



**CARBON
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Impact of CO₂ Utilization in Fresh Concrete on Corrosion of Steel Reinforcement



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Ready mix concrete producers in the United States, Canada and Singapore are using the CarbonCure Ready Mix Technology to adjust their concrete mix designs. The compressive strength improvements from an optimized injection of CO₂ enable the production of concrete without sacrificing performance or durability. Since being introduced commercially, more than 4 million cubic yards of concrete have been produced with the CarbonCure Technology, achieving material savings and avoiding CO₂ emissions that exceed 63,000 tons as of January 2020.

EXECUTIVE SUMMARY

Carbonation - The Good, The Bad and The Ugly: This paper discusses two different types of “carbonation,” both of which involve chemical reactions between carbon dioxide (CO₂) and cement but with very different impacts on concrete. The two reactions are summarized as follows:

Early carbonation (the good): In the CarbonCure process, CO₂ is injected into concrete during mixing. The CO₂ reacts rapidly—in a matter of minutes—with the calcium-silicate phases of the cement to form nanoparticles of calcium carbonate (CaCO₃) or calcite, which act as nucleation sites for the subsequent hydration (reaction with water) of the calcium silicates. This results in an acceleration of the setting and strength gain of the concrete.

Atmospheric carbonation (the bad): This occurs after the concrete has hardened and during its subsequent exposure. In this case, the source of the CO₂ is the atmosphere, where it is generally present at concentrations less than 0.04%. Over a period of years and decades, the CO₂ slowly penetrates the concrete and reacts with the normal products of cement hydration, converting them into a mixture of calcite with lesser amounts of silica, alumina and iron oxides. The process also results in a reduction in the alkalinity (pH) of the concrete. This process is not necessarily harmful to the concrete unless the CO₂ can penetrate deep enough into the concrete to reach embedded steel reinforcement, in which case the steel may start to corrode (the ugly).

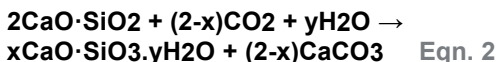
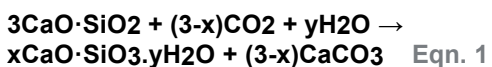
Despite the similarities in terminology and the processes involved (reactions with CO₂ producing CaCO₃), the two types of carbonation must not be confused. During early carbonation, only an infinitesimal amount (<< 1%) of calcium-silicate phases are carbonated and the subsequent hydration of the phases is not impacted beyond an acceleration in the rate of hydration at early ages. Consequently, the nature and quantity of the hydrates that form and the alkalinity (pH) of the concrete is unchanged. Early carbonation is not injurious to the behaviour of the embedded steel, and does not increase the risk of steel corrosion due to subsequent carbonation by atmospheric CO₂ or other process (such as chloride ingress).

Despite differences in the nature, timing and consequences of the process, the term “carbonation” has become synonymous with corrosion in the minds of many and this has created a misconception that “early carbonation” may be detrimental to steel corrosion in a similar manner to “atmospheric carbonation.” The benign impact of early carbonation on steel corrosion is demonstrated and explained in this paper.

1.0 INTRODUCTION: EARLY CARBONATION OF CALCIUM SILICATES (THE CARBONCURE PROCESS)

The CarbonCure process involves the injection of carbon dioxide (CO₂) into concrete during mixing. The CO₂ reacts within minutes with the calcium liberated from the calcium silicate phases (3CaO·SiO₂ and 2CaO·SiO₂) of the Portland cement during initial hydration to form nano-size particles of calcium carbonate or calcite (CaCO₃). These calcite nanoparticles act as nucleation sites for the subsequent hydration of the cement resulting in an acceleration in the setting behaviour and early strength gain of the concrete.

