

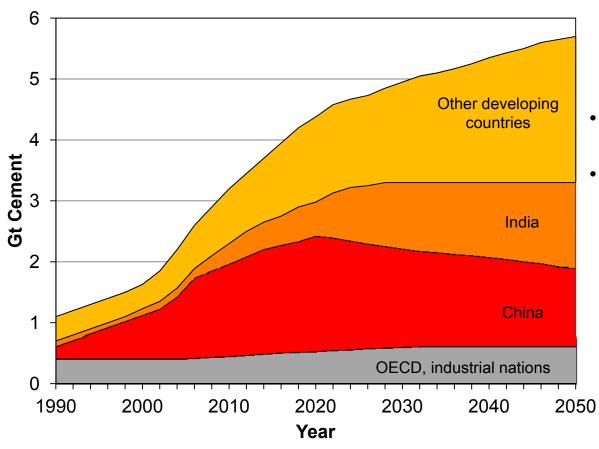
Co₂ Sequestration Through Early Age Concrete Carbonation

Sean Monkman, PhD VP Technology Development CarbonCure Technologies

> Anna Maria XIII Anna Maria, Florida 8 November 2012

CARBON CURE

CEMENT DEMAND IS GROWING

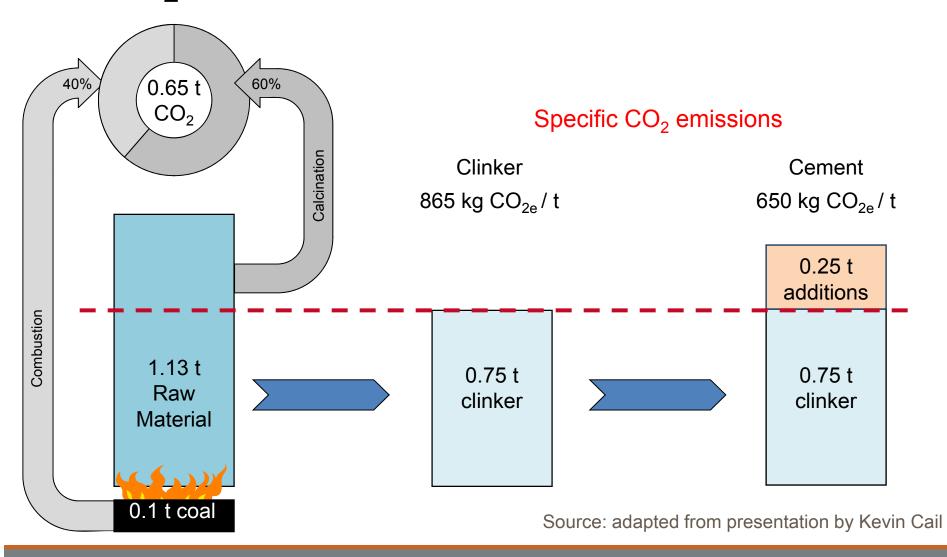


- Higher than it has ever been, and projected to rise ever higher
- Perhaps 600% growth from 1990 to 2050

