Types of Concrete Carbonation
TECHNICAL NOTE

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Two Types of Concrete Carbonation

Concrete can be subjected to two distinct types of carbonation. The first is weathering carbonation, which concerns mature concrete reacting over an extended period of time when it is exposed to carbon dioxide in the atmosphere. The second is early age carbonation, which involves utilizing carbon dioxide in the production of concrete wherein the reaction occurs at very early ages on fresh concrete. The carbonation can take place as early as concrete mixing stage and can end prior to, or in line with, the conclusion of accelerated curing (as much as 48 hours later). CarbonCure Technologies uses early age carbonation to sequester CO_2 into concrete. The following document explores both types of carbonation in more detail.

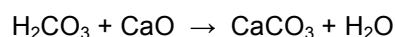## Weathering Carbonation

Weathering carbonation, or atmospheric carbonation, occurs in concrete when calcium compounds react with carbon dioxide (CO_2) from the atmosphere and water (H_2O) in the concrete pores.
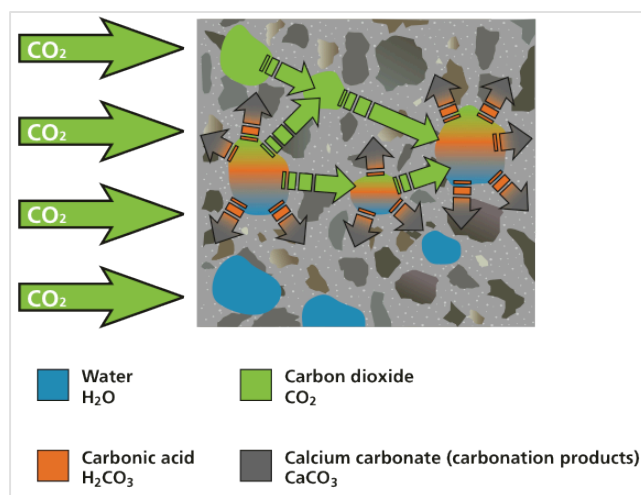
First, the CO_2 reacts with the water in the pores to form carbonic acid (H_2CO_3). The carbonic acid then reacts with the calcium compounds contained within the hydration products that are present in mature concrete, mainly calcium hydroxide (typically 25 – 50 % by weight of the cement paste). Calcium carbonate ($CaCO_3$) forms according to the following chemical reaction:

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$$
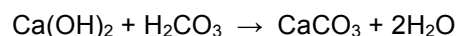
Once the $Ca(OH)_2$ has carbonated and is depleted from the cement paste, the calcium-silicate-hydrate gel (C-S-H) can be decalcified thereby allowing the liberated CaO to carbonate according to the following chemical reaction:

$$H_2CO_3 + CaO \rightarrow CaCO_3 + H_2O$$

Water
H_2O

Carbon dioxide
CO_2

Carbonic acid
H_2CO_3

Calcium carbonate (carbonation products)
$CaCO_3$

Source: Fibertex, www.fibertex.com

The depletion of calcium hydroxide will cause the concrete pore solution pH to drop below 13. The pH can reach as low as 8 for fully carbonated concrete. Concrete with ferrous reinforcement requires a high pH to ensure the stability of the protective passive layer on the surface of the reinforcement. A drop in the pH level can cause the passive layer to deteriorate, thereby making the reinforcement susceptible to
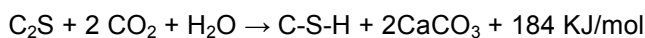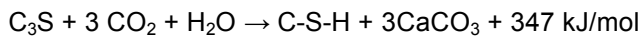
harmful corrosion. This is a particular issue if the reinforcement is exposed to aggressive agents such as chloride ions. The corrosion products occupy a greater volume than the original ferrous reinforcement and, in a hardened, mature microstructure, can create internal stresses that cause cracking of the concrete cover.

Exposure conditions, primarily the relative humidity, can have a significant effect on the depth of carbonation and the amount of CO_2 absorbed over time. In general, carbonation only occurs when the relative humidity is between 40 and 90%. If the relative humidity is too low then there is insufficient water in the pores for CO_2 to dissolve to form the carbonic acid needed to react with the calcium compounds. If the humidity is too high then the CO_2 pore network is full of water and ingress of the carbon dioxide is inhibited. When the relative humidity is in a moderate range the conditions are ideal to promote a greater carbonation depth and thus a higher CO_2 absorption.

Early age carbonation

Early age carbonation occurs when the carbonation reactions occur alongside the early hydration of the cement through a deliberate exposure of fresh concrete to CO_2. The carbonation occurs rapidly and can contribute to a denser and stronger concrete. The carbonate reaction product formation contributes to strength development. The duration and application method of the carbon dioxide varies depending on the process, but can be as short as a few seconds of exposure or as long as the initial accelerated curing.

The mechanism of the early age carbonation reaction is distinct from that of weathering carbonation. The general reaction of carbon dioxide with tricalcium silicate and dicalcium silicate phases in cement was described in 1974 by Young as:

$C_3S + 3\ CO_2 + H_2O \rightarrow$ C-S-H $+ 3CaCO_3 + 347$ kJ/mol

$C_2S + 2\ CO_2 + H_2O \rightarrow$ C-S-H $+ 2CaCO_3 + 184$ KJ/mol

These reactions are spontaneous and exothermic. A closer look at the early carbonation reaction of a concrete mix or product reveals nine discrete steps.