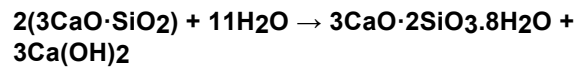
The chemical reactions are often referred to as “carbonation” and can be written as follows (Berger et al. 1972):



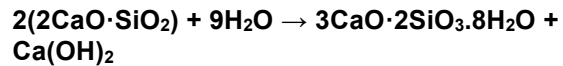
The CO₂ uptake during this “early carbonation” is typically less than 0.2% by mass of the cement in the mix. This means that only a very small portion (<< 1%) of the calcium available in the calcium silicates is converted into CaCO₃. As a result, more than 99% of the calcium silicates remain after “early carbonation” to undergo the normal hydration reactions which are discussed in

1.1 SUBSEQUENT HYDRATION OF CALCIUM SILICATES & PROTECTION (PASSIVATION) OF STEEL

The subsequent hydration (reaction with water) of the calcium silicates can be represented by the following reactions:



Eqn. 3



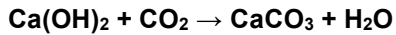
Eqn. 4

The calcium hydroxide produced by these reactions serves as a buffer to maintain a high pH (high level of alkalinity) in the concrete pore solution. The pH of saturated calcium hydroxide solution is approximately 12.4. The pore solution of concrete also contains alkali hydroxides (NaOH and KOH) resulting from the small amounts of sodium (Na) and potassium (K) in the Portland cement. As a result, the pH of the concrete pore solution is usually greater than 13 and may approach 14.

At this high pH level steel reinforcement embedded in the concrete develops a dense layer of ferric oxide on the surface which protects the steel from corrosion. The layer is known as the “passive layer” and process is called “passivation.”

1.2 LATER “ATMOSPHERIC CARBONATION” OF CONCRETE AND DE-PASSIVATION OF STEEL (CORROSION INITIATION)

During long term exposure of concrete to normal atmospheric conditions, CO₂ present in the atmosphere may penetrate in to the concrete and react with the calcium-bearing hydrates converting them into calcium carbonate (calcite). The reaction for calcium hydroxide is often written as follows:



Eqn. 5

This equation is somewhat of an oversimplification as the CO_2 first must dissolve in water; there will be no reaction in dry concrete. The hydrated calcium silicates and calcium aluminates also react with CO_2 forming more CaCO_3 . This process is also known as “carbonation” or “atmospheric carbonation”.

In the absence of steel this process is not generally harmful to concrete as what remains after the carbonation reaction is a solid matrix of calcite with good mechanical properties. However, the reaction results in a significant reduction in the pH from above 13 to approximately 8. At this lower pH, the passive layer on the steel is lost and unable to protect the steel from corrosion. If sufficient water and oxygen are present, the steel will corrode.

This process is also known as “carbonation” or “atmospheric carbonation”. This type of carbonation can be harmful to steel-reinforced concrete.

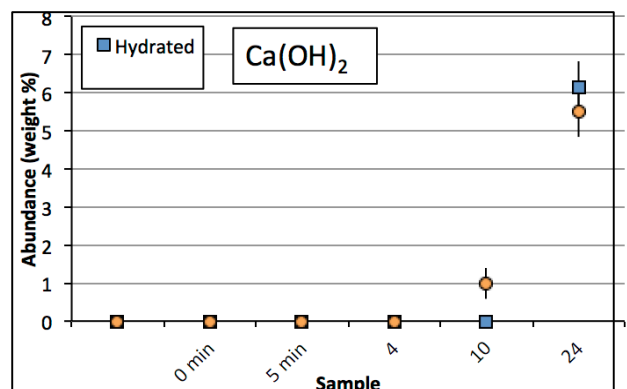
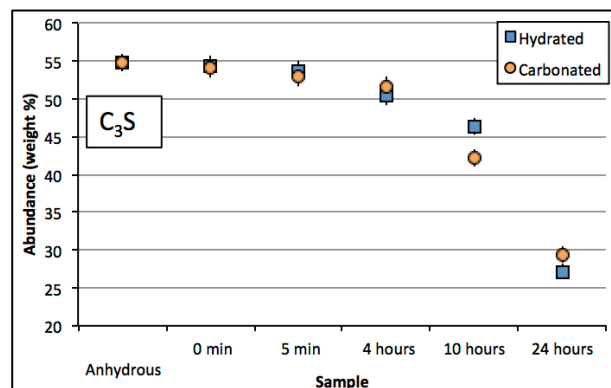
Atmospheric carbonation is very different to early carbonation. It results in the conversion to CaCO_3 of virtually all the calcium-bearing hydrates and of any residual un-hydrated calcium-silicate phases. There is no opportunity for subsequent hydration of unreacted phases and reinstatement of the alkalinity (high pH) of the system. Contrast this with the early carbonation process which results in the conversion to CaCO_3 of an almost infinitesimal quantity of calcium from the calcium-silica phases before hydration; subsequent hydration of what remains of these phases will result in abundant calcium-bearing hydrates that produce a highly alkaline (high-pH) environment that is conducive to passivation of embedded steel.

