

The Effect of In-Situ Development of Nano-Calcium Carbonate On Industrial Concrete

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Abstract The introduction of carbon dioxide gas into cement paste while mixing and during the first moments of hydration results in the production of thermodynamically stable carbonate reaction products. The so-produced nanocrystalline carbonates are homogeneously distributed throughout the fresh concrete mix and are present in the paste prior to the development of any significant hydration products. Industrial-scale experiments have used waste carbon dioxide gas as an upcycled feedstock in the production of concrete masonry blocks and ready mixed concrete. The in-situ development of small amounts of nanocrystalline calcite affected the concrete properties. The compactibility of the fresh masonry blocks was reduced but compensatory process adjustments allowed for the production of blocks with compressive strengths increased up to 19% and water absorptions 18% lower. The workability of the ready-mix concrete strength was reduced while compressive strengths were equivalent or improved up to 17%. A subsequent model investigation assessed the materials science impacts of the carbonation through Quantitative X-Ray Diffraction and scanning electron microscopy. The analysis identified the nature and morphology of the mineral phase development resulting from carbonation of the cement. Changes at the microstructural level were documented including reaction product grain size and morphology. The in-situ chemical formation of nanocrystalline calcite avoids issues related to intermixing and distribution commonly faced by additions of ex-situ sourced nanomaterials to cement mixes.

1 Introduction

Carbon dioxide emissions are recognized as a significant issue for the cement and concrete industry. It is estimated that 5% of the world's annual CO₂ emissions are attributable to cement production [1]. A number of approaches have been identified to reduce the emissions intensity of the cement produced and used [2]. Innovative approaches are sought and are likely to be a part of a portfolio strategy. The most significant improvements in efficiency and cement substitution are likely to be already known and available. Future emissions improvements will likely be incremental. Thus, a range of further approaches will also have to be pursued.

One potential method is to upcycle carbon dioxide into concrete products. The mechanism of the carbonation of freshly hydrating cement was systematically studied in the 1970s at the University of Illinois. The main calcium silicate phases in cement were shown to react in the presence of water to form calcium carbonate and calcium silicate hydrate gel [3] as shown in equations 1 and 2:



The carbonation reaction is exothermic. The carbonation heats of reaction for the main calcium silicate phases are 347 kJ/mol for C₃S and 184 kJ/mol for β-C₂S [4]. The calcium silicate hydrate (C-S-H) gel that forms is understood [3] to be intermixed with CaCO₃. C-S-H gel formation occurs even in an ideal case of β-C₂S and C₃S exposed to a 100% CO₂ at 1 atm given the observation that the amount of carbonate that forms does not exactly correspond to the amount of calcium silicate involved in the reaction [4]. By virtue of adding gaseous CO₂ to freshly mixing concrete the reaction products are anticipated to form in situ, nano-scale and with a homogenous distribution.

The reaction of carbon dioxide with a mature concrete microstructure is conventionally acknowledged to be a durability issue due to such effects such as shrinkage, reduced pore solution pH, and carbonation induced corrosion. In contrast, a carbonation reaction integrated into concrete production reacts CO₂ with freshly hydrating cement, rather than the hydration phases present in mature concrete, and does not have the same effects.

2 Methods

A series of industrial scale experiments were performed whereby gaseous carbon dioxide was injected into concrete products during their batching and mixing. The carbonation was integrated with both concrete masonry unit manufacture and

ready-mixed concrete production. The goal was to assess the potential of using the carbon dioxide to add, through in-situ chemical reaction during production, nano-scale carbonate reaction products and to determine the attendant material science impacts.

A tank of liquid CO₂ was connected to a gas control system and manifold. The liquid was expanded to a gas and metered for injection into the mixer (block) or mixing drum of the ready-mixed concrete truck. The gas was delivered, at a specified flow rate over a fixed injection interval, whereupon it reacted with the hydrating cement before the mixing was completed.

The carbon dioxide content of the concretes were determined by taking a fresh sample from the production, drying the concrete on a hot plate to remove the water, and subsequently sieving the dried sample through a 160 μm sieve. Samples of the raw materials also analyzed to determine how much of each component passes a 160 μm sieve. This information, along with the concrete mix design, allows for the calculation of a theoretical composition of the sample fines against which analyzed samples can be compared.