Source: WWF/Lafarge

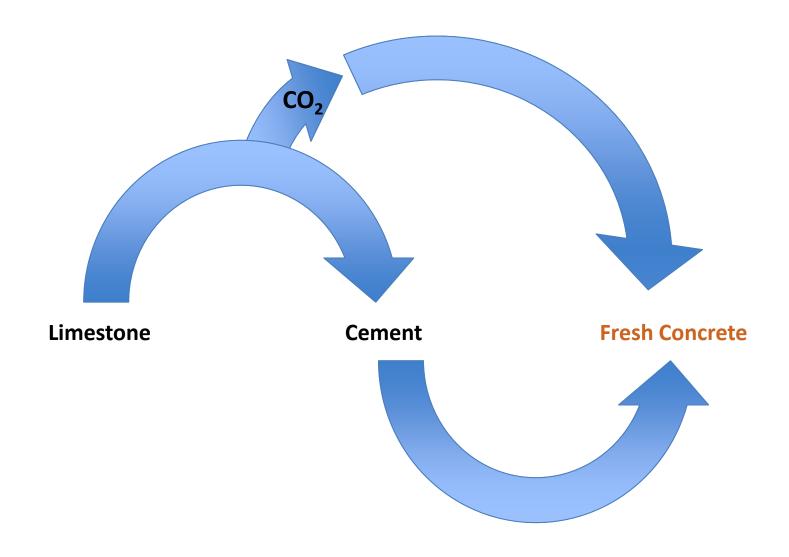
CEMENT PRODUCTION AND CO₂ EMISSIONS





CARBON CYCLE





OUTLINE



- Carbonation background
- Historical perspective
- The Technology
- Demonstration data

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$$C3S_{(alite)} + 3H^{+} \leftrightarrow 3Ca^{2+} + SiO_{2}^{0} + 3OH^{-}$$
 $C2S_{(belite)} + 2H^{+} \leftrightarrow 2Ca^{2+} + SiO_{2}^{0} + 2OH^{-}$

Cement Dissolution (Ca²⁺ Supply)



$$CO_{2 (g)} \leftrightarrow CO_{2 (aq)}$$
 $CO_{2 (aq)} + H_2O \leftrightarrow H_2CO_{3 (aq)}$
 $H_2CO_{3 (aq)} \leftrightarrow HCO_{3^- (aq)} + H^+$
 $HCO_{3^- (aq)} \leftrightarrow CO_{3^{-2} (aq)} + H^+$

CO₂
Dissociation
(CO₃-2 Supply)

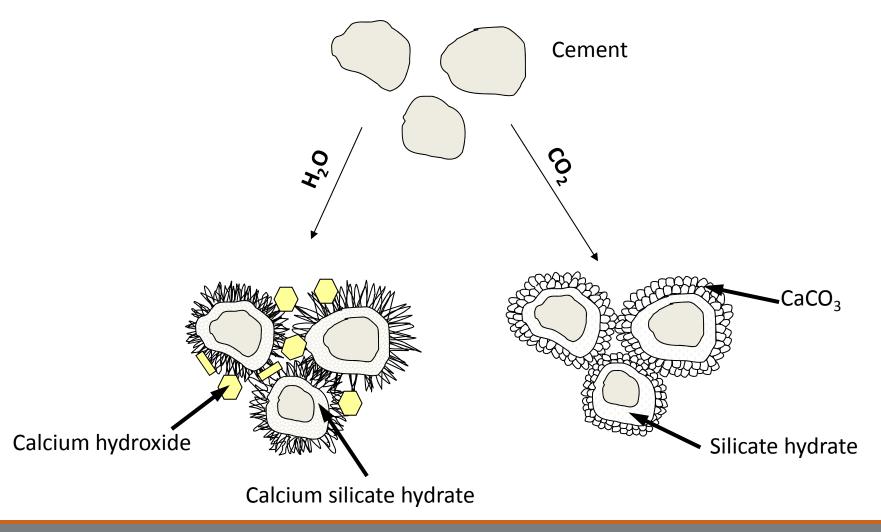


 $Ca^{+2}_{(aq)} + CO_3^{-2}_{(aq)} \leftrightarrow CaCO_3_{(s)}$

Precipitation (CO₂ Storage)

HYDRATION VS CARBONATION





CO₂ INTO CONCRETE IS TRADITIONALLY A PROBLEM



- Carbon dioxide reaction with a mature concrete microstructure can be associated with durability issues
 - Shrinkage
 - Reduced pore solution pH
 - Carbonation induced corrosion
- However, process applies CO₂ to fresh concrete rather than mature concrete

OUTLINE



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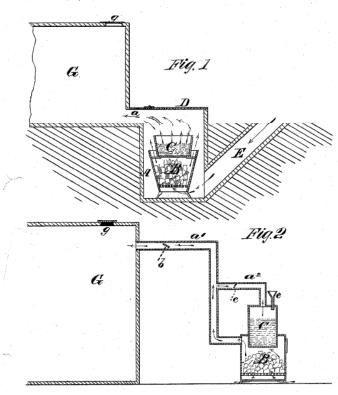
CARBON UTILIZATION BEFORE

J. L. ROWLAND.

Manufacture of Artificial Stone.

