

Carbonate bonding – safe and effective CO₂ sequestration

Research into the sequestration of CO₂ as a mineral carbonate that is used as a fill material or aggregate replacement is well underway and heading towards commercialisation. However, the use of carbonate as part of a bonding process is less well advanced. There are two companies leading the commercialisation in this exciting, new area.

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Many companies are looking at the possibility of permanently sequestering CO₂ as a mineral carbonate. The majority of these companies are looking at the mineral carbonate as, at best, a fill material or aggregate replacement. This form of mineral carbonation has been commonly referred to as ‘mineralisation’. The biggest drawback to these processes is that the mineral needs to be in a decarbonated form to begin with.

Two companies, Solidia Technologies^{®1} and CarbonCure², are investigating the use of the mineral carbonate as part of a bonding process. These solutions provide a higher-value end product while permanently sequestering CO₂. Solidia has developed a unique, non-hydrating calcium silicate cement formulation that can be manufactured in existing cement plants with current raw materials. CarbonCure injects CO₂ into fresh concrete to accelerate and improve its performance. Although carbonate bonding is a new topic, carbonation of concrete is a naturally-occurring process that continues all around us.

Natural carbonation

Carbonation of concrete can impact the long-term durability of the concrete itself. In this reaction, CO₂ from the atmosphere combines with lime, or more precisely, calcium hydroxide from the concrete’s calcium silicate hydrate matrix (C-S-H), to form calcium carbonate, as seen in Formula 1, below. This reaction in itself is not necessarily detrimental to concrete quality, but it does lower its pH.

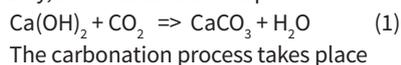
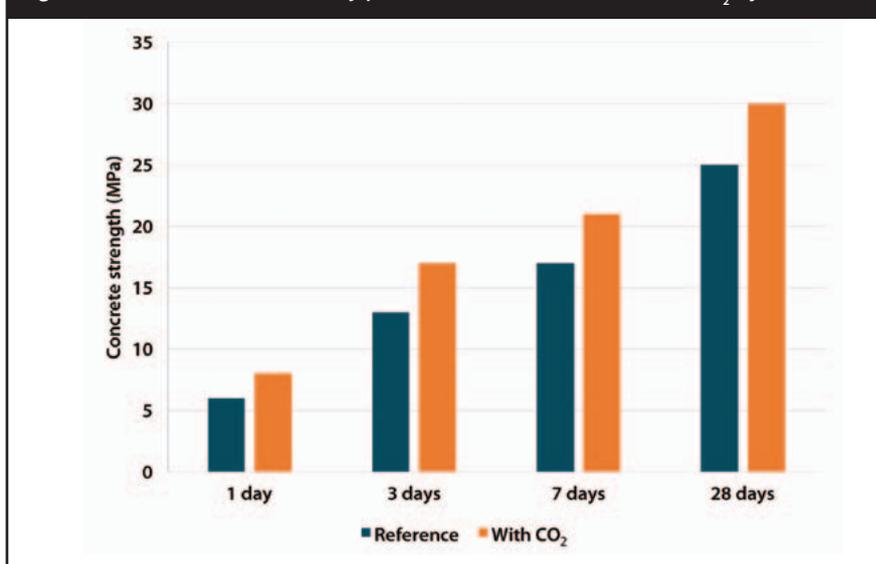
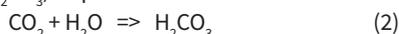


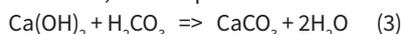
Figure 1: test results from industrially-produced concrete with and without CO₂ injection



under humid conditions as the CO₂ first dissolves in water, forming carbonic acid (H₂CO₃) as per Formula 2.



Therefore, the complete reaction is:



Carbonation of concrete can be an issue when reinforcing steel is used in the concrete as the reaction lowers the concrete’s pH, which is normally above 12. The trouble occurs when the pH drops to around seven, where the steel can start to deteriorate. The rate of carbonation is a function of many factors, including the porosity of the concrete and the exposure to humid conditions. The rate of carbonation has been defined by the following equation.

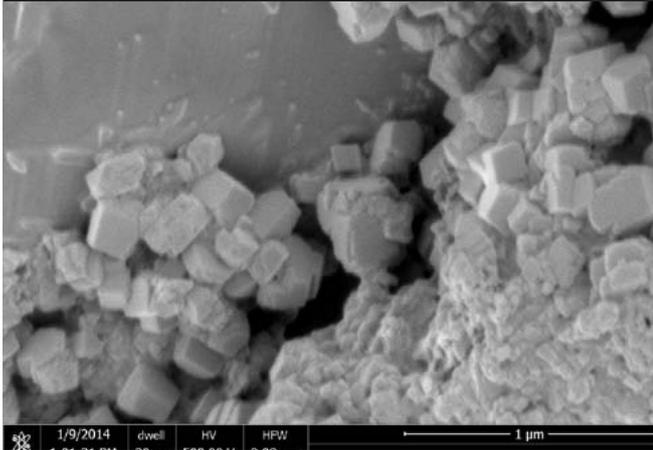
$$X_c = K_c * t^{1/2} \quad (4)$$

where: X_c = depth of carbonation
K_c = carbonation coefficient
t = time in years.

