25 to 1000°C , at a rate of $20^\circ\text{C}/\text{min}$, in nitrogen atmosphere. The weight loss information, obtained from TG curve and TG first derivative (DTG), were used to estimate the amount of the hydration phases; in particular $\text{Ca}(\text{OH})_2$ and CaCO_3 .

Powdered samples were analyzed using XRD, with PANalytical X'Pert PRO diffractometer, to identify the crystalline components. Diffraction patterns were collected between 5° and 65° 2θ with a step size of 0.016° . PANalytical X'Pert Highscore software with the Powder Diffraction File database was employed to elucidate the mineralogy of the samples based on the diffraction patterns.

To qualitatively identify CaCO_3 and $\text{Ca}(\text{OH})_2$ phases powdered samples were analyzed using FTIR. PerkinElmer Spectrum 100 Series FTIR Spectrometer with Attenuated Total Reflectance attachment was used. The spectra were gathered between 550 and 4000 cm^{-1} wavenumber at 4 cm^{-1} intervals. Essential FTIR software version 2.00.045 was used to analyze the FTIR spectra.

Scanning electron microscopy (SEM), with X ray microanalysis [Energy Dispersive X ray Spectroscopy (EDXS)], was used to study microstructure of paste samples. Fractured samples were analyzed using Jeol 6500F Field Emission SEM.

3. RESULTS AND DISCUSSION

3.1 CO₂ concentration in the environmental chamber

As expected, the gaseous CO₂ concentration for mix A was below atmospheric level (<0.04%), see Figure 3.

Figure 3. CO₂ concentration in the environmental chamber during mixing process.

For mix B, the initial gaseous CO₂ concentration was ca. 98% increasing to 100% when carbonated mixing water was admitted into the chamber. However, during mixing the CO₂ levels decreased due to its reaction with the hydrating cement paste. At the end of the mixing process ~40 vol.% of gaseous CO₂ had reacted with the paste, which in terms of CO₂ concentration dissolved in the mixing water equates to 1.655 mol L⁻¹. In addition, a part of the CO₂ dissolved in carbonated water was sequestered in paste B. Although this amount is difficult to quantify directly, the remaining concentration of dissolved CO₂ in carbonated water, once it was admitted to the chamber holding nearly 100% gaseous CO₂, was at least ~0.219 mol L⁻¹ (see Discussion in following paragraph).

Theoretical concentration of CO₂ dissolved in water carbonated under 40 bar of CO₂ is ~1.090 mol L⁻¹ (Dodds *et al.*, 1956). When the same volume of carbonated water as used for paste mixing was admitted to the mixing bowl alone, the environmental concentration of CO₂ raised and stabilized at ca. 38.1 vol.% (Fig. 3). Consequently, the equilibrium between concentrations of CO₂ dissolved in water and this in the chamber's atmosphere was reached. At this equilibrium the remaining concentration of CO₂ dissolved in the water was estimated at ~0.219 mol L⁻¹.

3.2 Mix temperature during mixing

Normalized temperatures of mixes A and B as a function of time are depicted in Figure 4.

Temperature of mix A increased by 2°C in the first minute of mixing and then increased more gradually by a further 2°C. This was obviously caused by initial reaction between water and cement compounds.

In the case of mix B, due to the highly exothermic reaction between CO₂ and the initial cement hydrates, or cement-originating ions dissolved in the mixing water, temperature increased rapidly with an increase in the mixing time. It is worth to note that at the end of the mixing process the paste reached apparent temperatures in excess of 45°C.

Moreover, it was observed that with the increase in the temperature of paste B more energy was required to mix it, which indicates the loss of workability with time. This was supported by visual observation such as partially dry lumps of cement particles were visible in the mixing bowl, indicating fast hydration of cement and subsequent partial dehydration.

Figure 4. Normalised temperature of the pastes during mixing.

3.3 Heat of hydration

The heat flow results between 1 h and 5 days after hydration began are shown in Figure 5.