No. 137.322.

Patented April 1, 1873.





Find Carbon Dioxide Gas Under Pressure an Efficient Curing Agent for Cast Stone

By JACOB WEBER and ROBERT MATTHEI The Liquid Carbonic Corporation Chicago, Illinois

THE use of carbon dioxide to produce ■ artificial stone goes back to the early. days of modern chemistry, when men learned that the composition of many limestones and marble was nearly pure calcium carbonate. The first commercial use of earbon dioxide in making stone was in sand-lime brick-making in Europe. Sand-and-lime bricks were made under pressure, placed in kilns, and carbon dioxide was caused to circulate around the bricks for many days until the desired hardness was obtained, through the formation of calcium carbonate.

In the early 1900's, T. M. Thom of England made artificial marble by treating a mixture of calcined materials, which approached marble in chemical composition, with earbon dioxide. He calcined his mixture with various mineral constituents, ground them finely, and then slacked and pressed the mixtures into the slabs of desired size under hydraulic pressure. The slabs were allowed to dry and then placed in a kiln, where carbon dioxide was introduced under high pressure. It was claimed for the stone thus produced that it compared very favorably with the natural stone in color and ap-pearance. It was also claimed that the artificial stone in reality had a higher specific gravity and greater strength than the natural stone.

Conduct Series of Tests

Various tests to determine the efficiency of carbon dioxide as a curing agent for the speedy curing of cast stone and other concrete products were conducted by the writers in the laboratory of The Liquid Carbonic Corporation. In preparation for our first test we made a small pressure vessel out of double extra heavy 8-in. pipe. One end of the pipe was welded shut, and the other end was fitted with a blind flange. Suitable fittings were welded on to the vessel for pressure gauges, vacuum gauges, and release valves. Small slabs of cast stone, 6 by 4 by 1 in thick, were placed in the cylinder, or pressure vessel, and carbon

CONCRETE

pressures. The pressures used were 25, 50, 100 and 150 lb. a sq. in. In the first test a vacuum was drawn on the vessel to eliminate the air completely, and then carbon dioxide was introduced to the desired pressure. To compare the possible effect of the presence or absence of air, another series of tests was run in which no vacuum was drawn, but carbon dioxide pressure was added directly to the atmosphere in the vessel; and in a third series of tests the air was flushed out with carbon dioxide before pressure was added.



A test under service conditions. After nearly two years of service, the step nearer the cam-era, not cured with carbon dioxide, shows much more wear than the treated specimen

Samples of cast stone treated in these tests were of various ages-freshly molded, 24 hours, 48 hours, one week and two weeks. After treatment with carbon dioxide gas the freshly molded samples were chalky and crumbly, most probably because the water of the mixture had formed carbonic acid and precipidioxide was introduced under various tated the lime as calcium carbonate be-

fore the hydrolosis of the aluminates and silicates. Beyond the age of 24 hours no difference was observed in the appearance or strength of the samples treated with carbon dioxide.

What the Tests Disclosed

Inasmuch as the samples used were very small, it was impossible to determine how much carbon dioxide was absorbed by weight. Since we wished to maintain a constant pressure during the period of cure in carbon dioxide, we could not obtain the amount of carbon dioxide absorbed by the fall in pressure. The samples were broken across and the depth of penetration of the carbon dioxide gas was determined by testing the face of the sample for free lime with phenolphthalein. It was found that the gas had penetrated to a depth of about 3's of an inch. From the apparent hardness of the surfaces observed during the honing and polishing process, and the depth of penetration of the gas, we found that the samples that were 24 hours old before treatment, which permitted the initial set of the portland cement to occur, were most satisfactory. The higher the pressure, the more total gas was absorbed; but that seemed to make little difference in so far as surface hardness was concerned.