The carbon contents of the sieved samples were then measured via the combustion infrared detection method using an Eltra CS 800 elemental analyzer. A 0.1 - 0.2 gram sample of sieved material is loaded into the induction furnace of the analyzer where it is heated to ~2500 °C in a pure oxygen environment. During the combustion process all carbon-containing compounds react with the available oxygen to produce carbon dioxide gas (CO₂). This gas is then passed through an infrared detection cell. Based on the amount of measured CO₂ the analyzer calculates the original carbon content of the sample. The carbon content can be recalculated to be an equivalent CO₂ content. A net increase in CO₂ is determined by comparison of the CO₂ contents for a carbonated sample to an uncarbonated control sample.

The carbon dioxide gas for the trials was sourced from an industrial gas supplier but conventionally such gas captured from a point-source emission. The capture step is performed in response to market demand for the industrial carbon dioxide and thus the industrial CO₂ can be understood to be CO₂ emissions repurposed for beneficial utilization. Had the utilization not demanded the gas then the gas would not have been processed and instead would have remained in an emission stream.

2.1 Masonry block production

The block experiment was conducted at an Illinois-based masonry concrete producer. Gaseous carbon dioxide was injected, at a rate of 1.5% by weight of the cement, into the concrete mixer once all the dry materials had been loaded. The injection took place over 180 seconds. A medium weight mix design, summarized in Table 1, was used to make standard 8" (200 mm) concrete blocks.

Table 1. Masonry mix design, per m³

Component	Quantity	Unit	Fraction
Washed gravel	311	kg	8.7%
Sand	1960	kg	54.8%
Silica Sand	567	kg	15.9%
Cement	454	kg	12.7%
Rainbloc 80	1478	ml	-
Mix water	7.9%	-	7.9%

The fresh concrete was assessed visually and via feedback from the machine (i.e. compaction time) and production personnel. Samples were taken periodically to assess the water content of the concrete and monitor whether the carbon dioxide had any impact on the “wetness” of the fresh product. Such samples were also processed for quantification of carbon dioxide uptake. The finished blocks were transported to a curing room heated with forced humid air.

Concrete performance compressive strength was measured at 7, 28 and 56 days at the producer’s testing laboratory with 5 blocks for each carbonated condition at each test age. Water absorption and density testing was also conducted on three blocks per condition. Testing was conducted according to ASTM C90 - Standard Specification for Loadbearing Concrete Masonry Units. The control dataset was comprised of two batches contributing 8 strength specimens (5 from the first batch, 3 from the second) and 6 absorption/density specimens.

2.2 Ready-mix concrete production

The ready-mixed concrete experiment was conducted at a Dartmouth, Nova Scotia ready-mixed concrete producer. The mix design is summarized in Table 2. The aggregates and cement were loaded into the ready-mix concrete truck mixing drum and mixed briefly before the addition of the carbon dioxide. The gas was injected at 1.5% by mass of cement by means of a gas delivery line retrofit onto the truck mixer. The injection was completed in 180 seconds whereupon the remaining mix materials were added after the conclusion of the CO₂ injection. The mixing procedure was modified to allow the application of carbon dioxide when the water to cement ratio was low; the reaction rates of carbon dioxide and cement are known to be higher at lower w/c [5]. The carbonated and control batches had the same amount of water rather than aiming for a specific workability. The mix design targeted 27.5 MPa (4000 psi).

Table 2. Ready-mix concrete mix design, per m³

Component	Quantity	Unit	Fraction
Sand	770	kg	33.5%
Stone	1030	kg	44.8%
GU Cement	336	kg	14.6%
Water	163	kg	7.1%
Daracem 50	1350	ml	-
Darex II	200	ml	-

The fresh concrete was characterized in terms of temperature, slump (ASTM C143), and air content (ASTM C231). The compressive strength of the hardened concrete was assessed at 1, 7, 28 and 56 days by testing 3 cylinders per condition according to ASTM C39.

2.3 Lab investigation of nano-crystalline reaction products

The microstructural analysis of carbonate reaction products in industrially produced concrete was difficult due to the available sampling approaches and conventional mix designs. An investigation was conducted to characterize the carbonate reaction products through carbonation of a model cement system. A high degree of carbonation was achieved to allow for direct observation of the crystalline reaction products.