The heat evolution of the control mix A follows the expected pattern for neat cement paste hydration (Taylor, 1990). The initial peak (Stage 1) and some of the dormant period (Stage 2) are missing in this graph. The main hydration period, as evidenced by the increase in heat flow, is observed between 8 h and 11 h. In addition, between 1.5 and 2.5 days, an additional peak can be identified, which is associated with further hydration of the remaining C₃A phase (Aitcin, 2008).

The heat evolution curve of mix B is very different from that obtained for mix A. It appears that only limited

hydration took place between 1 h and 1 day from the period when hydration began. This suggests that hydration was hindered, possibly as a consequence of the coating of the unreacted cement particles with the carbonation products (reaction of cement hydrates with CO_2 during the 25 min of mixing).

Figure 5. Rate of heat evolution of cement pastes.

3.4 TG results

Figure 6 depicts the Ca(OH)_2 and CaCO_3 contents in mix A (non-carbonated) and mix B (carbonated) at different times during the first 25 h after beginning of hydration. Results are compared with the quantity of these two compounds obtained from unreacted cement (CEM I).

For the mix A, the Ca(OH)_2 content changed from the level measured for the unreacted cement (0.3%) to ca. 0.2, 8.0, and 11.4% at 0.5, 10, and 25 h of hydration, respectively. These results are in a good agreement with the literature (Ramachandran, Paroli, Beaudoin, & Delgado, 2002). In the case of mix B, the amount of Ca(OH)_2 at these particular testing times was 1.1, 1.7, and 3.7%, respectively.

Where the CaCO_3 content is concerned, the non-carbonated mix A had approximately 50% increase in the presence of CaCO_3 when compared with the unreacted cement (from 1.05% for unreacted cement to 1.59% at 25 h of hydration). In contrast, mix B exhibited a sharp increase (nearly 400%) in CaCO_3 content just within first 30 min of hydration (value of 5.2%). The content at 25 h increased marginally to ca. 5.5%.

These results clearly indicate that early carbonation (which in this case was purposefully accelerated) significantly increased the kinetics of the hydration in the first 30 min of the hydration process. On the other hand, the lower content of Ca(OH)_2 at 10 and 25 h suggests that further reaction was hindered, as alluded to by the results from the heat of hydration test.

Figure 6. Contents of Ca(OH)_2 and CaCO_3 in cement pastes.

3.5 FTIR results

The FTIR spectra of the mixes A and B and unreacted cement (CEM I) are shown in Figure 7.

As opposed to mix B, at the age of 0.5 h no Ca(OH)_2 was detected in unreacted cement and in mix A (narrow peak due to OH stretching at wavelength of ca. 3643 cm^{-1}). In contrast, at the age of 10 and 25 h, sharper Ca(OH)_2 peak was observed when comparing to mix B.

In comparison to CEM I, it is clear from the graph that water was present in both mixes at all tested ages (stretching and bending vibrations of water are at ν_1 and ν_2 of approximately 3430 and 1642 cm^{-1} , respectively).

CaCO_3 is identified at wavenumber of 712 cm^{-1} (ν_4 —split in-plane bending vibration), 847 and 873 cm^{-1} (ν_2 —out of plane bending of CO_3^{2-}), and 1429 – 1492 cm^{-1} (ν_3 —asymmetric stretching of CO_3^{2-}). Therefore, it can be noted that at each investigated age peaks assigned to CaCO_3 were more pronounced for mix B than for mix A, suggesting higher CaCO_3 content in mix B. Most

Figure 7. FTIR patterns of cement pastes.

importantly, a very high quantity of CaCO₃ in mix B was observed directly after mixing, that is at 0.5 h.

Although the FTIR results are only of qualitative significance, they also indicate, similarly to results presented in Section 3.4, a more rapid initial hydration and considerably higher development of CaCO₃ where mix B is concerned.

3.6 XRD results

XRD data for mix A, mix B and unreacted cement (CEM I) are shown in Fig. 8.