It seemed to make no difference in the finished cure if the air in the veses! was removed by a vacuum or flushed out with gas, but it did seem to make a difference whether the air was removed or not.

To check the tendency of earbon dioxide-treated cast stone toward expansion, slabs were prepared as described above-that is, they were allowed to set 24 hours, then placed in a chamber for 24 hours, from which the air had been withdrawn. Then carbon dioxide was applied under 160 lb. of pressure, and the samples were soaked in water for 24 hours. For comparison, similar slabs untreated in carbon dioxide gas, but allowed to set for six weeks, were immersed in water at the same time. These slabs were then allowed to dry in the air for 24

CARBON CURE

NEW APPROACH

- Developed after research into carbonation curing at McGill University
- Goal: achieve the material benefits of carbonation curing
 - Improved strength
 - Reduced absorption
 - Improved resistance to chloride permeability
 - Improved freeze-thaw performance
- Goal: carbon dioxide absorption into the concrete
 - Closing the loop
 - Permanent CO₂ storage in the concrete product
 - Green positioning in the marketplace
 - Value added

OUTLINE

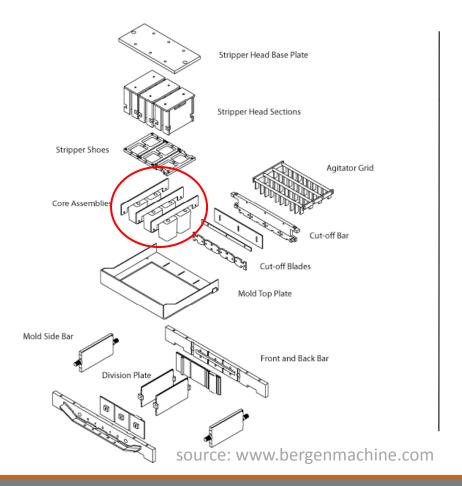


- Carbonation background
- Historical perspective
- The Technology
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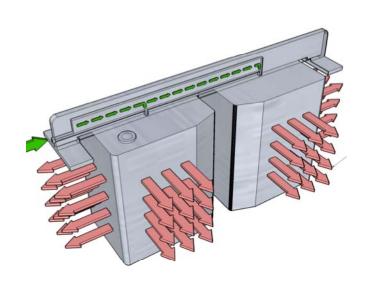
CARBONATION CURING INTEGRATION



Traditional mould design



Modified core bar

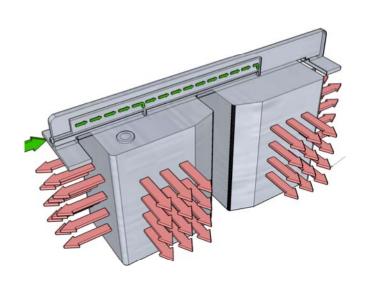


CARBONATION CURING INTEGRATION



Modified core bar

Gas delivery system





source: www.bergenmachine.com

TECHNOLOGY OFFERINGS



- Rapid installation with low CAPEX
- Plug and play
- Utilizes the existing production setup
 - Same plants
 - Same materials
 - Same practices
- Realize cost savings and environmental marketing benefits

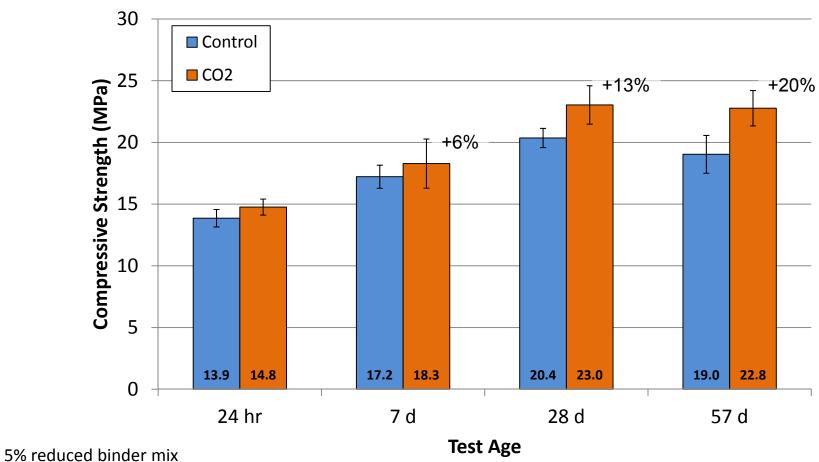
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15 SEC CARBONATION



