



Montréal, Québec
May 29 to June 1, 2013 / 29 mai au 1 juin 2013

Microstructure and properties of concrete subject to early carbonation curing

Vahid Rostami¹, Yixin Shao¹, Andrew J. Boyd¹ and Zhen He²

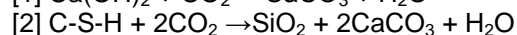
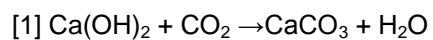
¹Department of Civil Engineering and Applied Mechanics, McGill University

²School of Water Resources and Hydropower Engineering Science, Wuhan University

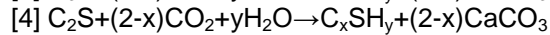
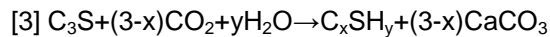
Abstract: Microstructure and properties of concrete subject to early age carbonation curing was studied to examine the effect of early carbonation on performance of concrete at different ages. The study was intended to understand the mechanism of concrete carbonation at early age through the microstructure development of its cement paste. Early carbonation was carried out after 18-hour initial controlled air curing and followed by a subsequent hydration. The microstructure characterized by XRD, TGA, ²⁹Si NMR and SEM was correlated to strength gain, CO₂ uptake and pH change. It was found that early carbonation was capable of accelerating early strength and allowing subsequent hydration after carbonation. The short term carbonation created a microstructure with more strength-contributing solids than conventional hydration. Calcium hydroxide was converted to calcium carbonates, and calcium-silicate-hydrate became intermingled with carbonates, generating an amorphous calcium silicate hydrocarbonate binding phase. Carbonation modified C-S-H retained its original gel structure. The re-hydration procedure applied after carbonation was essential in increasing late strength and durability. The pH of pore solution after early carbonation and re-hydration was of close value to reference. In addition to significant contribution to strength gain, the subsequent hydration helped improve durability. The proposed carbonation curing scheme seems to have the potential to be considered as an alternative to steam curing for various precast concrete products, offering technical, economical and environmental benefits.

1 Introduction

Carbonation curing is a procedure in which CO₂ is intentionally introduced to concrete at its early age in order to improve mechanical (Berger et al. 1972; Goodbrake et al. 1979; Young et al. 1974) and durability properties (Rostami et al. 2011). The governing carbonation reactions which occur at early age of concrete are different from those of detrimental weathering carbonation during concrete service life; in weathering carbonation, hydration products including calcium hydroxide (CH) and calcium silicate hydrates (C-S-H) are carbonated (Eqs.[1-2]), and calcium carbonate and silica gel are produced. These undesirable reactions lead to full decalcification of C-S-H and reduce alkalinity of the pore solution which adversely affect the mechanical properties and corrosion resistance of the steel reinforcement (Castellote et al. 2009; Slegers and Rouxhet 1976).



In early carbonation curing, however, calcium-silicates (C_2S and C_3S) contribute in the carbonation reactions and generate C-S-H and calcium carbonate (Eqs. [3-4]) leading to high early strength (Goodbrake et al. 1979; Young et al. 1974).



Early carbonation of concrete can be beneficial. It can function as an accelerated curing technique (Goodbrake et al. 1979; Young et al. 1974) and reduce carbonation shrinkage in service (Toennies 1960). In addition, early carbonation curing offers a CO_2 sequestration method by permanent storing of the greenhouse gas within precast concrete products (Shao and Mirza 2006) such as masonry blocks, concrete pipes, fiber-cement wallboards, concrete piles, and hollow core slabs.

Although early carbonation could be technically beneficial to concrete, it cannot be applied to fresh concrete, since the water saturated capillary pores prevent CO_2 penetration. Therefore a pre-conditioning procedure is required to remove enough free water from concrete in order to allow early carbonation reactions to proceed. It has been suggested that 18 hours of pre-conditioning in 60% relative humidity and $25^\circ C$ could make feasible early carbonation curing of concrete (Rostami et al. 2012).

This paper explores the performance of concrete cured by early carbonation. It also examines the microstructural effects of early carbonation in the material level using X-Ray diffraction (XRD) analysis, thermogravimetry analysis (TGA), ^{29}Si nuclear magnetic resonance (NMR) spectroscopy and Scanning Electron Microscopy (SEM).