Results indicate that after 30 min hydration mix A had a higher gypsum peak (located at 2θ of 11.7°) than mix B, see Figure 8a. As shown in Figure 8c, mix A had also higher C₃A peak (located at 2θ of 33.3°) and peaks assigned to C₂S and C₃S (located at 2θ of 32.3°, 32.7°, and 34.4°), see Figure 8b. Furthermore, AFt peaks (located at 2θ of 9.1° and 15.8°) appears to be higher for mix B (Figure 8a). All above observations suggest that, at this particular time, mix A had lower hydration degree than mix B.

At 25 h, all C₂S and C₃S peaks were lower for mix A (Figure 8b), whilst those assigned to Ca(OH)₂ were higher (located at 2θ of 18.1°, 28.7°, 34.1°,

47.1°, 50.8°, and 54.4°; see Figure 8b–d). These observations clearly indicate that at 25 h the degree of hydration for mix A was higher than that of mix B. Interestingly, AFt content of mix B was higher than that of mix A (Figure 8a).

It is worth mentioning that at both investigated times the calcite (CaCO₃) peaks (located at 2θ of 39.4°, 43.2°, and 48.6°; Figure 8d), and therefore calcite content, were slightly higher for mix B.

3.7 SEM/EDXS results

Figure 9 shows SEM images of the 25-h old non-carbonated (mix A) and carbonated (mix B) paste mixes, respectively.

It can be seen that the fractured surface of the mix A (Figure 9a) contains unreacted cement grains and products of cement hydration.

In contrast, the fractured surface of the sample B (Figure 9b) was covered with a layer of fibers/needles (<5 µm long and <0.5 µm width). Under the needles, a layer of very small lichen-like particles (<0.2 µm in cross-section) was found. Both the needle- and lichen-like particles appear to be well developed, with very high surface area. An additional

Figure 8. XRD patterns for 2θ of (a) 8–17°, (b) 17–24°, (c) 28–35°, and (d) 35–55°.

Figure 9. SEM micrographs of 25 h old (a) non-carbonated sample (mix A) and (b) carbonated sample (mix B).

EDS analysis revealed that both forms had a high concentration of CO_2 .

Considering morphological similarities with ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$), it can be speculated that needle-like structure is a carbonated ettringite with a chemical formula of $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{CO}_3)_3 \cdot 26\text{H}_2\text{O}$. Possibly, as a result of high CO_2 uptake during carbonation process, an ion exchange took place, that is SO_4^{2-} was fully or partially replaced by CO_3^{2-} . It was already mentioned by Taylor (1996) that if high quantity of CO_2 is present for carbonation “the carbonate analog of ettringite” will be formed. However, it was stressed that calcite is the more likely compound to occur. Nevertheless, more background research is needed to fully understand this very interesting phenomenon.

4. CONCLUSIONS

Two paste mixes were manufactured, namely, a non-carbonated one (mix A, control) and an extensively carbonated one (mix B, made with carbonated water under 40 bar CO_2 pressure and mixed in gaseous CO_2 for 25 min), with intention to study the changes caused by carbonation during mixing process. Based on the results presented in this article, following conclusions have been reached:

- Using direct measurement of CO_2 concentration in the chamber during the mixing process, it was demonstrated that it was possible to incorporate in the mix B a minimum of $1.655 \text{ mol of } \text{CO}_2 \text{ L}^{-1}$ of mixing water.
- Higher temperatures were recorded during mixing of cement with carbonated water in gaseous CO_2 environment compared to the control mix. This was a consequence of the reaction between the initial cement hydrates and CO_2 dissolved in the

mixing water (present in the carbonated water, or dissolved from the CO_2 rich environment).

- When compared to the non-carbonated mix A, the heat of hydration results indicate that the rate of initial hydration increased during mixing with carbonated water in gaseous CO_2 environment but was seriously hindered at later ages.
- TG, XRD, and FTIR studies revealed a substantial increase in the CaCO_3 content and decrease in the $\text{Ca}(\text{OH})_2$ content when carbonated water and gaseous CO_2 were used. SEM showed substantial differences in the microstructure of the carbonated mix—needle- and lichen-like hydrates with a high content of CO_2 covered the surface of the 25-h old fractured carbonated sample.

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