The experiment mixed 450 g of GU cement and 50 g of distilled deionized water in an airtight, resealable plastic bag. The materials were hand-agitated through the bag until homogeneously blended and the cement was moistened (30 seconds). The bag was inflated with 100% CO₂ gas and sealed. The system was allowed to react until all of the carbon dioxide had reacted (over several minutes) and the bag had deflated. This process was repeated a total of ten times over the course of 1 hour. A separate bag was prepared identically, but no carbon dioxide gas was added into the plastic bag.

Samples were pulverized using a mortar and pestle and stored in a sealed desiccator. Samples for QRXD testing were ring milled and micronized. The micronized samples were mounted and analyzed using a Bruker D8 Focus (0-20, LynxEye detector). Quantitative phase analysis of mixtures was conducted using the Rietveld method on Bruker Topas software.

Sub samples of the cement pastes were preserved for SEM/EDS analysis. Samples were mounted to aluminum stubs using carbon adhesive tabs. They were then sputter coated with 8 nm of Iridium, using a Leica EM MED020 Coating System, to enhance imaging quality. Imaging was conducted using a Helios NanoLab 650 Focused Ion Beam SEM. Images were collected at 0.5kV and a 25 PA current.

3 Results

3.1 Concrete masonry unit results

The first carbonated blocks produced during the masonry test were assessed to have a dry appearance with all other production inputs being equal. The batch report indicated that the carbonated batch included more water than the control, but there was 10% less water detectable by the mixer control sensor and 11% less as quantified with a bake off. The conclusion was that the CO₂ caused an apparent drying effect wherein more water had been added to the mix, but less water could be detected in or removed from the mix. The blocks were also observed to be underweight.

The operator created a second batch wherein additional mix water was added into the mixer after the CO₂ injection ended and prior to discharge. The mix was homogenized after the water addition. The amount of water was based upon the operator's assessment to produce a batch of concrete with the desired consistency and appearance. The water increase, as recorded by the w/c sensor on the batching system, was 11%. Further, a bake off found 3% more water removable from the fresh samples.

The temperature of the blocks was measured when they were sampled for carbon quantification. Samples were removed from blocks on the production line two to five minutes after the end of mixing. The control blocks were found to be 26.6 °C. The carbonation treatment increased the temperature of the concrete. The unadjusted batch was 30.5 °C while the water adjusted batch was 31.8 °C.

Carbon quantification testing showed that 70% of the supplied CO₂ for the first carbonated batch was absorbed to give an uptake of 1.05% by weight of cement. In contrast, 93% of the supplied CO₂ was absorbed by the water adjusted concrete for an uptake of 1.40% CO₂ by weight of cement. The temperature rise was higher for the second batch which is in alignment with the greater carbonation uptake and exothermic nature of the carbonation reaction.

The strength development of the concrete masonry units, in Figure 1, shows the impact of water adjustment on the carbonated blocks. The strength of the dry carbonated blocks was 62% of the control at 7 days, 68% at 28 days and 76% at 56 days. The water adjustment resulted in blocks strengths 18-19% higher than the control at all three test ages.

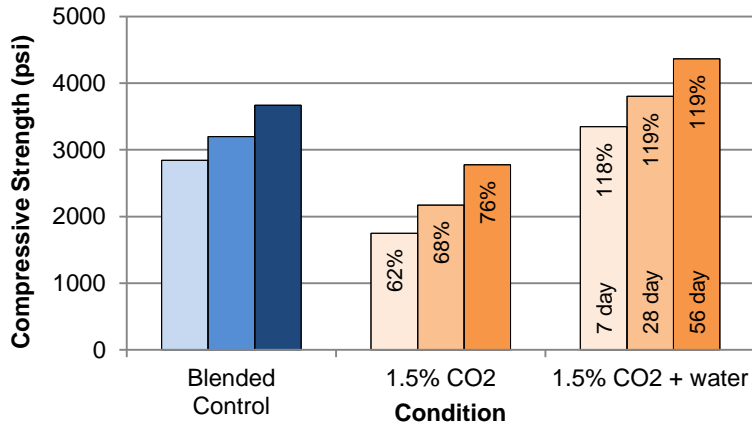


Fig 1. Strength development of carbonated and control concrete masonry units

The dry batch was found to have a density that was 94.9% of the control. The carbonation treatment made the concrete more difficult to compact given that less material was packed into the same mould cavity. The density of the water-adjusted batch was 99.8% of the control. The water adjustment successfully allowed the proper mass of concrete to be compact into the mould. The average water absorption of the blocks was decreased 11% for the dry batch and 18% for the water adjusted batch. The carbonation reaction products and impact on hydration served to reduce porosity of the blocks and this effect was greater at the higher density and higher carbonation uptake.