2 Experimental program

Concrete slab samples of 40 mm × 76 mm × 127 mm were cast using a mixture proportion representing general precast concrete products: cement (general use cement) = 320 kg/m³, water/cement=0.36, water = 115 kg/m³, fine aggregate = 1092 kg/m³ and coarse aggregate = 728 kg/m³. Immediately after vibration-compaction casting, different curing regimes were applied to the concrete samples, as summarized in Table 1.

Table 1: Curing conditions for concrete

| Batch ID | Curing procedure | Initial curing | Carbonation curing | Subsequent curing |
|----------|--|---------------------|-----------------------------|---------------------|
| B1, B8 | Air curing ^a | 20h open air curing | 0h Carbonation | Sealed ^e |
| B3, B10 | Carbonation ^b without water spray | 18h open air curing | 2h Carbonation | Sealed |
| B11 | Carbonation with water spray | 18h open air curing | 2h Carbonation+ water spray | Sealed |
| B4, B7 | Steam curing ^c | 4h steam curing | 0h Carbonation | Sealed |
| B2, B9 | Sealed curing ^d | Sealed curing | 0h Carbonation | Sealed |

^aAir curing: at 25 °C, 60%RH in an environmental chamber.

^bCarbonation curing: 0.15 MPa gas pressure.

^cSteam curing: at 63 °C in saturated steam.

^dSealed curing: at 25 °C, in a sealed container.

^eSealed: applied only to B5, B8, B10 and B9 up to 28 days.

Batches B1 and B8 served as a reference which was initially air cured for 20-h. Other reference batches were B4 (steam-cured) and B2 and B9 (sealed-cured). At the beginning of the steam curing, the temperature was gradually increased from the room temperature (25 °C) to 63 °C in one hour. The steam curing conditions were kept for four hours. The Batches B3, B10 and B11 were initially air-cured in an

environmental chamber in 60% RH and 25°C for 18-h before 2-h carbonation curing. The carbonation was conducted in a chamber wherein pure CO₂ was injected to reach a 0.15 MPa gas pressure and the mass of the system was monitored, as schematically shown in Figure 1.

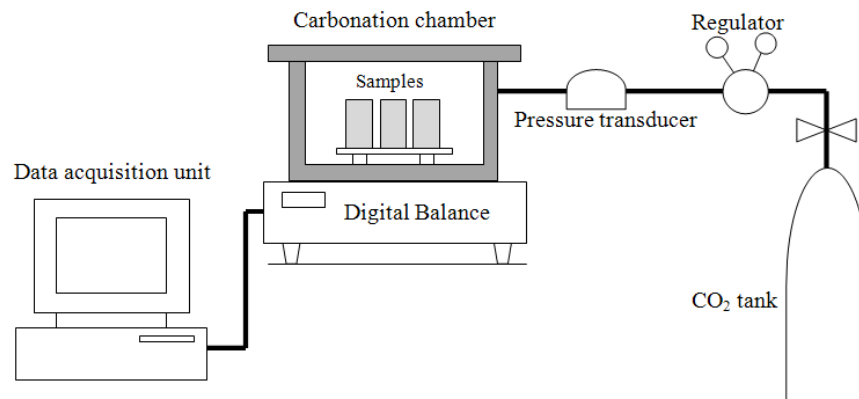


Figure 1: Schematic of early carbonation set up

Batch B11 was water compensated for the amount of water lost during the initial air curing and carbonation curing. The water compensation was done by spraying water equal to the amount the lost water, back on concrete samples. The samples were then sealed to allow gradual absorption of the sprayed water. Both batches B10 and B11 were kept sealed for subsequent hydration until the designated test date. To study the microstructure of the binding phase in the carbonated concrete, paste samples of 14×14×6 mm were prepared and cured exactly the same as the concrete.

The amount of CO₂ uptake was calculated by two independent methods. In the first method, mass gain, the mass of the samples before and after carbonation as well as the mass of water lost during the carbonation (according to Eqs. [1-2]) were recorded and Eq. [5] was used to find the CO₂ uptake. In the second method, mass curve, the curve obtained by monitoring the mass during the 2-h carbonation was used to calculate mass increase due to CO₂ absorption (Mass_{CO₂}) and find the CO₂ uptake using Eq. [6].

$$[5] \text{ CO}_2 \text{ uptake} = \frac{[\text{Mass}_{\text{after carbonation}} + \text{Water}_{\text{lost}}] - \text{Mass}_{\text{before carbonation}}}{\text{Mass}_{\text{cement}}}$$

$$[6] \text{ CO}_2 \text{ uptake} = \frac{\text{Mass}_{\text{CO}_2}}{\text{Mass}_{\text{cement}}}$$