The carbonation reaction slows as the depth of carbonation increases as seen by the square root factor used for time. The natural carbonation of concrete is only an issue when the depth of carbonation (X_c) reaches the depth of the reinforcing steel. At this point the pH can drop to a level at which the passivation of the steel is destabilised.

The following excerpt from a study of bridges in Florida gives a good idea of the ranges of carbonation that can occur.

“Concrete carbonation depths observed in the bridges were as high as 50mm, with an average value of ≈10mm. The carbonation coefficients [K_c] measured from bridge-extracted cores ranged from 0 to 14 mm/y^{1/2}, with a median value of 1.4 mm/y^{1/2}. Cores extracted from bridge decks presented higher values of X_c and K_c compared with the substructure. This difference was most pronounced on

Figure 2: nano particles of CaCO_3 (rhombohedral forms) in concreteFigure 3: liquid CO_2 being added to a concrete batch leaving the mixer (CO_2 pipe on lower right)

bridges built over water, where the average values of X_c were 12.3 and 2.1mm for the deck and the substructure, respectively.”³

Although concrete carbonation as described above has been seen as a durability issue for concrete, several companies are looking at carbonate bonding as an improvement to or possible replacement for the traditional OPC bonding mechanism based on calcium silicate hydrates.

CarbonCure

CarbonCure’s research started in 2004 when a McGill Engineering student, and future founder of CarbonCure, was examining the chemical interaction between fresh concrete and CO_2 . Rob Niven was delighted to find that some of the concrete properties were improved through the process. Today, over 20 concrete product manufacturers have signed on to license the technology. CarbonCure is now poised to move into the ready-mixed concrete space. So if natural carbonation can be a cause for concrete deterioration, how does CarbonCure actually improve the concrete?

The secret is in the way the CO_2 is introduced into the concrete. The release of liquid CO_2 into fresh concrete causes minute particles of ‘dry ice’ or frozen CO_2 to form. The dry ice forms as the CO_2 quickly expands from the liquid phase, absorbing heat and freezing into the solid phase. The solid CO_2 attaches itself to lime (CaO) in the concrete, forming homogeneously-dispersed nano crystals of CaCO_3 , the very material that was used to make the cement in the first place.

The nanocrystalline carbonates are believed to be created in the fresh concrete mix alongside the earliest development of the hydration products (C-S-H). The in-situ

formation of the particles also appears to be a superior means to achieve nano particle dispersion as opposed to mixing in pre-formed nano particles.

The nano particles of CaCO_3 form nucleation sites for the calcium silicate hydration reactions that cause concrete to harden. The early formation of the nucleation sites allows for a more rapid curing of concrete, enabling it to set faster and produce high strengths. This allows the ready-mix and concrete product companies to reduce the amount of cement in their concrete while maintaining its inherent strength.

So exactly how is the CO_2 injected into the concrete? That is the novel part. The CO_2 is carefully metered according to a proprietary system during the concrete batching process. Liquid CO_2 is brought to the concrete site in storage tanks. The tanks are then connected to the metering system and the CO_2 is released into the concrete batch using insulated hoses and a special nozzle design. Although it sounds rather complex, the metering technology fits into a large suitcase, and the hoses and tanks are commercially available. The trick is in obtaining the optimum CO_2 dosage for the concrete in question.

In many respects, the addition of CO_2 to concrete is similar to adding any admixture. Any concrete producer that is familiar with the optimisation steps involved in integrating a new admixture among its product offerings will be comfortable with integrating the CO_2 injection technology. The addition of liquid CO_2 when properly added has no known detrimental effects on the concrete’s other properties, such as slump, workability or durability.

The reduction of cement in the concrete with the additional injection of CO_2 is

a double win for reducing the carbon footprint of concrete. This is part of the reason that CarbonCure was the recipient of the BuildingGreen.com Top-10 Green Building Products for 2013.

The process is easy to apply in concrete product manufacturing and is gaining support in the ready-mix concrete business. The cost of CO_2 can be high, depending on local availability, but its use still represents an overall cost saving. The cost of CO_2 is also expected to decrease as more and more CO_2 capture technologies come online. CarbonCure’s dream is to one day utilise the CO_2 captured from Portland cement production and sequester it in the concrete made from the same cement.

Solidia Technologies

Solidia’s research started in a university on the other side of the US-Canadian border, namely Rutgers, the State University of New Jersey. There, Richard Riman and Vahit Atakan developed the first Solidia products and went on to start Solidia Technologies. Riman’s background was in materials science and engineering as was co-inventor Vahit Atakan, who is now Solidia’s R&D director. The initial work was carried out with a monocalcium silicate ore that is found in nature and known as ‘wollastonite’. Wollastonite ore occurs naturally but not in the abundance and geographic dispersion that would make it a replacement for traditional Portland cement.