3.2 Ready-mix concrete results

The carbonation of the ready-mix concrete was shown to have a significant effect on the workability of the concrete. The slump was 7 inches for the control and 3 inches for the carbonated batch. The workability of the concrete was improved by an admixture as a demonstration that conventional means could be used to address the consistency. The carbonated concrete was 28.6 °C, or more than 2°C higher than the control (25.8°C). The temperature rise is associated with the exothermic carbonation reaction. The compressive strength development of the concrete is presented in Figure 2. The carbonated concrete samples were produced prior to the addition of the admixture to the batch.

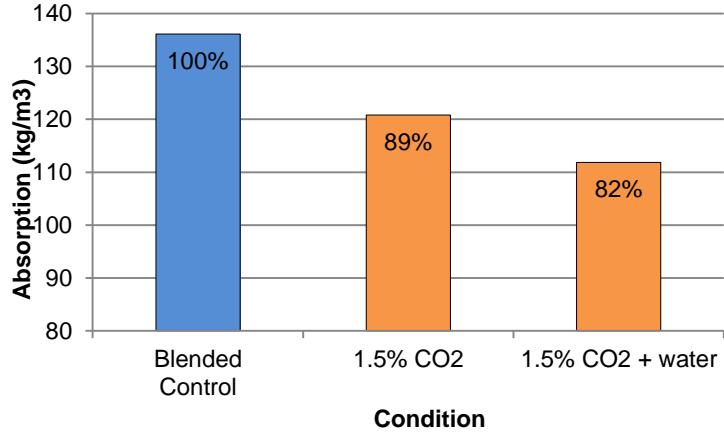


Fig 2. Absorption of carbonated and control concrete masonry units

The 1.5% CO₂ dosed batch was 98% of the control strength at 1 day, 98% of the control at 7 days, 117% at 28 days and 111% at 56 days. The air content was lower than for the control (4.5% versus 5.9%) and a possible contributing factor to the strength performance. It is not known if the carbon dioxide reaction directly impacted the air content or if another aspect of the production was responsible.

Carbon quantification revealed that the uptake was 1.69% CO₂ by weight of cement. This reading implies a reaction efficiency exceeding 100% so should be interpreted to be an overestimate. The uncertainty was concluded to be due to a complexity of the mix design used.

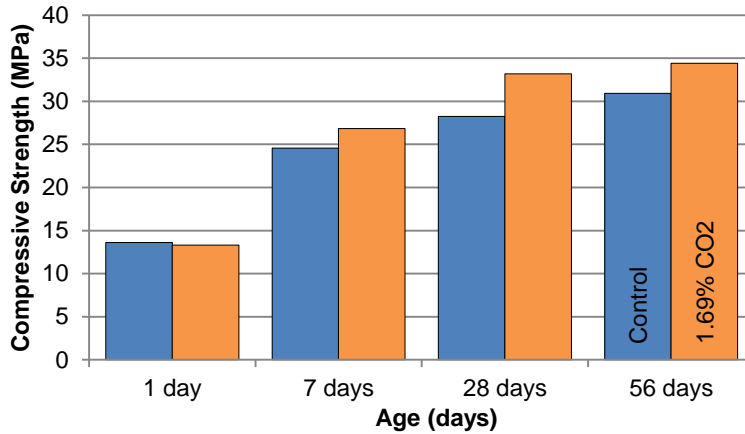


Fig 3. Strength development of carbonated and control ready-mix concrete mixes

3.3 Carbonate reaction product characterization

Quantitative X-ray Diffraction (as summarized in Table 3) revealed that the anhydrous cement sample contained 6.7% CaCO_3 (identified as calcite) by mass. The carbonate content of the uncarbonated sample was unchanged from the anhydrous condition while the carbonated sample was found to be 35.5% CaCO_3 by mass.