2.0 COMPOSITION AFTER EARLY CARBONATION

The “early carbonation” of the fresh concrete during mixing does not affect the subsequent hydration reactions (beyond the acceleration due to nucleation effects) or the composition of the pore solution as the amount of calcium-silicates consumed by the process is negligible. This is demonstrated in two separate studies conducted on Portland cement pastes where CO_2 was introduced during mixing and on a study on the impact of CO_2 injection on the passivity of steel embedded in concrete.

2.1 Effect of Early Carbonation on Subsequent Hydration

In this study (Monkman et al 2018) paste samples were made with a water-to-cementing-materials ratio (w/cm) of 0.50 and mixed in a high-speed food blender. The headspace in the blender was purged and continuously refreshed by a flow of 100% CO_2 gas for one minute. After mixing the batch was sampled immediately ($t = 0$) and at $t = 5$ minutes, 4, 10 and 24 hours. These samples were immediately frozen in liquid N_2 for later analysis. A parallel set of reference (hydrated) samples was produced in the same manner without CO_2 and sampled at the same times. Quantitative X-ray diffraction (QXRD) analysis was used to determine the amounts of crystalline phases in the pastes and the amorphous calcium-silicate-hydrate (C-S-H) was determined by difference. Figure 1 shows the reduction in the amount of anhydrous tri-calcium-silicate (C_3S) and the concomitant increase in the hydrates; these being calcium hydroxide [Ca(OH)_2] and amorphous calcium-silicate hydrate (C-S-H) during the first 24 hours.



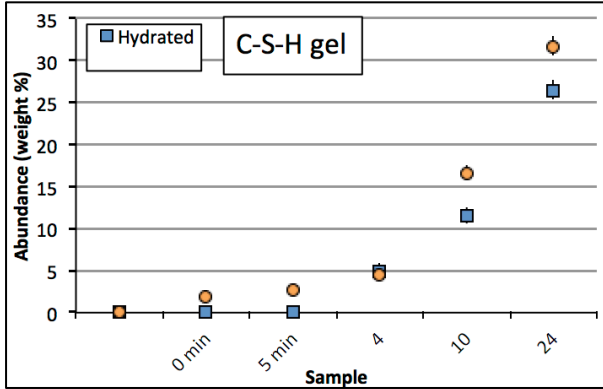


Figure 1 Impact of CO₂ Injection on the Change in the Quantity of Cement Phases During the First 24 Hours of Hydration

The data in Figure 1 show that the amount of Ca(OH)₂ and C-S-H that forms after the initial carbonation period is not significantly different to the amount that forms in the absence of CO₂ gas during mixing.

2.2 EFFECT OF EARLY CARBONATION ON PORE SOLUTION COMPOSITION

Portland cement pastes were produced with w/cm = 0.50 and mixed in a high-speed food blender. CO₂ was introduced during mixing to produce pastes with various levels of CO₂ uptake. The CO₂ uptake was later determined by combustion analysis. The pastes were cast into sealed cylindrical moulds and moist cured. At an age of 28 days the paste samples were placed in a high-pressure press to extract the pore solution which was subsequently analyzed using a pH meter. The pore solution pH is plotted against the measured CO₂ uptake in Figure 2.

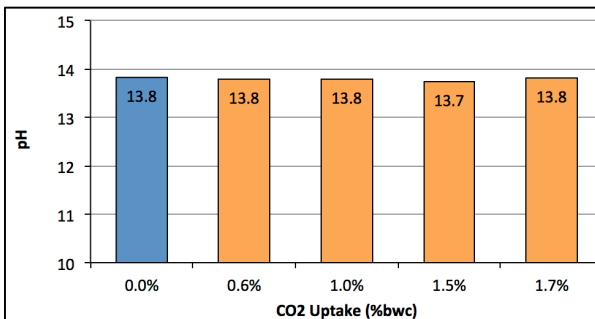


Figure 2 pH of Pore Solution Extracted from Carbonated Paste Samples at 28 days

The data indicates that there is no systematic change in the pH of the pore solution of pastes with CO₂ uptake. Although the measured pH of the solutions is slightly lower in all of the carbonated pastes compared with the uncarbonated control the differences are very small. All of the pH values are above 13.7 which is in the range of uncarbonated concrete and indicative of there being a significant quantity of alkali hydroxides (KOH and NaOH) in the pore solution. Recalling that pH is a measure of the hydroxyl ion concentration [OH⁻] on a log-scale, these pH values indicate [OH⁻] concentrations that are more than 10 times that of saturated-Ca(OH)₂ solution (pH = 12.4) and more than 100 times the [OH⁻] concentration generally considered to be required to maintain the passive layer on steel.