The compressive strength and the pH of the concrete samples were measured at early (20-h) and late (28-d) age. To examine the phase change due to the carbonation, XRD, TGA, ²⁹Si NMR and SEM analysis were conducted on the preserved paste samples. To find the concrete pH values, a simple ion extraction method (Heng and Murata 2004) using a pH meter with flat sensor was employed. XRD phase analysis was conducted on powder samples taken from the outer 2mm surface of the samples using a Phillips PW1710 Power Diffractometer (Cu K α radiation, scan interval 15-55° 2 θ , 0.02° and 0.5 s per step). Same powder samples were used thermogravimetry analysis using a NETZSCH thermal analyzer (TG 449 F3 Jupiter) with a resolution of 0.01 mg to run TGA and obtain the mass loss of the samples in the range 25 °C to 950 °C at the heating rate of 10 °/min. The silicate structure of C-S-H was studied by examining the ²⁹Si NMR spectra obtained at 59.5 MHz using an Agilent/Varian VNMRS-300 spectrometer. A spinning rate of 4000 Hz was applied to 100 μ g powder samples packed in 7.5 mm zirconia rotors. The morphology of the pastes was also studied on the fractures surface using a variable pressure (VP) SEM in SE mode.

3 Results

Table 2 presents the early and late strength of concrete under different curing conditions. At early age (20-h), the early carbonation cured concrete (B3) was considerably stronger than the sealed-cured (B2) and air-cured (B1). Nevertheless, compared to the steam-cured concrete, the carbonated sample has less strength at 20-h. The 28-day water-compensated carbonated concrete (B11) had comparable strength to the steam (B7) and the hydrated reference (B9). However, the carbonated concrete without water compensation had a poor strength at late age, manifesting the significant role of the subsequent hydration in the performance of carbonation-cured concrete.

Figure 2 shows the pH distribution at different depths of the carbonation-cured concrete at early and late age, and compares the values with those of the reference concrete. It was observed that the pH dropped only in the outer 10mm surface zone, while the alkalinity from the depth of 10mm to the concrete core was preserved above the threshold value (pH=10.5) needed to protect the passivation layer on the embedded reinforcing steel. This result supports the idea of utilizing carbonation curing for reinforced precast products.

Table 2: Strength gain and carbon uptake

| Curing condition | Age | Strength (MPa) | Carbon uptake (%) | | |
|------------------|------|----------------|-------------------|------------|---------|
| | | | Mass gain | Mass curve | Average |
| B1 | 20-h | 17.0±0.4 | 0 | 0 | 0 |
| B2 | 20-h | 18.7±0.9 | 0 | 0 | 0 |
| B3 | 20-h | 23.3±1.0 | 7.2±0.3 | 7.4±0.2 | 7.3±0.2 |
| B4 | 20-h | 26.5±1.4 | 0 | 0 | 0 |
| B7 | 28-d | 36.8±0.9 | 0 | 0 | 0 |
| B8 | 28-d | 22.1±1.1 | 0 | 0 | 0 |
| B9 | 28-d | 39.8±2.9 | 0 | 0 | 0 |
| B10 | 28-d | 28.8±1.7 | 6.9±0.2 | 7.3±0.2 | 7.1±0.2 |
| B11 | 28-d | 38.9±0.3 | 7.3±0.4 | 7.5±0.3 | 7.4±0.4 |

Figure 3 compares the XRD patterns of the paste samples associated with different curing regimes. Comparing the air cured (B1) with the carbonated (B3) patterns indicates a significant reduction of CH in the carbonated zone and an increase in the intensity of the peaks of calcium carbonates. Although the CH peak grew stronger in the carbonated and water-compensated batch (B11) due to further hydration, it remained weaker than that of the hydration reference (B9) up to 28 days. The reduced CH content in the carbonated zone can explain the pH drop on the concrete surface, as observed in Figure 2. It is worth noting that calcium silicates peaks in B3 are weaker compared to B1, due to the carbonation-hydration reactions (according to Eqs.[3-4]). This phase transformation which led to formation of C-S-H (carbonation-hydration) contributed to early strength gain in the carbonation-cured concrete (Young et al. 1974).