CO2 - 15 sec, 75 g

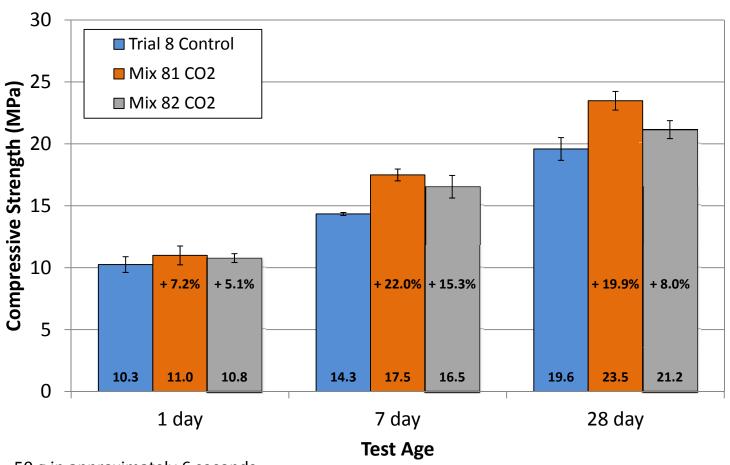
IMPROVING THE 15 SEC INJECTION TIME



- 15 sec of gas injection slows down the production cycle.
- An economically viable process needs to have minimal impact on the business as usual cycle.
- Must confine the gas injection to the 5-7 seconds that concrete is in the mould.

SHAW - CONVENTIONAL MIX AND CURING

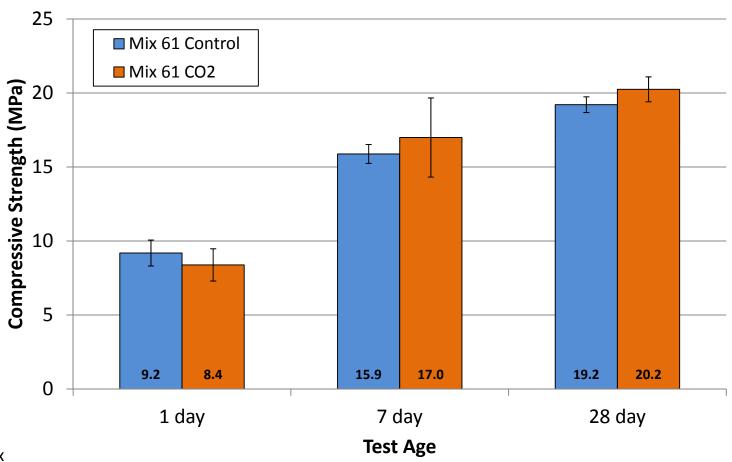




Mix 81 CO_2 - 50 g in approximately 6 seconds Mix 82 CO_2 - 68 g in approximately 6 seconds