Research indicated that monocalcium silicate and similar low-lime calcium silicates could be produced by thermally processing a combination of calcia and silica similar to how Portland cement is produced today. Since the ratio of calcium oxide to silica is lower than that of Portland cement, less limestone is required in the

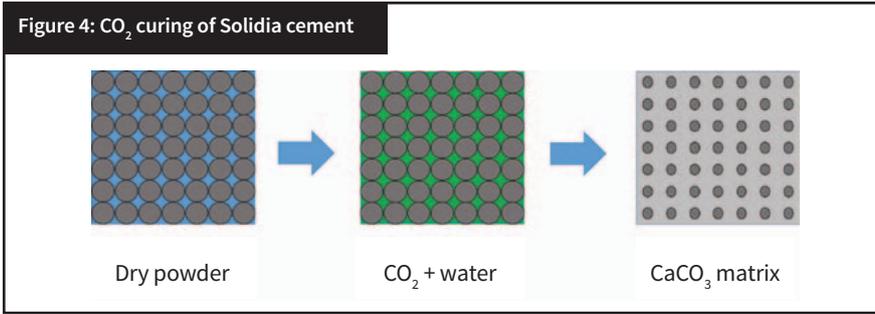


Table 1: independent laboratory test results for Solidia Concrete

Property	ASTM test reference	Solidia Concrete performance for concrete made with 400kg/m ³ cement content and 0.30 water-to-cement ratio
Compressive strength	C39	10,100psi (70MPa)
Split tensile strength	C496	1150psi (8MPa)
Flexural strength	C78	>850psi (>5.9MPa)
Young's modulus	C469	5100ksi (35GPa)
Poisson's ratio	C469	0.150
Thermal expansion coefficient	CRD-C39	~7-9 x 10 ⁻⁶ /C
Abrasion resistance	C770	<1mm
Durability factor after 350 freeze-thaw cycles	C666 Procedure A	88%

raw mix formulation. At the same time, the fusion temperature for the Solidia material is lower than that of ordinary Portland cement clinker. The lower fusion temperature and lower limestone requirements give Solidia's calcium silicate product a 30 per cent advantage in CO₂ release during production. That is, an equivalent amount of monocalcium silicate produces 70 per cent of the amount of CO₂ as an ordinary Portland cement. However, that is only half of the story.

Solidia's product uses carbonate bonding to cure. That is, CO₂ is introduced into the monocalcium silicate to form carbonate bonds that bind the calcium silicates. The amount of CO₂ sequestered during this process is roughly equal to 20-30 per cent by weight of the Solidia cement in the concrete. The process essentially mimics but greatly accelerates natural carbonation of concrete. As in nature, the Solidia process uses water as the medium to transfer the CO₂ from a gas to the carbonate bonds, only the concentration of CO₂ is much higher. Also, the temperatures are increased slightly to further enhance the reaction kinetics. The water is just the transport medium and can be almost completely recycled.

The difference with concrete carbonation is that the CO₂ is not attacking

the bonding matrix, but instead it is actually building it. The CO₂ dissolves in water and reacts with the dissolved Ca ions to form a CaCO₃ and SiO₂ matrix, similar to the C-S-H matrix in concrete made with OPC. The mechanism for carbonate bonding is shown in Figure 4.

Solidia Cement offers an enhanced sustainability profile, including a reduced carbon footprint and the ability to recycle up to 100 per cent of the water used during curing. Solidia Concrete™ also cures in less than 24h, compared to the typical 28 days required for OPC-based concrete. It is believed to provide superior product durability with resistance to freeze-thaw conditions, and chloride and sulphate attack (see Table 1).

However, some challenges still

remain. The pH of the Solidia Concrete stays low, similar to the natural carbonation of concrete. Although the low-pH environment is considered to be unfavourable for the corrosion of steel reinforcement in concrete, a recent study indicates that the rate of corrosion is similar when comparing Solidia Concretes to OPC-based concrete in mild exposure environments.

Since the CO₂ needs to be introduced into the concrete structure in an enclosed environment, Solidia's technology is initially more suitable for precast concrete products and sections than cast in place concrete. The cost of CO₂ can be high as noted previously but is expected to drop. These challenges and others will be overcome as the commercialisation of the product continues with financial and R&D support from such investors as KPCB, Bright Capital, BASF, BP, Lafarge, TOTAL and private investors.

Commercialisation processes in progress

Carbonation of concrete is a naturally-occurring process that happens all around us every day. This process can impact the durability of steel-reinforced concrete structures. However, at the same time CarbonCure and Solidia have shown that it can be harnessed for beneficial purposes that will assist in the capture and permanent sequestration of CO₂ from the atmosphere. Commercialisation of the CarbonCure and Solidia processes are in progress. They alone will not eliminate the large carbon footprint of the cement and concrete industries, but they may be able to take a substantial bite out of it. ■

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- ²<http://carboncure.com/>
- ³ SAGUES, A A, MORENA, E I, MORRIS, W AND ANDRADE, C (1997) *Carbonation in Concrete and Effect on Steel Corrosion*. Tampa, USA: University of South Florida, 256p.