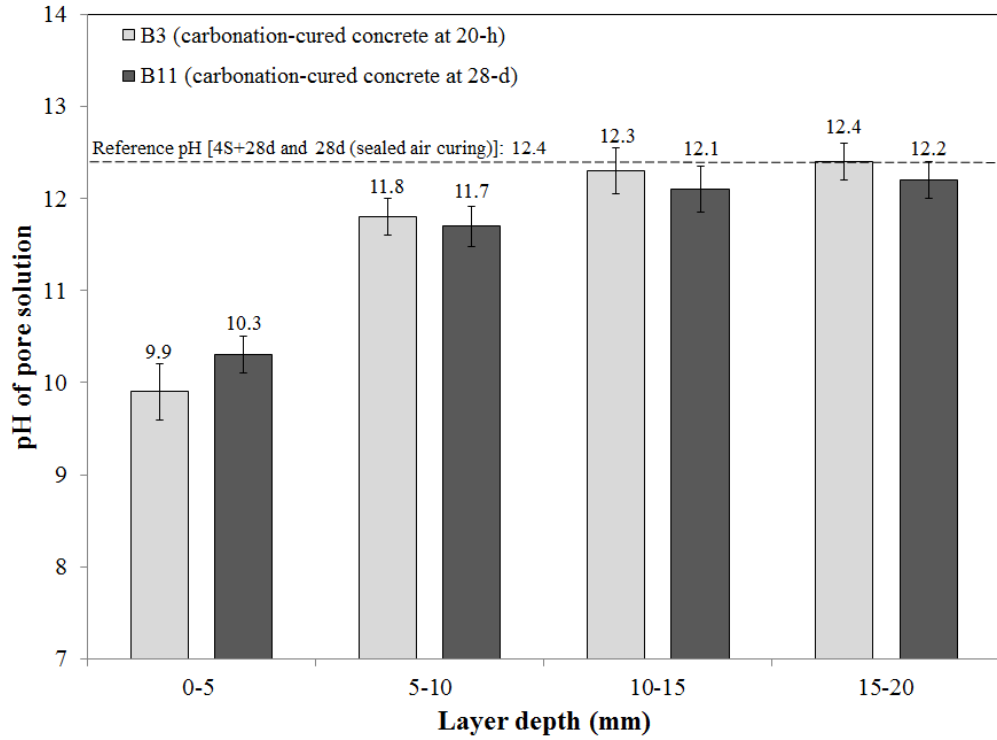


Figure 2: Distribution of pH values over thickness of carbonated concrete

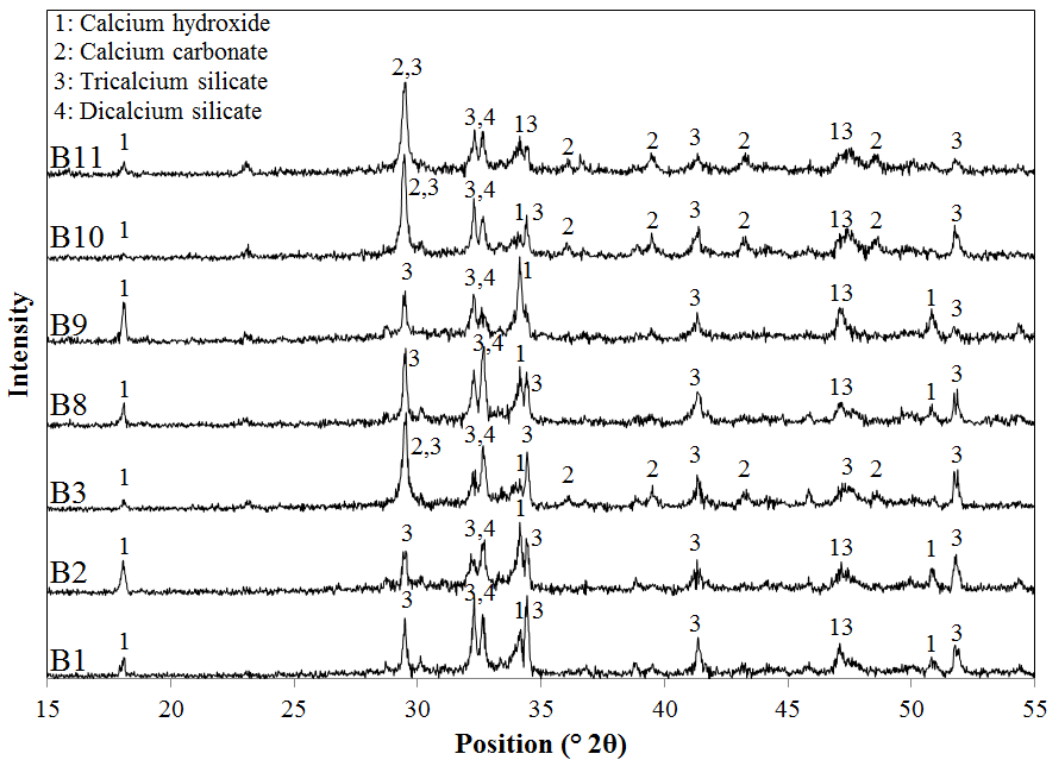


Figure 3: XRD patterns of paste samples

Figure 4 compares the DTG curves of cement paste batches obtained the temperature range 105 to 950 °C. The peaks shown in the DTG curves represent important endothermic events regarding decomposition of various phases. The mass loss in the range 105 to 420 °C is associated with dehydration of several hydration products such as calcium silicate hydrate, aluminate hydrate and ferrous aluminate hydrate (Ramachandran and Beaudoin 2001; Sha et al. 1999; Sharma and Pandey 1999). The dehydration of calcium hydroxide occurs between 420 and 540 °C (Ramachandran and Beaudoin 2001; Sha et al. 1999). Calcium carbonate is decomposed at higher temperatures: well-crystalline calcium carbonate is