Shaw - Reduced Curing Temperature

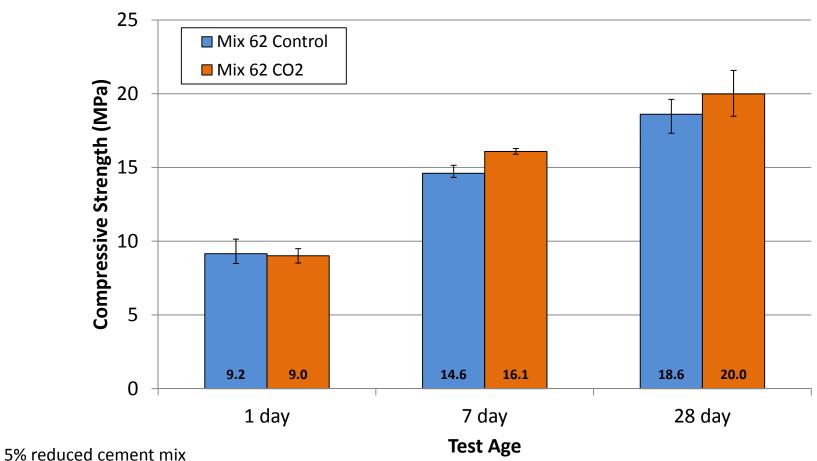




regular mix
Curing reduced 10°C
CO₂ - 65 g in approximately 7 seconds

SHAW - REDUCED CEMENT CONTENT



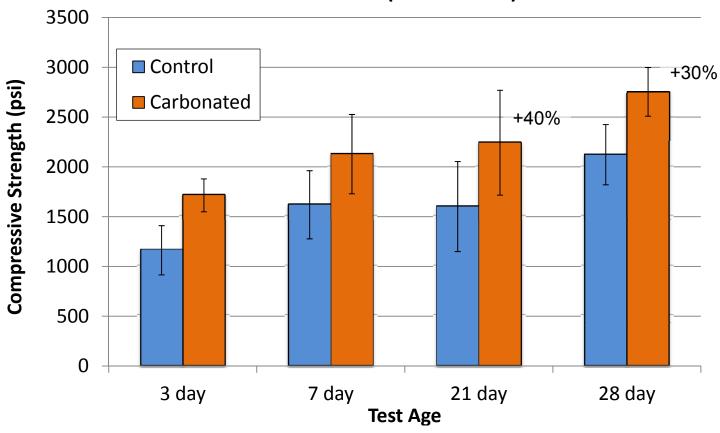


Normal curing
CO₂ - 65 g in approximately 7 seconds

BASALITE - WATER COMPENSATION







CO₂ - 50 g in approximately 5 seconds Used 16 block datasets for 21 & 28 days, (conclusions are statistically significant)

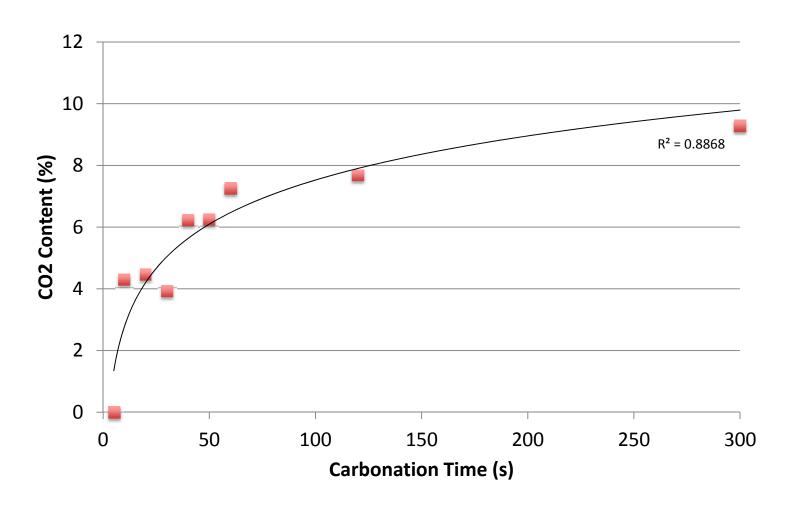
SENSITIVITIES



- Water content
 - Consistent product look
 - Compaction properties
- Achieving consistent product mass
- Keeping perforations clear
- How much CO₂ is absorbed?

QUICK AND DIRTY KINETICS





THANK YOU



CarbonCure Technologies 1.902.442.4020

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Source: City of Vancouver, Cisco and Pulse Energy