Table 3. Mineral composition by QXRD (in weight %) calculated for anhydrous cement, hydrated cement and carbonated cement

Component	Anhydrous	Hydrated	Carbonated
TiO_2	0.3	0.2	n.d.
C2S	17.5	21.3	15.5
C3A	5.1	5.1	4
C3S	53	45.2	29.8
C4AF	10.8	11.7	11.1
CaCO_3	6.7	6.5	35.5
Ca(OH)_2	n.d.	2.6	n.d.
Ettringite	3	6.4	2.6
Gypsum	3	0.3	0.7
SiO_2	0.5	0.8	0.9
Total	100.0	100.0	100.0
Total Ca	45.8	43.7	43.2

Interpretation must note that in the carbonated case the denominator has changed because the system has increased in mass through the addition of CO_2 as solid carbonate reaction products. The QXRD values can be normalized versus a total calcium content to improve the analysis and allow a direct comparison. The mass balance over the calcium content can allow the systems to be scaled to consider the same amount of calcium. A recalculated set of analytical results is presented in Table 4.

Table 4. Mineral composition (in weight %) rescaled for constant calcium content for anhydrous cement, hydrated cement and carbonated cement

Component	Anhydrous	Hydrated	Carbonated
TiO ₂	0.3	0.2	0.0
C2S	17.5	22.3	16.4
C3A	5.1	5.3	4.2
C3S	53.0	47.4	31.6
C4AF	10.8	12.3	11.8
CaCO ₃	6.7	6.8	37.7
Ca(OH) ₂	0.0	2.7	0.0
Ettringite	3.0	6.7	2.8
Gypsum	3.0	0.3	0.7
SiO ₂	0.5	0.8	1.0
Total	100.0	104.9	106.2

A net difference of the CaCO₃ content between the carbonated (37.7%) and the anhydrous (6.7%) conditions, in turn converted from %CaCO₃ to %CO₂, shows that the carbonated sample had a CO₂ content of 13.6% by weight of anhydrous cement. This level of carbonation ensures that the reaction products are found in considerably greater abundance than what is achieved in the industrial case. Nonetheless, it serves as an effective system for analysis given that the reaction products are easy to observe in a neat paste system that has a high degree of reaction.

The electron microscopy of the carbonated sample revealed that numerous rhombohedral nanocrystals were present in the system. The primary dimension of the particles generally exceeded 10 nm and was predominantly less than 150 nm. The size of the particles were too small to allow for an effective direct chemical assessment through EDS. However, the particle geometry is consistent with calcite and the QXRD identified the presence of large amounts of calcite so the conclusion is made that the carbonation process has achieved in-situ formation of nanocrystalline calcite. The production method (extensive and aggressive carbonation) has resulted in reaction products that are likely in larger sizes and in greater quantities than what would have been found in the industrial samples.

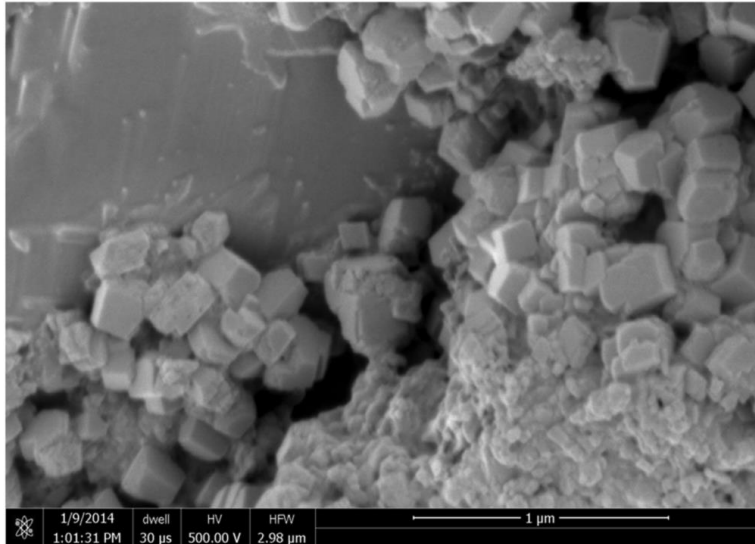


Fig 4. Nano-scale (10-150 nm) rhombohedral calcium carbonate reaction products produced through carbonating freshly hydrating cement

4 Analysis

The addition of the carbon dioxide to the masonry blocks suggested that the creation of nano-scale calcium carbonate reaction products in the fresh concrete made the blocks more difficult to compact. Further, a reaction time of 3 minutes and a carbon dioxide uptake of 1.05% by weight of cement was sufficient to impact the compaction.