1. CO_2 gas diffuses through the air to reach the concrete.

2. The carbon dioxide permeates through the air-filled porosity of the concrete mass.

3. Solvation of CO_2 (g) to CO_2 (aq) in the liquid phase of the fresh concrete.

4. Hydration of CO_2 (aq) to H_2CO_3 (a slow and rate determining step).

5. Ionisation of H_2CO_3 to H^+, HCO_3^-, CO_3^{2-}.
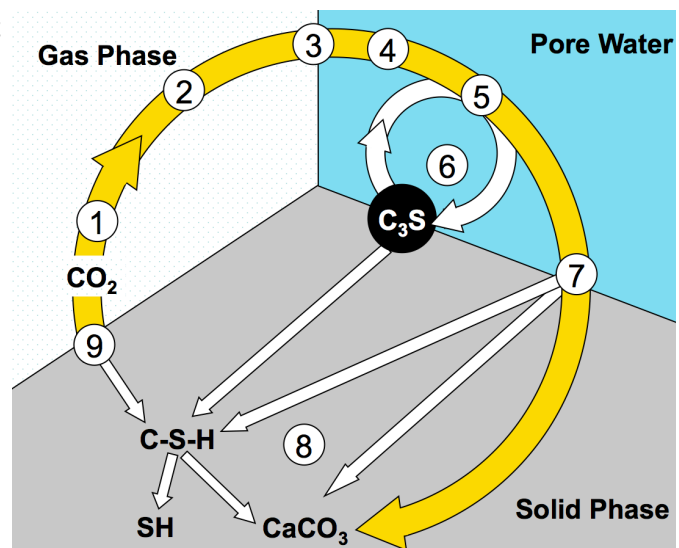
Adapted from Bertos et al, 2004

The presence of H$^+$ ions causes the pH of the developing cementitious system to drop. The pH can recover as the microstructure matures.

6. Dissolution of cement phases C_3S and C_2S. This occurs rapidly, cyclically, and exothermically. Cement grains are covered by a loose layer of calcium silicate hydrate gel that dissolves to release Ca^{2+} and SiO_4^{4-} ions.

7. Nucleation of thermodynamically stable $CaCO_3$ and conventional formation of C-S-H gel.

8. The $CaCO_3$ precipitates as a solid phase. Calcite is the preferred polymorph.

9. Secondary carbonation also occurs; sustained reaction of carbon dioxide and the cement paste can see C-S-H gel formed through the parallel early hydration decalcified and producing a calcium-depleted silicate hydration and $CaCO_3$.

Early age carbonation reactions can involve calcium that, on balance, would otherwise have hydrated to form calcium hydroxide and contribute to high pH. However, the early age carbonation does not hinder the long-term development of the concrete microstructure as the concrete matures. Therefore, calcium hydroxide will develop during later hydration and the pore solution pH development continues as normal once the carbonation application ends.

Recent research conducted by CarbonCure Technologies (at right) has shown that an early age carbonation process has a minimal effect on the pH of the pore solution of mature concrete. Paste samples we created with varying levels of carbonation (expressed as CO_2 content by weight of cement) that were achieved within 120 seconds of carbon dioxide injection during mixing. The paste was then cast into cylindrical specimens and moist cured. The pore solution was extracted at 28 days and the pH was measured. The decline was minimal and suggests no risk of depassivation of ferrous reinforcement.

Pore solution pH of carbonated paste samples
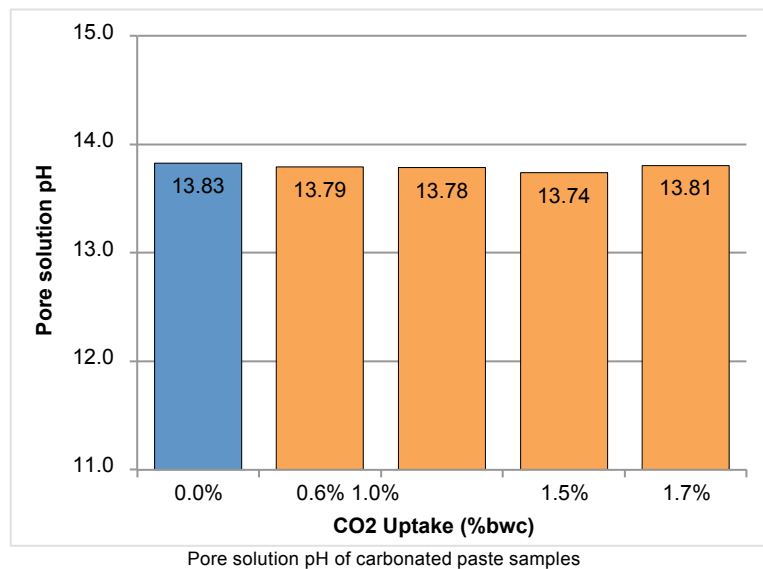
The effects of early age carbonation on the properties of concrete are being studied by several parties. In particular, ongoing research is developing an understanding about the impact of early age carbonation on carbonation shrinkage or carbonation uptake during the service life.

Context

The widely held notion that "carbonation is deleterious for concrete" is specifically rooted in the harmful effects of weathering carbonation on mature hydrated microstructures. Conversely, early age carbonation

involves different chemical reactions affecting an immature microstructure. The attendant material and environmental benefits of the carbon dioxide-cement interaction can be leveraged with a carefully considered carbonation approach.

CarbonCure Technologies focuses on using early age carbonation to sequester CO_2 in the cement paste to produce better concrete. While concrete carbonation has long been only considered to negatively impact concrete as a building material, the use of CO_2 now enables the development of a 'green' concrete building material.

Sources

Accelerated Curing Of Compacted Calcium Silicate Mortars On Exposure To CO_2. Young et al., Journal of the American Ceramic Society, Vol 57, Issue 9, 1974. doi:10.1111/j.1151-2916.1974.tb11420.x

A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2. Bertos et al., Journal of Hazardous Materials, Vol 112, Issue 3, 2004. doi:10.1016/j.jhazmat.2004.04.019