2.3 EFFECT OF EARLY CARBONATION ON PASSIVITY OF STEEL

In this study reinforced-concrete specimens were manufactured in accordance with ASTM G109; Figure 3 shows the experimental set-up for the corrosion testing. The concrete mixture contained approximately 20% fly ash and w/cm = 0.45 and was batched at a ready-mixed concrete plant and mixed and delivered to the laboratory in a transit mixer. CO₂ was injected into the truck at the laboratory. Concrete specimens were cast before injection of CO₂ (2201), after a single CO₂ injection (2202) and after a second injection (2203). The CO₂ uptakes were 0.2% and 0.5% CO₂ by mass of cementitious material for mixtures 2202 and 2203, respectively.

Reinforced-concrete specimens were moist-cured for 28 days and then subjected to repeated 28-day cycles consisting of 14 days ponded with 3% NaCl solution and 14 days air dry. The half-cell potential of the upper steel bar was measured against a copper-copper sulfate (CCS) standard half-cell at the mid-point of each cycle. The results for the first 6 months are shown in Figure 3. The values are significantly more positive than -200 mV which indicates that corrosion is almost certainly not occurring. This is consistent with the steel being in a passive condition regardless of the CO₂ injection and this is expected given the that tests on pastes (sections 2.1 and 2.2) indicated that the pore solution pH and the hydrate composition (that is the amounts of calcium hydroxide and calcium-silicate hydrate) are not impacted by CO₂ injection.

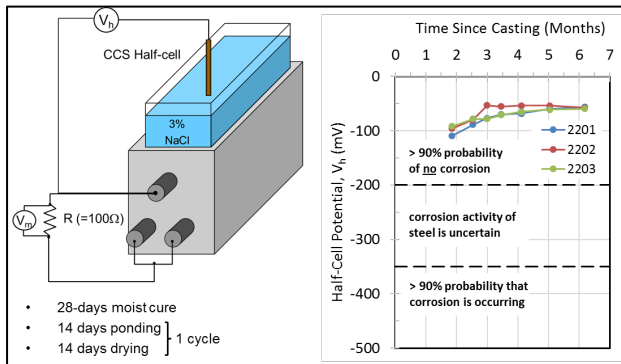


Figure 3 Set-Up for Corrosion Testing (ASTM G109) and Half-Cell Potential Results During the First 6 Months

3.0 EFFECT OF EARLY CARBONATION ON RISK OF CORROSION DURING SUBSEQUENT (LONG-TERM) EXPOSURE

Evidence was presented in Section 2 to demonstrate that the composition of the concrete in terms of the hydrates and pore solution is effectively unchanged by the small amount of CO_2 uptake during early carbonation and, thus, the passivity of the steel remains intact. However, questions have been asked regarding the impact of early carbonation on the subsequent rate of atmospheric carbonation of the mature concrete. If the rate is accelerated by early carbonation this could reduce the time to the onset of corrosion.

Corrosion of steel embedded in concrete can also be initiated by the penetration of chloride ions from external sources; this can occur when concrete is exposed to chloride-bearing de-icing or anti-icing salts (NaCl , CaCl_2 , MgCl_2) or seawater. Consequently, tests were conducted to determine whether early carbonation has an impact on the resistance of concrete to chloride-ion penetration.

Concrete specimens from mixes 2201, 2202 and 2203 described in Section 2.3 were also subjected to testing to determine the rate of atmospheric carbonation and chloride ingress.

3.1 ATMOSPHERIC CARBONATION OF CONCRETE TREATED WITH EARLY CARBONATION

Concrete prisms measuring 75 x 75 x 285 mm were moist-cured for either 1, 3 or 7 days and then placed in an outdoor exposure condition protected from

precipitation (see Figure 4). After approximately 4 years of exposure specimens were split open and the freshly-fractured surface sprayed with a 1% phenolphthalein solution (a pH indicator). This solution remains colourless if the pH is less than 9.2 but turns a vivid purple colour if the pH is greater than 9.2. The depth of the colourless zone (see Figure 4) represents the depth of carbonation.