The observations about the water content indicate that the water input into the mix was the same (carbonated mix 1) or higher (carbonated mix 2) than the control but was found through bake off to be, in turn, lower and equivalent. Effectively the reaction products have created new surface area in the fresh matrix.

The fact that the masonry block strength benefit was observed while the block density was unchanged versus the control suggests that the improvement was associated with the carbonation rather than having produced a denser block. The reduced water absorption indicates that the carbonate reaction products, or their attendant impact on the hydration, have resulted in an improved pore filling.

The creation of nano-scale carbonates in the fresh ready-mix concrete had a noticeable effect on the workability. As with the masonry case, the development of new surface area reduced the effective wetting of the water and decreased the ability of the matrix to shear or flow. Given that the carbonation step had a beneficial effect on strength (or at least neutral effect if the higher air content in the control was resulted in a lower strength as is possible [6]) the approach can be used as a

tool to modify the workability of fresh concrete and thereby influence rate of placement or finishing.

The performance improvement is achievable with amounts of carbon dioxide at 1.5% by weight of cement or lower. The in-situ production addresses one of the challenges of incorporating nano-CaCO₃ into cement systems, namely, achieving effective dispersion and fine distribution [7]. Given that the nano-CaCO₃ additions can reach 10% [8] the potency seen at the lower addition rate attests to the benefit of pursuing an in-situ approach.

An effort was made to estimate the increase in specific surface associated with the nanoparticle creation (Table 5). Both the block (1.40% uptake) and the ready-mix concrete (1.69%) were considered. The CO₂ content by weight of cement was recalculated to be a CaCO₃ content per cubic meter of concrete. The nano-crystalline calcite was modeled as a cube with a dimension of 50 nm. Assuming the nanoparticles had a density consistent with calcite (2.711 g/cm³) then a specific surface area associated with the calcite can be calculated. Further, the assumption is made that the particles are resting on another surface, such as a cement particle. A net new surface consideration assumes that 4 out of 6 faces of the nanoparticle represent new surface area in the system. Two of the faces are excluded since one is resting on an existing surface while one exposed surface is equivalent to the old surface that is covered by the particle. In practice the nanoparticles might not be resting on surface, particularly during the very early hydration or time interval such as when the concrete is formed or placed. As such, this calculation may be an underestimate.

Table 5. Surface area increase for in-situ nanoparticle creation

Component	Block Trial	RM trial	Unit
Cement	333	336	kg/m ³ concrete
CO ₂ Uptake	1.40%	1.69%	by weight cement
CaCO ₃ Level	3.18%	3.84%	by weight cement
Amount CaCO ₃	10.60	12.91	kg
Particle Dimension	50	50	nm
Surface Area per Particle	1.50E-14	1.50E-14	m ²
Volume per Particle	1.25E-22	1.25E-22	m ³
CaCO ₃ Density (Calcite)	2.711	2.711	g/cm ³
Single Particle Mass	3.39E-16	3.39E-16	g
Specific Surface Area	44,200	44,200	m ² /kg
Total CaCO ₃ Surface Area	468,520	570,622	m ²
New Surface Area	312,700	380,845	m ² /m ³ concrete

The calculation found that the calcite formation added about 312,000 m² of new surface per m³ of concrete in the masonry block case and about 380,000 in the ready-mix case. If the model particle size was reconsidered as 25 nm then the increased surface area become 625,000 m²/m³ in the masonry blocks and 760,000 in the ready-mix concrete. A comparison can be made to silica fume assumed to have a specific surface area of 20,000 m²/kg. The addition rates for silica fume that correspond to the new surface area in the system are 4.7% by weight of cement for the block and 5.7% for the ready-mix (or 9.4% and 11.3% for a 25 nm model nanoparticle). Given that silica fume additions on this order are known to affect the workability of concrete [9] it is concluded that the increase in surface area is a viable interpretation.

5 Conclusions

Industrial trials investigated a method of adding nano-CaCO₃ to concrete via an in-situ reaction between gaseous CO₂ and freshly hydrating concrete. The addition cause masonry blocks to be harder to compact though this could be addressed with a simple increase in mix water. The compressive strength and water absorption were both improved despite the block density being equivalent to the control. The reaction products similarly impacted the fresh properties of ready-mix concrete effectively reducing the workability. The compressive strength was comparable or better than the control. The side effects of the carbon dioxide addition are attributable to the new surface area associated with the reaction products as they are created in the fresh concrete.

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