decarbonated between 720 and 950 °C (Short et al. 2001) and the poorly-crystalline undergoes mass loss between 540 and 720 °C (Goto et al. 1995; Sauman 1971).

The DTG results confirmed the low CH content in the carbonated batches (B3, B10 and B11) as suggested earlier by the XRD phase analysis; this fact can be readily deduced from the reduced peak intensity at about 450°C corresponding to CH dehydration. All the batches, including the hydrated samples (B1, B2, B8 and B9) have a common DTG peak at about 750°C which shows the presence of carbonates in the as-received cement. The carbonated batches have additional endothermic peaks in the decarbonation temperature range corresponding to both poorly-crystalline and well-crystalline calcium carbonates.

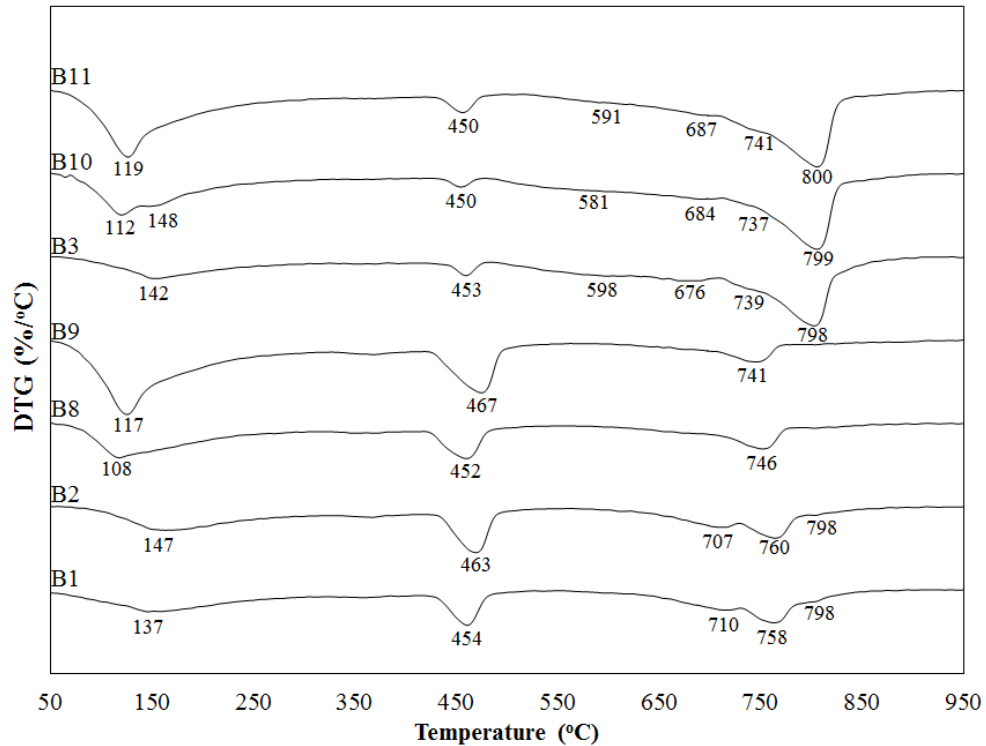


Figure 4: Comparison of DTG curves of paste samples at early (20h) and late (28d) age