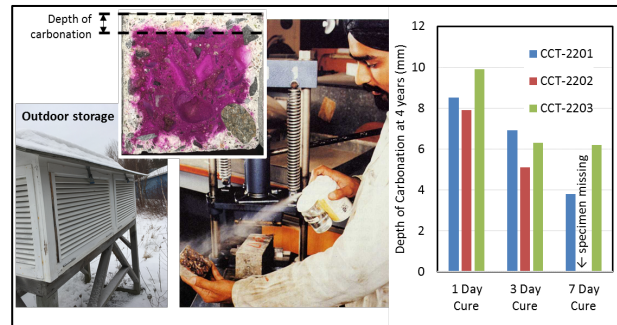


Figure 4 Outdoor Exposure and Testing of Concrete for Depth of Carbonation

The data show that the treatment with CO_2 during mixing (early carbonation) has no systematic effect on the subsequent rate of carbonation during outdoor exposure (atmospheric carbonation).

3.2 CHLORIDE RESISTANCE CONCRETE TREATED WITH EARLY CARBONATION

Concrete cylinders (100-mm diameter by 200-mm length) were moist-cured for 28 days prior to being tested in accordance with ASTM C1556. Briefly, this test involves cutting a 50-mm disc from the cylinder, coating the curved and one flat surface of the disc with epoxy, vacuum saturating the concrete and immersing it in a solution of sodium chloride (165 g/L NaCl). After a certain period of time, 180 days in this case, the disc is removed from solution and 1-mm increments of powder are ground from the exposed face down to a depth where the chlorides are expected to reach the original background concentration; the depth was 22 mm in this case. Each powder sample is subsequently tested for chloride content. The test set up and the 180-day chloride profile (chloride content versus depth from the exposed surface) are shown in Figure 5.

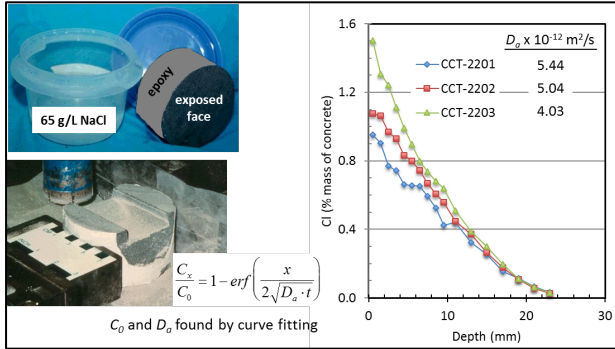


Figure 5 Test set-up for ASTM C1556 Bulk Diffusion Test and Chloride Profiles for Concrete after 180 Days Immersion in Salt Solution

The chloride profiles show some variability close to the surface (< 10 mm depth) but at greater depths the chloride contents are very similar. The depth of penetration of chlorides during the 180-day exposure period is approximately 21 to 22 mm regardless of the CO₂ injection. The calculated chloride diffusion coefficients are within the range of 4.0 to 5.5 x 10⁻¹² m²/s (lower numbers indicate greater resistance) and the differences between the values are not significant given the variability of the test.

4.0 SUMMARY

The “early carbonation” of concrete by CO₂ injection during the first few minutes of mixing has raised some concerns because of its perceived association with normal “atmospheric carbonation” that occurs long after the concrete has hardened. Atmospheric carbonation results in a loss of alkalinity (reduced pH) of the concrete which can lead to corrosion of embedded steel reinforcement. Early carbonation, on the other hand, has no measurable impact on subsequent hydration and the alkalinity (pH) of the concrete remains high providing protection to the steel (by passivation).

Furthermore, early carbonation has no negative impact on the subsequent rate of atmospheric carbonation or chloride ingress and, consequently, does not increase the risk of steel corrosion in any way.

REFERENCES

1. R. L. Berger, J. F. Young, K. Leung, *Nature: Physical Science*. 240, 16–18 (1972).
2. S. Monkman, P.A. Kenward, G. Dippl, M. MacDonald, and M. Raudsepp: “Activation of cement hydration with carbon dioxide.” *Journal of Sustainable Cement-Based Materials* (2018).