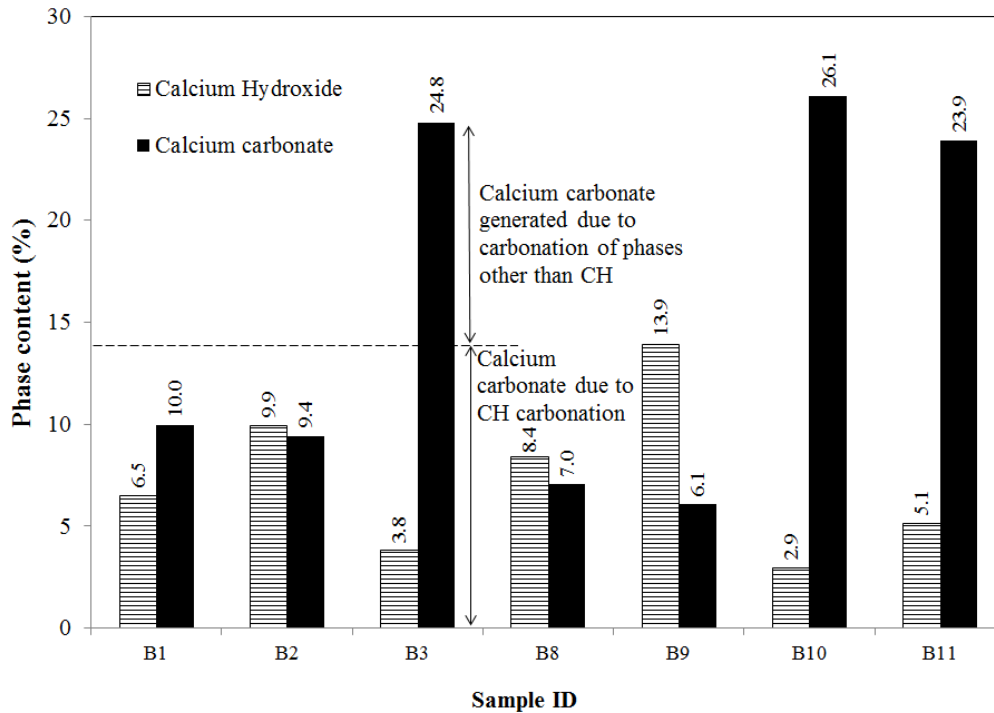


Figure 5: The calcium hydroxide and calcium carbonate content of the paste samples

A quantitative analysis on the CH and calcium carbonate phases was conducted based on the thermogravimetric results (Figure 5). It was observed that the amount of calcium carbonates that could possibly be produced at early age due to the CH to CaCO_3 transformation in the carbonated sample (B3) was considerably lower than the real calcium carbonate content. Therefore, it was concluded that the phases other than CH, such as C-S-H and calcium silicates could also be affected by the carbonation. The calcium carbonate produced by the carbonation curing was a stable phase and the content remained almost unchanged in the late age (B11).

Figure 6 compares the ^{29}Si NMR spectra of all batches. Q_0 is the representative of the unreacted calcium silicates phase content; Q_1 and Q_2 indicate the extent of dimer and linear chain bonds in C-S-H, respectively. The hydration reactions led to Q_0 decrease and Q_1 and Q_2 increase (B2 and B9). The early carbonation reaction clearly increased the relative intensity of Q_2 suggesting a higher polymerization degree in the C-S-H phase. Nevertheless, the original C-S-H structure was retained; the carbonation-induced polymerization was not such intense to form silica gel, since no sign of Q_3 and Q_4 was observed (Sauman 1971). This result suggested that the early carbonation curing was not detrimental to C-S-H structure, unlike weathering carbonation in which C-S-H could totally turn into silica gel (Slegers and Rouxhet 1976). The high early strength gained in the carbonated batch (B3) compared to the reference (B1) (Table 2), seems to be owing to the carbonation-modified C-S-H structure.

Typical SEM micrographs taken from the freshly fractured surfaces of the hydrated and carbonated pastes are presented in Figure 7. Typical features of a hydrated cement phase can be easily distinguished in Figure 7a: an amorphous C-S-H phase accompanying well-crystalline hexagonal CH. However, in the carbonated paste (Figure 7b) no crystalline features were detectable. Although the Energy Dispersive Spectroscopy (EDS) spot analysis suggested the presence of carbonates in the amorphous zone, no pure crystalline carbonate was visible at 2.5k magnification. This observation suggested the co-existence of carbonates and C-S-H in amorphous form, which is hypothesized to be calcium-silicate-hydro-carbonate.

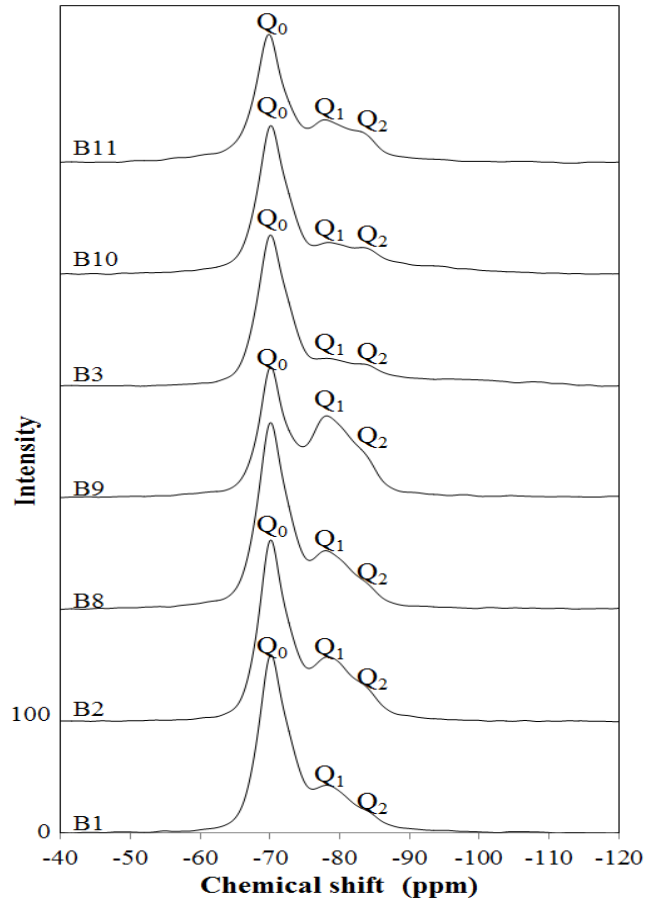


Figure 6: ^{29}Si NMR spectra of carbonated and reference samples (peaks are approximately at $Q_0=-70\text{ppm}$, $Q_1=-79\text{ppm}$ and $Q_2=-83\text{ppm}$).

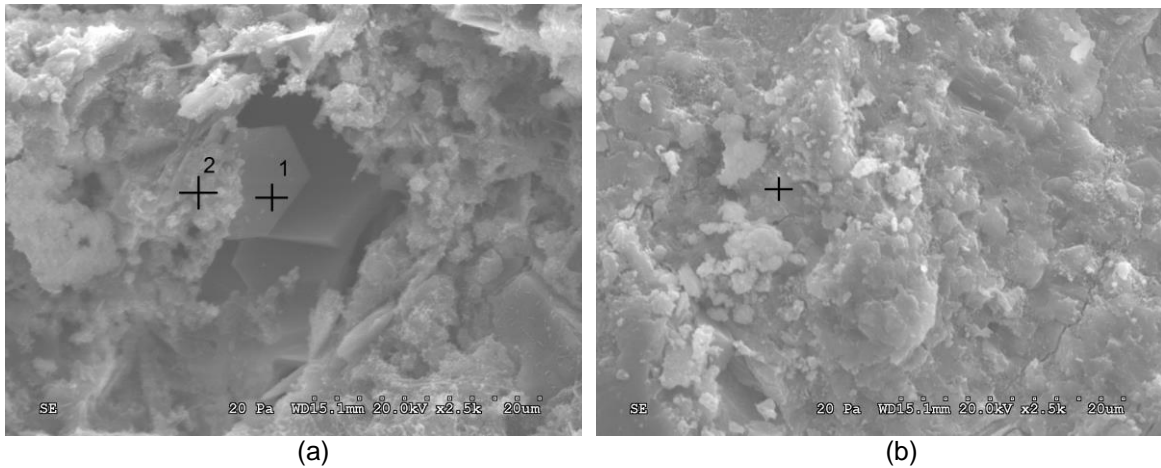


Figure 7: 10 SEM photomicrographs of: a) sealed cured OPC paste (B9) b) Carbonation-cured OPC paste (B11)

4 Conclusion

Early carbonation curing of concrete, which consists of pre-conditioning, short-term carbonation and subsequent hydration, offers a beneficial approach of recycling the CO₂ captured from the industrial emission sources.

The early carbonation curing regime promotes early strength gain. This advantage makes the early carbonation curing a suitable curing option for most of precast concrete products. The strength gain at early age is possibly due to the formation of the amorphous binding phase, C-S-H, with fully integrated calcium carbonate.

Carbonation-cured concrete has still the chance for further hydration when the water lost during the pre-conditioning and carbonation is compensated. The subsequent hydration stage is critical for carbonation-cured concrete. It plays an important role in late strength gain and durability of such concretes.

The short term carbonation led to a pH drop on the concrete surface due to the contribution of the major alkaline phases, calcium hydroxide, in the carbonation reactions. However, in the concrete core and in the vicinity of reinforcing bars, the pH was preserved above the threshold value (10.5) needed to keep the corrosion resistant passivation layer. Therefore, early carbonation curing application is extendable to reinforced precast products as well. The reduced CH content in the carbonation-cured concrete could contribute to improve the durability.

The early carbonation curing affected all the calcium based phases in concrete, including C-S-H. Nevertheless, the 2-h early carbonation did not damage the C-S-H structure. Although the degree of silicate polymerization was slightly increased, the carbonated C-S-H was far from silica gel. The original C-S-H binding structure could be preserved through the short carbonation curing.

References

- Berger, R. L., Young, J. F., and Leung, K. 1972. Acceleration of Hydration of Calcium Silicates by Carbon-Dioxide Treatment. *Nature-Phys Sci*, 240(97): 16-21.
- Castellote, M., Fernandez, L., Andrade, C., and Alonso, C. 2009. Chemical changes and phase analysis of OPC pastes carbonated at different CO₂ concentrations. *Materials and Structures*, 42(4): 515-525.
- Goodbrake, C. J., Young, J. F., and Berger, R. L. 1979. Reaction of Beta-Dicalcium Silicate and Tricalcium Silicate with Carbon Dioxide and Water Vapor. *Journal of the American Ceramic Society*, 62(3-4): 168-171.
- Goto, S., Suenaga, K., Kado, T., and Fukuhara, M. 1995. Calcium Silicate Carbonation Products. *Journal of the American Ceramic Society*, 78(11): 2867-2872.
- Heng, M., and Murata, K. 2004. Aging of Concrete Buildings and Determining the pH Value on the Surface of Concrete by Using a Handy Semi-Conductive pH-meter. *Analytical Sciences*, 20(7): 1087-1090.
- Ramachandran, V. S., and Beaudoin, J. J. 2001. Handbook of Analytical Techniques in Concrete Science and Technology. William Andrew Publishing/Noyes.
- Rostami, V., Shao, Y., and Boyd, A. 2012. Carbonation Curing versus Steam Curing for Precast Concrete Production. *J Mater Civil Eng*, 24(9): 1221-1229.
- Rostami, V., Shao, Y., and Boyd, A. J. 2011. Durability of concrete pipes subjected to combined steam and carbonation curing. *Construction and Building Materials*, 25(8): 3345-3355.
- Sauman, Z. 1971. Carbonization of porous concrete and its main binding components. *Cement and Concrete Research*, 1(6): 645-662.
- Sha, W., O'Neill, E. A., and Guo, Z. 1999. Differential scanning calorimetry study of ordinary Portland cement. *Cement and Concrete Research*, 29(9): 1487-1489.
- Shao, Y., and Mirza, M. S. 2006. CO₂ sequestration using calcium-silicate concrete. *Canadian Journal of Civil Engineering*, 33(6): 776-784.

- Sharma, R. L., and Pandey, S. P. 1999. Influence of mineral additives on the hydration characteristics of ordinary Portland cement. *Cement and Concrete Research*, 29(9): 1525-1529.
- Short, N. R., Purnell, P., and Page, C. L. 2001. Preliminary investigations into the supercritical carbonation of cement pastes. *Journal of Materials Science*, 36(1): 35-41.
- Slegers, P. A., and Rouxhet, P. G. 1976. Carbonation of the hydration products of tricalcium silicate. *Cement and Concrete Research*, 6(3): 381-388.
- Toennies, H. T. 1960. Artificial Carbonation of Concrete Masonry Units. *Journal of American Concrete Institute*, 56(2): 737-756.
- Young, J. F., Berger, R. L., and Breese, J. 1974. Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO₂. *Journal of the American Ceramic Society*, 57(9): 394-397.